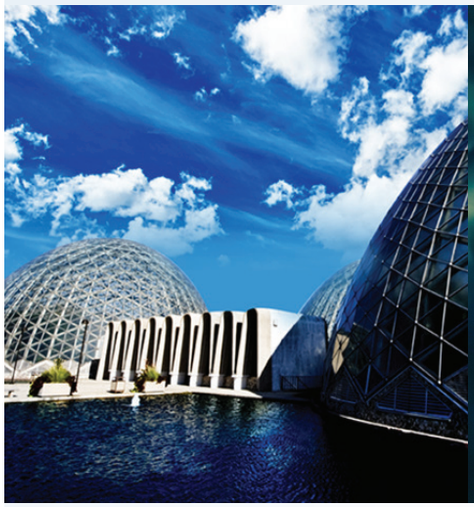
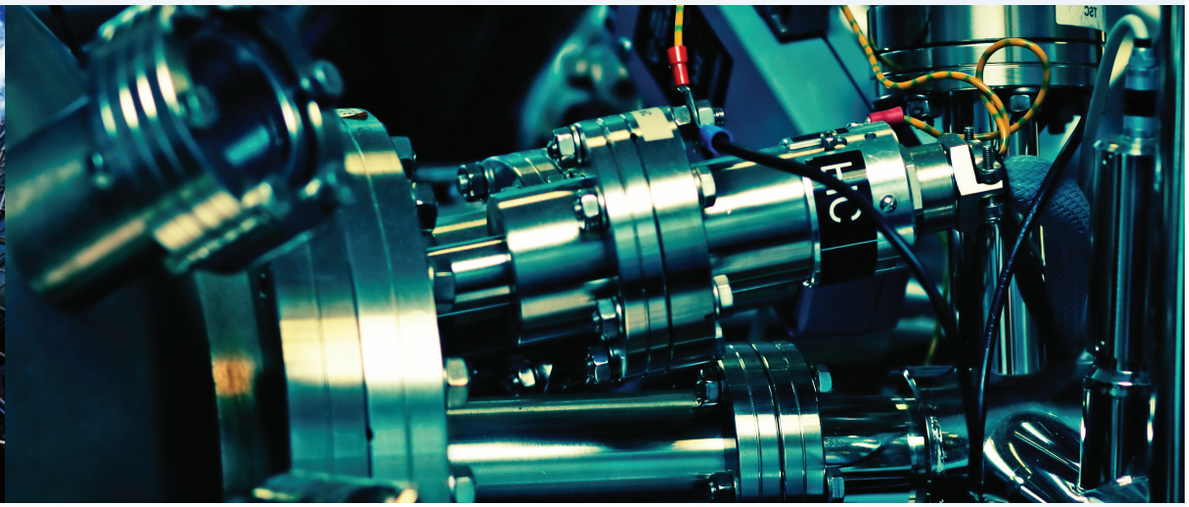
FACSS PRESENTS

SCIX2013

The Great SCIentific eXchange

FACSS 40TH





FINAL PROGRAM BOOK OF ABSTRACTS

SciX welcomes attendees from around the world to the 40th Annual Analytical Chemistry Meeting of FACSS: Right Size, Right Science, Right Conference!

MILWAUKEE, WI

Sept. 29 - Oct. 4, 2013

Hyatt Regency

Milwaukee and Wisconsin Center

SciXConference.org | FACSS.org

American Society for Mass Spectrometry

Networking
Resources
Professional Development
Learn more
www.asms.org

ASMS is one of the most dynamic scientific societies in the world and sponsors the following:

- **The Annual Conference on Mass Spectrometry and Allied Topics:** an open forum for the presentation of scientific research and the development of new applications and technology
- **Special topic short courses:** continuing education for those in the field and introductory courses for those entering the field
- **Journal of the American Society for Mass Spectrometry:** a peer reviewed monthly journal with a comprehensive range of research and development in mass spectrometry
- **Fall Workshop:** tutorial education on emerging technology
- **The Asilomar and Sanibel Conferences:** informal settings for highly focused conferences on specific research topics
- **Publications:** educational brochures for scientists and students, reprints of classic out-of-print mass spectrometry books
- **Educational Resources:** "how to" videos, tutorial lectures, historical interviews and more

Visit ASMS.org for details

American Society for Mass Spectrometry
2019 Galisteo Street
Bldg. I-1
Santa Fe, NM 87505
505-989-4517
office@asms.org

ASMS members receive:

- Subscription to the monthly Journal of the American Society for Mass Spectrometry
- Discounted registration for all conferences and short courses
- Access to private areas of the web site (www.asms.org):
  - Career Center
  - Membership Directory
  - Archives of the conference proceedings
  - Archives of the John Wiley mass spectrometry journals and IJMS
  - Collection of tutorial and plenary lectures

www.asms.org

TABLE OF CONTENTS

Attention Presenters: Check this final program to verify the schedule of your talk or poster. Changes may have occurred since the preliminary program.

SciX Conference and FACSS International Office
2019 Galisteo Street, Building I-1, Santa Fe, NM 87505
(505) 820-1653 ❍ (505) 820-1648 ❍ facss@facss.org ❍ www.scixconference.org ❍ www.facss.org

WELCOME TO SciX 2013

On behalf of the Federation of Analytical Chemistry and Spectroscopy Societies (FACSS) it is our pleasure to welcome you to Milwaukee for **SciX 2013**. This meeting marks the 40th year that FACSS has sponsored a conference devoted to advancing analytical chemistry and spectroscopy on behalf of its member organizations, although this is only the second year that FACSS has presented the meeting under the SciX name. **SciX - the great Scientific eXchange** – tries to encompass both the science and the community that have become the hallmark of FACSS's annual meeting. From its inception, FACSS has always been an extension of its member organizations, with the belief that these societies together could offer more to the scientific community than any one of them could do alone. The content and character of the conference is a reflection of the interests of those societies, and the science continues to grow as the federation grows, most recently with the addition of the Council for Near-Infrared Spectroscopy. Alongside the science are the lasting relationships, collaborations, and friendships fostered by these societies. FACSS, through SciX, continues to work to provide the venue to develop and renew these relationships. Ultimately, the FACSS organization is deeply indebted to each of the twelve member societies for the guidance of their leadership and the support of their membership.

As the FACSS organization grows and evolves, the foremost challenge each year is maintaining the high quality technical program of SciX year after year. The easiest solution is to have the same short list of big name speakers, which is a sure route to short term success and long term malaise. By featuring both established and young investigators, mixing academic, industrial, and government researchers, the program draws a dedicated audience year after year. For 2013 the conference will open with world-class plenary lectures on Green Chemistry from **Martyn Poliakoff CBE, FRS** from the University of Nottingham, followed by **Paul Anastas**, Yale University and former EPA science advisor. This year also marks the first time the LCGC magazine awards will be presented at SciX, including the **Lifetime Achievement Award in Chromatography** to **Pete Carr** from the University of Minnesota and the **Emerging Leader in Chromatography Award** to **Davy Guillarme** from the University of Geneva. While SciX is a proud host to these and the many prestigious society awards, there is arguably greater pride in the many contributed papers and posters that offer early career scientists and students opportunities to present their research to a truly international audience. These contributed papers provide the source for the third annual **FACSS Innovation Award,** presented for the most innovative new research debuted at SciX. The finalists are selected from the pool of all contributed papers, and present their work in a special session on Thursday afternoon. A panel of expert judges each talk on the basis of the novelty of their work and the impact of the science, with the winner announced at the Friday morning plenary. While scientists often compete for grants and recognition, it is a rare opportunity to see head-to-head competition for such a prestigious award, and this has rapidly become one of the signature events at SciX.

After long being the National Meeting for the SAS, SciX 2013 is also proud to host the National Meeting for NASLIBS, which became part of FACSS in 2012. FACSS and SciX chairs have promoted and delivered a "meeting within a meeting" concept that allows NASLIBS to maintain much of its historical identity while providing an opportunity for enhanced scientific exchange and visibility through interaction with the greater SciX attendees, member organizations, and scientific disciplines. In 2013 AES, the Electrophoresis Society has increased its commitment to FACSS and activity at SciX by increasing the number of sponsored sessions and supporting a student poster session. SciX 2013 also hosts the first official session organized by SpSJ. These new opportunities contribute to the FACSS vision of promoting enhanced **Sci**entific e**X**change at **SciX**.

With so many other meetings today being for-profit concerns run by large professional organizations, it is important to remember that SciX and FACSS are run by the consensus of the 12 non-profit member societies – by scientists, for scientists. The volunteer SciX 2013 team and the FACSS Executive Committee are also greatly indebted to the unwavering support at the FACSS / SciX International Office – Cindi Lilly and Marin Walker who do so much of the difficult work behind the scenes to make the conference, website, and federation run so smoothly.

We hope you enjoy SciX 2013. With an exceptional program, world-class plenary lectures, awards symposia, poster sessions, networking events, an extensive exhibition, all in the beautiful and welcoming city of Milwaukee, we're confident that this conference will herald 40 more years of great scientific exchange.

Fred LaPlant , General Chair
Heather Brooke, Workshop Chair
Ryan Schemeling , Local Chair
Rebecca Airmet, Advertizing Chair
Chad Atkins, Social Medial Chair
Ian R. Lewis, FACSS Governing Board Chair 2012-2013
Mike George, Program Chair
Mike Carrabba, Exhibits Chair
Kevin Yeh, Employment Chair
Jose Almirall, Awards Chair
Mark Hayes, FACSS/SciX Marketing Chair 2009-2013

GENERAL INFORMATION

LOCATION. All plenaries, symposia and the exhibits are located in the Wisconsin Center. Workshops are located in the Hyatt Regency Hotel and the Wisconsin Center.

PROGRAM. This printed program contains titles and abstracts as submitted by the authors.

SPEAKERS. There will be an LCD projector for each symposium. Speakers must supply their own computer with their presentation. Please arrive 30 minutes before your session begins. Each speaker should adhere to the time allotted for the talk.

POSTER SESSIONS.

Sunday SAS Sponsored Student Poster Session
Wisconsin Center, Ballroom Level, prefunction
7:15 – 9:00 pm SAS Poster Session and SciX Welcome Mixer

Monday Poster Session – *Ballroom Level, prefunction*
Set up posters between 7:00 – 8:00 am and remove by 5:00 pm
9:00 – 10:20 am - Poster Session
3:00 – 3:50 pm – Poster viewing and break

Tuesday and Wednesday Poster Sessions – *Exhibit Hall - Ballroom B/C/D*
Posters remain up all day on their designated day. Set up posters between 7:30 – 8:00 am and remove Tuesday posters by 4:30 pm and Wednesday posters by 4:00 pm.
9:00 – 10:20 am – Poster Session
3:00 – 3:50 pm – Poster viewing and dessert break

Thursday Poster Session – *102 Foyer*
Posters remain up all day. Set up posters between 7:00 – 8:00 am and remove at 3:50 pm
9:00 – 10:20 am – Poster Session
3:00 – 3:50 pm – Poster viewing and break

WORKSHOPS. A list of workshop, descriptions, and the locations begins on page 43. You must register for a SciX workshop at the conference registration desk

EMPLOYMENT BUREAU. The bureau is in the exhibit hall. See Page 4 for additional information

EXHIBITS. The exhibition is located in Ballroom B/C/D in the Wisconsin Center and will be open as follows. See page 31 for details.

Monday (Opening Reception)	5:30 pm – 7:30 pm
Tuesday	9:00 am – 4:30 pm
Wednesday	9:00 am – 4:00 pm

BREAKS.

Monday
9:00 – 10:20 am & 3:00 – 3:50 pm – B*allroom Level, prefunction*

Tuesday and Wednesday
9:00 – 10:20 & 3:00 – 3:50 pm – *Exhibit Hall - Ballroom B/C/D*

Thursday
9:00 – 10:20 am & 3:00 – 3:50 pm – *Ballroom Level, prefunction*

INTERNET ACCESS. Complimentary wireless internet access will be available in Exhibit Hall – Ballroom B/C/D

REGULATIONS. The following regulations are in the best interest of the conference.

1. There is no smoking in any conference areas.
2. An official name badge is required at all times.
3. No advertising may be placed in the conference area.
4. Only official exhibitors may display in the Exhibit Hall.
5. No distribution of product/meeting literature in sessions.
6. No Photography of PowerPoint Lectures or Posters

COMPANION REGISTRATION. Does not include access to symposia. Cost is $55 and includes the following: **Sun.** Evening Welcome Mixer. **Mon.** coffee/pastries 9:00 am and Exhibit Hall Opening Reception. **Wed.** Evening Event

SPECIAL EVENTS. *All the events below will take place in the Wisconsin Center unless otherwise indicated.*

SUNDAY

2:30 – 6:00 pm **"What's Hot" Exhibitor Presentations,** *Ballroom A*

6:15 pm **SciX 2013 Welcome**, Fred LaPlant
40 Years of the FACSS Conference, Ian R. Lewis
Keynote Lecture. From Test Tube to YouTube; **Martyn Poliakoff,** University of Nottingham. *Ballroom A*

7:15 – 9:15 pm **Welcome Mixer and SAS Sponsored Student Poster Session**. SAS, Coblentz Student and FACSS Student Award Presentations, *Ballroom Level, Prefunction*

MONDAY

7:50 am **Opening Address,** *Ballroom A*

8:00 am **Keynote Lecture.** Future Challenges in Green Chemistry; **Paul Anastas,** Yale University, *Ballroom A*

5:30 – 7:30 pm **Reception for Exhibit Opening** (wine, beer, light hors d'ouvres) *Exhibit Hall-Ballroom B/C/D*

TUESDAY

8:00 am **Coblentz Society Craver Award**. Emerging Trends in Infrared Spectroscopic Imaging: From Theory to Therapy; **Rohit Bhargava**, University of Illinois at Urbana-Champaign, *Ballroom A*

8:30 am **Charles Mann Award for Applied Raman Spectroscopy.** Nano Scale – Mega Challenge? Raman Spectroscopy Approaching Molecular Dimensions; **Volker Deckert,** Institute of Physical Chemistry and the Institute of Photonic Technology, University of Jena, *Ballroom A*

12:00 pm **Free Lunch and Employment Discussion for Students, sponsored by SABIC,** *Room 201B*

6:00 pm **Raman Reception,** *Regency A/B Hyatt Hotel*

7:30 pm **Society for Applied Spectroscopy Wine and Cheese Award Reception,** *Regency C/D Hyatt Hotel*

WEDNESDAY

8:00 am **Applied Spectroscopy William F. Meggers Award.** A New *in vivo* Raman Probe for Enhanced Applicability to the Body; **Paul Pudney,** Unilever, *Ballroom A*

8:30 am **SAS's Lester W. Strock Award.** Isotopic Analysis at Atmospheric Pressure in Laser Plasmas; **Richard Russo,** Lawrence Berkeley National Laboratory and Applied Spectra, Inc, *Ballroom A*

6:00 pm FACSStoberfest! An all inclusive event, *Regency Ballroom, Hyatt Regency Hotel*

THURSDAY

8:00 am **ANACHEM Award.** Capillary Electrophoresis of Bottom-Up Proteomics; **Norman Dovichi,** University of Notre Dame, *Ballroom A*

8:30 am ***LCGC* Lifetime Achievement in Chromatography Award.** Two-Dimensional Liquid Chromatography The Future of HPLC?; **Peter Carr,** Univ. of Minnesota, *Ballroom A*

3:50 pm **Plenary Session,** *Room 102C*
FACSS Distinguished Service Awards
FACSS Innovation Award Session

FRIDAY

8:00 am **Special Plenary Session:** Welcoming a New Member Organization into FACSS and much more….*Regency A/B Hyatt Hotel*

EVENTS OF SPECIAL INTEREST TO STUDENTS

SUNDAY EVENING, *Ballroom Prefunction, Wisconsin Center*

- Welcome Mixer: 7:15 – 9:15 pm
- SAS Sponsored Poster Session: 7:15 – 9:15 pm
    - SAS and Coblentz Student Award presentations
    - FACSS Student Award and Tomas Hirschfeld Scholar Award presentations

MONDAY through THURSDAY

- FACSS Student Poster Awards will be presented daily

MONDAY through THURSDAY

- Employment Bureau (Monday evening through Wednesday), Ballroom B/C/D

SPECIAL INVITATION TO STUDENT ATTENDEES

- Tuesday 8:00 am – noon. **Resume Writing and Interviewing Skills for Students.** *Room 201C*
  SABIC is hosting this free workshop. Your career search is one of the most influential investments in your future. This interactive half-day workshop will prepare attendees to make a positive and lasting impression both in-print and in-person. Receive tips and best practices, avoid common mistakes, learn how to tailor your resume for different prospective employers, and prepare yourself for important interview styles. Instructors: Derek Lake and Patrick Reuss from SABIC. Directly following the workshop, students are invited to join the Free Lunch and Employment Discussion hosted by SABIC.

- Tuesday 12:30 pm – **Free Lunch and Employment Discussion for Students. Hosted by SABIC**
  Eat lunch and chat with professionals from a wide range of professional fields (academic, government, chemical industry, pharmaceuticals, goods and services, etc.) It's a unique opportunity to ask questions, get helpful tips, and discuss topics that relate to your specific career-seeking situation within the current job market. *Room 201B* ***Check at conference registration desk for availability.***

- Wednesday 9:00 am – 5:00 pm. **Professional Analytical Chemists in Industry: What Does an Analytical Chemist Do?**
  This seminar begins with a discussion of the education requirements and salaries that an analytical chemist may expect in industry. The different roles (including scientific consultant, methods development and problem solver) of the industrial analytical chemists are explained. A majority of time is spent on problem solving, both the process and solving real-world problems. Students will learn a "framework" for approaching problems. Time will be available to ask questions on these topics and other related subject. The course text includes supplementary material on finding a job, summer employment, etc. The entire course, especially the problem solving, is structured for extensive participation and interaction. *Room 201C*
  Additional information is available at http://www.pg.com/science/prof_chemists.jhtml. The course is intended primarily for undergraduate students to educate them about careers as analytical chemists in industry. However, graduate students, high school teachers, and college faculty have indicated it was worth their time to attend. Instructors: Judson Haynes and Diane Parry, Procter and Gamble

EMPLOYMENT BUREAU

The Employment Bureau is located in the Exhibit Hall in conjunction with the internet café Monday evening and open through close of the hall on Wednesday afternoon.

EMPLOYERS: Bring either hard copy or electronic copy of job opportunities and display on poster board in the employment area. There will be copies of resumes for you to review or to take with you.

JOB SEEKERS: Bring an electronic copy of your resume and copies will be made available for prospected employers to review.

A message board will be available for employers and job seekers to communicate. There will also be space available to meet and conduct interviews. Contact Kevin Yeh yehkevin@gmail.com with any questions

FACSS and SciX CONFERENCE ORGANIZATION

MEMBER ORGANIZATIONS OF FACSS

American Chemical Society, Analytical Division
AES Electrophoresis Society
American Society for Mass Spectrometry
ANACHEM
The Coblentz Society
Council for Near Infrared Spectroscopy
The Infrared and Raman Discussion Group
International Society of Automation-Analysis Division
The North American Society for Laser-Induced Breakdown Spectroscopy
Royal Society of Chemistry Analytical Division
Society for Applied Spectroscopy
The Spectroscopical Society of Japan

SciX 2013 is the 40th Annual North American Meeting of FACSS
and the National Meeting
for the Society for Applied Spectroscopy
and the North American Society for Laser-Induced Breakdown Spectroscopy

---

2013 SciX Conference Chair Persons

General Chair	**Fred LaPlant**, *3M* Email: flaplant@mmm.com
Program Chair	**Mike George**, *University of Nottingham* Email: mike.george@nottingham.ac.uk
Exhibit Chair	**Mike Carrabba**, *The Hach Company* Email: mcarrabba@hach.com
Local Chair	**Ryan Schmeling**, *University of Wisconsin – Milwaukee*
Workshop Chair	**Heather Brooke**, *Merck & Co.*
Marketing Chair	**Mark Hayes**, *Arizona State University*
Advertising	**Rebecca Airmet**
Social Media Chair	**Chad Atkins**, *University of British Columbia*
Employment Center	**Kevin Yeh**, *University of Illinois*

2013 Program Section Chairs

Atomic Spectroscopy	**Carsten Engelhard**, *University of Siegen* and **Gerardo Gamez**, *Texas Tech University*
Awards	**Jose Almirall**, *Florida International University*
Biomedical and Bioanalytical	**Michael D. Morris** and **Francis Esmonde-White**, *University of Michigan*
Chemometrics	**Jeremy Shaver**, *Eigenvector Research, Inc.*
Chromatography	**Gregory Webster**, *AbbVie*
Electrophoresis	**Edgar Goluch**, *Northeastern University* and **Alexandra Ros**, *Arizona State University*
Laser-Induced Breakdown Spectroscopy	**Steve Buckley**, *TSI, Inc.*
Mass Spectrometry	**Rachel Loo**, *UCLA*
Molecular Spectroscopy	**Linda Kidder**, *Malvern Instruments*
Nanotechnology	**Wei Zhao**, *University of Arkansas*
Pharmaceutical Analysis	**John Wasylyk,** *Bristol-Myers Squibb*
Process Analytical Technology	**James Rydzak**, *GlaxoSmithKline*
Raman	**Duncan Graham**, *University of Strathclyde*; **Ian R. Lewis**, *Kaiser Optical Systems*; and **Pavel Matousek**, *Rutherford Appleton Laboratory*
Security and Forensics	**Greg Klunder**, *Lawrence Livermore National Laboratory*
Surface Science	**Anna Belu**, *Medtronic*
Surface Plasmon Resonance	**Jean-Francois Masson**, *Université de Montreal*

2013 FACSS Executive Committee

Governing Board Chair	**Ian R. Lewis**, *Kaiser Optical Systems, Inc.* Email: irlewis@kosi.com
Governing Board Chair Elect	**Greg Klunder**, *LLNL – Forensic Science Center*
Past Governing Board Chair	**S. Douglass Gilman**, *Louisiana State University*
Second Past Governing Board Chair	**Becky Dittmar**, *3M*
Secretary	**Christopher Palmer**, *University of Montana*
Treasurer	**Mark Druy**, *Physical Sciences, Inc.*

SciX CHAIRS

GENERAL CHAIR, SciX

Fred LaPlant

3M

Fred LaPlant received his B.S. in Chemistry from San Diego State University, and his Ph.D. in Analytical Chemistry from Purdue. Fred's research focused on developing novel applications of Raman spectroscopy and microscopy, including fiber-based sensors, detection of subsurface materials, and high-pressure high-shear modeling of fluids. Fred spent five years in product development at Perceptron in Ann Arbor, Michigan, a developer of process control and monitoring devices for the auto industry. His principle contribution was the development of a non-contact, laser-based ultrasound system to measure wet paint film thickness on the automobile assembly line in real time. He then moved into Analytical Research and Development at the Pfizer Ann Arbor site, where he applied his process monitoring experience to PAT, as well as promoting the use of spectroscopic tools in pharmaceutical development, including solid dosage form imagine, polymorph detection and quantitation, and materials characterization. He is currently part of the 3M Corporate Research Analytical Laboratory in Saint Paul, Minnesota. After 5 years as the spectroscopy group leader, overseeing numerous projects and technology initiatives, he switched to technical management and currently has responsibility for the mass spectrometry, separations, surface science (TOF-SIMS and XPS), SEM, and Microbiology groups. In addition, he is also the analytical liaison for nanotechnology EHS. Fred has been active in various capacities in the Society for Applied Spectroscopy, including national president of the SAS in 2010, and is the current General Chair for the 2013 SciX conference organized by the Federation of Analytical Chemistry and Spectroscopy Societies.

PROGRAM CHAIR, SciX

Mike George

University of Nottingham

Mike George received a PhD from the University of Nottingham under the supervision of Professor Martyn Poliakoff FRS and remained at Nottingham for 18 months where he began a very fruitful collaboration with Professor Jim Turner FRS in the area of using fast infrared spectroscopy for monitoring electron transfer in inorganic excited states. Fast infrared spectroscopy has continued to be a central feature of his research. He was awarded a Royal Society/STA of Japan postdoctoral fellowship to probe organic excited states with Professor Hiro-o Hamaguchi. He returned to Nottingham as an experimental officer (1993) and was promoted to research officer (1996), lecture (1998), reader (2001) and professor (2003).

Many of his research interests combine photochemistry, fast time-resolved infrared spectroscopy (TRIR) and instrument development particularly focused at elucidating inorganic, organic and biological reaction mechanisms. He is particularly interested in the coordination and reactivity of small molecules such as CO_2 and alkanes and noble gases including studies focusing on the factors affecting C-H activation. He is currently working in a consortium developing time-resolved X-ray measurements at the Research Complex at Harwell. He was involved in the development of two national facilities (PIRATE and ULTRA) at the Rutherford Appleton laboratory, Oxford and the latter facility is currently underpinning a range of ultrafast science in the UK. He also works in a range of other areas of analytical chemistry particularly combining using vibrational spectroscopic studies with supercritical fluids ranging from phase measurements associated with Carbon Capture and Storage (CSS) to new ways synthesizing antimalarial drugs for the developing world.

His work has been recognised by several awards including Royal Society of Chemistry Sir Edward Frankland Fellowship (2002/3); Corday-Morgan medal (2003), Photochemistry Award (2005) and Inorganic Reaction Mechanisms Award (2013) together with Horiba award (2005); Seaborg Lectureship UC Berkeley (2010) and the Craver award (2011) from The Coblentz Society. He was elected a Fellow of Society of Applied Spectroscopy in 2012 and he has severed on the committee of the Infrared and Raman Discussion Group (IRDG) since 1999.

SciX / FACSS CHAIRS

EXHIBITS CHAIR, SciX

Mike Carrabba

The Hach Company

Dr. Mike Carrabba joined the Hach Company in 2004 as the Director of Hach Homeland Security Air Systems and he is currently the Global Director of Open Innovation where he has the responsibility of finding and developing relationships for new and emerging technologies.

He received his B.S. in Chemistry (*magna cum laude*) from Salem State College in 1981 and his Ph.D. in Physical Chemistry from Tufts University in 1985. Dr. Carrabba's graduate work was conducted under the tutelage of Dr. Jonathan Kenny and focused on the utilization of laser-induced fluorescence to examine ultra-cooled gas phase molecules in a supersonic jet molecular beam. After graduate school, Dr. Carrabba joined EIC Laboratories where he eventually became Vice-President for the Spectroscopy Division. He conducted a variety of research programs, including photoelectrochemical etching of semiconductors, fiber optic chemical sensors and state-of-the-art Raman spectroscopy. During this time, he introduced the use of holographic filters for Raman spectroscopy and developed numerous types of field Raman instrumentation and techniques, several of which resulted in U.S. patents. After leaving EIC, he joined Chromex, Inc, a manufacturer of Raman spectroscopy systems, as Marketing Manager and was previously the OEM Division Manager at Jobin Yvon, Inc.

Dr. Carrabba has been very active in the Federation of Analytical Chemistry and Spectroscopy Societies (FACSS) over the years. He has served as Governing Board Chair (2002), Program Chair (2000), Program Section Chair for Raman (1992-1999, 2001), Chairperson of the Long Range Planning Committee (1999-2008) and as a member of the Governing Board. Since 2006 he has been serving as the FACSS/SciX Exhibits Chair.

In 2003 Dr. Carrabba received the Award of Merit and became a Fellow of ASTM for his 12 years of service as the Chairman of the ASTM Subcommittee on Raman Spectroscopy. In 2004 he received the FACSS Charles Mann Award for Applied Raman Spectroscopy and in 2007 he received the Williams-Wright Award for Industrial Vibrational Spectroscopy. He has also been honored with the Distinguished Service Awards from FACSS in 2009 and from the Society for Applied Spectroscopy (SAS) in 2011. In 2012, Dr. Carrabba was named a Fellow of the Society for Applied Spectroscopy (SAS). Dr. Carrabba is also member of the Coblentz Society.

GOVERNING BOARD CHAIR, FACSS

Ian R. Lewis

Kaiser Optical Systems

Ian R. Lewis was born in 1968, Somerset, UK. He obtained his undergraduate degree in Chemistry and Chemical Technology at the University of Bradford in 1989 and his Ph.D. in 1992 in the field of infrared and Raman spectroscopic characterization of polydienes in the IRC in Polymer Science and Technology under the joint direction of IRC associate director Professor Anthony Johnson and Professor Howell Edwards. Following his appointment as an Honorary Visiting Researcher to the IRC, he went to the University of Idaho in 1993 to work as a postdoc in Professor Peter Griffiths's lab. During this time he also acted as a consultant on the application of Raman spectroscopy to several industrial companies. In 1996 he joined Kaiser Optical Systems as a Laser Spectroscopy Specialist and is currently global Marketing Manager. In this later role, Ian has been able to collaborate with a number of laboratories and process scientists around the world on a variety of different projects. These collaborations have been extremely valuable and rewarding.

He has been an active participant in past-FACSS & SciX conferences as the Raman section chair in 2000, and from 2002 to the present, program chair for the Memphis meeting in 2007, and is current serving as the FACSS Governing Board Chair for 2012 and 2013. He has organized scientific sessions at several additional conferences including EAS and Pittcon, and participated as a program committee member for meetings including, ICORS (2010), and ICAVS (2011). He is the Chair of ASTM subcommittee E13.08 on Raman Spectroscopy (2002 to present), served as the secretary of E13.10 on Molecular Optic Imaging (2001-2003), and was the co-liaison from E13 to E55. From 2004 through 2008 he served on the Board of Managers of the Coblentz Society and from March 2009 to March 2011, he served as the president of the Coblentz Society. He has been a member of SAS since 1992 when he joined as an international student, he was/is the president of the Detroit section in 2011 and 2013, was elected as a Fellow of SAS in 2011, and is also currently president-elect. He has published 47 scientific papers in refereed journals, has co-authored 7 book chapters, and is co-editor of Handbook of Raman Spectroscopy: From Research Laboratory to the Process Line (published in 2001). He currently serves on the editorial advisory board of Spectroscopy Magazine, and American Pharmaceutical Review. He is an active reviewer for a number of international journals and a member of several scientific societies including ANACHEM, ACS AD, Coblentz Society, IRDG, MacroGroup UK, RSC, and SAS. In 2008, he was presented with the FACSS Charles Mann Award for Analytical Raman Spectroscopy.

Ian has been married to Dr. Mary Lewis, also a vibrational spectroscopist, since 1994. Mary and Ian met at University of Idaho where they both worked in the Griffiths lab. They currently have nine children, 5 girls and 4 boys. The children's ability to contribute in a creative way to deadlines (and to create new deadlines) is always a source of interest to their parents. Ian would like to take this opportunity to thank his family, especially his wife, for their support and his mum Valerie for encouraging him to come to the US and seek new opportunities.

PROGRAM and CONFERENCE SPONSORS

SciX 2013 and FACSS greatly appreciate the support it receives from its sponsors.

GENERAL CONFERENCE SPONSOR

B&W Tek
Ocean Optics
Pfizer

ATOMIC SPECTROSCOPY

Agilent Technologies
Bruker Elemental
Elemental Scientific Glassblowing
Enwave Optronics
GBC Scientific Equipment
Glass Expansion
IonSense
LECO
Meinhard
Olympus NDT, Analytical Instruments
Royal Society of Chemistry

AWARDS

Advantest America

BIOMEDICAL/BIOANALYTICAL

EmVision
Innovative Photonic Solutions

CHEMOMETRICS

B&W Tek
Eigenvector Research
FOSS

CHROMATOGRAPHY

Agilent Technologies
JASCO
Oxford University Press
Polymer Standards Service
Tosoh Bioscience

INFRARED/NEAR INFRARED SPECTROSCOPY

Advantest America
Anasys Instruments
Council for Near Infrared Spectroscopy
Infrared Associates
Kerith Foundation
LaserVision
Shimadzu Scientific Instruments
UpTek Solutions

LASER INDUCED BREAKDOWN SPECTROSCOPY

Applied Spectra
High Purity Standards
Laser Distance Spectrometry
TSI Incorporated

MASS SPECTROMETRY

Bruker Daltonics
Thermo Scientific
Waters

NANOTECHNOLOGY

Johnson Controls
Sigma-Aldrich

PHARMACEUTICAL

Optimal

PROCESS

Bruker Optics
Mettler Toledo

RAMAN

Analyst / RSC Publishing
Analytical Methods / RSC Publishing
HORIBA Scientific
Kaiser Optical Systems
Pfizer
Renishaw
Spectroscopy Magazine/Advanstar
Thermo Scientific
Wiley-Blackwell

SECURITY AND FORENSICS

1ST Detect
CRAIC Technologies
IonSense
Shimadzu Scientific Instruments
University of North Texas

STUDENT SPONSORS

Mike and Mary Carrabba
Meinhard Glass Products
Society for Applid Spectroscopy

SURFACE SCIENCE

Medtronic

SCIX 2013 AND FACSS THANKS ITS MEMBER ORGANIZATION FOR THEIR FINANCIAL SUPPORT

ACS, Analytical Division
AES Electrophoresis Society
American Society of for Mass Spectrometry
ANACHEM
The Coblentz Society
Council for Near Infrared Spectroscopy
The Infrared and Raman Discussion Group
International Society of Automation – Analysis Division
North American Society for Laser-Induced Breakdown Spectroscopy
Royal Society of Chemistry Analytical Division
Society for Applied Spectroscopy
The Spectroscopical Society of Japan

FACSS AWARDS

DISTINGUISHED SERVICE AWARDS

Awarded to an individual(s) for recognition of exceptional, long-term service to the FACSS organization. The 2013 recipients have served with excellence in many different capacities and contributed to the continuing success of FACSS through consistent dedication and sacrifice.

Awards will be presented Thursday, 3:50 pm, *Room 102C*

Mark A Hayes

Arizona State University

Dr. Mark A. Hayes holds an Associate Professorship in the Department of Chemistry and Biochemistry at Arizona State University, where he serves as an active researcher, mentor, teacher and colleague. His academic career has produced significant results across several disciplines within the analytical and physical chemistry community that includes aspects of engineering, physics, biology and medicine. While contributing to the knowledge base, Mark has energetically and creatively supported the wider profession at local, regional, national and international levels. He initially worked in private industry at a 'mom & pop' analytical laboratory and at J&W Scientific capillary gas chromatography column manufacturer (now part of Agilent) after earning his undergraduate degree at Humboldt State University (California). He then entered graduate school at Penn State University and studied under Professor Andrew G. Ewing, developing electroosmotic flow control mechanisms by an applied orthogonal field to refine the separations in small diameter capillaries and helped develop a time-of-flight mass spectrometer aimed at improving sensitivity allowing compatibility to other electrochemical and fluorescent measurements being performed on neurochemical systems. Postdoctoral studies were with Dr. Werner Kuhr at the University of California, Riverside focused on attaching enzymes directly to electrochemical probes to transduce non-electroactive targets to species which can be sensed via electron transfer. Dr. Hayes has contributed to several different research areas, ranging from creating bionanotubules from liposomes with electric fields to establishing a framework for vastly improved microscale array-based separations in more than seventy publications and book chapters. He has served on review panels for NIH, NSF, DOE, RSC, NAS, DOJ, GRE, DARPA, private industry, local (Mayo Clinic), and Romanian & Czech scientific and contributed peer review efforts to twenty-five journals, including Analytical Chemistry, The Journal of the American Chemical Society, Nature, Langmuir and The Royal Society. He was recently elected President (starting in 2014) of AES Electrophoresis Society. He has mentored fifty undergraduate and graduate students, producing fourteen doctorates while supporting them with research funds and prestigious fellowships (NSF, Kirkbright, ACS, Fulbright, FLAS and local awards). Federation of Analytical Chemistry and Spectroscopy Societies (FACSS) has been a valuable vehicle for him to serve the larger community as Program Chair (2003), Governing Board Chair (2005), Long Range Planning Chair (2009-2010) and Marketing Chair (2009-2013), along with presenting research talks, organizing sessions, and serving as section chair numerous times. He was instrumental in altering the management structure, changing the name of the North American meeting to SciX Conference, establishing a new development culture, and recruiting the AES Electrophoresis Society to join FACSS

Cynthia M. Lilly

Scientific Association Management

Cindi Lilly has been a conference planner at Scientific Association Management in Santa Fe, New Mexico for twenty-one years, since 1992. She has managed conferences for the Federation of Analytical Chemistry and Spectroscopy Societies since their 1997 conference in Providence, Rhode Island, working with a host of volunteer board members. Cindi's FACSS conference sites have included Austin, Detroit, Kansas City, Memphis, Orlando, Portland OR, Reno, Quebec City, Vancouver, and other sites throughout North America. Her work for FACSS includes association management, conference program planning and administration, board and delegate liaison, and other services. Cindi grew up in eastern Pennsylvania and holds a B.A. from Boston University. Relocating from New Hampshire to Santa Fe in 1992, Cindi is the mother of three daughters, one granddaughter, and another granddaughter due in August 2013. Her activities in Santa Fe include service with CASA (Court Appointed Special Advocate) for abused children and the Cancer Foundation for New Mexico.

PREVIOUS AWARDEES

1993	Edward Brame and Syd Fleming
1994	L. Felix Schneider
2001	David Coleman
2003	Jeanette Grasselli Brown
2009	Paul Bourassa and Mike Carrabba
2010	Scott McGeorge and Alexander Scheeline
2011	Jon W. Carnahan and Patricia B. Coleman
2012	Bruce Chase and O. Karmie Galle

FACSS AWARDS

The FACSS Student and the Tomas Hirschfeld Scholar Awards recognize outstanding contributions by individual who are Ph.D and M.Sc candidates.

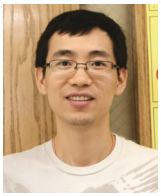
FACSS STUDENT AWARD

Larry R. Gibson II
University of Notre Dame

Oral Presentation: Monday, 3:50 pm, 103D

Larry Gibson received his B.S. in Chemical and Biomolecular Engineering from Johns Hopkins University in 2009. While at Hopkins, he worked as a research assistant under the direction of Dr. Richard Cone (Department of Biophysics) and Dr. Justin Hanes (Department of Chemical and Biomolecular Engineering), where his focus was on the development of drug delivery mechanisms to eradicate infectious STD pathogens. Presently, Larry is a Chemical and Biomolecular Engineering Ph.D. Candidate in Dr. Paul Bohn's group at the University of Notre Dame. His dissertation work targets the development of low-cost, hybrid microfluidic/nanofluidic devices for point-of-care medical diagnostics. Recently, Larry invented a robust method to swiftly screen patient biofluids for lipid biomarkers linked to debilitating neuroinflammatory and neurodegenerative diseases using non-aqueous microchip electrophoresis. His research interests include chromatographic and electrophoretic chemical separations coupled to spectroscopic and mass spectrometric detection, rapid prototyping, and finite element modeling. In addition to the 2013 Federation of Analytical Chemistry and Spectroscopy Societies Student Award, he has also achieved a Professional Development Award from the Graduate School at the University of Notre Dame. Larry has authored/coauthored 6 peer-reviewed publications to date.

TOMAS HIRSCHFELD SCHOLAR AWARDS



Bai Nie
Michigan State University

Oral Presentation: Monday, 4:30 pm, 103D

Bai Nie is a graduate student in the Physics Department of Michigan State University, working with Professor Marcos Dantus. Previously, he obtained his Bachelor and Master of Science in Physics from Nanjing University in China. His current research focuses on the development of novel ultrafast fiber lasers, pushing the limits of pulse duration and pulse energy of fiber oscillators. One of his works, which demonstrated the highest peak power generated from a simple Yb doped fiber oscillator, was featured as one of the most significant publications by 'Optics and Photonics News' in 2012. Beyond the fundamental laser research, he is also interested in and successfully demonstrated some applications using fiber lasers, such as multiphoton microscopy of living tissue and laser-induced breakdown spectroscopy. His work showed the great potential of ultrafast fiber lasers in practical applications. He has co-authored 12 peer reviewed papers and filed 1 patent. He also founded the Optical Society of America – Michigan State University student chapter and served as the president for the past two years.

Gloria Sheynkman
University of Wisconsin-Madison

Oral Presentation: Monday 4:10 pm, 103D

Gloria Sheynkman (formerly Kreitinger) graduated from the University of Notre Dame in June 2006 with a B.S. in Biochemistry. During her time at Notre Dame, she did undergraduate research in the laboratories of Dr. Mayland Chang and Dr. Shariar Mobashery, where she helped develop MS-based bioanalytical methods for the characterization of drug metabolites. During the year after graduation, she was an Americorp volunteer in San Francisco. Starting in 2007, she worked as a research associate at Gilead Sciences within Analytical Development, where she gained experience with a variety of analytical instrumentation while supporting the development of antiretroviral drug candidates. In 2009, these experiences led her to pursue an Analytical Chemistry PhD at the University of Wisconsin-Madison, where she was selected as a predoctoral fellow in the Genomic Sciences Training Program. She is currently working with Professor Lloyd M. Smith, who has driven the development of many technologies, including DNA sequencing. Her research project is at the interface of genomics and proteomics, where she is integrating next generation sequencing and mass spectrometry technologies for the improved characterization of sample-specific protein variations. Her most recent work describing the discovery of novel splice-junction peptides was just published in *Molecular & Cellular Proteomics*.

FACSS AWARDS

FACSS STUDENT AND TOMAS HIRSCHFELD SCHOLAR AWARDS – Call for Applications for 2014

The Tomas Hirschfeld Scholar and the FACSS Student Awards recognize the most outstanding papers submitted to FACSS by a graduate student. Recipients will receive financial support to help them attend the SciX 2014 conference in Reno, NV (September 28 – October 3). In 2013 one FACSS Student Award and two Tomas Hirschfeld Scholars are being presented. In order to have your presentation considered for a Tomas Hirschfeld Scholar Award or FACSS Student Award, students should submit their abstract using the SciX website submission form and indicate on the dropdown menu on the form their interest in these awards.

The submission process involves submitting an abstract, completing the website submission form, and submitting the following electronically to facss@facss.org

a) the form, available on the SciX website
b) a 250 word abstract of the work to be reported
c) two letters of nomination, one by the student's mentor. An explanation of the inventive contributions by the student to the work should be given. Creativity was a primary characteristic of Tomas's work, and thus should be a characteristic of the awardee
d) a copy of the candidates resumé
e) a copy of the candidate's graduate transcript
f) Copies of reprints and/or preprints of research accomplished.

The recipients will be included in either a session highlighting young scientists and their work or in an appropriate topic area. The SciX website will begin accepting abstracts and applications for FACSS student awards in January 2014. Go to www.scixconference.org to submit an application.

FACSS INNOVATION AWARD

The FACSS Innovation Award will be given for the most innovative and outstanding new research advancements debuted orally at the SciX Conference. All program areas are included. Only research finding presented for the first time in the public domain qualify for entry (work based on submitted papers not yet published electronically or in print at the time of abstract submission qualifies). Papers submitted for SciX will be considered for these awards – authors can check the appropriate box for their papers to be entered. Finalists will be selected for presentations at the SciX conference in special award sessions. Award winners will be selected after the award sessions are concluded. Each award includes: A cash prize of $1,500; a plaque; and publicity.

2012 INNOVATION AWARD WINNER:

Rohit Bhargava, *University of Illinois, Beckman Institute for Advanced Science and Technology*

Advancing Infrared Microscopy Instrumentation by Theory and Computation; Rohit Bhargava, P. Scott Carney, Rohith Reddy, Kevin Yeh, Thomas van Dijk, Matthew Gelber, Matthew V. Schulmerich; Univeristy of Illinois, Beckman Institute for Advanced Science and Technology

2013 FACSS INNOVATION AWARD FINALISTS

Thursday Afternoon 3:50 – 5:30 pm, *Room 201C*

Organizer: Jose Almirall: Presider: Michael George

The winner of the 2013 Innovation Award will be announced at the Friday morning session.

3:50 (762) **Imaging Quantum Effects in Biological Systems**; Gregory S. Engel[1]; [1]The University of Chicago

4:10 (763) **Ultra-compact LIBS Systems: Utilizing Microchip Laser Engines to Enable New Applications and Markets for LIBS**; Jason Eichenholz[1], Scott Buchter[2]; [1]Open Photonics Inc., [2]Lasersec

4:30 (764) **Biometrics from the Stable Isotope Analysis of Amino Acids in Human Hair**; Glen Jackson[1,2], Yan An[3], Kateryna Konstantynova[2]; [1]Forensic & Investigatice Science, WVU, [2]C. Eugene Bennett Department of Chemistry, WVU, [3]Department of Chemistry and Biochemistry, Ohio University

4:50 (765) **Portable Spectrometry: Making Good Use of CMOS Detectors**; Alexander Scheeline[1], Thu Anh Bui[1, 2]; [1]SpectroClick Inc., [2]Vietnam National University Hanoi

5:10 (766) **2D FT Electronic Spectroscopy of Quantum Dots in the Short-Wave Infrared**; David Jonas[1], Samuel Park[1], Dmitry Baranov[1], Byungmoon Cho[1]; [1]University of Colorado at Boulder

FACSS CHARLES MANN AWARD

For Achievements in the Field of Applied Raman Spectroscopy

VOLKER DECKERT

Institute of Physical Chemistry and the Institute of Photonic Technology, University of Jena

Presentation: Tuesday, 8:30 am

Ballroom A, Wisconsin Center

Volker Deckert holds a joint position at the Institute of Physical Chemistry, University of Jena, Germany and the Institute of Photonic Technology also in Jena. He obtained his Diploma and Ph.D. degree from the University of Würzburg, working on instrumental developments for Raman spectroscopy. As a post-doc he worked on non-linear and time-resolved laser spectroscopy at the University of Tokyo and KAST, in Kawasaki. During his habilitation at the ETH Zurich, he came into contact with near-field optical techniques and was among the first to combine this high spatial resolution technique with Raman spectroscopy. A major breakthrough was the development of tip-enhanced Raman spectroscopy (TERS), a combination of scanning probe microscopy with plasmonic probes. This technique brings together the sensitivity of surface enhanced Raman scattering and the high lateral resolution of near-field optics consequently provides a tool to investigate phenomena much beyond the diffraction limit of conventional optics. Since then his goal is to push the lateral resolution of Raman spectroscopy into smaller and smaller dimensions. In particular his interest is to apply the resolution capabilities of TERS towards nanoscale studies of bio molecules and recently to the investigation of fundamental dynamic processes of surface reactions.

SOCIETY FOR APPLIED SPECTROSCOPY AWARDS

DISTINGUISHED SERVICE AWARD

Recognizing members for their long-time service to the Society.

Bruce Chase

University of Delaware

Bruce Chase received his B. A. from Williams College in 1970 and his Ph.D. in physical chemistry from Princeton University in 1975, where he worked with Professor Donald S. McClure on studies of charge transfer excitation of transition metal ions in alkali fluorides. He then joined E. I. DuPont de Nemours as a research chemist in the Spectroscopy Division of the Central Research Department. He retired from DuPont in 2009 as a DuPont Fellow and Chair of the DuPont Fellows Forum. He is now a Research Professor in the Department of Materials Science and Engineering at the University of Delaware and the Chief Technical Officer of Pair Technologies, LLC. Dr. Chase's primary area of research is in vibrational spectroscopy, FT-IR and Raman techniques, and applications to industrial analytical problems. In collaboration with Dr. Tomas Hirschfeld (deceased) he developed an FT-Raman spectrometer which demonstrated the utility of near infrared excitation. Recent efforts include the development and utilization of polarized Raman scattering for the determination of orientation in fibers. Parallel work has involved developing multichannel detection instrumentation for the near infrared. In collaboration with Professor John Rabolt at the University of Delaware he has developed an approach to infrared spectroscopy based on focal plane area detectors. He was the 1989 winner of the Williams-Wright award and the 1990 EAS New York Section Gold Medal awardee. He also received the 1991 Delaware Valley ACS Section Award. He received the 1994 SSP Award from the Spectroscopy Society of Pittsburgh and is co-winner of the 1994 Bunsen-Kirchhoff Prize from the German Chemical Society. He received the 1998 Bomem-Michelson Award in March of 1998, and received the ACS Analytical Division Award in Spectrochemical Analysis in November 1999. In 2002 he received the Anachem Award and in 2005 the EAS Award for Analytical Chemistry. In 2007 he was recognized with the Hasler Award. In 2013 he received along with Professor John Rabolt, the MRS Innovation in Materials Science Award.

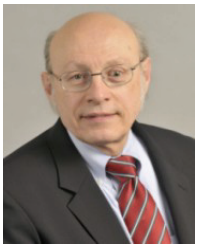
SOCIETY FOR APPLIED SPECTROSCOPY AWARDS

HONORARY MEMBERSHIP AWARD

Recognizing those individuals who have made exceptional contributions to spectroscopy.

Isao Noda
University of Delaware

Isao Noda was born in Tokyo, Japan. He came to the United States in 1969 and was graduated from Columbia University in the City of New York in 1974 with B.S. degree in chemical engineering. He also received his M.S. in bioengineering (1976), as well as M.Phil. (1978) and Ph.D. (1979) in chemical engineering from Columbia. In 1997 he received D.Sc. degree in chemistry from the University of Tokyo. After retiring from the Procter and Gamble Company in 2012, he became an Adjunct Professor at the Department of Materials Science and Engineering, University of Delaware. His research interest is in the broad area of polymer science and spectroscopy. He is known for the development of two-dimensional infrared (2D IR) correlation spectroscopy. He has also been actively involved in the research and development of a novel class of bio-based biodegradable plastics. He is a recipient of the 1991 William F. Meggers Award from the Society for Applied Spectroscopy and the 2002 Williams-Wright Award from the Coblentz Society. In 2002, he was appointed to the position of Honorary Adjunct Professor of the Department of Biological Science and Biotechnology at Tsinghua University in Beijing, China. He was selected as the 2005 Chemist of the Year by the Cincinnati Section of the American Chemical Society. He received the International Academic Cooperation and Exchange Medal in 2008 from the Chinese Chemical Society and Chinese Optical Society, New York State Society for Applied Spectroscopy's Gold Medal in 2009, the 2011 Bomem-Mechelson Award from the Coblentz Society, and the 2011 Ellis R. Lippincott Award jointly from the Optical Society of America, the Society for Applied Spectroscopy and the Coblentz Society. He became a Fellow of the Society for Applied Spectroscopy in 2011 and a Fellow of the Optical Society of America in 2012.



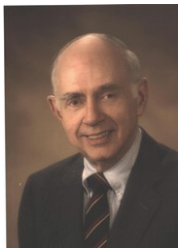
Richard P. Van Duyne
Northwestern University

Richard P. Van Duyne is the Charles E. and Emma H. Morrison Professor of Chemistry at Northwestern University. He discovered surface-enhanced Raman spectroscopy (SERS), invented nanosphere lithography (NSL), and developed ultrasensitive nanosensors based on localized surface plasmon resonance (LSPR) spectroscopy. His research interests include all forms of surface-enhanced spectroscopy, plasmonics, nanoscale biosensors, atomic layer deposition (ALD), atomic force microscopy (AFM), scanning tunneling microscopy (STM), ultra-high vacuum (UHV) STM, UHV-tip-enhanced Raman spectroscopy (UHV-TERS), and surface-enhanced femtosecond stimulated Raman spectroscopy (SE-FSRS). Professor Van Duyne has been recognized for his accomplishments with the Sir George Stokes Award from the Royal Society of Chemistry (2013), the Charles N. Reilley Award, Society for Electroanalytical Chemistry (2011), Election to the US National Academy of Sciences (2010), Analytical Chemistry Award, American Chemical Society, (2010), Bomem-Michelson Award, Coblentz Society (2010), Ellis R. Lippincott Award, Optical Society of America (2008), L'Oreal Art and Science of Color Prize (2006), Nobel Laureate Signature Award for Graduate Education, American Chemical Society (2005), Election to the American Academy of Arts and Sciences (2004), The Earle K. Plyler Prize for Molecular Spectroscopy, American Physical Society (2004), Excellence in Surface Science Award of the Surfaces in Biomaterials Foundation (1996), Pittsburgh Spectroscopy Award (1991), National Fresenius Award, American Chemical Society (1981), and the Coblentz Memorial Prize in Molecular Spectroscopy (1980). He is also a fellow of both the American Physical Society (1985) and the American Association for the Advancement of Science (1983). Van Duyne received his B.S. degree from Rensselaer Polytechnic Institute (1967) and a PhD. degree in analytical chemistry from the University of North Carolina (1971).

SOCIETY FOR APPLIED SPECTROSCOPY AWARDS

EMERITUS MEMBERSHIP AWARD

Recognizing those individuals who have who have contributed to spectroscopy and have been members of the Society for Applied Spectroscopy for 15 years, and now have retired from active scientific endeavor.

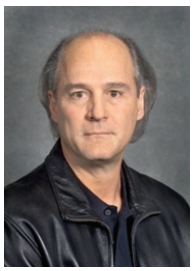


David M. Hercules

David M. Hercules was graduated from Juniata College with a B.S. in Chemistry and received a Ph.D. from MIT. His thesis research was performed under the direction of Prof. L. B. (Buck) Rogers; he received his basic education in spectroscopy from Prof. R. C. Lord. He has served on the faculties of Lehigh University, Juniata College, MIT, University of Georgia, University of Pittsburgh and Vanderbilt University. He was chairman of two major chemistry departments (ca. 9 years each) - Pittsburgh and Vanderbilt. He retired (officially) from Vanderbilt in 2007 as Centennial Professor Emeritus. His research over the years has been a random-walk through analytical spectroscopy. He began scientific life studying photoluminescence and contributed significantly to the broad adaptation of fluorescence methods. This expanded into studies involving electroluminescence, chemiluminescence and organic photochemistry. He was the first person to report the phenomenon of electrochemically generated chemiluminescence. He became interested in x-ray photoelectron spectroscopy (XPS) and, with the help of Prof. Kai Siegbahn, established one of the first XPS laboratories in the USA. He focused on the effectiveness of XPS for quantitative analysis and its application to studying heterogeneous catalysts. This led to a broader interest in surface analysis with focus on solution of real-world surface problems by using a combination of spectroscopic techniques. All of this led him to the application of secondary-ion mass spectrometry (SIMS) to the study of polymers; in collaboration with Prof. A. Benninghoven his lab did the first comprehensive correlations between polymer structure and their mass spectra. His current research involves the use of matrix-assisted laser desorption/ionization (MALDI) and electrospray mass spectrometry, coupled with ion mobility spectrometry, for studying synthetic polymers, particularly those that are complex and/or intractable. He has published over 500 scientific papers in peer-reviewed journals. Prof. Hercules has received a dozen national and international awards for his research, the first of which was the *Lester Strock Medal* from SAS. He has served on the advisory boards for a number of scientific journals, including *Applied Spectroscopy*. He has been mentor to more than 150 graduate students and postdoctoral research fellows. He has served on the Governing Board for the Council of Chemical Research, the Joint Board-Council Committee of Science for ACS, and as a member of the Chemistry Advisory Committee for the National Science Foundation. He was Chairman of Gordon Conferences on Analytical Chemistry and Photoelectron Spectroscopy. He was a member of the Executive Committee of the International Association of Environmental Analytical Chemists. While in Pittsburgh he was a member of the Pittsburgh Conference Committee. He currently serves as the Vanderbilt representative to the State of Tennessee EPSCoR Committee.

LESTER W. STROCK AWARD

Established by the SAS New England section to recognize an author(s) of an outstanding paper or series of papers.



Richard Russo

Lawrence Berkeley National Laboratory

Presentation: Wednesday, 8:30 am, Ballroom A

Russo is the founder and scientific director of the laser spectroscopy and materials group at the Lawrence Berkeley National Laboratory. His group pioneered the understanding and development of nanosecond and femtosecond pulsed laser ablation for chemical analysis with a 30 year contribution to fundamental and applied research. He is co-inventor of the nanowire laser and developer of a real-time standoff laser ultrasonic sensor (R&D100 2006). He also is co- inventor of a process for nano-texturing (ITEX process) thin-films, lead-inventor of the ion- assisted pulsed laser deposition (IBAD) process. Most recently, his Berkeley research group with the assistance of Applied Spectra staff demonstrated and patented the use of laser plasmas for real-time measurement of isotopes. The new technology named LAMIS (Laser Ablation Molecular Isotopic Spectroscopy) won a 2012 R&D100 Award, FACSS/SCiX Innovation Award and Spectrochimica Acta paper of the year for 2012. Russo has over 240 Scientific Publications; 45 Refereed Proceedings; 310 (215 Invited) Presentations, 9 Book Chapters and 18 Patents. Fourteen students received their PhD degree under his direction at the University of California Berkeley, as well as mentor to numerous PhD students from International Universities. Dr. Russo also is founder and president of Applied Spectra, Inc. (ASI). Russo founded ASI with the assistance of several of his PhD students from Berkeley. Together, they are world experts in laser ablation chemical analysis using LIBS and Laser Ablation with ICP-OES and ICP-MS. Company core expertise is research, development and manufacture of laser ablation chemical analysis instrumentation. ASI LIBS and Laser Ablation instruments are utilized in national and international markets, including academia, national laboratories, industry, energy, environmental and security applications. The company continues to advance laser ablation chemical analysis based on an expert in-house research team that provides superior analytical instrumentation and applications (methods) development.

SOCIETY FOR APPLIED SPECTROSCOPY AWARDS

BARBARA STULL GRADUATE STUDENT AWARD

Recognizing a graduate student for outstanding research in spectroscopy and presented in honor of our longtime colleague Barbara L. Stull

Andrew J. Schwartz
Indiana University
Presentation: Monday, 5:10 pm, 103D

Andrew (Andy) Schwartz hails from Adams County in northern Indiana. In 2010, Andy earned his B.S. degree in Chemistry with a minor in Physics from Huntington University. While attending Huntington University, Andy was actively involved in the chemistry department serving as the department's head laboratory assistant and chemical stockroom manager from January 2007 to May 2010. In addition to working in the department, Andy was also involved in a variety of chemical research projects at Huntington University. Two of the projects were performed under Dr. Ruth Nalliah, which involved fundamental studies of the effects of solvents on CdSe quantum dots and nickel porphyrins. Additionally, in collaboration with Dr. David Bell of the IU School of Medicine, Andy assisted in a research project that investigated the stability of varied anthocyanin molecules in artery ring media. Andy began his graduate studies at Indiana University in the fall of 2010, choosing to work under Prof. Gary Hieftje. In the Hieftje Lab he began work on further development, characterization, and application of a novel source for atomic spectrometry, the atmospheric-pressure solution-cathode glow discharge. Since beginning at the Hieftje lab, Andy has presented his work at the SciX conference in 2012, authored three publications, and was awarded the Robert & Marjorie Mann Fellowship for his research contributions. Andy has also served as an associate instructor for the chemistry department, which included assisting in teaching several undergraduate lab courses and one graduate course—Spectrochemical Methods of Analysis. Finally, in his free time, Andy enjoys drawing, hiking, reading, listening to music and playing the occasional video game.

Marie Richard-Lacroix
University of Montreal
Presentation: Monday, 4:50 pm, 103D

Marie Richard-Lacroix is currently a Ph.D. candidate under the supervision of Prof. Christian Pellerin at the Department of Chemistry of the University of Montreal. She received her bachelor's degree in chemistry in 2011 from the University of Montreal. During her undergraduate studies, she worked in Prof. Pellerin's group on the formation and characterization of supramolecular polymer complexes with small molecules into electrospun nanofibers. For this work, she received the Undergraduate thesis award from the Macromolecular science and engineering division of the Canadian Society for Chemistry. As a graduate student, her main research interest focusses on the characterization of molecular orientation and structural aspects of electrospun nanofibers by confocal Raman spectroscopy. She was the first to demonstrate that quantitative information can be obtained on individual nanofibers. She also established a new, experimentally simplified method with improved accuracy for orientation quantification by Raman spectroscopy. Up to now, she has published 6 peer-reviewed papers, including 5 as a first author. She is also author or coauthor of over 20 contributions presented in national and international conferences. Among other awards and scholarships, she received Ph.D. scholarships from NSERC-Canada and FRQNT-Québec.

SOCIETY FOR APPLIED SPECTROSCOPY AWARDS

WILLIAM F. MEGGERS AWARD

Recognizing the author(s) of an outstanding paper appearing in Applied Spectroscopy

Presented for *"A New in Vivo Raman Probe for Enhanced Applicability to the Body"* Volume 66, Issue 8, (August 2012), pp. 882-891.

Paul Pudney

Presentation: Wednesday, 8:00 am, Ballroom A

Paul Pudney has a BSc in chemistry from Liverpool University and obtained a PhD in Physical Chemistry from the University of East Anglia 'Spectroscopic studies of adsorbates on metal single crystal surfaces' under supervision of Prof Michael Chesters . After post doctoral studies at the Leverhulme Centre for Innovative Catalysis and the Interdisciplinary Research centre in Surface Science at Liverpool university he worked at the synchrotron at Daresbury before joining Unilever in 1994. Paul is now a science leader in vibrational spectroscopy at unilever discover. He has applied spectroscopy in a number of innovative ways to gain further understanding of both consumer products and their behaviour when they interact with our consumers. Examples include quantifying the complex microstructures of soft solid materials by confocal Raman spectroscopy such as foods and behaviour of molecules in ice using IR. He helped develop a novel in-situ Triboligical Raman instrument to help understand lubrication in a Soft Elasto-Hydrodynamic Contact. He has developed *in-vivo* Raman spectroscopic capability to measure and understand the delivery of actives to and their effect on the body, such as to the skin, scalp, axilla and oral mucosa. He has over 50 peer reviewed publications. He was nominated as one of the 'Prominent Young Vibrational Spectroscopists' in special addition of Vibrational Spectroscopy journal. He was runner up in the Meggers award in 2012.

Eleanor Bonnist studied chemistry at Imperial College London and received her PhD at Edinburgh University in the Anita Jones group working with fluorescence spectroscopy. She joined Unilever R&D Colworth Laboratory in 2008 and works with Raman spectroscopy to investigate how FMCG products interact with consumers.

Peter Caspers studied applied physics at the University of Twente. From 1997-2003 he did his Ph.D. research at the Erasmus MC in Rotterdam, the Netherlands, where he pioneered the technology and application of *in vivo* characterization of human skin based on confocal Raman microspectroscopy. From 2003-2012 he shared the university affiliation with River Diagnostics where he contributed to making the technology of Raman skin analysis commercially available. Currently he works for both the Erasmus MC and RiverD International to continue his work on research, development, and commercialization of biomedical applications of Raman spectroscopy.

Dr **Jean-Philippe Gorce** obtained his PhD in 2000 from Sheffield Hallam University (UK). His doctoral research was focused on the study of the crystallisation of n-alkane chains by vibrational spectroscopy. Dr JP Gorce joined the University of Surrey (UK) later that year as an ICI Research Fellow examining water filled microstructures in a range of materials (skin, cement, wood and coatings) using magnetic resonance imaging. In 2003, he joined the University of Sheffield (UK) as a Post-Doctoral Research Associate applying magnetic resonance relaxometry to the study of cement matrices used for the encapsulation of nuclear wastes. In 2006, Dr JP Gorce joined the Measurement Science unit of Unilever (Colworth Laboratory, UK) where, under the supervision of Dr Paul Pudney, he examined the diffusion of key chemicals into the human skin in-vivo. Since 2007, he has been a Higher Scientist at the Health and Safety Laboratory, an agency of the Health and Safety Executive (UK) where he is developing measurement protocols based on x-ray fluorescence spectroscopy for the assessment of occupational exposure to hazardous substances.

Chris Marriott is a design and manufacturing engineer having worked at Unilever R&D Colworth U.K. for over 40 years. During this time he gained expertise in 3D CAD modelling, welding and adhesives and introduced CADCAM to the in-house manufacturing facility. Chris has been very fortunate to have worked on projects for many of Unilever's business interests including:- animal feeds, meat, fish, vegetables (fresh and frozen), oils and fats, ice cream, beverages, oral, hair, skin, cosmetics, sensors and background science. There have been many varied, interesting and challenging projects that have involved the design of process equipment through construction to commissioning in the U.K. Europe, America and West Africa. But probably the most enjoyable work has been to help talented scientists at Colworth achieve their desired aims through an accurate interpretation of their requirements and then to design and build working solutions that fulfils their requirements. The work has often been of a novel nature leading to many patents over the years. He has been author/ co-author of many papers during this time including the presentation of a paper entitled 'The influence of product liability on the selection of materials for the construction of machines in the food industry', at an international conference in London.

Gerwin Puppels, PhD has been active in the field of Raman spectroscopy for over 25 years. His PhD-thesis (1991) concerned the development of sensitive Raman technology for recording spectra to be recorded of single biological cells and chromosomes. Moving to the Erasmus Medical Center in Rotterdam, the Netherlands in 1994, he started a research group to explore medical applications of Raman spectroscopy ... and found these in nearly every medical field, resulting in over 100 peer-reviewed papers in both spectroscopic and medical journals. He founded River Diagnostics in 2003 (and later RiverD International) to further develop the most successful applications. To date an *in vivo* skin analyzer, and a system for bacterial strain typing have been commercialized.

Scott Singleton joined Unilever in 1989 following completion of my PhD at the University of Edinburgh. He has worked in both the foreground and background research areas across all of Unilever's six R&D sites. His current role is global, working across Unilever R&D, where he leads the strategic advanced measurement and data modeling activities.

SOCIETY FOR APPLIED SPECTROSCOPY AWARDS

WILLIAM FL. MEGGERS AWARD - continued

Recognizing the author(s) of an outstanding paper appearing in Applied Spectroscopy

Presented for *"A New in Vivo Raman Probe for Enhanced Applicability to the Body"* Volume 66, Issue 8, (August 2012), pp. 882-891.

Martin van der Wolf, M.Sc. finished his engineering studies at the Technical University of Delft in 1991, specializing in micro-mechanical engineering. He has 20 years experience as a professional engineer specializing in design and engineering of advanced opto-mechanical products. He carried out numerous projects while at ASM lithography, Spark-Holland BV, TNO-Industry and as a team leader and instrument developer in a specialized group at the University of Maastricht Medical School. There innovative optical instrumentation for commercial clients in medical technology applications as well as for research projects at the university was developed. He joined River Diagnostics in 2004 where he learned the ins and outs of Raman spectroscopy and is responsible for system engineering and production.

SAS FELLOWS AWARD

Recognizes individual members for their outstanding service to the field of spectroscopy.

Paul Bourassa has been a member of the Society for Applied Spectroscopy for over 40 years and is currently completing his second term as SAS Treasurer. He has previously served SAS in wide variety of roles at the local section level and nationally including; President of the Chicago Section in 1981 and twice as National Tour Speaker Chairman. Paul is a member of the Coblentz Society where he served as a delegate to FACSS for a number of years. Paul has served FACSS in many roles. In 2007 he was the General Chairman of the FACSS conference in Memphis. For the ten years (1996 – 2006) as the Treasurer of FACSS. In 1994 he served as Governing Board Chairman and in 1989 he served as the General Chairman for the FACSS conference in Chicago. He has also served on the FACSS Long Range Planning Committee. In 2009, Paul received the FACSS Distinguished Service Award for his contributions to the federation. Having served on the Editorial Advisory Board of *Spectroscopy*, since the introduction of the journal, Paul has authored and coauthored a number of articles for the publication and served as editor of the Spectral Interpretation column. Paul has also served as a reviewer for the National Science Foundation. He is a member of the American Chemical Society. With colleagues Jim Rydzak and John Coates, Paul has taught courses in Molecular Spectroscopy for the Center for Professional Advancement in New Jersey and Amsterdam over a period of eight years. After graduating from the Illinois Institute of Technology, in Chicago, Paul started his career in spectroscopy, with a mass spectrometer at the University of Chicago. After learning how to polish salt crystal windows, Paul began a long career in Infrared Spectroscopy. Then, during his sixteen years at UOP, Paul widened his scope to include chromatography, NMR, UV-VIS-NIR, emission, x-ray and eventually became supervisor of the Spectroscopy Department at UOP. Paul and his wife Linda live in Germantown, Tennessee where Paul is active as the Clerk of Session at Farmington Presbyterian Church, a post he has served in for the past seventeen years. He is a member of the Germantown Coffee Club. Linda and Paul's daughter, Rachael, lives and works in Austin, Texas. Paul is currently the Vice President of Blue Moon, Inc. a Marketing and Public Relations firm owned by he and his wife. Paul is also a freelance writer, publishing a series of articles in the New 50, a magazine insert in the Memphis Commercial Appeal newspaper.

Deborah Bradshaw is an analytical chemist who has been working the field of atomic spectroscopy for over 30 years. She started working as a chemist using flame atomic absorption and then migrated into graphite furnace in the early 1980s, developing methods using Zeeman background corrected techniques for the analysis of seawater samples. It was then a natural progression to migrate into the plasma techniques. For the past 18 years, she has been working as a consultant in the field of atomic spectroscopy, conducting training classes and giving technical support for AA, ICP-OES and ICP-MS. Debbie has been a member of SAS since 1981, when she attended her first FACSS meeting. She has served in various capacities for the Society, including serving on several committees. Debbie was Treasurer from 2002-2004 and served as News Column Editor for Applied Spectroscopy for 14 years. In 2008, she was honored with the SAS Distinguished Service Award. In addition to her consulting efforts to promote education and support to the analyst using atomic spectroscopy techniques, Debbie was the FACSS Atomic Spectroscopy Symposia Chair in 2007 and 2008, has organized several technical symposia at both FACSS and PittCon, has been a short course instructor for SAS, and continues to be a short course instructor at the Winter Plasma Conference on Spectrochemical Analysis.

David J. Butcher is currently Professor of Chemistry and Associate Dean of the College of Arts and Sciences at Western Carolina University (WCU) in Cullowhee, NC. He is married to Dr. Karen Butcher and has two children, Emily 21 and Neil 20, with whom he enjoys leisure time. He received his bachelor's degree in 1982 from the University of Vermont. After three years of employment at Pfizer and Bowdoin College, he received his Ph.D. from the University of Connecticut in 1990. His graduate work, conducted under the direction of Robert G. Michel, involved the development of instrumentation for laser excited atomic fluorescence and ionization spectroscopies. He joined the faculty at WCU in 1990 as an Assistant Professor of Chemistry, was promoted to Associate Professor in 1997, was promoted to Professor in 2001, and became Department Head in 2002. Prof. Butcher became Associate Dean in April, 2004. Prof. Butcher has more than 50 publications in a variety of areas of analytical chemistry, including graphite furnace atomic absorption spectrometry, diode laser atomic absorption spectrometry, and ion trap mass spectrometry. Along with Prof. Joseph Sneddon, he is co-author of the volume "A Practical Guide to Graphite Furnace

SAS FELLOWS AWARD

Recognizes individual members for their outstanding service to the field of spectroscopy.

Atomic Absorption Analysis. His current research interests include environmental analytical chemistry and analytical atomic spectrometry. He has also been involved in a number of novel teaching innovations in general and analytical chemistry. He received the 1998 WCU University Scholar Award as the outstanding researcher. He serves on the Editorial Boards of Microchemical Journal, Spectroscopy Letters, and Applied Spectroscopy Reviews. In 2001, he served as Program Chair for 28th FACSS meeting held in Detroit, MI. In 2009, he became Editor-in-Chief of *Analytical Letters*, and the following year, he became Editor-in-Chief of *Instrumentation Science and Technology*. He served as the General Chair for the 37th FACCS meeting held in Raleigh, NC in 2010, and as Chair of the Western Carolinas American Chemical Society Section in 2011. He received the Distinguished Service Award from the Society for Applied Spectroscopy in 2012, and was named a Fellow of the Society in 2013.

Stanley R. Crouch is Professor Emeritus at Michigan State University. He was educated at Stanford University (1958-1963, MS 1963), where he worked with D. A. Skoog, and at the University of Illinois (Ph. D. 1967), working with H.V. Malmstadt. At Michigan State, he did research and taught from 1968 until retiring in 2000. His research interests are in spectrochemical analysis, kinetics, and chemical instrumentation. He received the ACS 1996 Analytical Division J. Calvin Giddings Award for Excellence in Education and the 2001 Analytical Division Award in Chemical Instrumentation. He has co-written textbooks in Spectrochemical Analysis (J. D. Ingle, Jr.), Electronic Measurements (H.V. Malmstadt and C. G. Enke), Analytical Chemistry (D. A. Skoog, D. M. West, and F. J. Holler), and Instrumental Analysis (D. A. Skoog and F. J. Holler). He currently resides in Minden, Nevada where he continues to write textbooks in his fields of interest.

In 2008, Dr. **David Christian ("Chris") Hassell** was named as an Assistant Director of the Federal Bureau of Investigation (FBI), where he serves as Director of the FBI Laboratory. Chris joined the Bureau from the Oklahoma State University Multispectral Laboratories, where he led Research, Development, Testing and Evaluation. He previously served as Assistant Vice President for Science and Technology at Applied Marine Technologies Incorporated. Prior to that position, he led programs in analytical chemistry, instrumentation development, and nuclear weapons forensics at Los Alamos National Laboratory. During this time, he also served as a subject matter expert for weapons of mass destruction with the Iraq Survey Group in Baghdad. Earlier in his career, Dr. Hassell was a Senior Research Chemist at DuPont, developing online analytical instrumentation for chemical and bioprocess facilities for both research and manufacturing. He received his PhD in analytical chemistry from the University of Texas at Austin with Professor Jim Holcombe.

Dr. **Kathryn S. Kalasinsky** currently serves as a Scientific Review Officer in the Bioengineering Sciences and Technologies Integrated Review Group at the National Institutes of Health. She previously spent more than 20 years at the Armed Forces Institute of Pathology (AFIP) on the Walter Reed Medical Center base. Dr. Kalasinsky has a PhD in chemistry in the area of spectroscopy from the University of South Carolina. She began working at AFIP in the area of Forensic Toxicology during which time she received a national award from the American Academy of Forensic Sciences for outstanding research. She then moved into microbiology developing pathogen detectors and digital databases of biological references. Dr. Kalasinsky also worked with physicians and pathologists in Infectious Disease Sciences at AFIP exploring spectroscopic techniques for diseases diagnosis and prognostic probabilities. Dr. Kalasinsky has served as President of the Society for Applied Spectroscopy as well as numerous committee appointments throughout the years. She also served as President of the Coblentz Society and on the Governing Board for several years.

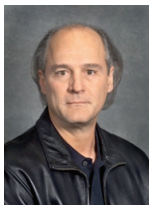
Dr. **Nancy Miller-Ihli** received her PhD in Analytical Chemistry from the U of MD under the direction of Professor Thomas O'Haver. Her early research focused on using multielement atomic absorption spectrometry in support of nutrition research at USDA. Later she combined separations technology with atomic spectroscopy techniques to do speciation analyses. She joined SAS as a graduate student and felt the society was a huge asset to her professional development (even allowed her to meet some molecular spectroscopists :-) Nancy served on many committees with SAS and was also part of the Executive Committee serving as Gov Board Chair in 1993. During her tenure she focused on internationalization of the Society. She served as a co-chair for the SAS web page and was a member of the Applied Spectroscopy Editorial Advisory Board. Nancy has always had an interest in teaching, mentoring and coaching so particularly enjoyed interactions with SAS student members and felt the student poster sessions were both fun and educational. Nancy currently serves on the clinical faculty of a nutrition company and trains health professionals about nutrition and genomics. She enjoys coaching people one-on-one to reach their health and weight loss goals. Nancy loves scuba diving and has recently taken up running (5K's). Personal goal statement: Be healthy. Be happy. Help others.

John Olesik is currently a Research Scientist, Adjunct Associate Professor and Director of the Trace Element Research Laboratory in the School of Earth Sciences at The Ohio State University. He received his B.S. degree in Chemistry from the University of Rochester in 1977 and is Ph.D. in Analytical Chemistry from the University of Wisconsin-Madison in 1982 (with Prof. John Walters). He was a Postdoctoral Research Associate at the University of Wisconsin-Madison in 1982 and at Indiana University from 1982 to 1984 (with Prof. Gary Hieftje). John was an Assistant Professor of Chemistry at the University of North Carolina-Chapel Hill from 1984 until he moved to The Ohio State University in 1991. He is currently the Chair of the SAS Publications Committee, Regional Associate Editor for the Americas for the *Journal of Analytical Atomic Spectrometry* and serves on the Editorial Advisory Boards of *Spectrochimica Acta Part B* and *Spectroscopy*. He was the Program Chair for the 1997 FACSS meeting, the ACS representative on the FACSS Governing Board from 1999-2005 and on the Editorial Boards of *Applied Spectroscopy* from 2001 to 2009 and the *Journal of Analytical Atomic Spectrometry* from 2006-2009. John received the Rappaport Award from the Ohio Valley Section of the SAS in 1998, the Lester Strock Award from the SAS in 2001 and the Spectrochemical Analysis Award from the ACS in 2009. His research interests include fundamental processes in plasmas used for emission

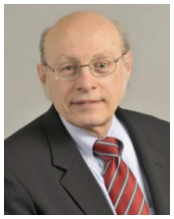
SAS FELLOWS AWARD - continued

Recognizes individual members for their outstanding service to the field of spectroscopy.

and mass spectrometry, time-resolved measurements in plasmas, laser ablation sampling, spectroscopic imaging detection systems, aerosol generation and transport, ion-molecule reactions to overcome spectral overlaps in ICP-MS, micro- and nano-particle analysis, analytical geochemistry and trace element biogeochemistry.



Richard Russo
See page 15 for biographical information



Richard P. Van Duyne
See page 14 for biographical information

Frank Vanhaecke (1966, Oostende, Belgium) obtained his PhD degree in 1992 from Ghent University (Belgium). Subsequently, he continued carrying out scientific research as a post-doctoral fellow at the same university and at the Johannes Gutenberg University of Mainz (Germany). In 1998, Frank became Professor of Analytical Chemistry in the rank of lecturer at Ghent University. He was promoted to Professor in the rank of senior lecturer in 2000, to Full Professor in 2006 and to Senior Full Professor in 2012. Frank has a passion for the determination, speciation and isotopic analysis of (trace) elements via ICP – mass spectrometry (ICP-MS). He is leading the 'Atomic & Mass Spectrometry A&MS' research group that studies fundamentally-oriented aspects of the technique and develops methods for solving challenging scientific problems in an interdisciplinary context. Nowadays, specific topics of research include the direct analysis of solid materials by means of ICP-MS using laser ablation (LA) for sample introduction and isotopic analysis using multi-collector sector field ICP-MS. In 2011, Frank received a 'European Plasma Spectrochemistry Award' for his contributions to this research field and he is a Fellow of the Royal Society of Chemistry RSC. So far, Frank's scientific research has resulted in >200 publications in peer-reviewed journals (~4800 citations, h-factor = 38 according to ISI's Web of Science). Additionally, Frank has also (co)authored ~15 book chapters and has edited a book (together with Patrick Degryse), entitled 'Isotopic analysis – fundamentals and applications using ICP-MS' for Wiley-VCH (2012). As of July 2012, he is the chairman of the editorial board of Journal of Analytical Atomic Spectrometry – JAAS. He is also a member of the advisory boards of 'ABC – Analytical and Bioanalytical Chemistry' and SAB – 'Spectrochimica Acta B'. Frank is married to Katia and they are the proud parents of a son called Daan.

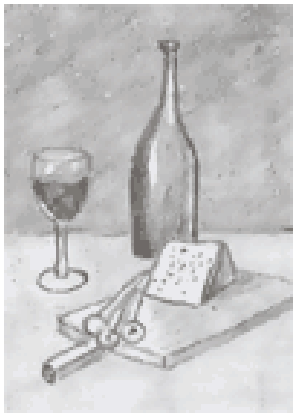
Professor **John Wright** is one of the pioneers in the field of laser spectroscopic applications in chemistry. He is recognized as the person responsible for the development of multidimensional laser methods that provide great selectivity in chemical measurement. His early work focused on the development of site selective laser spectroscopy. He applied this method to gain new insights into the fundamental factors that control solid state defect chemistry, to discover up-conversion processes that convert infrared light into visible light, to invent new ways for performing spectrochemical analysis, to perform high resolution laser spectroscopy of protein binding sites, and to study materials at very high pressures. More recently, he developed a new family of coherent laser methods collectively termed Multiresonant Coherent Multidimensional Spectroscopy (CMDS). They are based on creating multiple quantum coherences and are the optical analogue of multidimensional NMR methods. He is applying these methods to the chemical measurement of complex systems such as understanding the mechanism for oxygen evolution in the oxygen evolving complex of photosystem II and the nature of charge separation and transport in photovoltaic and photocatalytic nanoscale heterostructures. He has been recognized for his work by the ACS Award in Spectrochemical Analysis, the SAS William F. Meggars Award, the Andreas C. Albrecht Chair of Chemistry, and Fellowship in the American Association for the Advancement of Science and the American Physical Society. His teaching has been recognized by the Benjamin Smith Reynolds Award for Teaching Excellence in Engineering and the Chancellor's Excellence in Teaching Award.

LIPPINCOTT AWARD

Given to honor the memory of Ellis R. Lippincott for significant contributions to vibrational spectroscopy. The medal is sponsored jointly by the Society for Applied Spectroscopy, the Coblentz Society, and the Optical Society of America.

X. Sunney Xie
Harvard University

Xiaoliang Sunney Xie (born 1962 in Beijing, China) is the Mallinckrodt Professor of Chemistry and Chemical Biology at Harvard University. Xie is considered a founding father of single-molecule enzymology. He has also made major contributions to biomedical imaging by developing CARS microscopy. Xie received a B.S. in chemistry from Peking University, followed by his Ph.D. in 1990 from the University of California at San Diego. He conducted postdoctoral research at the University of Chicago and in 1992 joined Pacific Northwest National Laboratory, where he later became a Chief Scientist. In 1999, he became the first full professor at Harvard University from the People's Republic of China. Among the first to conduct fluorescence studies of single molecules at room temperature in the early 1990s, his research group has contributed to the emergence of the field of single-molecule biophysical chemistry and its application to biology. His work focuses on single-molecule enzymology, protein conformational dynamics, and the study of gene expression and regulation in living cells. His group also pioneered CARS microscopy and stimulated Raman scattering microscopy, sensitive biomedical imaging techniques that allow 3D imaging of live cells and organisms based on vibrational spectroscopy.



The Society for Applied Spectroscopy Cordially Invites You to Join Us at Our Annual Wine and Cheese Awards Reception Tuesday, October 1, 2013 7:30 p.m. At the Hyatt Regency Milwaukee in the Regency Ballroom

This is a member's only event.

COBLENTZ SOCIETY'S CLARA CRAVER AWARD

Recognizing a young individual under the age of 45, who has made significant contributions in applied analytical vibrational spectroscopy.

Rohit Bhargava

University of Illinois at Urbana-Champaign

***Presentation, Tuesday, 8:00 am,** Ballroom A, Wisconsin Center*

The Coblentz Society is pleased to announce that Professor Rohit Bhargava, Professor of Bioengineering at the University of Illinois at Urbana-Champaign has been selected as the recipient of the 2013 Craver Award. In 2006, The Coblentz Society created an award to recognize the efforts of young professional spectroscopists that have made significant contributions in applied analytical vibrational spectroscopy. The Society has named this award for Clara D. Craver in recognition of her pioneering efforts in promoting the practice of infrared vibrational spectroscopy and her many years of service to the Coblentz Society. Further, the Craver Award is the Society's complement of its prestigious 'Coblentz Award' that recognizes young spectroscopists for efforts in fundamental aspects of vibrational spectroscopy. This award is presented to Professor Bhargava in recognition of his work in the area of spectral chemical imaging, including the development of the fundamental theory and modeling of Raman and infrared chemical imaging. His work has included the application of imaging to the study of polymeric systems as well as biological systems. Professor Bhargava's research interests have spanned the areas of Instrumentation development and analysis including the development of high definition and ultrasensitive IR imaging systems, and of time-resolved IR imaging. He has also made advancements in the design and fabrication of nanostructures for optical sensing, advancements in chemometrics, high-performance computing and visualization. His work has spanned applications of spectroscopic imaging to solve various problems in composite polymers, cancer histopathology, forensics, molecular diffusion and seed grains. Rohit Bhargava is Bliss Faculty Scholar and Professor of Bioengineering at the University of Illinois at Urbana-Champaign, where he was previously Associate (2011-2012) and Assistant Professor (2005-2011). He is also a faculty member in Chemical and Biomolecular Engineering, Mechanical Science and Engineering and Electrical and Computer Engineering as well as the Beckman Institute for Advanced Science and Technology. Rohit received dual B.Tech. degrees (in Chemical Engineering and Polymer Science and Engineering) from the Indian Institute of Technology, New Delhi. His doctoral thesis work at Case Western Reserve University was in the area of polymer spectroscopy. Subsequently, he worked as a Research Fellow at the National Institutes of Health in the area of biomedical vibrational spectroscopy. Research in the Bhargava laboratories focuses on fundamental optical theory for vibrational spectroscopic imaging, developing new instrumentation, application of spectroscopic imaging to biomedical and polymer problems and numerical analyses. Current research in the Bhargava group is supported by several federal agencies, industry, private foundations and competitive programs at the University of Illinois. Rohit's work has been recognized with several research and teaching awards and he is routinely nominated to the list of teachers ranked excellent at Illinois. He is also two time recipient of the FACSS Innovation Award for novel work presented for the first time at the SciX conference (2011 and 2012). His work has also been recognized with the award of the William F. Meggers Award from the Society of Applied Spectroscopy (1999 and 2002).

The Coblentz Society – fostering understanding and application of vibrational spectroscopy

Call for Award Nominations - See http://www.coblentz.org/ for more information

ABB Bomem-Michelson Award: ABB sponsors the Bomem-Michelson Award to honor scientists whom have advanced the technique(s) of vibrational, molecular, Raman, or electronic spectroscopy. Contributions may be theoretical, experimental, or both. The recipient must be actively working and at least 37 years of age. The nomination should include a résumé of the candidate's career as well as a synopsis of the special research achievements that make the candidate an eligible nominee for the ABB sponsored Bomem-Michelson Award. Nominations for the award are open February 1st to **May 1st** each year. Further information: www.coblentz.org/awards/the-bomem-michelson-award.

Coblentz Award: The Coblentz Award is presented annually to an outstanding young molecular spectroscopist under the age of 40. The candidate must be under the age of 40 on January 1st of the year of the award. Nominations should include a detailed description of the nominee's accomplishments, a curriculum vitae and as many supporting letters as possible. Annual updates of files of nominated candidates are encouraged. Nominations for the Coblentz Award are open between January 3rd and **July 15th** each year. Further information regarding the Coblentz Award is available at www.coblentz.org/awards/the-coblentz-award.

Craver Award: The Craver Award is presented annually to an outstanding young molecular spectroscopist whose efforts are in the area of applied analytical vibrational spectroscopy. The candidate must be under the age of 45 on January 1st of the year of the award. The work may include any aspect of (near-, mid-, or far-infrared) IR, THz, or Raman spectroscopy in applied analytical vibrational spectroscopy. Nominees are welcome from academic, government, or industrial research. Nominations must include a detailed description of the nominee's accomplishments, curriculum vitae or résumé, and a minimum of three supporting letters. Nominations for the Craver Award are open between March 30th and **August 30th** each year. Further information: www.coblentz.org/awards/the-craver-award.

Ellis R. Lippincott Award: The Ellis R. Lippincott Award is presented annually in recognition of significant contributions and notable achievements in the field of vibrational spectroscopy. The medal is jointly sponsored by the Coblentz Society, the Optical Society of America and the Society for Applied Spectroscopy. Recipients must have made significant contributions to vibrational spectroscopy as judged by their influence on other scientists. Because innovation was a hallmark of the work of Ellis R. Lippincott, this quality in the contributions of candidates will be carefully appraised. Nominations for the award are open January 1st to **October 1st** each year. Nominations should be submitted to: Lippincott Award Chairperson, awards@osa.org. Further information: www.coblentz.org/awards/the-lippincott-award.

Honorary Membership: The Coblentz Society awards honorary memberships in the Society to people who have made outstanding contributions to the field of vibrational spectroscopy or any other field related to the purposes of the Society. Nominations close on **February 1st** each year, with awards announced at the Annual Members Meeting at Pittcon and presented at SciX. Send your nomination for 2014 to James Rydzak, Coblentz Society President at James.W.Rydzak@gsk.com

COBLENTZ SOCIETY'S WILLIAM G. FATELEY STUDENT AWARD

The William G. Fateley Student Award is given by the Coblentz Society annually to recognize outstanding contributions to vibrational spectroscopy during a current Ph.D. program. William G. (Bill) Fateley was among the first winners (1965) of the Coblentz award, and worked tirelessly to promote the Pittsburgh Conference and FACSS. Author of more than 350 publications and recipient of numerous other awards, he returned to his alma mater, Kansas State University, as chairman of his department in 1972 and served there until his retirement 1997 and beyond. He served as the Editor of *Applied Spectroscopy* for 20 years, and served as mentor to a generation of spectroscopists

In 2013 the Coblentz Society's William G. Fateley Student Award will be announced at the SciX 2013 conference at the SciX/SAS sponsored poster session following the Sunday evening conference opening and special plenary session.

The Coblentz Society – fostering understanding and application of vibrational spectroscopy
Call for Student Award Nominations
Visit www.coblentz.org for more information

In addition to Awards for professionals in industry, academia and government laboratories, the Coblentz Society encourages young scientists to pursue studies in all forms of vibrational spectroscopy through the presentation of Student Awards. The Coblentz Student Award recognizes excellence in research involving vibrational spectroscopy and/or coursework including vibrational spectroscopy. The William G. Fateley Student Award is presented to one of the nominees each year in honor of Bill Fateley, former editor of Applied Spectroscopy and an early recipient of the Coblentz Award. Nominators must be members of the Coblentz Society. To become a member, contact Mark Druy at druy@psicorp.com, visit the Coblentz Society website at www.coblentz.org, or register when renewing your Society for Applied Spectroscopy membership at www.s-a-s.org.

Coblentz And William G. Fateley Student Awards: The Coblentz Society seeks nominations of outstanding students for the Coblentz Student Awards. Awardees receive a copy of the Society's Desk Book, a certificate, and a year's membership in the Society. Their names and the names of their faculty advisors appear in the Society's Newsletter. All awardees who attend FACSS will receive their award in person from the Coblentz Society's president at a presentation during Sunday Evening's SAS Student Poster session. All nominees for the Coblentz Student Award will automatically be considered for the William G. Fateley Student Award. The William G. Fateley award recipient will be given the opportunity to speak in the Student Awards session at FACSS or in another appropriate venue, and will receive a $1000 prize supported by an endowment established in Professor Fateley's name by his former students, friends and colleagues.

Nominations for the Coblentz and William G. Fateley Student Awards must be submitted by **February 1st**. Additional information regarding eligibility for the Coblentz Society student awards and nomination requirements can be found at www.coblentz.org/awards/coblentz-student-awards.

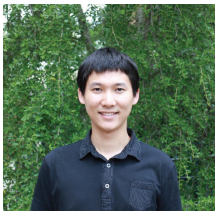
COBLENTZ SOCIETY'S STUDENT AWARDS

For many years, the Coblentz Society has encouraged young scientists to pursue studies on spectroscopy by seeking nominations of outstanding students for the Coblentz Student Awards. The awardees receive a copy of the Society's Deskbook, a certificate, and a year's membership in the Society. Their names, the names of their faculty advisors, their institute, and their anticipated graduation date appear in the Society's Fall Newsletter published in an issue of the Journal, Applied Spectroscopy.

Tomasz P. Wrobel graduated from "Advanced Spectroscopy in Chemistry" Erasmus Mundus master programme in 2010, yielding a double diploma of USTL Lille 1 (France) and Jagiellonian University (Krakow, Poland). He completed a master thesis about atherosclerotic tissue imaging with FT-IR spectroscopy and is continuing this topic throughout his PhD studies under supervision of Professor Malgorzata Baranska. He is also an assistant in Jagiellonian Centre for Experimental Therapeutics (JCET). He has published 10 peer-reviewed articles (another 4 are in the process of revision) and 2 book chapters (another one is being reviewed). He has received several awards and stipends including an award by the Polish Chemical Society for the best presentation of master thesis results, regional "Doctus" fund for the best doctoral students and an award given by the polish Ministry of Education for the best doctoral students.

Sarah Holton received her B.S in chemical engineering at the University of South Carolina in 2008 before joining the Department of Bioengineering and the Medical Scholars Program (M.D/Ph.D) at the University of Illinois at Urbana-Champaign. During her time at Illinois, she worked with Professor Rohit Bhargava, she focused on developing advanced cell culture models to study early breast tumor dynamics. She is interested in applying FTIR spectroscopic imaging to the practice of pathology in order to improve patient diagnostic and prognostic strategies. Sarah defended her doctoral thesis in Summer 2013 and is continuing her medical studies.

Rachel Masyuko is a chemistry PhD student in Dr. Paul W. Bohn's research group at the University of Notre Dame. Her research interests include label- free molecular imaging of biological systems and the development of correlated imaging technologies for chemical analysis. Her work involves chemically communicating microbial communities in complex microenvironments. Her research focuses on understanding the biological processes and interactions that occur at the cellular and multi-cellular level during the biofilm formation process by following the spatial and temporal characteristics of the molecular species in the matrix.



Tao Liang is a PhD candidate working on helium nanodroplet spectroscopy for Prof. Gary Douberly in the Department of Chemistry at the University of Georgia. His research focuses on using high resolution infrared laser spectroscopy to study species solvated in superfluid helium nanodroplets, which are ideal matrixes for trapping metastable molecules as well as for forming molecular clusters for fundamental research in chemistry. Currently he is working on gaining a molecular level understanding of the interactions that drive atmospheric chemistry involving the OH radical, such as its complexes with O_2. He also uses state-of-the-art *ab initio* methods like Møller–Plesset perturbation theory and coupled-cluster theory to help with the interpretation of the experimental data, which is important for understanding the properties of these species. He published 10 papers, 3 of which he is first author, and is active in many projects that will make contributions to the field of molecular spectroscopy.

COBLENTZ SOCIETY'S HONORARY MEMBERSHIP AWARD

Recognizing those individuals who are deemed by the Board of Managers of the Society to have made outstanding contributions to the field of vibrational spectroscopy or to any other field related to the purposes of the society.

2013 Recipients

James W. Cooley
Professor Emeritus of Electrical Engineering at the University of Rhode Island

For development of the Cooley-Tukey Fast Fourier Transform algorithm and its subsequent contributions to the development of FTIR.

Charles H. Townes
Professor of Astrophysics at UC Berkeley

For development of the laser and its subsequent applications to the technology of Raman spectroscopy.

ACS DIVISION OF ANALYTICAL CHEMISTRY AWARD IN CHEMICAL INSTRUMENTATION
Sponsored by Dow Chemical

Charles L. Wilkins
University of Arkansas
Presentation: Tuesday, 3:50 pm
Room 102E

Charles Wilkins, Distinguished Professor of Chemistry and Biochemistry at the University of Arkansas, has been awarded the 2013 American Chemical Society Division of Analytical Chemistry Award in Chemical Instrumentation, sponsored by the Dow Chemical Company. The award recognizes Wilkins for his contributions to a broad range of analytical instrumentation techniques that have been documented in over 300 publications in Analytical Chemistry, Journal of the American Chemical Society, Journal of Physical Chemistry and many other books and journals. He has also authored and or co-edited nine books covering a variety of analytical instrumentation methods. These publications have been cited extensively in the chemical literature and include a dozen papers cited more than 100 times each and a lifetime total of over 7,000 citations. Wilkins is distinguished by his leading contributions in a wide range of analytical instrumentation, including advances in Fourier transform infrared spectroscopy, FT- nuclear magnetic resonance spectrometry, ion cyclotron resonance mass spectrometry and computerized laboratory data acquisition and analysis. He has primarily been recognized for his contributions to the development of "hyphenated" instrument approaches to couple distinct types of instrumentation for analytical purposes. He was the first to combine GC-infrared and mass spectrometry into a single analysis system and also was a leader in the combination of HPLC analysis and nuclear magnetic resonance, in ways that opened the current use of HPLC-NMR for metabolomics studies. His work, in collaboration with Michael Gross, also pioneered the use of ICR-mass spectrometry for analytical applications, Wilkins has served in numerous professional capacities, including terms both as Chair of the Analytical Chemistry Division and Chair of the Computers in Chemistry Division of the American Chemical Society. He also was Chair of the Department of Chemistry at the University of California, Riverside for seven years. He served on the Advisory Board of the National Center for Toxicological Research of the FDA and has served on many other advisory boards and panels. Wilkins also serves on the editorial advisory boards of numerous journals, among them Mass Spectrometry Reviews, Applied Spectroscopy Reviews, and, previously, two terms on the Analytical Chemistry editorial board. He is a Contributing Editor of Trends in Analytical Chemistry, and serves as Associate Editor of International Journal of Analytical Chemistry. Wilkins has received awards and honors throughout his career, including designation as a Fellow of the American Association for the Advancement of Science, as a Fellow of the American Chemical Society, and as a Fellow of the Society for Applied Spectroscopy. Honors include the Lester Strock Award of the Society for Applied Spectroscopy in 1982, the Tolman Medal of the Southern California Section of the American Chemical Society in 1993, and the Pittsburgh Analytical Chemistry Award, in 1994. In 1996 he was awarded the Gold Medal Award of the New York Section of the Society for Applied Spectroscopy and in 1997 the American Chemical Society Franklin & Field Award for Outstanding Achievement in Mass Spectrometry. More recent honors include the 2002 Eastern Analytical Symposium Award for Outstanding Achievement in the Fields of Analytical Chemistry, the 2003 University of Arkansas Alumni Faculty Distinguished Achievement Award for research, and in 2004 the University of Oregon Department of Chemistry Alumni Achievement Award, Distinguished Awardee in Pure Science. In 2009 there was publication of a Special Issue of the International Journal of Mass Spectrometry in honor of Charles Wilkins.

ANACHEM AWARD

The ANACHEM Award is presented annually to an outstanding analytical chemist based on activities in teaching, research, administration or other activity, which has advanced the art and science of the field

Norman Dovichi
University of Notre Dame

Presentation: Thursday, 8:00 am
Ballroom A, Wisconsin Center

Norman Dovichi holds the Grace-Rupley Professorship in the department of Chemistry and Biochemistry at the University of Notre Dame. He received his BSc with a dual major in Chemistry and Mathematics from Northern Illinois University and his PhD in Physical Analytical Chemistry from the University of Utah, where he was Joel Harris's first PhD student. He spent two years at Los Alamos Scientific Laboratory with Dick Keller. Since then he has held faculty positions at the Universities of Wyoming, Alberta, and Washington before taking his current position at Notre Dame. Dovichi has graduated 57 PhD students, has published over 250 papers, holds seven US patents, and has given over 350 invited talks. He has served on the editorial advisory boards of 16 journals and now serves as Associate Editor for *Analytical Chemistry*. He holds an honorary professorship with the Chinese Academy of Sciences.

Research Interests

Dovichi has primarily focused his research on the use of capillary electrophoresis and ultrasensitive laser-induced fluorescence for analysis of minute amounts of biological molecules. In the 1980s, he introduced the concept of single molecule detection to the chemical literature. In the 1990s, his group employed that technology to measure the activity and activation energy of single enzyme molecules. His group also developed capillary array electrophoresis instruments for high-throughput DNA sequencing. This technology was patented and commercialized as the Applied Biosystems model 3700 DNA sequencer. He was recognized for this work by the journal *Science* as an "Unsung Hero of the Human Genome Project". More recently, his group has focused its attention on chemical cytometry, which is the chemical analysis of the content of single cells. This chemical cytometry work has developed a suite of powerful tools for the characterization of glycosphingolipids in single neurons and glia. Most recently, his group has developed capillary electrophoresis-tandem mass spectrometry as a tool for analysis of zeptomole amounts of peptides and for characterization of the protein content of single cells. This group has developed diagonal capillary electrophoresis, which has the potential to be a powerful tool in identification of phosphorylated peptides with no interference from other components within the sample. Finally, the group has also developed on-column digestion systems that allow analysis of picogram amounts of protein homogenates.

THE *LCGC* LIFETIME ACHIEVEMENT IN CHROMATOGRAPHY AWARD

The LCGC Lifetime Achievement in Chromatography Award is presented annually to a separation science professional for a lifetime of contributions to the advancement of chromatographic techniques and applications.

Peter W. Carr
University of Minnesota

Presentation: Thursday, 8:30 am
Ballroom A, Wisconsin Center

Peter W. Carr is a professor of chemistry at the University of Minnesota (UMN), Twin Cities. He received his B.S. in chemistry from the Polytechnic Institute of Brooklyn in 1965 and his PhD in chemistry from Pennsylvania State University in 1969, followed by postdoctoral studies at Stanford University Medical School. Carr became an assistant professor at the University of Georgia in in 1969 and was promoted to Associate Professor in 1975. In 1977, he accepted a post as an Associate Professor of Chemistry at the University of Minnesota, where he was made a full professor in 1981. During his career at UMN he has also been the Associate Director of the Cooperative Center for Bioanalytical Processing (1987-1990) and an Associate Member of the Graduate Faculty for Microbial Engineering (1990-present).

Carr is well known for his pioneering contributions to the fundamental theory and practice of liquid chromatography, which have resulted in more than 400 highly cited publications and 18 patents. Among his most significant accomplishments are detailed thermodynamic measurements and solvatochromic modeling of retention and selectivity. These studies, together with their careful and thorough interpretation, have provided a clearer understanding of the role of the mobile and stationary phases in liquid chromatography as well as the relative contributions of polarizability-dipolarity, hydrogen-bond donor, and hydrogen-bond acceptor interactions.
Another important advance made by Carr is the development of chemically and thermally stable zirconia stationary phases with a variety of surface chemistries. These phases have enabled separations to be performed over a wider pH range and at much higher temperatures than possible using conventional silica-based stationary phases. This has led to the most recent groundbreaking work by Carr in ultrafast and two-dimensional liquid chromatography.

During his academic career, Carr has mentored 14 MS students, 50 PhD students, and 36 postdoctoral associates. Some of these students have chosen academic careers at high-quality undergraduate institutions and leading research universities in the United States, Europe, and Asia. Others have gone on to prominent industrial careers at small companies as well as Fortune 500 companies.

Carr has received numerous awards and recognitions. These have included the R.S. Palmer Award from the Minnesota Chromatography Forum (1984), the Merit Award from the Chicago Chromatography Discussion Group (1987), the Benedetti-Pichler Award from the American Microchemical Society (1990), the Award in the Fields of Analytical Chemistry from the Eastern Analytical Symposium (1993), the Stephen Dal Nogare Award from the Delaware Valley Chromatography Forum (1996), the Award in Chromatography from the American Chemical Society (1996), the Award for Outstanding Achievements in Separation Science from the Eastern Analytical Symposium (2000), the Pittsburgh Conference Award in Analytical Chemistry from the Society for Analytical Chemists of Pittsburgh (2004), the Award in Analytical Chemistry from the American Chemical Society (2009), the A.J.P. Martin Gold Medal from the Chromatographic Society, United Kingdom (2010), and the Csaba Horvath Medal from the Connecticut Separation Science Council and Hungarian Chromatographic Society (2010).

THE *LCGC* EMERGING LEADER AWARD

The LCGC Emerging Leader Award is presented annually to a talented young separation science professional who has made strides early in his or her career toward the advancement of chromatographic applications and techniques.

Davy Guillarme
University of Geneva, University of Lausanne

Presentation: Wednesday, 1:20 pm
101C

Davy Guillarme is a senior lecturer in Analytical Pharmaceutical Chemistry at the School of Pharmaceutical Sciences at the University of Geneva and the University of Lausanne, Switzerland. He received his MS in analytical chemistry in 2001 and his PhD in chemistry in 2004, both from the University of Lyon, France, followed by postdoctoral studies at the University of Geneva, Switzerland. In 2006 he became an Assistant Master at the University of Geneva, and in 2010, was appointed Senior Lecturer there.

Guillarme has made significant contributions in fast and high-resolution chromatography, particularly in the comparison of available approaches, using various types of samples. He has been working on ultrahigh-pressure liquid chromatography (UHPLC) since 2004, and has published extensively on the possibilities offered by this method. He has also made an Excel calculator, available for free on his website (and downloaded more than 7000 times to date), that can be used to determine the new isocratic and gradient conditions to be used when transferring a method between HPLC and UHPLC. He has also recently co-edited a book with Jean-Luc Veuthey, *UHPLC in Life Sciences.*

More recently, he has published a series of papers dealing with the possibilities of modern wide-pore reversed-phase LC phases for the analysis of intact biomolecules, including therapeutic peptides, proteins and monoclonal antibodies. Other areas of focus include hydrophilic interaction liquid chromatography (HILIC) for the analysis of polar and other ionizable compounds, the evaluation of supercritical fluid chromatography (SFC) using conventional and sub-2-µm particles, and LC-MS and UHPLC-MS applied to pharmaceutical analysis.

PREVIOUS FACSS BOARD AND MEETING CHAIRS

1973	
Jeannette Grasselli	Governing Board Chair
1974 – Atlantic City	
James White	Governing Board Chair
George Heinz	General
James White	Program
Edward Ruffing	Exhibit
1975 - Indianapolis	
James Holcombe	Governing Board Chair
Gerald Wallace	General
James Holcomb	Program
Edward Ruffing	Exhibit
1976 - Philadelphia	
Edward Brame	Governing Board Chair
Edward Brame	General
Edward Dunlap	Program
Douglas Robinson	Arrangements
Edward Ruffing	Exhibit
1977 - Detroit	
Edgar Peck	Governing Board Chair
Mitch Kapron and James Burns	General
Jeannette Grasselli	Program
L. Felix Schneider	Arrangements
Edward Ruffing	Exhibit
1978 - Boston	
James Williamson	Governing Board Chair
Paul Lublin	General
James Cosgrove	Program
James Cornwell	Arrangements
Edward Ruffing	Exhibit
1979 - Philadelphia	
Peter Keliher	Governing Board Chair
Douglas Robinson	General
Philip LeFleur	Program
Sydney Fleming	Arrangements
Edward Ruffing	Exhibit
1980 - Philadelphia	
L. Felix Schneider	Governing Board Chair
Sydney Fleming	General
Theodore Rains	Program
Robert Barford	Arrangements
Edward Ruffing	Exhibit
1981 - Philadelphia	
Jack Katon	Governing Board Chair
Robert Barford	General
Mary Kaiser	Program
James Cavanaugh	Arrangements
Peter Keliher	Exhibit
1982 – Philadelphia	
Sydney Fleming	Governing Board Chair
James Cavanaugh	General
Andrew Zander	Program
Matthew O'Brien	Arrangements
Peter Keliher	Exhibit
1983 - Philadelphia	
Mary Kaiser	Governing Board Chair
Matthew O'Brien	General
John Lephardt	Program
D. Bruce Chase	Arrangements
Peter Keliher	Exhibit
1984 - Philadelphia	
Theodore Rains	Governing Board Chair
D. Bruce Chase	General
Patricia Rouse Coleman	Program
Fred Corcoran	Arrangements
Peter Keliher	Exhibit
1985 - Philadelphia	
Robert Barford	Governing Board Chair
Fred Corcoran	General
Matthew Klee	Program
Marshall Fishman	Arrangements
Peter Keliher	Exhibit
1986 - St. Louis	
Ronald Schroeder	Governing Board Chair
Marshall Fishman	General
Alexander Scheeline	Program
Terry Hunter	Arrangements
Edward Brame	Exhibit
1987 - Detroit	
Patricia Rouse Coleman	Governing Board Chair
David Coleman and L. Felix Schneider	General
John S. Beaty	Program
Edward Brame	Exhibit
1988 - Boston	
James Cavanaugh	Governing Board Chair
Frank Plankey and John S. Beaty	General
Roger Gilpin	Program
Edward Brame	Exhibit
1989 - Chicago	
Alexander Scheeline	Governing Board Chair
Paul Bourassa	General
Robert G. Michel	Program
Edward Brame	Exhibit
1990 - Cleveland	
Nancy Miller-Ihli	Governing Board Chair
Charles Belle	General
Steven Hughes	Program
Edward Brame	Exhibit
1991 - Anaheim	
David Coleman	Governing Board Chair
Richard Deming and Constance Sobel	General
James Holcombe	Program
Edward Brame	Exhibit
1992 - Philadelphia	
Karmie Galle	Governing Board Chair
Matthew Klee	General
Barry Lavine	Program
Edward Brame	Exhibit
1993 - Detroit	
Robert Watters	Governing Board Chair
L. Felix Schneider and David Coleman	General
Julian Tyson	Program
Mildred Barber	Exhibit
1994 - St. Louis	
Paul Bourassa	Governing Board Chair
Terry Hunter	General
John Koropchak	Program
Mildred Barber	Exhibit

PREVIOUS FACSS BOARD AND MEETING CHAIRS

1995 – Cincinnati

Jon W. Carnahan	Governing Board Chair
Joseph A. Caruso	General
Richard F. Browner and R. Kenneth Marcus	Program
Mildred Barber	Exhibit

1996 – Kansas City

Rachael Barbour	Governing Board Chair
O. Karmie Galle	General
William Fateley	Program
Scott McGeorge	Exhibit

1997 - Providence

Mildred Barber	Governing Board Chair
Chris Brown	General
John Olesik	Program
Scott McGeorge	Exhibit

1998 - Austin

John Graham	Governing Board Chair
David Laude	General
Isiah Warner and Linda McGown	Program
Scott McGeorge	Exhibit

1999 - Vancouver

Robert G. Michel	Governing Board Chair
Michael Blades	General
Ronald Williams	Program
Scott McGeorge	Exhibit

2000 - Nashville

John Koropchak	Governing Board Chair
Arlene Garrison	General
Michael Carrabba	Program
Scott McGeorge	Exhibit

2001 – Detroit

David A. Laude	Governing Board Chair
David Coleman and L. Felix Schneider	General Co-Chairs
David J. Butcher	Program
Scott McGeorge	Exhibit

2002 – Providence

Michael Carrabba	Governing Board Chair
Robert G. Michel	General Chair
Mark A. Hayes	Program Chair
Scott McGeorge	Exhibit

2003 – Fort Lauderdale

Ronald Williams	Governing Board Chair
Rina Dukor	General
James Rydzak	Program
Scott McGeorge	Exhibit

2004 – Portland

Michael Blades	Governing Board Chair
David Trimble	General
George Agnes	Program
Scott McGeorge	Exhibit

2005- Quebec City, Canada

Mark Hayes	Governing Board Chair
Denis Boudreau	General
Paul Farnsworth	Program
Scott McGeorge	Exhibit

2006 – Orlando

Diane Parry	Governing Board Chair
Christine Wehlburg	General
S. Douglass Gilman	Program
Mike Carrabba	Exhibit

2007 – Memphis

James Rydzak	Governing Board Chair
Paul Bourassa	General
Ian R Lewis	Program
Mike Carrabba	Exhibit

2008 – Reno

Gary Brewer	Governing Board Chair
John Hellgeth	General
Greg Klunder	Program
Mike Carrabba	Exhibit

2009 – Louisville

Becky Dittmar	Governing Board Chair
Jessica Jarman	General
Curtis Marcott	Program
Mike Carrabba	Exhibit

2010 – Raleigh

S. Douglass Gilman	Governing Board Chair
David J. Butcher	General
André J. Sommer	Program
Mike Carrabba	Exhibit

2011 – Reno

S. Douglass Gilman	Governing Board Chair
Greg Klunder	General
Pavel Matousek	Program
Mike Carrabba	Exhibit

2012 – Kansas City

Ian R. Lewis	Governing Board Chair
Brandye Smith-Goettler	SciX General
Steven Ray	SciX Program
Mike Carrabba	SciX Exhibits

SOCIETY AND COMMITTEE MEETINGS AND EVENTS

FACSS/SciX ORGANIZATION

Sunday, September 29, *Executive Ballroom C/D at Hyatt Hotel*

8:30 – 10:30 am FACSS Long Range Planning Meeting (Federation)
4:00 – 6:00 pm SciX Long Range Planning Meeting (Conference)
7:15 – 7:45 pm Program Committee

Monday, September 30, *Executive Ballroom C/D at Hyatt Hotel*

12:30 – 1:15 pm SciX 2014 Reno Meetings: Budget, and Planning
3:00 – 3:45 pm Site Selection Meeting

Tuesday, October 1, *Executive Ballroom A at Hyatt Hotel*

12:30 – 1:15 pm SciX 2014 Reno Meetings: Program
3:00 – 3:45 pm Budget and Finance Committee

Wednesday, October 2, *Executive Ballroom C/D at Hyatt Hotel*

12:30 – 1:15 pm SciX 2015 Providence Meetings: Budget, Program and Planning

Thursday, October 3, *Executive Ballroom C/D at Hyatt Hotel*

Noon Executive Committee Meeting *(for the Executive Committee only)*
6:00 pm Governing Board Meeting (light dinner will be provided)
9:30 pm Governing Board Chair Reception (delegates and invitees) location TBD

COBLENTZ SOCIETY

Monday, September 30, *Executive Ballroom B at Hyatt Hotel*

12:00 pm Board Meeting

NASLIBS

Monday, September 30, *Executive Ballroom*

7:30 pm NASLIBS Reception (open to all)

Tuesday, October 1, *Executive Ballroom B at Hyatt Hotel*

12:00 pm NASLIBS Annual Board Meeting

SOCIETY FOR APPLIED SPECTROSCOPY

Saturday, September 28, *Executive Ballroom C/D at Hyatt Hotel*

3:00 – 8:00 pm SAS Executive Committee

Sunday, September 29

12:00 – 4:00 pm SAS Member Only Event, Tour of Pabst Brewery

Monday, September 30

Noon – 2 pm Editorial Board Meeting, *Room 201C, Wisconsin Center*
After Exhibit Opening Student Event, visit the SAS booth for more information, *Executive Ballroom C/D at Hyatt Hotel*

Tuesday, October 1

8:00 – 10:00 am Membership Committee, *Executive Ballroom C/D at Hyatt Hotel*
12:00 – 2:00 pm Publication Committee, *Executive Ballroom D/D at Hyatt Hotel*
4:30 – 6:30 pm SAS Governing Board Meeting, *Executive Ballroom D/D at Hyatt Hotel*
7:30 pm SAS Wine and Cheese Reception, *Regency Ballroom C/D at Hyatt Hotel*

SAS PAT TECHNICAL SESSION

Monday, September 30, ***103C***

1:00 pm SAS PAT Technical Section Meeting"

SciX EXHIBITORS

The exhibit is one of the focal points of the SciX Conference. Exhibits are the realization of the research presented during the scientific symposia and include innovation instrumentation, software, and supplies. New technologies and products will be shown and you will find an interesting mix of sales, scientific, and engineering expertise among their representatives.

Sunday, 3:30 pm, What's Hot Exhibitor Presentations in Ballroom A
Tuesday and Wednesday poster session are held in the Ballroom B-D (exhibit hall) as well as the coffee and dessert breaks.
Tuesday and Wednesday, 9:00 – 10:20 am – Poster Session and Coffee Break
Tuesday and Wednesday, 3:00 – 3:50 pm – Poster Viewing and Dessert Break

Refer to back inside cover for exhibit hall layout

ACS Division of Analytical Chemistry	807
Advantest America, Inc.	708
AES Electrophoresis Society	702
Agilent Technologies, Inc.	111
AIST-NT Inc.	504
Anasys Instruments Corp.	406
Andor Technology	803
Applied Spectra, Inc.	606
Avantes	319
B&W Tek, Inc.	506
BaySpec, Inc.	208
Block Engineering	115
Bruker Corporation	512
Catalina Scientific Instruments, LLC	301
CeramOptec Industries Inc.	205
Coates Consulting	516
Coblentz Society	808
Eigenvector Research, Inc.	415
Elemental Scientific, Inc	113
Energetiq Technology, Inc.	612
Enwave Optronics, Inc.	601
FACSS/SciX	
FiberTech Optica, Inc.	313
Fiveash Data Management, Inc.	715
GBC Scientific Equipment	607
Harrick Scientific	110
HORIBA Scientific	401 Island
Ibsen Photonics	617
ICP Information Newsletter, Inc.	604
INDATECH	802
Innovative Photonic Solutions	405
Iridian Spectral Technologies	615
Kaiser Optical Systems, Inc.	500
Light Age, Inc.	413
Milestone, Inc.	212
Neaspec GmbH	106
New Folder Consulting	613
Ocean Optics, Inc.	417/420
Ondax, Inc.	600/602
OPOTEK, Inc.	805
Optigrate Corp	404
Oriel Instrument, Inc.	214
P&P Optica Inc.	800
PD-LD, Inc.	418
Photonic Cleaning Technologies	416
PIKE Technologies	700
Pittcon	713
Princeton Instruments, Inc.	100
Quantel USA	303
Renishaw, Inc.	603/605
Retsch Inc.	108
Rigaku Raman Technolgies	411
Royal Society of Chemistry	614
RPMC Lasers, Inc.	203
SciAps, Inc.	201
Scinco	317
Shimadzu Scientific Instruments, Inc.	210
Snowy Range Instruments	806
Society for Applied Spectroscopy	809-811
Spectral Systems LLC	716
Spectroscopy Magazine / Advanstar	318
Technology Networks.com	316
Thermo Scientific	312
Thorlabs	704
Tornado Spectral Systems	412/414
TSI Incorporated	109
Wasatch Photonics	305/307
Waters	207
Wiley-Blackwell	315
WITec Instruments Corp.	400

EXHIBITOR DESCRIPTIONS

ACS Division of Analytical Chemistry **Booth 807**
2019 Galisteo St., Bldg I-1
Santa Fe, NM 87505
www.analyticalscience.org
With 8,000 members, the Analytical Division is the third largest division of the American Chemical Society. It organizes programming at the spring and fall ACS meetings, Pittcon and the SciX Conference. The division website provides a variety of information and member services, including the Analytical Sciences Digital Library. The division has a wide range of outreach programs including student travel grants and regional meeting support. Its award program includes undergraduate, graduate and professional awards. This member oriented and directed group works for you! Please join or volunteer to help. Visit our website at www.analyticalsciences.org for more information.

Advantest America, Inc. **Booth 708**
201 West 72nd St 4G
New York, NY 10023
www.advantest.com
A world-class technology company, Advantest is the leading producer of automatic test equipment (ATE) for the semiconductor industry and a premier manufacturer of measuring instruments used in the design and production of electronic instruments and systems, The company also focuses on R&D for emerging markets that benefit from advancements in nanotech and terahertz technologies, and has recently introduced critical dimension scanning electron microscopes essential to photomask manufacturing, and 3D THz spectroscopy/imaging analysis systems to the pharmaceutical industry. Its configurable and compact TAS7500 THz Spectroscopy/Imaging Systems uses proprietary terahertz wave technology to acquire characteristic spectra. Founded in Tokyo in 1954, Advantest established its first subsidiary in 1982, in the USA, and now has subsidiaries worldwide. More information is available at www.advantest.com

AES Electrophoresis Society **Booth 702**
1202 Ann St
Madison, WI 53713
www.aesociety.org
AES Electrophoresis Society is a unique non-profit, international organization founded to improve and promote the wide variety of techniques and technologies relying upon electric field mediated separations and manipulations. The field of electrophoresis is broad including isoelectric focusing, 2-D gel electrophoresis, SDS polyacrylamide gel electrophoresis (PAGE), capillary, free-flow, dielectrophoresis as well as wide forms of electrokinetics. Electrokinetic fields now intersect microfluidics and microdevices, biotechnology, and material synthesis. Electrophoretic technologies play a central role in scientific investigations in clinical, basic, and applied disciplines from cancer research to molecular biology. Thus, promoting excellence in electrophoretic technologies and their use will improve the overall quality and sophistication of vast endeavors. Membership is open to everyone with an interest in electrophoretic applications.

Agilent Technologies, Inc. **Booth 111**
2850 Centerville Rd.
Wilmington, DE 19808
www.agilent.com/chem
Agilent manufactures and distributes a complete line of instrumentation serving the clinical, analytical, biotech, environmental, pharmaceutical, forensic science, food and flavor, academia, and all other laboratory markets that have needs for the best in quality, performance, and serviceability in the instruments they purchase.

AIST-NT Inc. **Booth 504**
359 Bel Marin Keys Blvd
Ste 20
Novato, CA 94949
www.aist-nt.com
Key Products/ Description: Atomic Force/ Scanning Probe Microscopes; Combined AFM & Raman Spectroscopy systems; TERS-enabled Solutions AIST-NT manufactures the only Scanning Probe Microscope system that has been designed from the ground up for spectroscopy applications and specifically for Nano-Raman and TERS. With individual members having 15 or more years of AFM, STM and Nano-Raman development experience, AIST-NT brings to bear on your projects the capabilities of the most innovative team in the industry. Advanced Integrated Scanning Tools for Nano Technologies is exactly what AIST-NT stands for. Please visit our booth and see our technology in real time – you will feel most welcome!

Anasys Instruments Corp. **Booth 406**
121 Gray Avenue, Ste 100
Santa Barbara, CA 93101
www.anasysinstruments.com
Anasys Instruments is dedicated to delivering innovative products and solutions that measure nanoscale material properties. Understanding structure-property correlation, especially for samples with spatially varying physical and chemical properties, is critical in a diverse range of fields, including polymers, materials science, life science, semiconductors, and data storage, to name but a few. Anasys Instruments introduced nanothermal analysis (nano-TA™) based on self-heating ThermaLever™ AFM cantilever probes in 2006, allowing nanoscale measurements of thermal properties. In 2010, Anasys Instruments proudly introduced the breakthrough multiple award-winning nanoIR™ technology. This AFM-based solution enables chemical characterization utilizing infrared spectroscopy techniques at the nanoscale. By combining AFM and infrared spectroscopy, Anasys Instruments offers researchers an unprecedented suite of chemical, mechanical, and thermal property measurement capabilities. Anasys Instruments unveiled the afm+ in Fall 2011. The afm+ is the first fully integrated AFM platform which offers three important analytical capabilities. The afm+ includes Anasys' proprietary thermal probe technology (nano-TA™), Scanning Thermal Microscopy (SThM) and Transition temperature microscopy (TTM™) capabilities. The afm+ is fully upgradable to the Anasys nanoIR system.

Andor Technology **Booth 803**
425 Sullivan Ave. #3
S. Windsor, CT 06074-1942
www.andor.com
Andor Technology is a global leader in the pioneering and manufacturing high performance scientific imaging cameras, spectroscopy solutions and microscopy systems for research and OEM markets. Andor has been innovating the photonics industry for over 20 years and aims to continue to set the standard for high performance light measuring solutions that allow consumers to perform light measurements previously considered impossible. Through continuous dialogue with customers and strong teamwork, Andor continues to innovate ground-breaking products that improve the world in which we live.

EXHIBITOR DESCRIPTIONS

Applied Spectra, Inc. **Booth 606**
46665 Fremont Blvd
Fremont, CA 94538
www.appliedspectra.com
We are a leading supplier of analytical instruments based on laser ablation technology. We offer a comprehensive suite of innovative LIBS (Laser Induced Breakdown Spectroscopy), LA (Laser Ablation) and tandem LIBS/LA instruments for rapid elemental and isotopic analysis without sample prep. Our analytical products are helping our customers perform effective and efficient forensic analysis, QC work during solar and battery manufacturing, and hazardous substance detection in the environment. We are world class LIBS/LA experts ready to support our customers with measurement method and application development.

Avantes **Booth 319**
9769 W. 119th Dr., ste 4
Broomfield, CO 80021-2560
www.avantes.com
Avantes is a leader in field of fiber optic spectroscopy offering a range of spectrometers, light sources, and fiber optics to support measurements in the range from 190-2500 nm. With an installed base of over 10,000 systems throughout the world and 17 years of experience in fiber optic spectroscopy, Avantes is equipped to meet the challenges presented by applications facing our customers. Avantes instruments and system configurations support fluorescence, UV/VIS absorbance, reflectometry/thin film metrology, LIBS, Raman, UV/VIS and NIR radiometry, optical emission spectroscopy and many other spectroscopic techniques

B&W Tek, Inc. **Booth 506**
19 Shea Way, ste 301
Newark, DE 19713
www.bwtek.com
B&W Tek is an advanced instrumentation company producing optical spectroscopy, laser instrumentation and laboratory, portable and handheld Raman systems. B&W Tek provides solutions for the pharmaceutical, biomedical, physical, chemical, LED lighting and research communities. Our commitment to innovating solutions has made B&W Tek a leader in Raman spectroscopy solutions worldwide. With a strong vertical integration capability, B&W Tek also provides custom product development, design and manufacturing.

BaySpec, Inc. **Booth 208**
1101 McKay Drive
San Jose, CA 95120
www.bayspec.com
BaySpec, Inc., founded in 1999 with 100% manufacturing in the USA (San Jose, California), is a vertically integrated spectroscopy company. The company designs, manufactures and markets advanced spectral instruments, from UV-VIS-NIR and Raman spectrometers to handheld and portable NIR and Raman analyzers, to bench-top in-line process and Raman microscopes for the biomedical, pharmaceuticals, chemical, food, semiconductor, and homeland security industries. BaySpec's core technologies include: ultra-high throughput Volume Phase Gratings (VPGTM), optimized deep-cooled detector/cameras, and high power narrowband lasers, which allow for cost effective customized solutions without the custom expenses. Designs are optimized for performance and long-term reliability featuring no moving parts. The company has experience shipping over 35,000 spectral engines of all types. For more information visit us at www.bayspec.com.

Block Engineering **Booth 115**
377 Simarano Dr. #130
Marlborough, MA 01752
www.blockeng.com
Founded in 1956, Block Engineering, LLC is a leading manufacturer and marketer of high performance Quantum Cascade Laser (QCL) and FTIR spectrometers for military, government, commercial, and industrial customers. Block's Mobile Chemical Agent Detector (MCAD) system is a fixed site, passive FTIR spectrometer offered in partnership with Northrop Grumman Corp. Block's PORTHOS™ is a portable, passive FTIR spectrometer system that remotely detects chemical threats as far as three miles and protects against chemical warfare agents and weapons of mass destruction. Block Engineering is also manufacturing and selling a line of revolutionary QCL-based spectrometers, including LaserScan™, LaserBench™ and LaserScope™ for non contact, non destructive, real time surface chemical analysis for applications ranging from detection of explosives and liquid/solid chemical warfare agents to control of manufacturing operations and verification of surface conditions in a variety of industrial processes.

Bruker Corporation **Booth 512**
19 Fortune Dr.
Billerica, MA 01821
www.bruker.com
Bruker is a leading provider of high-performance scientific instruments and solutions for molecular and materials research, as well as for industrial and applied analysis. www.bruker.com

Catalina Scientific Instruments, LLC **Booth 301**
1870 West Prince Road, Ste 21
Tucson, AZ 85713
www.catalinasci.com
Catalina Scientific Instruments. Our products include an innovative cross-dispersing echelle spectrograph and KestrelSpec™ imaging spectroscopy software. Our portable Echelle Multiplex Unit (EMU) has high resolution up to 50,000 resolving power with high throughput at F/2 or F/3. Each echelle image covers the entire UV-VIS-NIR spectral region in one exposure, without scanning. The echelle systems are ideal for Laser Induced Breakdown Spectroscopy (LIBS), OES, bioluminescence, photoluminescence, fluorescence, and Raman applications using multiple laser wavelengths.

CeramOptec Industries Inc. **Booth 205**
515 Shaker Road
East Longmeadow, MA 06062
www.ceramoptec.com
CeramOptec Industries Inc a world leader in specialty silica optical fiber production including non-circular core fibers, bundles, assemblies/vacuum products. All silica fibers 190nm to 2500 operation with NA's from 0.12 - 0.53. Hard polymer clad, plastic clad fibers, Silver halide fibers for MIR. Custom engineered solutions with competitive prices.

Coates Consulting **Booth 516**
12 North Branch Rd
Newton, CT 06471
http://www.coates-consulting.com/
Coates Consulting is celebrating its 17th year in business as a leading scientific and technology-based consulting company. Coates Consulting LLC was formed in 2010 to expand its business operations, and to position the company as an instrument and sensor designer and as a producer of prototypes and manufactured hardware. The company continues to provide traditional consulting services noted below:
Analytical Services: Coates Consulting LLC has an operational 2000 sq. ft laboratory

Technology Resource: Company supports new sensor technology, from applications to new products and product marketing
Spectroscopy Expert Services: Utilizing nearly 50 years experience in analytical chemistry and spectroscopy.
Product Development Services: Company is well established in instrument and sensor product development; providing designs, prototypes and concept models

Coblentz Society **Booth 808**
Dept of Chemistry and Biochem
Univ of South Carolina
Columbia, SC 29208
www.coblentz.org
Professional organization that fosters the understanding and application of vibrational spectroscopy. Through the voluntary efforts of its members, the society sponsors scientific conferences, creates symposia for research presentations, provides social activities to stimulate informal discussion, and recognizes excellence in vibrational spectroscopy through four sponsored awards (the Coblentz, Craver, Williams-Wright, and Lippincott Awards). The society also administers the ABB Bomem-Michelson Award. The Coblentz website can be found at http://www.coblentz.org.

Eigenvector Research, Inc. **Booth 415**
3905 West Eaglerock Dr
Wenatchee, WA 98801
http://www.eigenvector.com
Eigenvector Research, Inc. (EVRI) is a full-service Chemometrics company, offering software, training and consulting. EVRI provides advanced chemometrics support for a wide variety of industries and academia. Our chemometric software products include our flagship MATLAB-based PLS_Toolbox and stand-alone Solo. We also offer MIA_Toolbox and Solo+MIA for Multivariate Image Analysis and applications for putting chemometric models on-line, such as Solo_Predictor. EVRI offers chemometrics training, such as our short courses here at SCIX, plus our renowned Eigenvector University (EigenU) held each May in Seattle. We also do in-house training for many Fortune 500 companies and government agencies. Our consulting services have been an important part of projects in both start-up and large established companies. Our staff of six consultants has over 100 years of combined chemometric experience. Make EVRI your complete source of chemometric tools and know-how!

Elemental Scientific, Inc **Booth 113**
1500 N. 24th Street
Omaha, NE 68110
www.meinhard.com/www.icpms.com
Elemental Scientific offers Sample introduction for ICP, ICPMS, and AA that includes: Meinhard and PFA nebulizers, scientific glassware, laboratory automation, FAST systems, preconcentration systems, elemental speciation, peristaltic pumps, syringe pumps, automated inline and offline sample dilution. Visit us at: www.icpms.com | www.meinhard.com

Energetiq Technology, Inc. **Booth 612**
7 Constitution Way
Woburn, MA 01801
www.energetiq.com
Energetiq Technology, Inc. is a developer and manufacturer of broadband light sources for use in analytical instrumentation. Energetiq has introduced a novel new technology for broadband DUV/VIS/NIR high brightness light source. The EQ-99 and EQ-1500 LDLS™ are Laser-Driven Light Sources that have a repeatable, long life with extremely stable output.

Enwave Optronics, Inc. **Booth 601**
18200 W. McDurmott St., Ste B
Irvine, CA 92614
www.enwaveopt.com
Enwave provides a full range of Raman solutions from low cost routine Raman instruments to high sensitivity Raman instruments with a variety of configurations to meet your applications needs. Five categories of products to fulfill your routine Raman application needs:
•Handheld and Field Portable Raman Instruments
•High Performance On-line Process Raman Analyzers
•Laboratory Raman, Including Confocal Raman Microscopes
•OEM and Custom Raman Instruments
•Gas-Phase Raman Analysis Systems

FACSS / SciX
2019 Galisteo St., Bldg I-1
Santa Fe, NM 87505
www.facss.org / www.scixconference.org
SciX 2014 presented by FACSS will be held September 28 – October 3 in Reno, Nevada at the Grand Sierra Resort. The conference attracts top scientists from academia and industry for a powerhouse collection of lectures, poster, exhibits, and more. Symposia includes groundbreaking research and prestigious internationally recognized awards. SciX offers daily networking opportunities through its exhibits and social events.

FiberTech Optica, Inc. **Booth 313**
330 Gage Avenue, Ste 11
Kitchener, ON, N2M 5C6 CANADA
www.fibertech-optica.com
Designer and manufacturer of specialty fiber optic solutions! Broad range of fiber assemblies such as: Our new feature product – Raman Filtered Probe, patchcords, couplers, pigtails, spot-to-line converters, bundles, reflectance probes, OCT probes, Raman probes, linear and spaced v-groove arrays and high power laser cables. Fiber optic components such as: Vacuum feedthrough and LED modules. Spectral bands coverage from deep UV to MIR (190-5500nm)! Applications are biomedical imaging, process control, laser power delivery. Whether you need one prototype to test a concept or a large batch to be integrated into your products, we are here to assist you.

Fiveash Data Management, Inc. **Booth 715**
211 Vista Rd.
Madison, WI 53726
www.fdmspectra.com
FDM provides ATR and transmission FTIR libraries, and Raman libraries. Six of our ATR libraries were expanded and rerun on a monolithic diamond ATR (4000 to 400 cm-1). These libraries include the FDM ATR Polymers, FDM ATR Organics, FDM ATR Inorganics, FDM ATR Essential Oils, and the FDM ATR Retail A&S. The new FDM ATR Dyes were run on both diamond and Ge ATR crystals to get excellent spectra of high refractive index compounds. Our Raman libraries now include the FDM Raman Polymers(3400 to 200 cm-1), Organics(3400 to 200 cm-1), Inorganics (3400 to 50 cm-1), and the FDM Raman Retail A&S(3400 to 200 cm-1). The FDM Raman Minerals, which now has more than 11,500 spectra, is the world's most extensive and detailed collection of Raman mineral spectra. Ask about these new libraries: the FDM ATR Drugs Mixtures, the FDM HiRes VPFTIR Mixtures and the FDM HiRes VPFTIR Refrigerants Mixtures.

EXHIBITOR DESCRIPTIONS

GBC Scientific Equipment **Booth 607**
151A N. State St./ PO Box 339
Hampshire, IL 60140
www.gbcscientific.com
The Optimass 9500 ICP-MS Time-of-Flight Mass Spectrometer performs 30,000 acquisitions each second, simultaneously measuring every mass and isotope from 1 to 260 amu. This ICPMS offers unique fingerprinting software option and semi-quantitative retrospective analysis. Our Mass Spec is 5 times faster than a quadrupole! GBC offers a wide range of atomic absorption spectrophotometers for flame, furnace and hydride analysis, from the most automated instrument on the market, the SavantAA Sigma, to the low-cost, high-value SensAA. gbcscientific.com (USA) - gbcsci.com (worldwide)

Harrick Scientific **Booth 110**
141 Tompkins Ave.
Pleasantville, NY 10570
www.harricksci.com
The leading innovator in molecular spectroscopy sampling for over 40 years, **Harrick** offers an extensive array of accessories for FTIR, UV-Vis, Raman, and x-ray spectroscopy. Sampling techniques include ATR, diffuse reflectance, specular reflectance, transmission, and controlled environmental chambers for in-situ Operando catalysis and photochemistry research. We work with researchers to develop effective solutions for challenging research studies

HORIBA Scientific **Booth 401 Island**
Attn: Raman Spectroscopy
3880 Park Avenue
Edison, NJ 08820
www.horiba.com/scientific
See surprising new innovations in Raman, ICP/GD-OES, Fluorescence and many other areas of optical spectroscopy. At least one major new instrument is being released at FACSS, sorry SCIX, to send you over the rainbow and in to the real Kansas. Our team of scientists will be available for science and fun. We will be showing the latest developments in Raman microscopy, AFM/Raman, low cost and high cost Raman, transmission Raman, microsecond and millisecond Raman imaging. We offer the highest sensitivity Fluorescence systems on the market - including TCSPC and EEM/UV-VIS analysis, fast Surface Plasmon Resonance (SPR) imaging and combined CL/PL/Raman accessories for SEM. For elemental analysis we provide advanced ICP/GD-OES systems, C/S/O/N/H analyzers and smallest spot XRF microscopes. We have analyzers for particles from 1nm to 30mm in size providing size, shape, zeta potential and surface area. If you have a special application or want systems that combine any of the above techniques stop by we may already do what you want. We will certainly be interested talk with you about what interests you and where we can help.

Ibsen Photonics **Booth 617**
Ryttermarken 15-21
Farum, Other, Denmark DK-3520
www.ibsenphotonics.com
Ibsen Photonics is the global leader in transmission gratings and OEM spectrometer modules for UV, VIS, and NIR spectral ranges.
The overall key benefits of our products and technologies are:
Very high efficiency/throughput (low optical loss)
High thermal stability and robustness
Our spectrometer products include:
ROCK for high throughput
FREEDOM for ultra compact size and low cost
EAGLE for high resolution
I-MON wavelength interrogation monitor for FBG sensing systems in the 850, 1310, and 1550 nm wavelength ranges
Custom built OEM spectrometers to match our customer's exact needs
Our grating products include:
Phase Masks for Fiber Bragg Grating manufacturing
Pulse Compression Gratings for high power lasers
Polarization insensitive gratings (PING) for Telecom WSS, OCM and tunable filters
High efficiency spectrometer gratings

ICP Information Newsletter, Inc. **Booth 604**
PO Box 666
Hadley, MA 01035-0666
http:/icpinformation.org
ICP Information Newsletter, Inc. is a nonprofit corporation established in 1997 to foster science education, research, and study in spectroanalytical chemistry. The corporation includes three division: the ICP Information Newsletter, a monthly publication with international distribution that gathers all conference and published information related to plasma spectrochemistry; the Winter Conference on Plasma Spectrochemistry, a biennial meeting with international participation featuring state-of-the-art research developments in plasma spectrochemistry, and the University Research Institute for Analytical Chemistry, the research and development branch that provides specialty plasma spectrochemical analysis, consulting, method development, training, and applied research with ICP atomic emission and mass spectrometry. The 2014 Winter Conference is planned for January 5-11, 2014 in Amelia Island, Florida. The ICP Information Newsletter now in its 39th year of publication is distributed to subscribers in computer – readable format on CD-ROM. Visit http://icpinformation.org for subscription and conference details.

INDATECH **Booth 802**
385 Avenue Les Baronnes
Prades Le Lez
Herault, France 34730
www.indatech.eu
Industrial products are produced by complex processes and involve multi-phase systems such as suspension of particles in liquids or mixtures of particles (powders, tablets, polymer composites etc.). In order to monitor and control the processes generating these products, it is necessary to assess, in real-time, both physical and chemical attributes non-destructively ('PAT' approach). Usually it is necessary to implement many different sensors which can be both costly and complex. INDATECH has developed novel and dedicated solutions, combining the advantages of Hyperspectral imaging with VIS-NIR spectroscopy in order to predict physical and chemical attributes using spatially resolved spectroscopy techniques. These solutions rely on a hyperspectral terminal unit (Hy-Ternity®) combined with SAM-Flex® probes (biotechnology, crystallisation, filtration, dissolution,..) or SAM-Spec® specifically designed interfaces (fluid bed drying, compaction, filling, polymerisation, etc..). We also provide new solutions for in-line Raman Spectroscopy, Hyperspectral imaging and classical NIR spectroscopy.

Innovative Photonic Solutions **Booth 405**
4250 U. S. Highway 1, Ste 1
Monmouth Junction, NJ 08852
www.innovativephotonics.com
IPS specializes in the manufacture of high performance wavelength stabilized semiconductor lasers for use in Raman spectroscopy, FTIR, fiber laser seeding & pumping, remote sensing, interferometry, speckle free illumination and homeland security applications. Our proprietary wavelength stabilization technology enables us to lock the

laser to a specific wavelength without complex feedback mechanisms. The technology is applicable to both single and multi-mode lasers and enables the manufacture of both high power multi-mode and narrow linewidth (<100 KHz) single frequency lasers. Our products span the ~400 nm – 2400 nm wavelength range and are available in TO-56, 14-Pin BF packages or in turn-key modules with integral laser and temperature control electronics. New products include a 638 nm single frequency HeNe laser replacement source, an integrated laser and Raman probe, and OEM Raman spectroscopy engines

Iridian Spectral Technologies **Booth 615**
2700 Swansea Cres.
Ottawa, ON, K1G 6R8 CANADA
www.iridian.ca
Iridian Spectral Technologies, the leader in optical filter solutions, designs and manufactures thin film optical filters and coatings for UV, visible, and IR applications. Our dielectric thin film filters provide long term durability and reliability while offering industry-leading optical performance. We are happy to provide custom filter solutions to address specific functional needs in benchtop, probe, or handheld Raman applications. We offer long-pass, short-pass, notch, laser line and multi-band filters. Our spectroscopy filters offer high transmission (>90%), steep edges (cut-offs as low as 40 cm-1) and deep blocking (>OD6). This provides more signal with less background for Raman spectroscopy and allows you to capture better images for fluorescence or microscopy applications by providing brighter images with improved contrast.

Kaiser Optical Systems, Inc. **Booth 500**
371 Parkland Plaza
Ann Arbor, MI 48103
www.kosi.com
Kaiser Optical Systems, a Rockwell Collins Company, is recognized as a world leader in the design and production of Raman analyzers and components for spectroscopy. Our RamanRxn Systems™ suite of Raman analyzer includes ATEX certified process analyzers for classified installations, reaction analysis analyzers, bulk solids analyzers, gas-phase analyzers, Raman microscopes, and the Raman WorkStation™ featuring Kaiser's revolutionary fast, quantitative PhAT technology and transmission Raman capability. Our components product lines include performance filters, high F/# spectrographs, and OEM systems. Raman analyzer installation locations include R&D, Pilot plant, manufacturing, and QA/QC. Pharmaceutical PAT applications include reaction monitoring, API production, polymorphic form quantitation, drug product unit operations (including blending, granulation, and tableting), and end product testing. Other Applications areas for RamanRxn Systems™ analyzers include biotech, semiconductors, nanotechnology, petrochemical, polymers, and specialty chemical. We invite you to visit our booth, learn about our products, and discuss your applications needs.

Light Age, Inc. **Booth 413**
500 Apgar Dr.
Somerset, NJ 08873
www.lightage.com
Since its founding in 1986, Light Age, Inc. has been the inventor, innovator, and preeminent developer of alexandrite laser technology and several other advanced laser technologies. It has also played a major role in pioneering and establishing numerous advanced applications based on solid-state laser media and nonlinear optical processes. Today, Light Age is the leading supplier of alexandrite laser systems worldwide for almost every application from fundamental research to laser hair removal to atmospheric lidar. Its products are sold under its own name brands and in OEM and embedded products distributed by other device manufacturers.

Milestone, Inc. **Booth 212**
25 Controls Drive
Shelton, CT 06484
www.milestonesci.com
Milestone Inc., a global leader in the field of microwave sample prep and mercury analysis, offers a complete suite of productivity tools for today's modern chemist to obtain the highest throughput for metals digestions, accelerated organic extractions, and mercury analysis (Direct, CVAAS, CVAFS, and Simultaneous CVAAS/AFS). Come see the new UltraWAVE as it revolutionizes microwave digestion through the use of our patented Single Reaction Chamber technology (SRC) - run mixes batches and enjoy hassle free cleaning with disposable vials.

Neaspec GmbH **Booth 106**
Bunsenstrasse 5
Martinsried, Bava, Germany 82152
www.neaspec.com
Neaspec is dedicated to delivering innovative solutions for nanoscale optical imaging & spectroscopy for researchers in industry and academic institutions. Neaspec's NeaSNOM – the ultimate nanoanalytic microscopy platform for materials research and photonics – enables optical analysis of complex material systems at visible, infrared and terahertz frequencies at a spatial resolution of 10nm.

New Folder Consulting **Booth 613**
19 Lynbrook Circle
Durham, NC 27712
http://www.newfolderconsulting.com/
New Folder consulting develops graphical user interfaces for chemometrics to help you understand your data and easily develop real-time processing streams. New Folder also provides personalized consulting to help you develop new algorithms for your specific data.

Ocean Optics, Inc. **417/420**
830 Douglas Avenue
Dunedin, FL 34698
www.oceanoptics.com
Ocean Optics is the inventor of the world's first miniature spectrometer and a global leader in optical sensing technologies for research, education, industry and quality. Ocean Optics also provides a full range of complementary technologies such as optical fibers, probes, sensors and sampling accessories. From UV through NIR, from modular components to full LIBS and Raman systems, Ocean Optics has a solution for virtually every application need and every budget.

Ondax, Inc. **Booth 600/602**
850 E. Duarte Rd.
Monrovia, CA 91016
www.ondax.com
Ondax Inc. manufactures a full line of high-performance Raman lasers and filter accessories to enable best-in-class Raman systems in a compact, portable footprint. SureLock™ wavelength-stabilized Raman lasers deliver either single-frequency or line-narrowed performance with very low power consumption. Wavelengths from 405nm to 808nm with powers up to 800mW are available, in compact TO cans, pigtailed butterfly, free-space and fiber-coupled module configurations. Ondax also offers a full range of wavelength-matched NoiseBlock™ ASE filters (fiber-coupled or free-space), and ultra-narrow-band (<10cm-1) SureBlock™ Notch filters. These filters enable simultaneous detection of extremely low frequency Stokes and

Anti-Stokes Raman signals. The filters are manufactured using an extremely robust glass material that does not degrade over time and can withstand harsh environmental conditions. Custom laser wavelengths and filters are available. Ondax offers excellent technical customer support to help you design and optimize these components into your Raman system. For more information visit www.ondax.com or contact sales@ondax.com

OPOTEK, Inc. **Booth 805**
2233 Faraday Avenue
Suite E
Carlsbad, CA 92008
www.opotek.com
Manufacturer of efficient, broadly tunable ultraviolet, visible and infrared solid-state laser systems based on patented OPOTEK Optical Parametric Oscillators (OPO). These products stand out in their reliability and robustness to produce compact and portable designs. The systems are computer controlled via a USB connection and require no expertise in laser operation.

Optigrate Corp **Booth 404**
3267 Progress Drive
Orlando, FL 32826
www.optigrate.com
OptiGrate Corp is a pioneer and world leader in commercial volume Bragg gratings (VBGs) and VBG-based ultra-narrow band optical filters. For over a decade OptiGrate has designed and manufactured a full range of VBGs in inorganic photo-thermo-refractive silicate glass and supplied VBG-based filters to more than 300 customers on 5 continents. OptiGrate's product line of Raman optical filters includes ultra-narrow band Notch filters (BragGrate™ Notch Filter) and laser-line cleaning filters (BragGrate™ Bandpass Filter) with a linewidth narrower than 5 cm-1 at FWHM. Such filters are fully environmentally stable, do not degrade in high intensity light irradiation, and enable simultaneous measurements of Stokes and Anti-Stokes frequencies down to 5 cm-1 with a single-stage monochromator Raman systems. Standard filters are available at 488, 514, 532, 633, 785, and 1064 nm, while any custom wavelength in a range from 400 to 2000 nm can be ordered.

Oriel Instrument, Inc. **Booth 214**
A Brand of Newport Corporation
150 Long Beach Blvd
Stratford, CT 06349
www.newport.com/oriel
Oriel® Instruments, a brand of Newport Corporation, is recognition in the optical research field as a highly reliable source for well engineered, durable Light Sources and their dedicated Power Supplies, as well as Light Detection Systems and Spectroscopy Instrumentation. Oriel also manufactures dedicated broadband light sources, monochromatic light sources and detectors for light measurement & characterization in sophisticated dedicated instrumentation.

P&P Optica Inc. **Booth 800**
680-A Davenport Road
Waterloo, ON N2V 2C3 CANADA
www.ppo.ca
P&P Optica is your partner for optimized spectral imaging systems. We take pride in developing systems with our customers, and bridge the gap between "custom" and "turn-key" solutions. Our spectrometers provide a more sensitive, faster, and more accurate tool for use across a variety of industries and applications. Through innovative design and components P&P Optica spectrometers provide sensitivity unprecedented for optical spectrometers, so that less time or illumination is required to reach the same levels of sensitivity as other systems on the market. The flexibility of our design allows for an application optimized system while considering your project's specific needs

PD-LD, Inc. **Booth 418**
30-B Pennington-Hopewell Rd
Pennington, NJ 08534
www.pd-ld.com
Since 1993, PD-LD Inc. is focused on volume production of innovative photonic components for high performance spectroscopic systems. PD-LD developed and patented Volume Bragg Grating (VBG®) technology which is incorporated in many standard wavelength stabilized laser products used for Raman and SERDS system solutions. These stabilized lasers are available as full turnkey, enclosed modules.. Standard wavelengths available include: 450nm, 514.5nm, 530nm, 647nm, 785nm and many others in the NIR. New products for SciX 2013 include 632.8nm single mode series, SMS, He ne laser alternative and the brilliant green GB-530 laser module. PD-LD is also demonstrating the Prism Award winning LS-2 LabSource Dual Laser System for research innovators of Shifted excitation Raman Difference Spectroscopy, SERDS. The LS-2 provides the two closely matched wavelengths required to greatly reduce or completely eliminate fluorescence from low Raman sample emissions. From component to bench-top, PD-LD has the product and the experience for your spectroscopic performance requirements.

Photonic Cleaning Technologies **Booth 416**
1895 Short Lane
Platteville, WI 53818
www.photoniccleaning.com
Photonic Cleaning Technologies is the manufacturer of First Contact PolymersTM - "THE Cleaning and Protection System." Available in Colorless and Red and each in Spray and Non-Spray Formula. Apply liquid polymer solutions to surfaces and peel the resulting dried film leaving the surface nearly atomically clean. Listed on NASA's Outgassing website as meeting the collected volatile condensable mass (CVCM) requirements for space applications. Independent XPS/ESCA and Laser Damage Threshold testing shows no residue down to the molecular level! Safe with high power laser optics. Remove Dust & Fingerprints. Reduce Solvent Waste. Non-Toxic Inert Polymer and solvents. Clean Nanostructures, Gratings & Masks! Protect and clean microscope optics.

PIKE Technologies **Booth 700**
6125 CottonWood Drive
Madison, WI 53719
www.piketech.com
PIKE Technologies, Inc., is the leading manufacturer of sampling accessories for FT-IR, NIR and UV-Vis spectrometers. PIKE products include attenuated total reflectance (ATR), diffuse reflectance, specular reflectance, integrating spheres, polarization, gas cells, IR microscope, beam condensers, remote sensing, and a complete line of transmission sampling accessories. Many of these products are available with optional heating and automation for increased sampling speed and productivity. PIKE Technologies, Inc. also offers design and consulting services for development of specialized and custom products for a wide range of spectroscopy applications. PIKE products are used in the petrochemical, food, forensic, pharmaceutical, semiconductor, agriculture, government and the material science industries as well as in many academic institutions around the world. They can be used for the analysis of organic and inorganic materials and are compatible with all major brands of spectrometers.

EXHIBITOR DESCRIPTIONS

Pittcon 2014 **Booth 713**
300 Penn Center Blvd, Ste 332
Pittsburgh, PA 15235
www.pittcon.org
Pittcon 2014, the world's largest annual conference and exposition for laboratory science, will be held March 2- 6, 2014, in Chicago, Illinois. If you identify, quantify, analyze, or test the chemical or biological properties of compounds or molecules, Pittcon is a must attend event for you. See all the innovations in instrumentation from leading companies from around the world, learn about the latest techniques used in your industry, select from over 2,000 technical presentations and over 100 short courses, and participate in networking opportunities with world renowned scientists. Register today at www.pittcon.org.

Princeton Instruments, Inc. **Booth 100**
3660 Quakerbridge Rd.
Trenton, NJ 08619
www.princetoninstruments.com
Princeton Instruments is a world-renowned designer and manufacturer of high-performance spectrographs; CCD, ICCD, EMCCD, and InGaAs cameras; and optics-based solutions for the scientific research, industrial imaging, and OEM communities. We take pride in partnering with our customers to solve their most challenging problems in unique, innovative ways. We are excited to feature the new IsoPlane aberration-free, imaging spectrograph that "deters the blur." The exclusive, state-of-the-art optical design utilized in the IsoPlane means this revolutionary instrument provides a sharply focused image across the entire focal plane, compared to the smeared image of the traditional Czerny-Turner models. With the IsoPlane more photons end up in the peak, increasing the height and effective signal-to-noise ratio (SNR), rather than in the wings, where they contribute to the background noise. Stop by the Princeton Instruments booth for a demonstration. Visit www.deter-the-blur.com or www.princetoninstruments.com for more information.

Quantel USA **Booth 303**
601 Haggerty Lane
Bozeman, MT 59715
www.quantel-laser.com
Quantel group is an international leader in providing pulsed laser technologies for research, industrial, commercial, military, and medical applications. Founded in 1970, the Group has a consistent record of investment leading to numerous innovative and successful products distributed worldwide. Quantel corporate headquarters is in Paris with manufacturing subsidiaries in the USA, Germany, and France.

Renishaw, Inc. **Booth 603/605**
5277 Trillium Blvd.
Hoffman Estates, IL 60192
www.renishaw.com
Renishaw is a global company with core skills in measurement, motion control, spectroscopy and precision machining. We develop innovative products that significantly advance our customers' operational performance - from improving manufacturing efficiencies and raising product quality, to maximizing research capabilities and improving the efficacy of medical procedures. Renishaw Raman spectrometers are configurable to include: multiple excitation sources from the UV through NIR with automated laser switching and alignment; quick-launch fiber-optic probes; AFM/NSOM/Raman interfaces, SEM-Raman interfaces, microscope accessories including hot/cold cells, macro-sampling; global Raman imaging, near the excitation line analysis (<5 cm-1). Renishaw Raman spectrometers provide chemical/molecular information confocally and can be configured for sub-micron spatial resolution with options for auto-alignment, internal calibration & performance validation. For more information on Renishaw's Raman microscope go to www.renishaw.com/raman

Retsch Inc. **Booth 108**
74 Walker Lane
Newtown, PA 18940
www.retsch-us.com
Retsch is the world leader in solid material sample preparation equipment for quality control and research and development laboratories. Our expertise and devotion to providing the highest quality products for accurate and reproducible sampling methods is unsurpassed. Our selection of mills, sieve shakers, and sample dividers offer the industry standards for sample preparation.

Rigaku Raman Technolgies **Booth 411**
1101 McKay Dr., Ste B
San Jose, CA 95131
www.rigaku.com
Rigaku's new handheld Raman instruments combine patented optics and proven spectral analysis techniques with state-of-the-art, low-cost Telecom-developed optical components, providing our customers with fast, economical, easy to use, handheld chemical identification and composition analyzers for explosives detection, including improvised explosive device (IED) detection; narcotics and other controlled substances detection and identification; counterfeit drug detection, food contaminant detection; and detection and identification of many other sample types; for homeland security; pharmaceutical, cosmetics, food, wine, beer and agricultural feed quality assurance and quality control; medical diagnostics; petrochemical exploration and process control; forensics; archeometry; and many other applications. For over 60 years Rigaku has been the global leader in x-ray spectrometers. With our exclusive line of handheld Raman analysis instrumentation, Rigaku continues the tradition of bringing high quality spectrometers for real world sample analysis. At Rigaku Raman Technologies we are dedicated to providing our customers with the tools that solve their analysis problems today.

Royal Society of Chemistry **Booth 614**
Thomas Graham House
Science Park, Milton Road
Cambridge, UK CB4 0WF
www.rsc.org
The Royal Society of Chemistry (RSC) is the largest organisation in Europe for advancing the chemical sciences, supported by 45,000 members worldwide and an internationally acclaimed publishing business. The Analytical Division of the RSC advances analytical chemistry and science by providing a forum for analytical chemists and scientists to exchange information and ideas. It organises meetings and via, the Analytical Chemistry Trust Fund, finances studentships, Schools Analyst competitions, awards, lectureships and VSO students. Our analytical portfolio of journals features wide coverage across all areas of analytical science, from chemistry and physics to biology and engineering. From Analyst which highlights premier fundamental discoveries, inventions and applications in the analytical and bioanalytical sciences, Analytical Methods which publishes early applied demonstrations of new analytical methods with clear societal impact, to Journal of Analytical Atomic Spectrometry (JAAS) which is considered to be the number-one journal for innovative research in the theory, practice and application of spectrometric techniques to elemental research. Analytical Methods also now features AMC Technical Briefs published on behalf of the Analytical Methods Committee. These articles are free to access and provide up-to-date technical information, concentrating on items that are important for analytical scientists, currently topical,

and which are not readily available from other sources. Whether it's to become an RSC member, engage with the RSC Analytical Division in advancing analytical chemical science, meet a member of RSC Publishing staff or find out the latest news from our analytical journals, please come and visit our booth at SCIX 2013!

RPMC Lasers, Inc. **Booth 203**
203 Joseph Street
Ofallon, MO 63366
www.rpmclasers.com
RPMC Lasers, Inc. offers innovative Diode Pumped Solid-State Lasers and Laser diode Modules for industrial and scientific applications. Its compact laser modules, featuring wavelengths in the visible and near-UV spectrum, have outstanding performance with market-leading power levels. The SLIM line features a monolithic resonator technology that ensures true single-frequency emission along with excellent power, wavelength and pointing stability

SciAps, Inc. **Booth 201**
2 Constitution Way
Woburn, MA 01801
www.sciaps.com
SciAps, Inc. is a Boston-based instrumentation company specializing in portable analytical instruments. Our mission is to provide durable, field-tested, portable instruments to identify any compound, any mineral, any element - any place on the planet. Manufacturing, service and customer support is operated out of our fully ISO-certified facility located in Laramie, WY

Scinco **Booth 317**
2935 S. Fish Hatchery Rd
Madison, WI 53711 The SCINCO S-3100 UV-Vis spectrophotometer is designed for research, routine and high-throughput applications that require rapid and accurate analysis. By utilizing advanced photodiode array technology and the See-through optical design the S-3100 offers better sample throughput when compared to traditional monochromator-based spectrophotometers. This robust optical design offers superior wavelength accuracy of less than ± 0.2 nm and repeatability of less than 0.02 nm. Featuring only one moving part and a 10,000-hour tungsten lamp, the design of the S-3100 enables longer uninterrupted operation. SCINCO, in the USA will offer a new unprecedented standard warranty coverage of 3 years. Visit SCINCO at booth 317 for information and a demonstration or contact CPS Analytical at (608) 274-7719 or info@CPSanalytical.com. You can also visit our website to see this an other products offered by CPS at http://cpsanalytical.com/CPSanalytical_scinco_S3100.htm

Shimadzu Scientific Instruments, Inc. **Booth 210**
7102 Riverwood Dr.
Columbia, MD 21046
www.ssi.shimadzu.com
Shimadzu offers a full line of analytical instrumentation, including UV Visible and Fluorescence Spectrophotometers; FTIR Spectrometers; Automated FTIR Microscope; HPLC systems and components; LC/MS; Gas Chromatography; GC/MS; MALDI-TOF Mass Spectrometers; Data Stations for Spectroscopy and Chromatography; Thermal Analyzers, TOC, Atomic Absorption Spectrometers, ICP, EDX, Particle Size Analyzers, Balances, Capillary Rheometers, Mooney Viscometers, Universal Testing Equipment and more.

Snowy Range Instruments **Booth 806**
628 Plaza Lane
Laramie, WY 82070
www.wysri.com
Snowy Range Instruments (SnRI) uses a wide range of optical, electrical, mechanical, and software methods to solve difficult spectroscopic problems. Creative, cost-effective solutions are made possible by SnRI's experience with diverse optical technologies and our experience with complex applications. Our team takes pride in our on-time delivery of cost-effective designs and instrumentation. SnRI introduces its Sierra Series of spectroscopic readers. Built on a decade of experience in Raman instrument design the Sierra readers address many of the issues of optical analysis. Our spectrometers are constructed from the best components in a solid aluminum body for rugged long-life time usage.

Society for Applied Spectroscopy **Booth 809-811**
201B Broadway Street
Frederick, MD 21701-6501
www.s-a-s.org
The Society for Applied Spectroscopy is a non-profit membership organization representing scientists in all areas of spectroscopy. Members receive numerous benefits including a subscription to the internationally recognized, peer reviewed journal Applied Spectroscopy. Visit our booth for more information and to join!

Spectral Systems LLC **Booth 716**
6350 Pheasant Lane
Verona, WI 53593
www.spectral-systems.com/
Precise infrared FTIR Spectroscopy components for 30 years, Spectral Systems has a renewed commitment to providing high quality and innovative optical components, coatings, system integration and consulting services from concept to production for products supporting FTIR spectroscopy, including laboratory, remote sensing and miniature hand held instruments. A long and distinguished history supplying components to JSLSCAD, Space flight thru NASA, and many commercially found IR applications. Our custom coating products, such as BBAR for IR materials, protective anti-humidity for halides, solderable, thorium free, dichroic, and FTIR beamsplitters set the industry standard for quality and performance. We succeed when our customers succeed.

Spectroscopy Magazine / Advanstar **Booth 318**
485F US Highway 1 South, Ste 100
Iselin, NJ 08830
www.spectroscopyonline.com
Spectroscopy's mission is to enhance productivity, efficiency, and the overall value of spectroscopic instruments and methods as a practical analytical technology across a variety of fields. Scientists, technicians, and laboratory managers gain proficiency and competitive advantage for the real- world issues they face through unbiased, peer-reviewed technical articles, trusted troubleshooting advice, and best-practice application solutions. We serve subscribers by using print and digital media to disseminate highly focused editorial content that combines peer-reviewed scientific articles with practical, solutions-based information, helping readers to become better spectroscopists whether they work in the laboratory, on the process line, or in the field.

Technology Networks.com **Booth 316**
Woodview, Bull Lane
Sudbury
Suffolk CO10 0FD, UK
www.technologynetworks.com/spectroscopy
Since our foundation in 2000, running just one website based on combinatorial chemistry, Technology Networks has expanded its portfolio to include 27 communities dedicated to a wide range of disciplines within the life science and drug discovery sectors. Providing a base for our members to access the latest news, products and research from their chosen fields, our communities have been designed to be easy to navigate, interactive, with clearly displayed unique content, as well as offering a rich source of product and technical information.

Thermo Scientific **Booth 312**
5225 Vernona Road
Madison, WI 53711
www.thermo.com
As the largest Raman instrument supplier in the world, Thermo Fisher is committed to continued innovations in Raman microscopy. The DXR family of Raman systems is known for making research performance Raman more accessible and useable by a wider number of users. This year we extend our solutions to materials science research to include an integrated AFM-Raman solution that allows multifaceted analysis of advanced materials with nanoscale resolution. Come see up close what's new and how we can help you accelerate your work. Whether you're in academic or government research or an analytical laboratory in industry the DXR family can get you there faster.

Thorlabs **Booth 704**
56 Sparta Ave
Newton, NJ 07860
www.thorlabs.com
Thorlabs, a vertically integrated photonics products manufacturer, was founded in 1989 to serve the laser and electro-optics research market. As that market has spawned a multitude of technical innovations, Thorlabs has extended its core competencies in an effort to consistently serve its industry at the research end, as well as the industrial, life science, medical, and defense segments. The organization's highly integrated and diverse manufacturing assets include semiconductor fabrication of Fabry-Perot, DFB, QCL, ICL, and VCSEL lasers, fiber towers for drawing glass optical fibers (silica, fluoride, tellurite, and hollow core), MBE crystal growth machines, brushless DC motor technology for advanced microscopy positioning stages, extensive glass and metal fabrication facilities, advanced thin film deposition capabilities, and optomechanical and optoelectronic shops. Headquartered in Newton, NJ, the company has over 1000 employees at 11 manufacturing and sales offices throughout the United States, United Kingdom, Germany, France, Sweden, Japan, China, and Brazil.

Tornado Spectral Systems **Booth 412/414**
555 Richmond Street West, Ste 705
Box 218
Toronto, ON M5V 3B1 Canada
www.tornado-medical.com
Tornado Spectral Systems develops optical spectroscopy solutions for sample identification, detection, diagnosis, and imaging. Our "powered by Tornado" partnership model enables OEMs to turbo-charge their end-user applications and products with our high-performance free-space spectroscopy and nanophotonics (aka spectroscopy-on-chip) technologies. Tornado's HyperFlux line of high-sensitivity, high-resolution spectrometers overcomes the trade-off between light throughput and spectral resolution, typically offering a 10-15x increase in throughput over conventional spectrometer designs. HyperFlux is available in several off the shelf models and can be easily customized with the band pass, resolution, footprint, and branding required to meet OEM needs. Tornado's nanophotonic spectrometer is an on-chip solution which never requires alignment and can be customized for high resolution or broad bandwidth preferences. Extreme miniaturization allows for multiple independent spectrometers in one integrated system

TSI Incorporated **Booth 109**
500 Cardigan Road
Shoreview, MN 55126
www.tsi.com
The TSI 3000 Series Desktop LIBS Elemental Analyzer offers rapid elemental analysis for minute quantities of solid materials. Based on advanced laser-induced breakdown spectroscopy (LIBS), the TSI 3000 Series instruments are designed to analyze organic elements (C, H, O, N) and heavy metals simultaneously to determine impurities in powders like Carbon Nanotubes and empirical formulas. TSI's LiquiScan ES for liquid nano material characterization will also be displayed.

Wasatch Photonics **Booth 305/307**
4020 Stirrup Creek Dr., Ste 115
Durham, NC 27703
www.wasatchphotonics.com
Wasatch Photonics, Inc. is the leader in high performance Volume Phase Holographic Gratings (VPHGs) and Volume Phase Holographic Optical Elements (VHOEs). Products developed by our world class design team include; Raman sensors and instrumentation, advanced holographic components for spectroscopy, hyperspectral imaging, astronomy and OCT. Company headquarters and the holographic component manufacturing facility are located in Logan, Utah. Instrumentation is manufactured at our Systems Division facility located in Research Triangle Park, NC. High efficiency VPH Gratings combined with low F number optics allow unprecedented throughput for our Raman spectrometers. Our Raman systems provide ultimate sensitivity for process control, rapid SERS tag identification and unknown substance identification for homeland security.

Waters **Booth 207**
34 Maple Street
Milford, MA 01757-3696
Waters Corporation, the premium brand in the analytical instruments industry, creates business advantages for laboratory-dependent organizations by delivering practical and sustainable scientific innovation to enable significant advancements in healthcare delivery, environmental management, food safety, and water quality worldwide. Bringing keen understanding and deep experience to those responsible for laboratory infrastructure and performance, Waters helps customers make profound discoveries, optimize laboratory operations, deliver product performance, and ensure regulatory compliance. Pioneering a connected portfolio of separations and analytical science, laboratory informatics, mass spectrometry, as well as thermal analysis, Waters' technology breakthroughs and laboratory solutions provide an enduring platform for customer success.

Wiley-Blackwell **Booth 315**
The Atrium Southern Gate
Chichester
West Sussex, UK PO19 8SQ
http://www.wiley.com
Wiley publishes a large range of top quality consumer, professional, educational and research material, from the well-known 'For

Dummies' guides, to college textbooks, highly ranked peer-reviewed primary research and evidence based medicine. Wiley-Blackwell, the scientific, technical, medical and scholarly publishing business of John Wiley & Sons, publishes on behalf of societies and membership associations and offers libraries and individuals 1250 online journals, thousands of books in print and online, reviews, reference works, databases, and many other innovative resources for teaching and learning. At the SciX conference we will be providing free copies of our leading spectroscopy-related journals as well as promotional details for our print and electronic books spectroscopy books programme.

WITec Instruments Corp. **Booth 400**
130G Market Place Blvd
Knoxville, TN 37922
www.WITec-Instruments.com
WITec is a manufacturer of high resolution optical and scanning probe microscopy solutions for scientific and industrial applications. A modular product line allows the combination of different microscopy techniques such as Raman, NSOM or AFM in one single instrument for flexible analyses of optical, chemical and structural properties of a sample.

WORKSHOPS

Workshops are a valuable component of the SciX conference and are conducted by leading experts. There is an additional charge for most workshops. See on-site registration form for costs.

UW MADISON SYNCHROTRON TOUR

Carol Hirschmugl, *University of Wisconsin at Madison*

Saturday, 10:00 am – 4:00 pm

Synchrotron Radiation Center (http://www.src.wisc.edu/about.html) is a world class facility located about 80 miles from Milwaukee at the University of Wisconsin at Madison. The center is among a handful of synchrotron facilities in the world that are optimized for spectroscopy. The high photon intensities available allow for a variety of ground-breaking studies. Carol Hirschmugl from the University of Wisconsin, Milwaukee, has extensive experience at the facility, and will be leading the tour. Vans will leave from the Hyatt Hotel at 10:00 AM and transport attendees to the synchrotron, where there will be an overview of the technology and applications, followed by a tour of the facilities. Lunch at the facility will be included, and we will be back to the Hotel at approximately 4:00 PM.

ADVANCED CHEMOMETRICS WITHOUT EQUATIONS

Barry Wise, *Eigenvector Research*

Saturday and Sunday, 9:00 am – 4:30 pm

Advanced Chemometrics without Equations (ACWE) takes up where our popular Chemometrics without Equations course leaves off. It is assumed that participants will have a working knowledge of Principal Components Analysis (PCA) and regression with Partial Least Squares (PLS). ACWE concentrates on improving chemometric models via 1) advanced preprocessing methods, 2) variable selection and 3) non-linear methods. The critical difference between inadequate and successful chemometric models is often data preprocessing, i. e. what is done to the data before using PCA, PLS etc. The goal of preprocessing is to remove variation not related to the problem of interest so that the variation of interest is more evident and can be more easily modeled. The variables selected, e. g. spectral regions, can also greatly affect the success of the application. In some instances, the relationship between predictor and predicted variables is non-linear and modeling can be improved through the use of methods that account for this. ACWE focuses on advanced preprocessing methods, including Extended Multiplicative Scatter Correction (EMSC) and Generalized Least Squares (GLS), for improving models. Variable selection techniques, such as inteval PLS (iPLS) are also considered. Locally Weighted Regression (LWR) and Support Vector Machines (SVM) are demonstrated. The effect of preprocessing, variable selection and non-linear methods on robustness of the final models is also considered. Students will work problems using MATLAB and PLS_Toolbox on computers provided (maximum of two students per computer). More information can be found at http://www.eigenvector.com/courses/ACWE.html

NOT YOUR FATHER'S INFRARED SPECTROMETER: MID-IR QUANTUM CASCADE LASER (QCL) SYSTEMS

Mark Norman, *Block Engineering*

Sunday, 8:00 am – 12:00 pm

Mid-infrared quantum cascade laser (QCL) spectrometers have recently become available for applications outside the research laboratory. Though similar to Fourier transform infrared (FTIR) in some respects, QCL systems provide distinct characteristics including a highly collimated light source, high spectral brightness, and a small beam diameter. These features, coupled with wide tuning over the mid-IR fingerprint region, enable certain key applications previously difficult for FTIR including long open-path gas measurements and standoff surface analysis. This workshop will educate attendees on the theoretical and practical aspects of QCLs with a combination of lecture and hands-on exercises.

INTRODUCTION TO PORTABLE RAMAN SPECTROMETERS

Travis Thompson, *B&W Tek, Inc*

Sunday, 8:00 am – 12:00 pm

This workshop will discuss the basics of how to use portable Raman spectrometers, the importance of portable Raman spectrometers in a variety of applications, and hands-on training

HANDS-ON MICROFLUIDICS - AES ELECTROPHORESIS SOCIETY

Yoland Fintschenko, *Labsmith*

Sunday, 8:00 am – 12:00 pm

Content Overview – In this course there is a 1.5 hour lecture component and 2 hour hands-on component using LabSmith equipment with time for breaks. The course objectives are as follows: Introduce experimental parameters that are important for successful microfluidic experiments using electrokinesis and hydrodynamic flow techniques. Provide practical experience constructing microfluidic circuits using tubing and microfluidic chips. Provide practical experience in controlling and imaging fluid movement in microfluidic circuits using manual and automated solution delivery.

DEPTH PROFILE ANALYSIS OF THIN/THICK FILMS USING PULSED RF GLOW DISCHARGE OPTICAL EMISSION SPECTROSCOPY (GD-OES) AND PLASMA PROFILING TOF-MS

Philippe Hunault, *Horiba Scientific*

Sunday, 9:00 am – 4:30 pm

The workshop will feature a detailed presentation of the main characteristics of the technique, with illustrative results showing the key features of Pulsed RF GDOES, including multi-element depth profiling, rapid analysis-feedback, high dynamic range, and complimentary use with XPS and SEM. Detailed applications will be covered including thin film photovoltaics, electrodes for Li batteries, and plasma deposition optimization and control. Introduction and comparison with PP TOF-MS will also be presented.

SPECTRAL ANALYSIS USING MULTI-BAND RAMAN

Bayspec, Inc.

Sunday, 1:00 – 5:00 pm

Often the question is asked when configuring a Raman instrument "which excitation wavelength is best?" Many options for excitation wavelengths, and multiple laser wavelengths may be employed so technologists can have the flexibility to address different sample materials. For many samples, especially those of an organic or biological nature, fluorescence is a particular concern. Exciting these samples with a laser in the green (532 nm) may promote this fluorescence, and may swamp any underlying Raman spectrum to such an extent that it is no longer detectable. In this instance, the use of a laser in the red (633 nm) or NIR (785 nm) may provide a solution. With the lower photon energy, a red or NIR laser may not promote the electronic transition (and hence the fluorescence) so the Raman scatter may be far easier to detect.

FUNDAMENTALS OF LASER-INDUCED BREAKDOWN SPECTROSCOPY

Steve Buckley, *TSI, Inc.*

Sunday, 1:00 – 5:00 pm

This course will provide a comprehensive overview of Laser-Induced Breakdown Spectroscopy, starting from an overview of the fundamentals and continuing through some of the major applications

of LIBS. Selection of hardware, including options for lasers and detectors, will be covered in detail. Use of LIBS for rapid positive materials identification and quantitative analysis will be covered with applications from industry (metals, glass, nanoparticles) and research. Students will emerge from the class with a solid understanding of LIBS fundamentals and an appreciation of where LIBS can be successfully applied in practice, for research or commercial applications

ADVANCED METHODS IN SPECTROMETER CALIBRATION
Brian Smith, *Princeton Instruments*
Sunday, 1:00 – 5:00 pm

The course will cover the need for wavelength and intensity calibrations for dispersive spectrographs, the problems traditionally encountered with these calibrations, and how new developments in lamp technology, software, and algorithms can give wavelength and intensity calibrations that are of high accuracy and are easy to obtain.

RÉSUMÉ WRITING AND INTERVIEWING SKILLS FOR STUDENTS
Drew Manica, *SABIC*
Tuesday, 8:00 AM – 12:00 pm

SABIC is hosting this free workshop for Students. Your career search is one of the most influential investments in your future. This interactive half-day workshop will prepare attendees to make a positive and lasting impression both in-print and in-person. Receive tips and best practices, avoid common mistakes, learn how to tailor your résumé for different prospective employers, and prepare yourself for important interview styles. Directly following the workshop, students are invited to join the **FREE lunch and Employment Discussion hosted by SABIC.**

PROFESSIONAL ANALYTICAL CHEMISTS IN INDUSTRY: WHAT DOES AN ANALYTICAL CHEMIST DO?
Judson Haynes and Diane Parry, *Procter and Gamble*
Wednesday, 9:00 am – 4:30 pm

This seminar begins with a discussion of the education requirements and salaries that an analytical chemist may expect in industry. The different roles (including scientific consultant, methods developer, and problem solver) of the industrial analytical chemist are explained. A majority of time is spent on problem solving, both the process and solving real-world problems. Students will learn a "framework" for approaching problems. Time will be available to ask questions on these topics and other related subjects. The Course text includes supplementary material on finding a job, summer employment, etc. The entire course, especially the problem solving, is structured for extensive participation and interaction. Additional information is available at http://www.pg.com/science/prof_chemists.jhtml. The Course is intended primarily for undergraduate students to educate them about careers as analytical chemists in industry. However, graduate students, high school teachers, and college faculty have indicated it was worth their time to attend.

THE FOLLOWING ACS WORKSHOPS ARE BEING PRESENTED ON SATURDAY AND SUNDAY:

Methods Development, Validation Procedures and Regulatory Compliance Issues
Learn the fundamentals of quality assurance, quality control, and analytical methods validation and how to improve your FDA, WHO and OECD regulatory compliance directives for analytical data submissions. Key topics covered include: conformity assessment; analytical method optimization during development; case studies in the improvement of validation characteristics; data integrity and statistical evaluation of analytical data; and more.

Laboratory Safety
Learn best practices to minimize personal injury, health impairment, property loss, fines, and liability in your laboratory. This course gives you an overview of the practical and latest regulatory measures for the prevention of accidents, incidents, or exposures that may cause health impairment, injury, fire, or interference with laboratory operations. It includes the OSHA training requirements for a Chemical Hygiene Officer.

PROGRAM OVERVIEW

SUNDAY

2:30 – 6:00 pm **"What's Hot" Vendor Presentations,** *Ballroom A*

6:15 pm **KEYNOTE LECTURE**. From Test Tube to YouTube; **Martyn Poliakoff,** *Ballroom A,* page 52

7:15 – 9:15 pm **Welcome Mixer, SAS Sponsored Student Poster Session, Coblentz Student Awards, FACSS Student and Tomas Hirschfeld Scholar Awards,** *Ballroom Level Prefunction*

MONDAY MORNING

7:50 am Opening Address

8:00 am **KEYNOTE LECTURE**. Future Challenges in Green Chemistry, **Paul Anastas**, *Ballroom A,* page 53

9:00 am **POSTER SESSION**, *Ballroom Level Prefunction,* page 53
AES Poster Session
Infrared Spectroscopy and THz Spectroscopy
Atomic and Laser Induced Breakdown Spectroscopy

10:20 am **SYMPOSIA,** page 55
Technological Advances and New Applications using Quantum Cascade Lasers, *101A*
New Instrumentation in LIBS, *101B*
Applied Spectroscopy Focal Point Session: Bioimaging and Bioanalysis with Quantum Dots, *101C*
Ion Structure and Energetics, *102A*
Electrically Driven Processes in Nanofluidic Devices, *102B*
Pharmaceutical Raman, *102C*
Nuclear Forensics, *102D*
ACS-RSC Symposium on Sustainability in Atomic Spectroscopy, *102E*
Chemistry in Art and Archaeology, *103B*
Industrial Process Analytical Real Time Assurance, *103C*
Contributed papers in Chemometrics, *103D*

MONDAY AFTERNOON

1:20 pm **SYMPOSIA,** page 57
Chemistry in Art and Archaeology, *101A*
Biological Applications of LIBS, *101B*
Materials Characterization Using Vibrational Spectroscopy, *101C*
Chemometrics for Hand Held, Embedded, and Medical Devices, *102A*
AES Award Session Honoring Todd Squires, *102B*
Emerging Raman Techniques and Applications, *102C*
Analytical Chemists Easing World Poverty, *102D*
Six Degrees of Separation: Jim Holcombe's Career in Atomic Spectroscopy, *103B*
SAS PAT Section Pharmaceutical and Biopharmaceutical PAT Session I, *103C*
Contributed Papers in Surface and Nanotechnolgy and Material Characterization, *103D*

3:00 pm **POSTER VIEWING AND BREAK**

3:50 pm **SYMPOSIA**, page 60
Ionic Liquid Facilitated Smart Materials for Analytical Chemistry, *101A*
Fundamentals of LIBS Plasmas, *101B*
Contributed Papers in Bioanalytical Research, *101C*
Practical Chemometrics for Industry, *102A*
Dielectrophoresis, *102B*
Recent Innovations in Stand-Off Raman for the Detection of Hazards, *102C*
Biological MS and Proteomics, *102D*
Nanotechnology and Sustainability, *Room 102E*
Understanding the Underlying Mechanisms in Plasma Spectrochemistry: Gateway to Improved Performance in Elemental Analysis, *103B*
SAS PAT Tech Section – Biopharmaceutical and Pharmaceutical PAT Session II, *103C*
FACSS / SAS Student Awards, *103D*

TUESDAY MORNING

PLENARY LECTURES, *Ballroom A,* page 63

8:00 am **Coblentz Society Craver Award.** Rohit Bhargava

8:30 am **Charles Mann Award for Applied Raman Spectroscopy.** Volker Deckert

9:00 am **POSTER SESSION,** *Ballroom B/C/D,* page 63
Environmental Analysis
Mass Spectrometry
Pharmaceutical Analysis
RAMAN

10:20 am **SYMPOSIA,** page 65
ACS-RSC Symposium on Sustainability in Molecular Spectroscopy and Mass Spectrometry, *Room 101A*
Planetary LIBS: Geological and Gemological Applications, *101B*
Mass Spectrometry in Forensics, *101C*
Tandem MS Big and Small, *102A*
Cell and Organelle Electrophoresis, *102B*
Advances in Biological SERS Analysis, *102C*
The Birth of Chemometrics – In Honor and Memory of Bruce Kowalski I, *102D*
FACSS Charles Mann Award Session Honoring Volker Deckert, *102E*
Nanoparticles, Metals, and More: Young Investigators in Atomic Spectroscopy, *103B*
Flow/Continuous PAT I, *103C*
Spectroscopy and Surface Characterization of Semiconductor Nanomaterials, *103D*

TUESDAY AFTERNOON

1:20 pm **SYMPOSIA,** page 67
Electrophoresis and Omics, *101A*
Quantifications in LIBS Plasmas, *101B*
Security and Forensics, *101C*
Spray Desorption Ionization Methods, *102A*
Analytical Chemists Easing World Poverty, *102B*
Low Field NMR, *102C*
The Birth of Chemometrics – In Honor and Memory of Bruce Kowalski II, *102D*
Coblentz Society Craver Award Honoring Rohit Bhargava, *102E*
Chemical Imaging in Pharmaceutical Manufacturing, *103B*
Flow/Continuous PAT II, *103C*
Contributed Papers in Bio-Medical and Bio-Analytical Research, *103D*

TUESDAY AFTERNOON, continued

3:00 PM **POSTER VIEWING AND DESSERT BREAK**

3:50 pm **SYMPOSIA**, page 69
Nanoscale IR, *101A*
Industrial Applications of LIBS, *101B*
Ion Chromatography, *101C*
Pharmaceutical Mass Spectrometry, *102A*
Nano-Facilitated Sensing, *102B*
A New Age of Raman Imaging, 102C
The Birth of Chemometrics in Honor and Memory of Bruce Kowalski III, *102D*
ACS Analytical Chemistry Division Award in Chemical Instrumentation Honoring Charles Wilkins, *102E*
Advances in Materials Characterization via Glow Discharge Spectrometry, *103B*
Analytics in Pharmaceutical Counterfeit Detection, *103C*

WEDNESDAY MORNING

PLENARY LECTURES, *Ballroom A,* page 73

8:00 am **SAS's Applied Spectroscopy William F. Meggers Award.** Paul Pudney

8:30 am **SAS's Lester W. Strock Award.** Richard Russo

9:00 am **POSTER SESSION,** *Ballroom B/C/D,* page 73
Atomic
Biological, Bioanalytical, and Biomedical
Chemometrics
Microscopy, Imaging Spectroscopy, Forensics, and Education

10:20 am **SYMPOSIA**. page 75
Coherent Two-Dimensional Spectroscopy I, *101A*
Chemometrics for LIBS, *101B*
Gel Permeation Chromatography, *101C*
Active Nanocomposites, *102A*
Applications of Analytical Sciences in Diabetes, *102B*
Spectroscopic Techniques in Forensic Investigation, *102C*
Home Made Explosives, *102D*
Applied Spectroscopy Meggers Award Accepted by Paul Pudney, *Room 102E*
Advances and Atypical Applications of Novel Plasmas, *103B*
Macromolecular Biopharmaceuticals: Recent Trends and New Analytical Challenges, *103C*
Contributed Papers in Instrument Development and Sensor Design*, 103D*

WEDNESDAY AFTERNOON

1:20 pm **SYMPOSIA,** page 77
Coherent Two-Dimensional Spectroscopy II; *Room 101A*
Analytical LIBS, *Room 101B*
Fast LC: Honoring *LCGC* Young Investigator Award Winner Davy Guillarme, *Room 101C*
Terahertz Spectroscopy and Imaging, *102A*
Analytical Science Applications in Burns, Trauma and Wound Care, *102B*
SERS – State of the Art by the Artists, *102C*
Making the Most of Spectral and Other Process Analysis Data, *102D*
SAS's Lester W. Strock Award Honoring Richard Russo, Isotope Measurements in Laser Plasmas, *102E*
Surface Analysis of Organic and Pharmaceutical Materials, *103B*
Pharmaceutical Applications of Near Infrared Spectroscopy, *103C*
Vibrational Spectroscopy in Pharmaceutical Analysis, *103D*

3:00 pm **POSTER VIEWING AND DESSERT BREAK**

3:50 pm **SYMPOSIA**, page 79
Coherent Two-Dimensional Spectroscopy III, *101A*
LIBS-Plus, *101B*
UV Raman Spectroscopy: Instrumentation Development and Application, *101C*
Terahertz Spectroscopy and Imaging. *102A*
Spectral Analysis of Pathogens, *102B*
Novel Raman Techniques, *102C*
Contributed Papers in Raman Spectroscopy, *102D*
Real-World Applications of Surface Analysis, *102E*
New Instrumentation and New Approaches at the Frontier of Atomic Spectroscopy, *103B*
Industrial Applications of Spectroscopy, *103C*
Bioanalytical Applications of Plasmonics, *103D*

THURSDAY MORNING

PLENARY LECTURES, *Ballroom A,* page 82

8:00 am **ANACHEM Award.** Norman Dovichi

8:30 am ***LCGC* Lifetime Achievement in Chromatography Award.** Peter Carr

9:00 am **POSTER SESSION,** *102 Foyer,* page 82
Biological and Bioanalytical Applications
Chromatography, Microfluidics, and Separation Science
Molecular Spectroscopy
Nanotechnology and Materials Characterization

10:20 am **SYMPOSIA,** page 83
Contributed Papers in Molecular Spectroscopy, *101A*
The Next Frontier: The Future of LIBS, *101B*
Nanomaterials for Plasmonics I, *101C*
Women in Science, *101D*
A Spectroscopic Slant on Lab-on-Chip Diagnostics, *102A*
Contributed Papers in LIBS and Atomic Spectroscopy, *102B*
Raman in Biochemical Analysis, *102C*
The Digital Crystal Ball, *102D*
2D HPLC: Honoring *LCGC* Lifetime Achievement Award Winner Peter Carr, *102E*
Metallomics: The Vibrant Role of Metals in Biology, Disease, and Treatment, *103B*
Translation and Commercialization in Biomedical Applications*103C*

THURSDAY AFTERNOON

1:20 pm	**SYMPOSIA,** page 86 IRENI – Synchrotron-Based Widefield Infrared Microspectroscopy, *101A* New Applications of LIBS, *101B* Supercritical Fluid Chromatography, *101C* Contributed Papers in Raman Imaging, *101D* Tobacco Analysis by MS, *102A* Medical Applications, *102B* Early Career Scientists in Raman Spectroscopy, *102C* Nanomaterials for Plasmonics II, *102D* ANACHEM Award Session Honoring Norman Dovichi, *102E* Innovative Applications of MID- and Near-IR Spectroscopy, *103B* What is the State of Process Analytical Technology? A Technical Panel, *103C*
3:00 PM	**POSTER VIEWING AND BREAK**
3:50 pm	**PLENARY SESSION,** *102C*, page 88 **FACSS DISTINGUISHED SERVIE AWARD** **FACSS INNOVATION AWARDS,** *102C*

FRIDAY MORNING SPECIAL PLENARY SESSION,
Regency A/B – Hyatt Hotel

8:00 am	Welcoming a New Member Organization into FACSS and Much More…., page 89

WEDNESDAY EVENING EVENT, 6:00 PM
FACSSTOBERFEST! AN ALL INCLUSIVE EVENT
Regency Ballroom, Hyatt Hotel

In honor of the season and the German heritage of Milwaukee, the SciX Wednesday Night Event will be a very special Octoberfest celebration, featuring a full menu of all your German favorites, including sausage, schnitzel, spaetzle, a full bar ... and beer! Entertainment will be provided by a live Polka band, with a DJ taking over to keep the dancing going until midnight. So put on your dirndl or your lederhosen, and come help us celebrate the best FACSStoberfest ever!

TECHNICAL PROGRAM OVERVIEW BY TOPIC

ATOMIC SPECTROSCOPY

Monday AM
- ACS-RSC Symposium on Sustainability in Atomic Spectroscopy, *102E*
- Chemistry in Art and Archaeology, *103B*

Monday PM (1:20 pm session)
- Six Degrees of Separation: Jim Holcombe's Career in Atomic Spectroscopy, *103B*

Monday PM (3:50 pm session)
- Understanding the Underlying Mechanisms in Plasma Spectrochemistry: Gateway to Improved Performance in Elemental Analysis*, 103B*

Tuesday AM
- Atomic Spectrometry and the Analysis of Nanomaterials, *103B*

Tuesday PM (3:50 pm session)
- Advances in Materials Characterization via Glow Discharge Spectrometry*, 103B*

Wednesday AM
- Advances and Atypical Applications of Novel Plasmas, *103B*

Wednesday PM (3:50 pm session)
- New Instrumentation and New Approaches at the Frontier of Atomic Spectroscopy*, 103B*

Thursday AM
- Contributed Papers in LIBS and Atomic Spectroscopy, *102B*
- Metallomics: The Vibrant Role of Metals in Biology, Disease and Treatment, *103B*

BIOMEDICAL AND BIOANALYTICAL SCIENCE

Monday AM
- Applied Spectroscopy Focal Point Session: Bioimaging and Bioanalysis with Quantum Dots, *101C*

Monday PM (1:20 pm session)
- Biological Applications of LIBS, *101B*
- SAS PAT Section Pharmaceutical and Biopharmaceutical PAT Session I, *103C*

Monday PM (3:50 pm session)
- Contributed Papers in Bioanalytical Research*, 101C*
- Biological MS and Proteomics, *102D*
- SAS PAT Section Pharmaceutical and Biopharmaceutical PAT Session II, *103C*
- FACSS / SAS Student Awards, *103D*

Tuesday AM
- Cell and Organelle Electrophoresis, *102B*

Tuesday PM (1:20 pm session)
- Contributed Papers in Bio-Medical and Bio-Analytical Research, *103D*

Wednesday AM
- Applications of Analytical Sciences in Diabetes, *102B*

Wednesday PM (1:20 pm session)
- Analytical Science Applications in Burns, Trauma and Wound Care*, 102B*

Wednesday PM (3:50 pm session)
- Spectral Analysis of Pathogens*, 102B*

Thursday AM
- Translation and Commercialization in Biomedical Applications, *103C*

Thursday PM (3:50 pm session)
- Innovation Awards Session

CHEMOMETRICS

Monday AM
- Contributed Papers in Chemometrics, *103D*

Monday PM (1:20 pm session)
- Chemometrics for Handheld, Embedded, and Medical Devices, *102A*

Monday PM (3:50 pm session)
- Practical Chemometrics for industry, *102A*

Tuesday AM
- The Birth of Chemometrics – In Honor and Memory of Bruce Kowalski I, *102D*

Tuesday PM (1:20 pm session)
- The Birth of Chemometrics – In Honor and Memory of Bruce Kowalski II, *102D*

Tuesday PM (3:50 pm session)
- The Birth of Chemometrics – In Honor and Memory of Bruce Kowalski III, *102D*

CHROMATOGRAPHY

Tuesday PM (3:50 pm session)
- Ion Chromatography*, 101C*

Wednesday AM
- Gel Permeation Chromatography, *101C*

Wednesday PM (1:20 pm session)
- Fast LC: Honoring *LCGC* Emerging Leader in Chromatography Award Winner Davy Guillarme, *101C*

Thursday AM
- 2D HPLC: Honoring *LCGC* Lifetime Achievement Award Winner Peter Carr, *102E*

Thursday PM (1:20 pm session)
- Supecritical Fluid Chromatography, *101C*

ELECTROPHORESIS AND MICROFLUIDICS

Monday AM
- Electrically Driven Processes in Nanofluidic Devices, *102B*

Monday PM (1:20 pm session)
- AES Award Session Honoring Todd Squires, *102B*

Monday PM (3:50 pm session)
- Dielectrophoresis, 1*02B*
- FACSS / SAS Student Awards, *103D*

Tuesday AM
- Cell and Organelle Electrophoresis, *102B*

Tuesday PM (1:20 pm session)
- Electrophoresis and Omics, *101A*

Thursday PM (1:20 pm session)
- ANACHEM Award Honoring Norman Dovichi, *102E*

FORENSICS AND SECURITY

Monday AM
- Nuclear Forensics, *102D*

Tuesday AM
- Mass Spectrometry in Forensics*, 101C*

Tuesday PM (1:20 pm session)
- Department of Defense Forensic Needs and Application, *101C*

Tuesday PM (3:50 pm session)
- Analytical Chemistry as Detective: Case Studies in Forensic Science, *103D*

Wednesday AM
- Forensics and Vibrational Spectroscopy, *102C*
- Home Made Explosives*, 102D*

Thursday PM (3:50 pm session)
- Innovation Awards Session

INSTRUMENTATION AND CHEMICAL SENSORS

Monday AM
- Technological Advances and New Applications Using Quantum Cascade Lasers, *101A*
- Applied Spectroscopy Focal Point Session: Bioimaging and Bioanalysis with Quantum Dots, *101C*

Tuesday PM (3:50 pm session)
- Nano-facilitated Sensing, *102B*
- ACS Analytical Chemistry Division Award in Chemical Instrumentation*, 102E*

Wednesday AM
- Contributed Papers in Instrument Development and Sensor Design, *103D*

INSTRUMENTATION AND CHEMICAL SENSORS continued

Wednesday PM (3:50 pm session)
Real-World Applications of Surface Analysis, *102E*
Thursday PM (3:50 pm session)
Innovation Awards Session

LASER INDUCED BREAKDOWN SPECTROSCOPY

Monday AM
New Instrumentation in LIBS, *101B*
Monday PM (1:20 pm session)
Biological Applications of LIBS, *101B*
Monday PM (3:50 pm session)
Fundamentals of LIBS Plasmas, *101B*
FACSS / SAS Student Awards, *103D*
Tuesday AM
Planetary LIBS: Geological and Gemological Applications, *101B*
Tuesday PM (1:20 pm session)
Quantification in LIBS Plasmas, *101B*
Tuesday PM (3:50 pm session)
Industrial Applications of LIBS, *101B*
Wednesday AM
Chemometrics for LIBS, *101B*
Wednesday PM (1:20 pm session)
Analytical LIBS, *101B*
SAS's Lester W. Strock Award Honoring Richard E. Russo, *102E*
Wednesday PM (3:50 pm session)
LIBS-Plus, *101B*
Thursday AM
The Next Frontier: The Future of LIBS, *101B*
Nanomaterials for Plasmonics I, *101C*
Contributed Papers in LIBS and Atomic Spectroscopy, *102B*
Thursday PM (1:20 pm session)
New Applications of LIBS, *101B*
Thursday PM (3:50 pm session)
Innovation Awards Session

MASS SPECTROMETRY

Monday AM
Ion Structure & Energetics, *102A*
Monday PM (3:50 pm session)
Biological MS and Proteomics, *102D*
FACSS / SAS Student Awards, *103D*
Tuesday AM
Tandem MS Big and Small, *102A*
Mass Spectrometry in Forensics, *101C*
Tuesday PM (1:20 pm session)
Spray Desorption Ionization Methods, *102A*
Tuesday PM (3:50 pm session)
Pharmaceutical Mass Spectrometry, *102A*
Thursday PM (1:20 pm session)
Tobacco Analysis by MS, *102A*

MOLECULAR SPECTROSCOPY (IR and NIR)

Monday AM
Technological Advances and New Applications Using Quantum Cascade Lasers, *101A*
Monday PM (1:20 pm session)
Chemistry in Art and Archaeology, *101A*
Contributed Papers in Surface and Nanotechnology and Material Characterizations; *103D*
Monday PM (3:50 pm session)
Ionic Liquid Facilitated Smart Materials for Analytical Chemistry, *101A*
Tuesday PM (1:20 pm session)
ACS-RSC Symposium on Sustainability in Molecular Spectroscopy, *101A*
Coblentz Craver Award Honoring Rohit Bhargava, *102E*
Tuesday PM (3:50 pm session)
Nanoscale IR, *101A*
Wednesday AM
Coherent Two-Dimensional Spectroscopy I, *101A*
Forensics and Vibrational Spectroscopy, *102C*
Wednesday PM (1:20 pm session)
Coherent Two-Dimensional Spectroscopy II, *101A*
Terahertz Spectroscopy and Imaging, *102A*
Pharmaceutical Applications of Near Infrared Spectroscopy, *103C*
Wednesday PM (3:50 pm session)
Coherent Two-Dimensional Spectroscopy III, *101A*
Terahertz Spectroscopy and Imaging, *102A*
Industrial Applications of Spectroscopy, *103C*
Thursday AM
Contributed Papers in Molecular Spectroscopy, *101A*
A Spectroscopic Slant on Lab-on-Chip Diagnostics, *102A*
Thursday PM (1:20 pm session)
IRENI – Synchrotron Based Widefield Infrared Microspectroscopy, *101A*
Innovative Applications of Mid- and Near-IR Spectroscopy, *103B*
Thursday PM (3:50 pm session)
Innovation Awards Session

NANOTECHNOLOGY

Monday PM (1:20 pm session)
Contributed Papers in Surface and Nanotechnology and Material Characterizations; *103D*
Monday PM (3:50 pm session)
Nanotechnology and Sustainability, *102E*
Tuesday AM
Spectroscopy and Surface Characterization of Semiconductor Nanomaterials, *103D*
Tuesday PM (3:50 pm session)
Nano-facilitated Sensing, *102B*
Wednesday AM
Active Nanocomposites, *102A*
Thursday AM
Nanomaterials for Plasmonics I, *101C*
Thursday PM (1:20 pm session)
Nanomaterials for Plasmonics II, *102D*
Thursday PM (3:50 pm session)
Innovation Awards Session

PHARMACEUTICAL AND INDUSTRIAL SPECTROSCOPY

Monday AM
Pharmaceutical Raman for Industry, *102C*
Industrial Process Analytical Real Time Assurance, *103C*
Monday PM (3:50 pm session)
Practical Chemometrics, *102A*
SAS PAT Section Pharmaceutical and Biopharmaceutical PAT Session II, *103C*
Tuesday AM
Flow/Continuous PAT I, *103C*
Tuesday PM (1:20 pm session)
Low Field NMR, *102C*
Chemical Imaging in Pharmaceutical Manufacturing, *103B*
Flow/Continuous PAT II *103C*
Tuesday PM (3:50 pm session)
Industrial Applications of LIBS, *101B*
Analytics in Pharmaceutical Counterfeit Detection, *103C*
Wednesday AM
Macromolecular Biopharmaceuticals: Recent Trends and New Analytical Challenges, *103C*

PHARMACEUTICAL AND INDUSTRIAL SPECTROSCOPY continued

Wednesday PM (1:20 pm session)
Making the Most of Spectral and Other Process Analysis Data, *102D*
Surface Analysis of Organic and Pharmaceutical Materials, *103B*
Vibrational Spectroscopy in Pharmaceutical Analysis, *103D*

Thursday AM
The Digital Crystal Ball, *102D*

Thursday PM (1:20 pm session)
Medical Applications, *102B*
What is the State of Process Analytical Technology: A Technical Panel, *103C*

PROCESS ANALYTICAL SPECTROSCOPY

Monday AM
Industrial Process Analytical Real Time Assurance, *103C*

Monday PM (1:20 pm session)
SAS PAT Section Pharmaceutical and Biopharmaceutical PAT Session I, *103C*

Monday PM (3:50 pm session)
SAS PAT Section Pharmaceutical and Biopharmaceutical PAT Session II, *103C*

Tuesday AM
Flow/Continuous PAT I, *103C*

Tuesday PM (1:20 pm session)
Flow/Continuous PAT II *103C*

Thursday PM (1:20 pm session)
What is the State of Process Analytical Technology: A Technical Panel, *103C*

RAMAN

Monday AM
Pharmaceutical Raman, *102C*

Monday PM (1:20 pm session)
Materials Characterization Using Vibrational Spectroscopy, *101C*
Emerging Raman Techniques and Applications, *102C*
Contributed Papers in Surface and Nanotechnology and Material Characterizations; *103D*

Monday PM (3:50 pm session)
Recent Innovations in Stand-off Raman for the Detection of Hazards, *102C*
FACSS / SAS Student Awards, *103D*

Tuesday AM
Advances in Biological SERS Analysis, *102C*
FACSS Charles Mann Award Session Honoring Volker Deckert, *102E*
Spectroscopy and Surface Characterization of Semiconductor Nanomaterials, *103D*

Tuesday PM (3:50 pm session)
A New Age of Raman Imaging, *102C*

Wednesday AM
Forensics and Vibrational Spectroscopy, *102C*
SAS's Meggers Award Session Honoring Paul Pudney, *102E*

Wednesday PM (1:20 pm session)
SERS – State of the Art by the Artists, *102C*

Wednesday PM (3:50 pm session)
Contributed Papers in Raman Spectroscopy, *102D*

Wednesday PM (3:50 pm session)
UV Raman Spectroscopy: Instrumentation, Development and Application, *101C*
Novel Raman Techniques, *102C*

Thursday AM
Raman in Biochemical Analysis, *102C*

Thursday PM (1:20 pm session)
Contributed Papers in Raman Imaging, *101D*
Early Career Scientists in Raman Spectroscopy, *102C*
Nanomaterials for Plasmonics II, *102D*

SURFACE PLASMON RESONANCE

Wednesday PM (3:50 pm session)
Bioanalytical Applications of Plasmonics, *103D*

Thursday AM
Nanomaterials for Plasmonics I, *101C*

Thursday PM (1:20 pm session)
Nanomaterials for Plasmonics II, *102D*

SUSTAINABILITY

Monday AM
ACS-RSC Symposium on Sustainability in Atomic Spectroscopy, *102E*

Monday PM (1:20 pm session)
Analytical Chemists Easing World Poverty, *102D*

Monday PM (3:50 pm session)
Nanotechnology and Sustainability, *102E*

Tuesday AM
ACS-RSC Symposium on Sustainability in Molecular Spectroscopy, *101A*

Tuesday PM (1:20 pm session)
Analytical Chemists Easing World Poverty, *102B*

Thursday AM
Nanomaterials for Plasmonics I, *101C*

PROGRAM HIGHLIGHTS

SATURDAY	SUNDAY	MONDAY	TUESDAY	WEDNESDAY	THURSDAY	FRIDAY
		Ballroom Prefunction 7:30 am Wake Up Coffee	*Ballroom Prefunction* 7:30 am Wake Up Coffee	*Ballroom Prefunction* 7:30 am Wake Up Coffee	*Ballroom Prefunction* 7:30 am Wake Up Coffee	*Regency A/B Hyatt Hotel* 7:30 am Wake Up Coffee and Muffins
9:00 am – 4:30 pm Workshop	8:00 am – 4:30 pm Workshops	*Ballroom A* 7:50 am Opening Remarks **Michael George** 8:00 am Keynote Lecture **Paul Anastas** *Yale University*	*Ballroom A* 8:00 am Coblentz Society's Craver Award **Rohit Bhargava** University of Illinois at Urbana-Champaign 8:30 am FACSS Charles Mann Award **Volker Deckert** University of Jena	*Ballroom A* 8:00 am SAS Applied Spectroscopy William F. Meggers Award **Paul Pudney** *Unilever* 8:30 am SAS Lester W. Strock Award **Richard Russo** Berkeley National Lab and Applied *Spectra, Inc.*	*Ballroom A* 8:00 am ANACHEM Award **Norman Dovichi** *University of Notre Dame* 8:30 am LCGC Chromatography Award **Peter Carr** *University of Minnesota*	8:00 – 10:30 am Special Plenary Session: Welcoming a New Member Organization into FACSS and Much More….
			8:00 am – 12:00 pm Workshop for Students	9:00 am – 4:30 pm Workshop for Students		
			Ballroom B/C/D 9:00 am – 4:30 pm Exhibits Open	*Ballroom B/C/D* 9:00 am – 4:00 pm Exhibits Open		
10:00 am – 4:00 pm UW Madison Synchrotron Tour		*Ballroom Prefunction* 9:00 – 10:20 am Poster Session and Break	*Ballroom B/C/D* 9:00 – 10:20 am Poster Session and Break	*Ballroom B/C/D* 9:00 – 10:20 am Poster Session and Break	*Room 201 Foyer* 9:00 – 10:20 am Poster Session and Break	
		10:20 – 12:00 pm Oral Symposia	10:20 – 12:00 pm Oral Symposia	10:20 – 12:00 pm Oral Symposia	10:20 – 12:00 pm Oral Symposia	
		Noon Lunch on own	Noon Lunch on own	Noon Lunch on own	Noon Lunch on own	
			Room 201B 12:30 pm Lunch and Roundtable discussion for students. Sponsored by SABIC			
	Ballroom B/C/D 2:30 – 6:00 pm What's Hot Vendor Presentations	1:20 – 3:00 pm Oral Symposia	1:20 – 3:00 pm Oral Symposia	1:20 – 3:00 pm Oral Symposia	1:20 – 3:00 pm Oral Symposia	
		Ballroom Prefunction 3:00 – 3:50 Poster Viewing and Break	*Ballroom B/C/D* 3:00 – 3:50 Poster Viewing and Break	*Ballroom B/C/D* 3:00 – 3:50 Poster Viewing and Break	*Room 201 Foyer* 3:00 – 3:50 Poster Viewing and Break	
	B*allroom A* 6:15 pm Keynote Lecture: **Martyn Poliakoff**	3:50 – 5:30 pm Oral Symposia	3:50 – 5:30 pm Oral Symposia	3:50 – 5:30 pm Oral Symposia	3:50 – 5:30 pm Plenary Session FACSS DSA Awards Innovation Award Session	
	Ballroom Prefunction 7:15 – 9:15 pm Welcome Mixer and SAS Sponsored Student Poster Session Coblentz Student Awards FACSS Student and Tomas Hirschfeld Scholar Awards	*Ballroom B/C/D* 5:30 – 7:30 pm Exhibit Opening Reception	Regency A/B Hyatt Hotel 6:00 pm Raman Reception Sponsored by Kaiser Optical Systems, Inc.	Regency Ballroom Hyatt Hotell 6:00 pm FACSStoberfest! All inclusive event		
			Regency C/D Hyatt Hotel 7:30 pm SAS Reception			

SATURDAY and SUNDAY WORKSHOPS, see page 43 for a list

SUNDAY

"What's Hot" Symposium, Presider: Brian Dable, Arete Associates, *Ballroom A*

2:30 **HORIBA;** XploRA-ONE: One Shot Raman...Power and Affordability at the Push of a Button
2:40 **Indatech**
2:50 **Neaspec;** Introducing nano-FTIR – imaging and spectroscopy at 10nm spatial resolution
3:00 **Eigenvector Research;** Eigenvector's Automated Modeling and Interactive Deployment Tools
3:10 **BaySpec**; Dual band Agility Raman Analyzer
3:20 **TSI**; ChemReveal LIBS: The Next Generation Tool in Rapid Elemental Analysis of Solids
3:30 **Photonic Cleaning Technologies;** First Contact Polymer: Protecting and Cleaning Previously Uncleanable Optical Surfaces
3:40 **Wasatch**
3:50 **B&W Tek;** Portable Raman Detects Methanol-Laced Spirits
4:00 **Ibsen Photonics**; New Raman OEM Spectrographs with Ultra High Efficiency Transmission Gratings
4:10 **Princeton Instruments;** Imaging and Multichannel Spectroscopy with the IsoPlane SCT-320 Spectrograph
4:20 **Renishaw;** Capturing a True Chemical Picture of Your Sample: High Definition Raman Imaging
4:30 **Ondax**
4:40 **WITec;** True Surface Imaging in Confocal Raman Microscopy
4:50 **Advantest America**
5:00 **Thermo Scientific;** New Integrated AFM-Raman Solution Connects Performance and Flexibility at the Sample to Ease of Use and Reliability for the Researcher
5:10 **Thorlabs;** Mid-IR Innovations from Thorlabs
5:20 **Kaiser Optical Systems, Inc.**
5:30 **Innovative Photonic Solutions**; Advancements in Raman and FTIR Laser Sources
5:40 **HORIBA**; Customizable Multiplexed SPR and OpenPlex
5:50 **Ocean Optics**; Advances in Raman Sampling

6:15 **Keynote Lecture;** *Ballroom A*

(1) From Test Tube to YouTube
Martyn Poliakoff
University of Nottingham

7:15 **Welcome Mixer • SAS Sponsored Student Poster Session • Coblentz Student Awards • FACSS Student and Tomas Hirschfeld Scholar Awards** – *Ballroom Prefunction*

SAS
Student Poster Showcase and Awards

Please join us in celebrating the
future of spectroscopy as SAS students showcase their research and compete for the annual SAS Student Poster Awards.

Sunday, September 29, 2013, 7:15-9 p.m.
(during the SciX mixer in the Wisconsin Center)

Sponsored by
The Society for Applied Spectroscopy and SciX

TECHNICAL PROGRAM – MONDAY
Welcome 7:50 am and Keynote Lecture – 8:00 am; Ballroom A
Presider: Michael George

8:00 am Keynote Lecture
(2) Future Challenges in Green Chemistry; **Paul Anastas**, Yale University

Professor Anastas is the Director of the Center for Green Chemistry and Green Engineering at Yale University. He also served for many years at the EPA, where he coined the term 'Green Chemistry'

Monday Poster Session
9:00 – 12:20 am
Ballroom Prefunction

All Monday posters should be put up between 7:30 – 8:00 am and removed by 4:30 pm

AES Poster Session

Board #

1 (3) **Protonation-Deprotonation Processes of 2-(4'-pyridyl)benzimidazole in its Inclusion Complex with cucurbit[n]uril**; Vijay Kant[1], Uma Nudurupati[1], Sohidul Mondal[1], Anindya Datta[1], [1]Indian Institute of Technolohy Bombay

2 (4) **Monitoring the Uniformity of α-Helices in Lipophilic Environments**; Anahita Zare[1], Jian Xiong[1], Jason Cooley[1], Renee Jiji[1], [1]University of Missouri-Columbia

3 (5) **Secondary Structure of Poly-L-Alanine in Solution Studied by Raman and ROA with Quantum Chemical Computation**; Tatsuya Furukawa[1], Shigeki Yamamoto[1, 2], Yukihiro Ozaki[1]; [1]Department of Chemistry, Graduate School of Science and Technology, Kwansei Gakuin University, [2]Department of Chemistry, Graduate School of Science, Osaka University

4 (6) **Rapid Dialysis within Microfluidic Channels: Spatiotemporal Control of Solution Micro-environment using Hydrogel Membrane Microwindows**; Joel Paustian, Todd Squires[1]; [1]University of California, Santa Barbara

5 (7) **Human Red Blood Cell Deformation and Crenation under High Frequency Spatial AC Field**; Ran An[1], Adrienne Minerick[1]; [1]Michigan Technological University

6 (8) **Determination and Quantification of Water-Soluble and Fat-Soluble Vitamins in Human Biofluids with HPLC/MS**; Maryam Khaksari[1], Chunhai Ruan[1, 2], Peng Song[1, 2], Neil Hershey[1, 2], Robert Kennedy[1, 2], Mark Burns[1, 2], Dave Burke[1, 2], Adrienne Minerick[1]; [1]Michigan Technological University, [2]University of Michigan,

7 (9) **High Sensitive Detection of Antigen-Antibody Reaction using quantum Crystal SERS Substrate**; Daichi Araki[1], Yuuki Hasegawa[1, 2], Katsuyuki Hasegawa[1, 2], Yuko S. Yamamoto[1, 3], Tamitake Itoh[1, 3], Yasutaka Kitahama[1], Yukihiro Ozaki[1]; [1]Kwansei Gakuin University, [2]Mytech Corporation, [3]AIST

8 (10) **Powder XRD of Pharmaceutical Ingredients with PPM Detection Limits**; Scott Toth[1], Matthew Jackson[1, 2], Justin Newman[1], Christopher Dettmar[1], Michael Becker[1, 3], Robert Fischetti[1, 3], Lynne Taylor[1, 2], Garth Simpson[1]; [1]Purdue University, Department of Chemistry, [2]Purdue University, Department of Industrial and Physical Pharmacy, [3]GM/CA@APS, Advanced Photon Source, Argonne National Laboratory

9 (170) **Using Gradient Insulator-based Dielectrophoresis to Capture Small Molecular Weight Proteins**; Ryan Yanashima[1], Mark Hayes[1]; [1]Arizona State University

Board #

10 (273) **Manipulation of Mitochondria by Insulator-based Dielectrophoresis**; Jinghui Luo[1], Gregory Wolken[1, 2], Edgar Arriaga[1, 2], Alexandra Ros[1]; [1]Department of Chemistry and Biochemistry, Arizona State University, [2]Department of Chemistry, University of Minnesota

11 (632) **Novel On-Chip Capacitively Coupled Contactless Conductivity Detection using Injected Metal Electrodes**; Leigh D. Thredgold[1], Dmitriy Khodakov[1], Amanda V. Ellis[1], Claire E. Lenehan[2]; [1]Flinders Centre for NanoScale Science and Technology, Flinders University, GPO Adelaide, [2]School of Chemical and Physical Sciences, Flinders University, Adelaide

Infrared Spectroscopy and THz Spectroscopy

12 (11) **Chemometrics applied to terahertz spectroscopy**; Josette El Haddad[1,2], Frédérick De Miollis[1, 2], Bruno Bousquet[1, 2], Lionel Canioni[1, 2], Patrick Mounaix[1, 2] ; [1]Univ. Bordeaux, [2]CNRS

13 (12) **Microwave and Infrared Spectral Studies of Cyclobutylcarboxylic Acid Chloride**; Joshua J. Klaassen[1], Peter Groner[1], James R. Durig[1]; [1]University of Missouri Kansas City

14 (13) **Heterodyne Electro-Optic Sampling of THz PulsedWaves**; Masahiko Tani[1], Tetsuya Kinoshita[1], Tomohiro Nagase[1], Shinpei Ozawa[1], Shogo Azuma[1], Satoshi Tsuzuki[1], Daiki Takeshima[1], Tatsuya Joja[1], Atsushi Iwamae[1], Stefan Funkner[1]; [1]Research Center for Development of Far-Infrared Region, University of Fukui, [2]University of Philippines Diliman, 1101 Philippines, [3]Faculty of Education and Regional Stduies, Uiversity of Fukui, [4]University of Nizhny Novgorod

15 (14) **The Determination of Silicon Concentration on Hair Tresses Using FTIR**; Alex Augatis[1], Eugene Oldham[1], Chi-san Wu[1], Musa Osama[1], Courtney Usher[1], Bret Clark[1] ; [1]Ashland Specialty Ingredients

16 (15) **Detection Limits for Blood on Four Fabric Types Using Infrared Diffuse Reflection Spectroscopy in Mid-- and Near--Infrared Spectral Windows**; Stephanie A. DeJong[1], Stephen L. Morgan[1], Michael L. Myrick[1] ; [1]University of South Carolina

17 (16) **Electrochemical Cell Developed to Measure Heating at an Electrode Surface During Cyclic Voltammetry**; Stephanie A. DeJong[1], Donna Chen[1], John Monnier[1], John Weidner[1]; [1]University of South Carolina

Board #

18 (17) ***In Situ* Infrared Spectroscopy of Polystyrene Brush Growth by ATRP Grafted From Initiator on Au Shows Two Kinetic Regimes**; Richard Osibanjo[1], Arrash Yasovolian[1], Taylor Brickey[1], Kaye Caburnay[1], Tonya Kuhl[1], Donald Land[1]; [1]University of California Davis

19 (18) **Examining the Structure and Formation of varying Length Alkyl Silane Monolayers on TiO2 Nanoparticles using *in situ* Attenuated Total Reflectance Infrared Spectroscopy**; Catherine G. McKenas[1], Karla S. McCain[1] ; [1]Austin College

20 (19) **Rapid Characterization and Quality Control of Cell Proliferation -SPECCs Shedding Light on Culture Media Solutions**; Miriam Unger[1], Inka Pfitzner[2]; [1]CETICS Healthcare Technologies GmbH, Esslingen am Neckar, Germany, [2]BioTeSys GmbH, Esslingen am Neckar, Germany

Atomic and Laser Induced Breakdown Spectroscopy

21 (20) **Improved Detection of Trace Elements for a Microwave Plasma Atomic Emission Spectrometer (MP-AES) Coupled with an Ultrasonic Nebulizer**; Fred Smith[1], Steve Wall[2]; [1]CETAC Technologies, [2]Agilent Technologies

22 (21) **Qualitative and Quantitative Elemental Analysis using a Tandem System That Combines Laser-Induced Breakdown Spectroscopy (LIBS) and Laser Ablation Inductively Coupled Plasma Spectrometry (LA-ICP-MS)**; Jhanis Gonzalez[1,3], José Chirinos[2], Dayana Oropeza[1], Meirong Dong[1], Richard Russo[1, 3]; [1]Lawrence Berkeley National Laboratory, [2]Escuela de Quimica, Universidad Central de Venezuela, [3]Applied Spectra, Inc.

23 (22) **Differential Laser Absorption Spectroscopy in an atmospheric Pressure Laser-Induced Plasma: Measurement of Fundamental Uranium Parameters**; Nicholas Taylor[1], Mark C. Phillips[1]; [1]Pacific Northwest National Laboratory

24 (23) **LIBS: Hydrogen Balmer Series Plasma Spectroscopy in Air**; Lauren Swafford[1], Christian Parigger[1]; [1]University of Tennessee Space Institute

25 (24) **Manifold Regression of LIBS Data from Geological Samples for Application to ChemCam on Mars**; M. Darby Dyar[1], Thomas Boucher[2], Marco Carmosino[2], Sridhar Mahadevan[2], Samuel Clegg[3], Roger Wiens[3]; [1]Mount Holyoke College, [2]University of Massachusetts Amherst, [3]Los Alamos National Laboratory

26 (25) **On the Effects of Distance between a Laser and its Target in LIBS Measurements**; Alissa Mezzacappa[1], Noureddine Melikechi[1], Agnes Cousin[2], Nina Lanza[2], Sam Clegg[2], Gilles Berger[3], Steve Bender[2], Jeremie Lasue[3], Roger Wiens[2], Sylvestre Maurice[3]; [1]Delaware State University, [2]Los Alamos National Laboratory, [3]Institut de Recherche en Astrophysique et Planetologie (IRAP)

27 (26) **Advancing the Analytical Capabilities of Laser Ablation Molecular Isotopic Spectrometry (LAMIS) for Boron Isotopic Analysis**; Arnab Sarkar[1,2], Xianglei Mao[1], Meirong Dong[1], Richard Russo[1]; [1]Lawrence Berkeley National Laboratory, Berkeley, California, [2]Fuel Chemistry Division, Bhabha Atomic Research Centre, Mumbai, India

Board #

28 (27) **Boron Isotopic Compositional Mapping by Laser Ablation Molecular Isotopic Spectrometry (LAMIS)**; Arnab Sarkar[1,2], Jose R. Chirinos[1], Dayana D. Oropeza[1], James K. Wu[1], Jhanis J. Gonzalez[1], Meirong Dong[1], Xianglei Mao[1], Richard E. Russo[1]; [1]Lawrence Berkeley National Laboratory, Berkeley, California, [2]Fuel Chemistry Division, Bhabha Atomic Research Centre, Mumbai, India

29 (28) **Oscillator Strength Measurements in Lanthanides and Transition Metals Using Laser-Induced Breakdown Spectroscopy**; Russell Putnam[1], Caleb Ryder[2], Steven Rehse[1] ; [1]Department of Physics - University of Windsor, [2]National Superconducting Laboratory - Michigan State University

30 (29) **Atomic Emission Lifetimes of Quiescent Air, AP and AN from ns laser Induced Plasma Plume vis-à-vis Laser Induced Breakdown Spectroscopy**; Manoj Kumar G[1], Leela Ch[1], Suman Bagchi[2], Sreedhar S[1], Ashwin Kumar M[1], Prem Kiran P[1]; [1]ACRHEM, University of Hyderabad, Hyderabad, India, [2]Raja Ramanna Centre for Advanced Technology, Indore, M. P, India

31 (30) **Temporal Characterization of Nanosecond Pulsed Laser Initiated Breakdown Threshold in Liquid Water**; Bhamidipati Sitalakshmi[1], Sunku Sreedhar[2], Ashoka Vudayagiri[1, 2] ; [1]University of Hyderabad, [2]ACRHEM

32 (31) **Spectral analysis of RF Emissions from laser Produced Plasma of Atmospheric Air and Metals**; Manoj Kumar[1], Vinoth Kumar L[1], Manikanta Elle[1], Leela Chelikani[1], Prem Kiran Pathuri[1] ; [1]Advanced Centre of Research in High Energy Materials (ACRHEM), University of Hyderabad

33 (32) **A Reinterpretation of Depth Profiling Data Using LIBS**; Carlos Montoya[1], Nancy Mcmillian[1], Warren Chesner[2]; [1]New Mexico State University, [2]Chesner Engineering

34 (33) **Calibration Issues in Deep-Ocean LIBS: The Use of H and O as Internal Standards**; Joseph Bonvallet[1], S. Michael Angel[1]; [1]University of South Carolina

35 (34) **Dynamics of Ultrafast Laser Ablation Plumes in the Presence of Gases: Implications to LA-ICP-MS and LIBS**; Prasoon Diwakar[1], Sivanandan Harilal[1], Ahmed Hassanein[1]; [1]Center for Materials Under eXtreme Environment, School of Nuclear Engineering Purdue University, 500 Central Drive, West Lafayette, Indiana

36 (35) **Isomer Identification using laser Induced Breakdown Spectroscopy**; Manoj Kumar Gundawar[1], Ashwin Kumar Myakalwar[1], Shiv Kumar Anubham[1], Ishan Barman[2], Narahara Chari[2] ; [1]University of Hyderabad, [2]Massachusetts Institute of Technology

37 (36) **Discrimination Analysis of Nitroimidazoles Studied with Femtosecond Laser Induced Breakdown Spectroscopy**; Manoj Kumar Gundawar[1], Nageswara Rao Epuru[1], Sreedhar Sunku[1], Venugopal Rao Soma[1]; [1]ACRHEM, University of Hyderabad, India

38 (37) **Fast Steel Analysis Using Laser-Induced Breakdown Spectroscopy**; Markus Gaelli[1]; [1]TSI Incorporated

39 (38) **Elemental Analysis of Thin Cu(In,Ga)Se_2 Solar Cell Films using femtosecond Laser-Induced Breakdown Spectroscopy**; Seokhee Lee[1,2], Jhanis Gonzalez[2, 3], Jong Yoo[3], Xianglei Mao[2], Richard Russo[2, 3], Sungho Jeong[1]; [1]School of Mechatronics, Gwangju Institute of Science and Technology, [2]Lawrence Berkeley National Laboratory, [3]Applied Spectra Inc

Board #

40 (39) **Spatially Resolved vs. Spatially Integrated Measurements of Parameters of Laser Induced Plasma**; Igor Gornushkin[1], Alexandr Demidov[1], Ulrich Panne[1, 2], Ebo Ewusi-Annan[, 3], Ben Smith[, 3], Nicolo Omenetto[, 3]; [1]Federal Institute for Materials Research and Testing (BAM), [2]Humboldt-Universität zu Berlin, Department of Chemistry, [3]Department of Chemistry, University of Florida

41 (40) **Absorption Laser-Induced Breakdown Spectroscopy**; Igor Gornushkin[1], Michael Asgill[1], Ulrich Panne[, 2]; [1]Optical Spectroscopy Working Group, Federal Institute for Materials Research and Testing, Berlin, [2]Humboldt-Universität zu Berlin, Department of Chemistry, Berlin

42 (41) **Concepts of Operation for LIBS-based Exploratory Geochemistry and Chemostratigraphy**; Pablo Sobron[1,2]; [1]SETI Institute, [2]MalaUva Labs

43 (42) **Study of Plasma Dynamics for Dicarboxylic Acids Induced by NdYAG-CO_2 Enhanced Dual Laser Pulses**; Staci Brown[1,2,3], Charlemagne Akpovo[1, 2, 3], Jorge Martinez[1, 2, 3], Lewis Johnson[1, 2, 3]; [1]Florida A & M University, [2]Physics Department, [3]Center for Plasma Science and Technology

44 (43) **Multivariate optimization and sample Preparation for Analysis of Fertilizers by laser Induced Breakdown Spectroscopy**; Lidiane Cristina Nunes, Edenir Rodrigues Pereira-Filho[, 2], Francisco José Krug[1]; [1]Center for Nuclear Energy in Agriculture (CENA-USP), [2]Federal University of São Carlos (UFSCar)

Monday Morning, *Room 101A*
TECHNOLOGICAL ADVANCES AND NEW APPLICATIONS USING QUANTUM CASCADE LASERS
Organizer and Presider: Bernhard Lendl

10:20 (44) **New Applications of Quantum Cascade Lasers in Analytical Chemistry**; Bernhard Lendl[1], Markus Brandstetter[1], Christoph Reidl-Leuthner[1], Georg Ramer[1], Johannes Waclawek[1], Harald Moser[1]; [1]Vienna University of Technology

10:40 (45) **Quantum Cascade Laser Arrays for integrated Optics**; Mathieu Carras[1], Sergio NIcoletti[, 2], Mickael Brun[2], Gregory Maisons[1], Fahem Boulila[1], Pierre Labeye[, 2], Pierre Barritault[, 2]; [1]III-V Lab, [2]CEA-LETI

11:00 (46) **Monolithic Tuning of Quantum Cascade Lasers for Compact Infrared Spectroscopy**; Christian Pfluegl[1], Mark Witinski[1], Laurent Diehl[1]; [1]Eos Photonics Inc.

11:20 (47) **Mid-Infrared Microspectroscopic Imaging with a Quantum Cascade Laser**; Kevin Yeh[1], Matthew Schulmerich[1], Rohit Bhargava[1]; [1]University of Illinois at Urbana-Champaign

11:40 (48) **Broadly-Tunable Room Temperature Terahertz Quantum Cascade Laser Sources: Devices and Applications**; Mikhail Belkin[1], Yifan Jiang[1], Karun Vijayraghavan[1], Frederic Demmerle[, 2], Gerhard Boehm[2], Markus-Christian Amann[2]; [1]Department of Electrical and Computer Engineering, The University of Texas at Austin, [2]Walter Schottky Institute, Technical University of Munich

Monday Morning, *Room 101B*
NEW INSTRUMENTATION IN LIBS
Organizer and Presider: Arel Weisberg

10:20 (49) **Design and Performance of a Person-Portable LIBS Instrument for the Detection of RNE Threats**; David Cremers[1], Melissa Bostian[1], Gary Smith[1], C. Randy Jones[1], Rosalie Multari[1], James Barefield II[, 2], Beth Judge[2], John Berg[2], Leonardo Trujillo[, 2], [1]Applied Research Associates, Inc., [2]Los Alamos National Laboratory

10:40 (50) **Design and Application of a New LIBS Desktop Analyzer**; Phillip Tan[1], Dan Jensen[1], Gregg Lithgow[1], Kregg Philpott[1], Markus Gaelli[1], Robert Robinsky[1]; [1]TSI Inc

11:00 (51) **In Search of Robust Multivariate Classification Method for Identification of High Energy Materials using laser Induced Breakdown Spectroscopy**; Manoj Kumar Gundawar[1], Ashwin Kumar Myakalwar[1], Shiv Kumar Anubham[1], Narahara Chari Dingari[, 2], Ishan Barman[, 2]; [1]University of Hyderabad, [2]Massachusetts Institute of Technology

11:20 (52) **Application of Laser-Induced Breakdown Spectroscopy for Quality Assessment of Pharmaceutical Products**; Gang Li[1], Sergey Arzhantsev[1], John Kauffman[1]; [1]US Food and Drug Administration

11:40 (53) **LIBS: Plasma Containing Titanium as a Probe for Temperature**; Alexander Woods[1], Christian Parigger[1], James Hornkohl[2]; [1]University of Tennessee Space Institute

Monday Morning, *Room 101C*
APPLIED SPECTROSCOPY FOCAL POINT SESSION: BIOIMAGING AND BIOANALYSIS WITH QUANTUM DOTS
Organizer: Russ Algar; Presider: Mike Blades

10:20 (54) **Sensing More with LessNew Strategies for Assays with Quantum Dots**; Russ Algar[1]; [1]University of British Columbia,

11:00 (55) **Energy Transfer Based Biosensing with Luminescent Semiconductor Quantum Dots**; Igor Medintz[1]; [1]U.S. Naval Research Laboratory

11:20 (56) **From Nanobodies to Antibodies: Time-Resolved Long-Lifetime FRET for Homogeneous Immunoassays**; Niko Hildebrandt[1]; [1]Université Paris-Sud

11:40 (57) **Nanoparticles in Theranostics: The Good, the Bad, and the Predictable**, David Cramb[1], [1]University of Calgary

Monday Morning, *Room 102A*
ION STRUCTURE AND ENERGETICS
Organizer and Presider: Mary T. Rodgers

10:20 (58) **Reactions of Iron and Iron Oxide Clusters with Carbon Monoxide Using Guided Ion Beam Tandem Mass Spectrometry**; Peter Armentrout[1], Christopher McNary[1], Oscar Wheeler[1]; [1]Department of Chemistry, University of Utah

10:40 (59) **Collision-induced Dissociation Energetics of Gly-Gly-Gly and Gly-Gly-Gly-NH2 Explored Using Tandem Mass Spectrometry and Theoretical Calculations**; Michael Van Stipdonk[1,2], Allison Williams[, 2], Benjamin Bythell[, 3], Abhigya Mookherjee[, 4], Peter Armentrout[, 4]; [1]Duquesne University, [2]Lawrence University, [3]University of Missouri-St. Louis/National High Magnetic Field Laboratory, Florida State University, [4]University of Utah

11:00 (60) **Guided Ion Beam Studies of Proton-Bound Dimers of Cytosines: Determination of Hydrogen-Bond Stabilization Energies and Relative Proton Affinities**; Bo Yang[1], Mary Rodgers[1] ; [1]Wayne State University

11:20 (61) **Computational Studies of Ion-neutral Reactions of Astrochemical Relevance**; Zhibo Yang[1]; [1]University of Oklahoma

11:40 (62) **Structure and Reactivity of Gas-Phase Peptide Radical Ions**; Victor Ryzhov[1]; [1]Northern Illinois University

Monday Morning, *Room 102B*
ELECTRICALLY DRIVEN PROCESSES IN NANOFLUIDIC DEVICES
Organizer and Presider: Stephen C. Jacobson

10:20 (63) **Electrokinetic Transport of Single DNA Molecules through Nanochannel Networks**; J. Michael Ramsey[1], Laurent D. Menard[1], Jinsheng Zhou[1]; [1]University of North Carolina at Chapel Hill

10:40 (64) **Coupling Electrokinetic Flow to Spectroelectrochemistry in Low-Dimensional Nanostructures for Chemical and Biochemical Sensing**; Paul W. Bohn[1,2], Jing Zhao[1], Nicholas M. Contento[1], Dane A. Grismer[1], Lawrence P. Zaino, 2, Sneha Polisetti[1]; [1]Department of Chemical & Biomolecular Engineering, University of Notre Dame, [2]Department of Chemistry & Biochemistry, University of Notre Dame

11:00 (65) **Bioanalytical Measurement with Scanning Ion Conductance Microscopy**; Lane Baker[1], Chiao-Chen Chen[1], Yi Zhou[1], Jianghui Hou, 2, Beth Yuilli[1], Anumita Saha[1], Alicia Friedman[1], Steve Ray[1] ; [1]Indiana University, [2]Washington University

11:20 (66) **Using Super-Resolution Optical Microscopy to Study Molecular Diffusion on Interfaces and in Nanopores**; Gufeng Wang[1], Luyang Zhao[1], Fang Chen[1], Bhanu Neupane[1] ; [1]North Carolina State University

11:40 (67) **Nanofluidic Circuits for Monitoring Single Virus Particles and Their Assembly**; Stephen C. Jacobson[1], Zachary Harms[1], Andrew Kneller[1], Lisa Selzer[1], Adam Zlotnick[1]; [1]Indiana University

Monday Morning, *Room 102C*
PHARMACEUTICAL RAMAN
Organizers and Presiders: Ian R. Lewis and Pavel Matousek

10:20 (68) **Monitoring of Continuous Crystallization using Non-Invasive Raman and Acoustic Emission Spectroscopies**; Laura Palmer[1], David Littlejohn[1], Alison Nordon[1], Jan Sefcik[1], Alastair Florence[1]; [1]University of Strathclyde

10:40 (69) **Raman Spectroscopy in Biopharmaceutical Manufacturing: Measuring the Media.**; Alan Ryder[1], Boyan Li[1], Bridget Kissane[1], Amandine Calvet[1] ; [1]Nanoscale Biophotonics Laboratory, National University of Ireland Galway

11:00 (70) **Pharmaceutical Tablet Matrix Effects in Quantitative Transmission Raman Spectroscopy**; Anders Sparén[1], Olof Svensson[1], Madeleine Hartman, 2, Magnus Fransson[1], Jonas Johansson[1]; [1]AstraZeneca R&D Mölndal, Sweden, [2]Uppsala University, Sweden

11:20 (71) **Tablet Assay of Acetaminophen by Transmission Raman**; Carl A. Anderson[1], Benoît Igne[1], MD Nayeem Hossain[1], James K. Drennen[1] ; [1]Duquesne University Center for Pharmaceutical Technology

11:40 (72) **Portable Spectrometers: The First Step in Pharmaceutical Counterfeit Investigation**; Ravi Kalyanaraman[1]; [1]Bristol-Myers Squibb

Monday Morning, *Room 102D*
NUCLEAR FORENSICS
Organizer and Presider: Greg Klunder

10:20 (73) **Laser-Induced Breakdown Spectroscopy for Real-Time Nuclear Forensics**; François R. Doucet[1], Paul Bouchard[1], Mohamad Sabsabi[1], Rick Kosierb[2]; [1]National Research Council Canada, Energy, Mining and Environment, [2]Canadian Nuclear Safety Commission, Directorate of Security and Safeguards

10:40 (74) **The Analysis of Special Nuclear Materials using Laser-Induced Breakdown Spectroscopy (LIBS)**; Elizabeth J. Judge[1], James E. Barefield II[1], John M. Berg[1], Stephen P. Willson[1], Loan A. Le[1], Leon N. Lopez[1], Leonardo Trujillo[1]; [1]Los Alamos National Laboratory

11:00 (75) **High Spatial Resolution Surface Analysis via Femtosecond Laser Ablation-Multi-Collector-Inductively Coupled Plasma Mass Spectrometry**; Greg Eiden[1], Andrew Duffin[1], Jesse Ward[1], Kellen WE Springer[1], Albert J. Fahey[1], John W. Robinson[1]; [1]Pacific Northwest National Laboratory

11:20 (76) **Surrogate Nuclear Explosion Debris (SNED): New Materials for Testing, Evaluation, and Research**; Greg Eiden[1], April Carman[1], Scott Harvey[1], Martin Liezers[1], Albert Fahey[1], Janet Cloutier[1]; [1]Pacific Northwest National Laboratory

11:40 (77) **Infrared and Near Infrared Spectroscopy of Uranium Ore Concentrates for Nuclear Forensic Analysis**; Gregory Klunder[1], Paul Spackman[1], Patrick Grant[1], Ian Hutcheon[1]; [1]Lawrence Livermore National Laboratory

Monday Morning, *Room 102E*
ACS-RSC SYMPOSIUM ON SUSTAINABILITY IN ATOMIC SPECTROSCOPY
Organizers: David W. Koppenaal and May Copsey;
Presider: David W. Koppenaal

10:20 (78) **Mass Spectrometry As an Indispensable Tool to Build and Maintain a Sustainable Future**; Jacob Shelley[1], Christopher Kuhlmann[1], Joshua Wiley, 2, R. Graham Cooks, 2, Carsten Engelhard[1]; [1]Institute for Inorganic and Analytical Chemistry, University of Muenster, [2]Department of Chemistry, Purdue University

10:40 (79) **Towards the Development of Greener Methods using Direct Solid Sampling**; Martin Resano[1], Esperanza Garcia-Ruiz[1], Miguel A. Belarra[1]; [1]University of Zaragoza

11:00 (80) **Novel Calibration Strategies for Quantitative Iron Imaging of Soft Tissues using Laser Ablation with ICPMS**; Jennifer O'Reilly[1], Liuxing Feng[2], Wang Jun[2], Heidi Goenaga-Infante[1]; [1]LGC Limited, [2]Division of Metrology in Chemistry, National Institute of Metrology

11:20 (81) **Laser Ablation for Chemical Analysis: Contribution to Sustainability of Atomic Spectroscopy**; Jhanis Gonzalez[1,2], Jose Chirinos[1], Dayana Oropeza[1], Meirong Dong[1], Huaming Hou[1], Vassilia Zorba[1], Xianglei Mao[1], Rick Russo[1,2]; [1]Lawrence Berkeley National Laboratory, [2]Applied Spectra, Inc.

11:40 (82) **Sustainability & Analytical Chemistry: Developing Greener Methods in the Mass Spectrometry Laboratory**; Carsten Engelhard[1,2], Anastasia Albert[2], Britta Vortmann[2], Wolfgang Buscher[2], Christopher Kuhlmann[2], Sascha Nowak[2], Jacob T. Shelley[2]; [1]University of Siegen, [2]University of Muenster

Monday Morning, *Room 103B*
CHEMISTRY IN ART AND ARCHAEOLOGY
Organizers: Mary Kate Donais and Peter Vandenabeele;
Presider: Mary Kate Donais

10:20 (83) **X-ray Spectroscopy and Imaging of Painted Works of Art: from the Nanometer to the Meter Scale**; Koen Janssens[1], Matthias Alfeld[1], Geert Van der Snickt[1], Joris Dik[2], Letizia Monico[1,3], Jo Verbeeck[1]; [1]University of Antwerp, [2]Delft University of Technology, [3]University of Perugia

10:40 (84) **Chemical Characterization of Pegmatite Quartz Quarries in the Churchill River Basin using SIMS**; Rachel ten Bruggencate[1], Mostafa Fayek[1], Brooke Milne[1], Kevin Brownlee[2], Scott Hamilton[3]; [1]University of Manitoba, [2]Manitoba Museum, [3]Lakehead University

11:00 (85) **Spectroscopic Examination of First Pyramidal Hypogeum Found in Etruria and Italy**; Mary Kate Donais[1], David George[2]; [1]Saint Anselm College Department of Chemistry, [2]Saint Anselm College Department of Classics

11:20 (86) **Using Non-Destructive Portable X-Ray Fluorescence Spectrometers on Archaeological Material in Museums: The Good and the Bad for Analyzing Stone, Ceramics, Metals, and Other Materials**; Robert Tykot[1]; [1]University of South Florida

11:40 (87) **Authenticating Art With Raman Spectroscopy: An Undergraduate Instrumental Analysis Laboratory Experiment**; Sara Nielsen[1], Ellen Yezierski[1], Jonathan Scaffidi[1] ; [1]Miami University

Monday Morning, *Room 103C*
INDUSTRIAL PROCESS ANALYTICAL REAL TIME ASSURANCE
Organizer and Presider: Richard Escott

10:20 (88) **To Hyternity and Beyond**; Fabien Chauchard[1], Richard Escott[1], Audrey Zilliox[2], Charles Ghommidh[3]; [1]INDATECH, [2]GSK, [3]Joint research unit Agropolymer Engineering and Emerging Technologies

10:40 (89) **Development of Real Time Assurance for Oligonucleotide Synthesis**; James Rydzak[1], David White[1], Christian Airiau[1], Don Clancy[1]; [1]GlaxoSmithKline Pharmaceuticals

11:00 (90) **Development of a Control Strategy for Real Time Release Testing of Ciprofloxacin HCl Controlled Release Multiparticulate Beads**; Stephen W. Hoag[1]; [1]University of Maryland, Baltimore

11:20 (91) **Spectral Imaging for Real Time Release**; Rudolf Kessler[1]; [1]Process Analysis and Technology, Reutlingen Research Institute, Reutlingen University

11:40 (92) **Can Calibrations Based on Light Propagation Theories Lead to Better Performance for real Time Monitoring?**; Suresh Thennadil[1], Yi-Chieh Chen[1], Nicolau Dehanov[1]; [1]University of Strathclyde

Monday Morning, *Room 103D*
CONTRIBUTED PAPERS IN CHEMOMETRICS
Organizer: Michel George; Presider: Keith Gordon

10:20 (93) **Extending the Dynamic Range of Photon Counting using Digital Filters Designed by Linear Discriminant Analysis (LDA)**; Garth Simpson[1]; [1]Purdue University

10:40 (94) **Evaluation of a Calibration Matrix for heavily Overlapped Ultra-Violet Spectra by Target Factor Analysis**; Huggins Z. Msimanga[1], Newsha Tavakoli[1]; [1]Kennesaw State University

11:00 (95) **Development of a Data Abstraction Strategy to Model Critical Properties of Navy Mobility Fuels from Mass Spectral Data**; Jeffrey Cramer[1], Robert Morris[1], Mark Hammond[1]; [1]U.S. Naval Research Laboratory

11:20 (96) **Raman Spectroscopy to Explore the Chemical Structure of Hypomineralised Teeth and Monitor Treatment with Dental Resins**; Sara Fraser[1], Arun Natarajan[2], Bernadette Drummond[2], Keith Gordon[1]; [1]MacDiarmid Institute of Advanced Materials and Nanotechnology, Department of Chemistry, University of Otago; [2]Oral Sciences, Faculty of Dentistry, University of Otago

11:40 (97) **Predicting Rheological Behavior of Wheat Dough Based on Machine Learning and Front-Face Fluorescence Spectroscopy on Wheat Flour**; Lyes Lakhal[1], Larbi Rhazi[1], Jean-Paul Bonhoure[1], Thierry Aussenac[1]; [1]Institut Polytechnique LaSalle Beauvais, [2]Institut Polytechnique LaSalle Beauvais, [3]Institut Polytechnique LaSalle Beauvais, [4]Institut Polytechnique LaSalle Beauvais

Monday Afternoon, *Room 101A*
CHEMISTRY IN ART AND ARCHAEOLOGY
Organizers: Mary Kate Donais and Peter Vandenabeele;
Presider: Peter Vandenabeele

1:20 (98) **Analysis with XRF and Raman Spectroscopies of 18th Century Böttger Red Stonewares: Unraveling Chemistry, Technology and Possible Provenance**; Francesca Casadio[2], Gulsu Simsek[1], Philippe Colomban[1], Ludovic Bellot-Gurlet[1], Katherine Faber[3], Ghenete Zelleke[2], Veronique Milande[4]; [1]Ladir, Universite Pierre et Marie Curie, Paris, [2]Art Institute of Chicago, Chicago, IL, [3]Northwestern University, [4]Cité de la Céramique

1:40 (99) **Chemical Insights on Modern Art Paintings**; Colombini Maria Perla[1]; [1]University of Pisa

2:00 (100) **Raman spectroscopy for the Characterization of Ceramic and stone Pottery**; Danilo Bersani[1]; [1]University of Parma, Department of Physics and Earth Sciences

2:20 (101) **Mobile Raman Spectroscopy in Art Analysis: Pros and Cons**; Peter Vandenabeele[1]; [1]Ghent University

2:40 (102) **Novel Sampling Strategies for Trace Element Quantification in Ancient Copper Artifacts using LA-ICP-MS**; Marcel Burger[1], Reto Glaus[1], Vera Hubert[2], Samuel van Willigen[2], Marie Wörle-Soares[2], Detlef Günther[1]; [1]ETH Zürich, Laboratory of Inorganic Chemistry, [2]Swiss National Museum

Monday Afternoon, *Room 101B*
BIOLOGICAL APPLICATIONS OF LIBS
Organizers and Presider: Matthieu Baudelet and Steve Rehse

1:20 (103) **Precise Cranial Surgery With Femtosecond Laser Ablation, Laser Induced Breakdown Spectroscopy and Second Harmonic Generation**; Philbert Tsai, Diana Jeong[1], David Kleinfeld[1]; [1]University of California, San Diego

1:40 (104) **Healing Humanity One Spark at a Time: Medical Applications of LIBS**; Steven Rehse[1]; [1]University of Windsor

2:00 (105) **Quantitative Analysis with LIBS at Low Ablative Energies**; M.A. Meneses-Nava[1], V. Contreras[1], O. Barbosa-Garcia[1], J.L. Maldonado[1], G. Ramos-Ortiz[1]; [1]Centro de Investigaciones en Optica A.C.

2:20 (106) **Chemometric Data Analysis Strategies for Optimizing Pathogen Discrimination and Classification Using Laser-Induced Breakdown Spectroscopy (LIBS) Emission Spectra**; Russell Putnam[1], Khadija Sheikh[1, 2], Andrew Daabous[1], Steven Rehse[1]; [1]Department of Physics - University of Windsor

2:40 (107) **Femtosecond Laser-Induced Breakdown Spectroscopy (fs-LIBS) of Electrode/Electrolyte Interfaces**; Sid Ahmed Beldjilali[1,2], Ulrike Vogl[1, 3], Simon Lux[1], Jaroslaw Syzdek[1], Huaming Hou[1], Xianglei Mao[1], Vassilia Zorba[1], Martin Winter[3], Robert Kostecki[1], Richard E. Russo[1]; [1]Environmental Energy Technologies Division, Lawrence Berkeley National Laboratory, [2]LPPMCA, USTOMB - Université des Sciences et de la Technologie d'Oran, Oran, Algeria, [3]MEET - Münster Electrochemical Energy Technology, Institute of Physical Chemistry, University of Muenster

Monday Afternoon, *Room 101C*
MATERIALS CHARACTERIZATION USING VIBRATIONAL SPECTROSCOPY
Organizer: Michael George; Presider: Katherine Cilwa

1:20 (108) **Ultra-Low Frequency Raman Spectroscopy: A New Technique for Polymorph Characterization of Pharmacuetical Drug Substances**; Peter Larkin[1], Marta Dabros[1], Beth Sarsfield[1], James Carriere[2], Brian Smith[3]; [1]Bristol Myers Squibb, [2]Ondax, [3]Princeton Instruments

1:40 (109) **Raman Spectroscopy of Oil Shale**; David Tuschel[1]; [1]HORIBA Scientific

2:00 (110) **Nanoscale Chemical and Thermal Identification of Inclusions in Polymers and Engineered Thermoplastic Blends using AFM Coupled to IR spectroscopy, Thermal and Mechanical Analysis**; Anne M. Simon[1], Nancy L. Jestel[1], Bing Zhou[1], Michael Lo[2]; [1]SABIC, [2]Anasys Instruments, Inc

2:20 (111) **Assessing Intermediate Degrees of Acylation of Starch Granules via Infrared Microspectroscopy**; Mark Boatwright[1,2], Meng Xue[2, 3], Yongcheng Shi[2, 3], David Wetzel[2]; [1]Department of Biochemistry and Molecular Biophysics, Kansas State University, Manhattan, KS, [2]Microbeam Molecular Spectroscopy Laboratory, Kansas State University, [3]Department of Grain Science, Kansas State University

2:40 (112) **Infrared Microspectroscopic Assessment of Hydrophilic Surface Treatment of Polydimethylsiloxane (PDMS) for Use in Microfluidics**; David Wetzel[1,3], Mark Boatwright[2, 3], Christopher Culbertson[1], Makund Koirala[1,3]; [1]Department of Chemistry, Kansas State University, [2]Department of Biochemistry and Molecular Biophysics, Kansas State University, [3]Microbeam Molecular Spectroscoy Laboratory, Kansas State University

Monday Afternoon, *Room 102A*
CHEMOMETRICS FOR HANDHELD, EMBEDDED, AND MEDICAL DEVICES
Organzier and Presider: Lin Zhang

1:20 (113) **Threat Specific Spectral Searches in the Detection of Explosives**; Kevin Judge[1], Greger Andersson[1]; [1]Smiths Detection

1:40 (114) **A Modified Exponential Gaussian Hybrid Function and Its Application to Processing the Data Obtained by Ultra-high Resolution TOFMS Coupled with Chromatography**; Jihong Wang[1], Peter M Willis[1]; [1]LECO Corporation

2:00 (115) **Muscle Oxygenation Measurement in Humans by Noninvasive Optical Spectroscopy and Locally Weighted Regression**; Lorilee Arakaki[1], Kenneth Schenkman[1], Wayne Ciesielski[1], Jeremy Shaver[2]; [1]University of Washington, [2]Eigenvector Research, Inc.

2:20 (116) **Multivariate Models for Rapid Identification with Handheld Spectrometers**; Katherine Bakeev[1], Dawn Yang[1]; [1]B&W Tek, Inc

2:40 (117) **A Chemometric Algorithm for Detection of Lipid Core Coronary Plaques Using Intravascular Near-Infrared Spectroscopy**; Huwei Tan[1], Craig Gardner[1], Stephen Sum[1], Sean Madden[1], Chunsheng Jiang, Zhehua He[1], Tianchen Shi[1], Edward Hul[1]l, Jay Caplan[1], James Muller[1]; [1]InfraReDx Inc.

Monday Afternoon, *Room 102B*
AES AWARD SESSION HONORING TODD SQUIRES
Organizers and Presiders: Edgar Goluch and Alexandra Ros

1:20 (118) **Solvo-, Chemi-, Diffusio- and Electro-Phoretic Migration: New Techniques to Measure Exotic Phoretic Mobilities and Characterize Colloidal Surfaces**; Todd Squires, Joel Paustian[1], Rodrigo Nery-Azevedo[1]; [1]University of California, Santa Barbara

2:00 (119) **Moving Charges to Order Particles: The Disorder-Order Transition for Dielectrophoretic Colloidal Assembly**; Eric Furst[1]; [1]University of Delaware

2:20 (120) **Fluid and Ion Transport at the Nanoscales: Application to Osmotic Energy Harvesting**; Lyderic Bocquet[1,2]; [1]ILM - University of Lyon, [2]MIT

2:40 (121) **Ion Correlation and Ion Steric Effects on Electrophoresis of a Colloidal Particle**; Aditya Khair[1], Robert Stout[1]; [1]Department of Chemical Engineering, Carnegie Mellon University

Monday Afternoon, *Room 102C*
EMERGING RAMAN TECHNIQUES AND APPLICATIONS
Organizers and Presiders: Ian R. Lewis, Duncan Graham and Pavel Matousek

1:20 (122) **Ultrafast Plasmonics: Surface-Enhanced Femtosecond Stimulated Raman Spectroscopy**; Richard Van Duyne, Renee Frontiera[1], Natalie Gruenke[1], Anne-Isabelle Henry[1]; [1]Northwestern University

1:40 (123) **Raman Microscopy for Imaging Cellular Dynamics**; Katsumasa Fujita[1]; [1]Osaka University

2:00 (124) **Investigation of Nanostructure Dynamics by Femtosecond Time-Resolved Spectroscopy with Nanometer Spatial Resolution**; Arnulf Materny[1]; [1]Jacobs University Bremen

2:20 (125) **Quantitative Raman Spectroscopy in Turbid Matter: Reflection or Transmission Mode?**; Rudolf Kessler[1], Dieter Oelkrug[2], Edwin Ostertag[1]; [1]Process Analysis and Technology, Reutlingen Research Institute, Reutlingen University, Reutlingen, [2]Institute of Physical and Theoretical Chemistry, University of Tübingen, Tübingen

2:40 (126) **Investigating the Degradation of Stored Red Blood Cells Using Raman Spectroscopy**; Chad Atkins[1,2], H. Georg Schulze[2], Deborah Chen[3], Peter Schubert[3, 4], Katherine Serrano[3, 4], Dana Devine[3, 4], Michael Blades[1], Robin Turner[1,2]; [1]University of British Columbia, Chemistry Department, [2]Michael Smith Laboratories, [3]University of British Columbia, Centre for Blood Research, [4]Canadian Blood Services

Monday Afternoon, *Room 102D*
ANALYTICAL CHEMISTS EASING WORLD POVERTY
Organizers and Presider: Diane Parry

1:20 (127) **Worker Exposure Assessment in Developing Countries**; Kevin Ashley[1]; [1]Centers for Disease Control and Prevention, National Institute for Occupational Safety and Health (CDC / NIOSH)

1:40 (128) **Vaccine Adjuvant Development for Neglected Diseases: An Analytical Approach**; Christopher Fox[1], Steven Reed[1]; [1]IDRI

2:00 (129) **Developing Analytical Centers for Excellence at Local Universities in Africa**; Aloysius Ike Ononye[1]; [1]Procter and Gamble

2:20 (130) **Improving Global Nutrition and Medical Care with Inexpensive Paper Analytical Devices**; Marya Lieberman[1], Nicholas Myers[1]; [1]University of Notre Dame

2:40 (131) **Establishing Innovative Sustainable Pharmaceutical Quality Assessment Capacity in Resource Constrained Settings**; Thomas Layloff[1], Eliangiringa Kaale[, 2], David Jenkins[, 3], S. Michael Hope[4]; [1]Supply Chain Management System, [2]Muhimbili University of Health and Allied Sciences, [3]FHI 360, [4]United States Agency for International Development

Monday Afternoon, *Room 103B*
SIX DEGREES OF SEPARATION: JIM HOLCOMBE'S CAREER IN ATOMIC SPECTROSCOPY
Organizer and Presider: John L. Molloy

1:20 (132) **Glow Discharge Mass Spectrometry and its Application to Determination of Purity to Support Global Traceability of Chemical Measurements**; Ralph Sturgeon, Bradley Methven, Scott Willie; [1]National Research Council of Canada, [2]National Research Council of Canada, [3]National Research Council of Canada

1:40 (133) **Amerithrax: The Most Complex Investigation in the FBI's History Explained in 20 Minutes**; Vahid Majidi[1]; [1]TASC

2:00 (134) **What Jim Taught Me In Graduate School That Helped My Career in the semiconductor Industry. P.S. It Wasn't the Academics**; Chris Sparks[1]; [1]Air Liquide Electronics US - Balazs NanoAnalysis

2:20 (135) **Chemical Investigation of Novel Psychoactive Substances Sold in the UK**; Jacqueline L. Stair[1], Sulaf Assi[1], Kathryn Kellet[1], Suzanne Fergus[1], Sheelagh Halsey[2]; [1]University of Hertfordshire, [2]Thermo Fisher Scientific

2:40 (136) **Pearls of Wisdom from a Proteomic Chemist: Passed Down from Father to Daughter to You**; Brook Nunn[1]; [1]University of Washington

Monday Afternoon, *Room 103C*
SAS PAT SECTION PHARMACEUTICAL AND BIOPHARMACEUTICAL PAT SESSION I
Organizers: Brandye Smith-Goettler and Edita Botonjic-Sehic; Presider: Edita Botonjic-Sehic

1:00 **SAS PAT Technical Section Meeting**

1:20 (137) **Kinetics-Based Reaction Monitoring Using In-Line Raman Spectroscopy**; Ming Huang[1], Robert Wethman[1], John Wasylyk[1]; [1]Bristol-Myers Squibb

1:40 (138) **On-line Application of NIRS for Monitoring of PPM Level Water in Manufacturing-Scale Distillation Process**; Zhenqi Shi[1], Gordon Lambertus[1], Robert Forbes[1], Steven Doherty[1], James Hermiller[1], Norma Scully[1], Sze Wing Wong[1], Mark LaPack[1]; [1]Eli Lilly and Company

2:00 (139) **Infrared Calibration Life-Cycle Management of the Active Content of an Oral Dosage Form**; Benoit Igne[1], Md. Nayeem Hossain[1], Carl Anderson[1], James Drennen[1]; [1]Duquesne University

2:20 (140) **Quantitative Predictions of Nifedipine Polymorphic Transitions Using In-Line Raman Spectroscopy, Principle Component Analysis and Multivariate Curve Resolution**; Shweta Raina[1], David E. Alonzo[3], Yi Gao[2], Geoff g. Z. Zhang[2], Lynne S. Taylor[1]; [1]Purdue University, Department of Industrial and Physical Pharmacy, [2]NCE Formulation - LC, Research and Development, AbbVie, Inc., [3]Formulation & Process Development, Gilead Sciences, Inc.

2:40 (141) **In-Process Monitoring of API Dissolution in Softgel Capsule Manufacturing using ATR-UV and Raman Spectroscopy**; Boyong Wan[1], Christopher Zordan[1], Xujin Lu[1], Gary McGeorge[1]; [1]Bristol-Myers Squibb Co.

Monday Afternoon, *Room 103D*
CONTRIBUTED PAPERS IN SURFACE AND NANOTECHNOLOGY AND MATERIAL CHARACTERIZATION
Organizer: Michael George; Presider: Pete Licence

1:20 (142) **Extreme Spatial and Temporal Resolution in Tip-Enhanced Raman Spectroscopy**; Norihiko Hayazawa[1,2], Chi Chen[1], Kentaro Furusawa[1, 4], Satoshi Kawata[1, 3]; [1]RIKEN, [2]Tokyo Institute of Technology, [3]Osaka University, [4]Tohoku University

1:40 (143) **Confocal Raman Microscopy to Investigate the Chemistry of Silane Ligands Immobilized on Porous Silica Particles**; Natascha Knowlton[1], Jay Kitt[1], Joel Harris[1]; [1]University of Utah

2:00 (144) **Polarized Raman Spectroscopy of Individual electrospun Nanofibers**; Christian Pellerin[1], Marie Richard-Lacroix[1]; [1]University of Montreal

2:20 (145) **Spectrophotometric Determination of Sn (IV) in Solutions for Electrodeposition of Sn and Sn Alloys**; Jingjing Wang[1], Chuannai Bai[1], Eugene Shalyt[1]; [1]ECI Technology

2:40 (146) **Non-Invasive Monitoring of Powder Drying by Broadband Acoustic Emission Spectrometry in Comparison with Spectroscopic Techniques**; Alison Nordon[1], Denise Logue[1], Laura Wurker[1], David Littlejohn[1]; [1]University of Strathclyde

Monday Afternoon, *Room 101A*
IONIC LIQUID FACILITATED SMART MATERIALS FOR ANALYTICAL CHEMISTRY
Organizer and Presider: Chieu D. Tran

3:50 (147) **Ionic Liquids in GC for Water Analysis and for LC-MS of Trace Anions**; Daniel Armstrong[1]; [1]University of Texas at Arlington

4:10 (148) **Chemical Sensing Platforms Based on Ionic Liquid-Xerogel Hybrids**; Frank Bright ; [1]UB, SUNY

4:30 (149) **Ionic Liquid Facilitated Surface Modification of Natural Materials**; Paul Trulove[1], Luke Haverhals[1], E. Kate Brown[1], David Durkin[1], Aimee Brenner[1], Matthew Foley[1], Hugh De Long[2]; [1]U.S. Naval Academy, [2]Air Force Office of Scientific Research

4:50 (150) **Continuing Investigation of the Polyionic Ionic Liquid Stationary Phases for Capillary GC**; Leonard M. Sidisky, Greg Baney, Jamie Desorcie, Katherine Stenerson, Gustavo Serranoe, Daniel Shollenberger ; [1]Supelco

5:10 (151) **Supramolecular Polysaccharide Composites: Synthesis and Analytical Application**; Chieu Tran[1]; [1]Marquette University

Monday Afternoon, *Room 101B*
FUNDAMENTALS OF LIBS PLASMAS
Organizer: Steven Buckley; Presider: Martin Richardson

3:50 (152) **Time-Dependent Studies of LIBS Plasmas: Correlation between Plasma Dynamics and LIBS Emission Signal**; Alessandro De Giacomo[1], Marcella Del[2], Rosalba Gaudiuso[1], Olga De Pascale[2]; [1]University of Bari, Department of Chemistry, [2]CNR-IMIP

4:10 (153) **Thomson Scattering from Aluminum Laser Plasmas in Air**; Matthieu Baudelet[1], Yuan Liu[1], Bruno Bousquet[2], Martin Richardson[1] ; [1]Townes Laser Institute, CREOL – The College of Optics and Photonics, University of Central Florida, [2]Univ. Bordeaux, LOMA, UMR 5798

4:30 (154) **Sefl-Consistent Three-Dimensional Modeling of Laser Induced Pasma for LIBS Applications**; A. Hassanein[1], T. Sizyuk[1], S. Harilal[1]; [1]Purdue University

4:50 (155) **Plasma Modeling for Calibration-Free LIBS: Expectations and Reality**; Igor Gornushkin[1,2], Ulrich Panne[1], S. V. Shabanov[3]; [1]BAM Federal Institute for Materials Research and Testing, [2]Humboldt-Universität zu Berlin, Department of Chemistry, [3]Department of Mathematics, University of Florida

5:10 (156) **Fraunhofer-type Absorption Line Splitting and Polarization in Confocal Double-Pulse Laser Induced Plasma**; Lev Nagli[1], Michael Gaft[1]; [1]Laser Distance Spectrometery

Monday Afternoon, *Room 101C*
CONTRIBUTED PAPERS IN BIOANALYTICAL RESEARCH
Organizer: Michael George; Presider: Francis Esmonde-White

3:50 (157) **Sub-diffraction Imaging and Single Particle Tracking in Cultured Cells**; Aleem Syed[1], Neha Arora[1], Michael Lesoine[1], Dipak Mainali[1], Emily Smith[1]; [1]Iowa State University

4:10 (158) **Evaluation of Multilayer SERS Nanoprobes for Enhanced Intracellular Sensing**; Pietro Strobbia[1], Adam Mayer[1], Charles Klutse[1], Brian Cullum[1]; [1]University of Maryland Baltimore County

4:30 (159) **Variable Pathlength Spectroscopy in Biochemical Studies**; Darrell McCaslin[1], Daniel Wirz[1]; [1]University of Wisconsin

4:50 (160) **Melittin-Membrane Interactions through the Eyes of Deep Ultraviolet Resonance Raman Spectroscopy and Circular Dichroism**; Michael K. Eagleburger[1], Jason W. Cooley[1], Renee D. JiJi[1]; [1]University of Missouri

5:10 (161) **Detection of Pollen Allergens in the Air**; Jeremy Pronchik[1], M Thibaudon[2], M Hrabina[3], J Barberon[3], K Mercier[4], C Frydman[4]; [1]HORIBA Scientifc, USA, [2]RNSA, France, [3]Stallergenes, France, [4]Horiba Scientific, France

Monday Afternoon, *Room 102A*
PRACTICAL CHEMOMETRICS FOR INDUSTRY
Organizer and Presider: Curtis Marcott

3:50 (162) **Design and Analysis of NMR Relaxation Measurements for Understanding Complex Multiphase Mixtures**; Charles Eads[1], Carrie Furnish[1], Allison Talley[1]; [1]Procter & Gamble

4:10 (163) **Applications of Target PLS in R&D**; Boiana Budevska[1]; [1]DuPont Crop Protection

4:30 (164) **Applied Chemometrics and Near Infrared Spectroscopy in Grain and Vegetable Quality Assurance**; Bin Dai[1], Patrick Lann[1], Ping Feng[1]; [1]Monsanto Company

4:50 (165) **Chemometrics in Polymer Research and Development at SABIC**; Nancy Jestel[1], Yusuf Sulub[1], Michael Hall[1], Cherie Pomeranz[1]; [1]SABIC

5:10 (166) **Hyperspectral NIR Imaging to Determine Defects Localization for Epoxy Resins as an Insulator Material**; Nicolas Spegazzini[1], Yukihiro Ozaki[1]; [1]Kwansei Gakuin University

Monday Afternoon, *Room 102B*
DIELECTROPHORESIS
Organizer and Presider: Zachary Gagnon

3:50 (167) **Programmed Assembly and Manipulation of Complex Particles by Electric Fields**; Orlin Velev[1]; [1]North Carolina State University

4:30 (168) **Dielectrophoretic Polarization of DNA Molecules**; Hui Zhao[1]; [1]University of Nevada Las Vegas

4:50 (169) **Particle Electrokinetics in Non-Newtonian Fluids**; Xiangchun Xuan[1]; [1]Clemson University

5:10 (170) **Using Gradient Insulator-based Dielectrophoresis to Capture Small Molecular Weight Proteins**; Ryan Yanashima[1], Mark Hayes[1]; [1]Arizona State University

Monday Afternoon, *Room 102C*
RECENT INNOVATIONS IN STAND-OFF RAMAN FOR THE DETECTION OF HAZARDS
Organizer and Presider: Bernhard Lendl

3:50 (171) **Development and Application of a Flexible Standoff Raman Imaging System**; Henric Östmark; [1]FOI Sweden

4:10 (172) **Noninvasive Identification of Concealed Hazards by Standoff Deep Raman Spectroscopy**; Emad Izake[1], Biju Cletus[1], Shankaran Sundarajoo, William Olds[1], Peter Fredericks[1], Esa Jaatinen[1]; [1]Queensland University of Technology

4:30 (173) **Development of Trace Explosive Optical Standards for the Evaluation of Stand-off Raman Sensors**; Augustus Fountain[1], Raphael Moon[1], Ashish Tripahti[1, 2], Jason Guicheteau[1], Steven Christesen[1]; [1]Research and Technology Directorate, Edgewood Chemical Biological Center, Aberdeen Proving Ground, [2]Science Applications International Corporation, Gunpowder Branch, Aberdeen Proving Ground

4:50 (174) **Standoff Detection and Imaging Based on Coherent Single-Beam Raman Spectroscopy**; Marcos Dantus[1,2], Marshall Bremer[2] ; [1]Michigan State University, Department of Chemistry, [2]Michigan State University, Department of Physics and Astronomy

5:10 (175) **Wide Field-of-View Standoff Raman Using a Small Spatial Heterodyne Raman Spectrometer**; Stanley Angel[1], Nirmal Lamsal[1]; [1]The University of South Carolina, Department of Chemistry & Biochemistry

Monday Afternoon, *Room 102D*
BIOLOGICAL MS AND PROTEOMICS
Organizer and Presider: Victor Ryzhov

3:50 (176) **MS-based Strategies for the Elucidation of Nucleic Acid – Ligand Interactions**; Daniele Fabris[1]; [1]University at Albany

4:10 (177) **Characterization of the Breast Cancer Marker Candidate LAG3 in Human Plasma by Hyphenated SPRi-MALDI-MS Analysis**; Chiraz Frydman[1], F Remy-Martin[2], M El Osta[1, 3], G Lucchi[3], R Zeggari[2], T Leblois[2], S Bellon[1], D Suckau[4], P Ducoroy[3], W Boireau[2, 3]; [1]HORIBA Scientific, France, [2]Institut FEMTO-ST, Université de Franche Comté, CLIPP, [3]CLIPP, Université de Bourgogne, [4]Bruker Daltonik GmbH

4:30 (178) **Quantifying Proteoforms Using High-Throughput Top-Down Proteomics**; John Savaryn[1], Adam Catherman[1], Archer Smith IV[1], Ryan Fellers[1], Bryan Early[1], Richard LeDuc[2], Paul Thomas[1], Neil Kelleher[1]; [1]Northwestern University, [2]Indiana University

4:50 (179) **Multiplex Quantification through Neutron-Encoded Mass Signatures (NeuCode)**; Nicholas M. Riley[1], Alexander S. Hebert[1], Joshua J. Coon[1]; [1]University of Wisconsin

5:10 (180) **Virtual 2D Gel Electrophoresis: Mass Spectrometric Imaging of Immobilized pH Gradient-Isoelectric Focusing Gels Reveals Intact Protein Heterogeneity in Proteomics**; Rachel Loo[1], Karen Lohnes[1], Joseph Loo[1]; [1]University of California-Los Angeles

Monday Afternoon, *Room 102E*
NANOTECHNOLOGY AND SUSTAINABILITY
Organizer: Rober Hamers; Presider: Joel Pedersen

3:50 (181) **Quantitative Analysis of Nanoparticle Interactions with Environmental and Biological Interfaces**; Howard Fairbrother[1], Julie Bitter[1], Gregg Duncan[1, 2], Mike Bevan[2]; [1]Johns Hopkins University, Department of Chemistry, [2]Johns Hopkins University, Department of Chemical and Biomolecular Engineering

4:30 (182) **Nanoparticle Toxicity Assessment in a Bacterial Model**; Christy Haynes[1], Ian Gunsolus[1], Benjamin Meyer[1], Catherine Murphy[3], Robert Hamers[2], Rebecca Klaper[4], Joel Pedersen[2]; [1]University of Minnesota, [2]University of Wisconsin, Madison, [3]University of Illinois, Champaign-Urbana, [4]University of Wisonsin, Milwaukee

4:50 (183) **Two High Aspect Ratio Nanoparticles Elicit Unique Molecular Responses That Explain Their Distinct Level of Cytotoxicity**; Galya Orr[1], Susan Tilton[1, 4], Norman Karin[4], Ana Tolic[1], Yumei Xie[1], Xianyin Lai[2], Raymond Hamilton[3], Katrina Waters[4], Andrij Holian[3], Frank Witzmann[2]; [1]Environmental Molecular Sciences Laboratory, Pacific Northwest National Laboratory, [2]Department of Cellular and Integrative Physiology, Indiana University School of Medicine, [3]Department of Biomedical and Pharmaceutical Sciences, University of Montana, [4]Fundamental & Computational Sciences Directorate, Pacific Northwest National Laboratory

5:10 (184) **Surface Functionalization of Diamond Nanoparticles for Nanotoxicity Studies**; Robert Hamers[1], Marco Torelli[1], Joel Pedersen[1], Randy Goldsmith[1], Galya Orr[2], Franz Geiger[3]; [1]University of Wisconsin-Madison, [2]Pacific Northwest National Laboratory, [3]Northwestern University

Monday Afternoon, *Room 103B*
UNDERSTANDING THE UNDERLYING MECHANISMS IN PLASMA SPECTROCHEMISTRY: GATEWAY TO IMPROVED PERFORMANACE IN ELEMENTAL ANALYSIS
Organizer and Presider: Gerardo Gamez

3:50 (185) **Spatial Distributions of Analyte Ions in an Inductively Coupled Plasma with Laser Ablation Sample Introduction**; Paul Farnsworth[1], Lance Moses[1]; [1]Brigham Young University

4:10 (186) **Implications of Fundamental Processes on ICP-MS Measurements**; John Olesik[1], Fang Liu[1], Shi Jiao[1], Anthony Lutton[1]; [1]The Ohio State University

4:30 (187) **Gas Flow Dynamics in ICPMS: Description, Explanation and Optimization**; Maryam Aghaei[1], Annemie Bogaerts[1]; [1]University of Antwerp

4:50 (188) **Spectrochemical Analysis and Diagnostics via Modeling**; Igor Gornushkin[1], Sergei Shabanov[2], Alexander Kazakov[3], Alexander Demidov[1], Ulrich Panne[1,4]; [1]BAM Federal Institute for Materials Research and Testing, Berlin, Germany, [2]Department of Mathematics, University of Florida, [3]State University of Aerospace Instrumentation, St. Petersburg, Russia, [4]Humboldt-Universität zu Berlin, Department of Chemistry

5:10 (189) **Assessment of the Liquid Sampling-Atmospheric Pressure Glow Discharge (LS-APGD) Rotational Temperature, Excitation Temperature, and Electron Number Density**; Benjamin T. Manard[1], Jhanis J. Gonzalez[2], Meirong Dong[2], Arnab Sarkar[2], Jose Chirinos[2], Xianglei Mao[2], Richard E. Russo[2], R. Kenneth Marcus[1]; [1]Clemson University, [2]Lawrence Berkeley National Laboratory

Monday Afternoon, *Room 103C*
SAS PAT SECTIONPHARMACEUTICAL AND BIOPHARMACEUTICAL PAT SESSION II
Organizers: Brandye Smith-Goettler and Edita Botonjic-Sehic; Presider: Edita Botonjic-Sehic

3:50 (190) **Model Diagnostics as Quality Control Tools for Near Infrared Calibration Models – Application to Raw Material Variability**; Benoit Igne[1], Carl Anderson[1], James Drennen[1]; [1]Duquesne University

4:10 (191) **Process Mass Spectrometers - Now a PAT Tool for Cell Culture**; Peter Traynor[1], Graham Lewis[1], Todd Colin[1]; [1]Thermo Fisher Scientific, [2]Thermo Fisher Scientific, [3]Thermo Fisher Scientific

4:30 (192) **Application of a TDLAS-based Water Vapor Mass Flow Rate Monitor for Lyophilization**; William Kessler[1], Michael Pikal[2], Puneet Sharma[2], Timothy Zwack[3]; [1]Physical Sciences Inc., [2]University of Connecticut, [3]IMA Life, NA

4:50 (193) **The Extra Absorptions of Amino Acid Mixtures in THz Range**; Zhaohui Zhang[1], Haixia Su[1], Xiaoyan Zhao[1], Zhi Li[1], Han Zhang[1], Katherine Dunn[2], Micheal Johnston[2]; [1]University of Science and Technology Beijing, [2]University of Oxford

Monday Afternoon, *Room 103D*
FACSS / SAS STUDENT AWARDS
Organizer and Presider: Jose Almirall

FACSS Student Award

3:50 (194) **Non-Aqueous Microchip Electrophoresis: A Promising Strategy for Biomarker Detection**; Larry Gibson[1], Paul Bohn[1]; [1]University of Notre Dame

Tomas Hirschfeld Scholar Award

4:10 (195) **Using RNA-Seq and Mass Spectrometry to Expand the Detection of Protein Variations**; Gloria Sheynkman, Michael Shortreed[1], Brian Frey[1], Mark Scalf[1], Lloyd Smith[1]; [1]University of Wisconsin-Madison

Tomas Hirschfeld Scholar Award

4:30 (196) **Yb Fiber Oscillator Developed for Laser-Induced Breakdown Spectroscopy**; Bai Nie[1], Greg Parker[1], Vadim Lozovoy[1], Marcos Dantus[1]; [1]Michigan State University

Barbara Stull Graduate Student Award

4:50 (197) **Confocal Raman Spectroscopy: An Efficient Tool for the Fine Characterization of Single Electrospun Nanofibers**; Marie Richard-Lacroix[1], Christian Pellerin[1]; [1]University of Montreal

Barbara Stull Graduate Student Award

5:10 (198) **Analytical Performance of a Solution-Cathode Glow Discharge for Optical Emission Spectrometry with an Interference-Filter Wheel Spectral Sorter**; Andrew Schwartz[1], Steven Ray[1], Gary Hieftje[1]; [1]Indiana University

TECHNICAL PROGRAM – TUESDAY
Plenary Lectures, Ballroom A
Presider: Jose Almirall

8:00 am – Coblentz Society's Craver Award.
(199) Emerging Trends in Infrared Spectroscopic Imaging: From Theory to Therapy; **Rohit Bhargava**, University of Illinois at Urbana-Champaign

8:30 am – FACSS Charles Mann Award for Applied Raman Spectroscopy.
(200) Nano Scale – Mega Challenge? Raman Spectroscopy Approaching Molecular Dimensions; **Volker Deckert,** Institute of Physical Chemistry and the Institute of Photonic Technology, University of Jena

TUESDAY POSTER SESSION
9:00 – 10:20 AM
Ballroom B/C/D

All Tuesday posters should be put up between 7:30 – 8:00 am and removed by 4:30 pm

Environmental Analysis

Board #

1 (201) **Environmental Discourses in Borana Oromo: A Focus on Narratives**; Teshome Tafesse[1]; [1]Addis Ababa University

2 (202) **Screening Method for Emerging Contaminants; for Ethenylestradiol and Chlormadinoneacetate, in Water by Derivative Spectrophotometry**; M. Ines Toral[1], Diego Pino[1], Gabriela Arriagada[1], Romina Otipka[1], Cesar Soto[2], David Contreras[2], Jorge Yanez[2]; [1]University of Chile, [2]University of Concepcion

3 (203) **Silica Nanoparticles Releases Fertilisers and Fungicides Slowly in Soil**; Erastus Gatebe, Harrison Wanyika[1], Paul Kioni[1, 2], Zhiyong Tang[3]; [1]JKUAT, [2]DKUT, [3]National center for nanoscience and nanotechnology

4 (204) **Development of PVC Calibration Standards Having Elemental Mass Fraction Values Traceable to Values for Standard Reference Materials (SRM)**; John Molloy[1], Matthew Boyce[1], Caroline Bibb[1], John Sieber[1]; [1]National Institute of Standards and Technology

5 (205) **Heavy Metals Levels in Urban Gardens and Lawns**; Ibrahim Saeed[1], John Peters[1]; [1]University of Wisconsin-Madison

Mass Spectrometry

6 (206) **The Qualitative Identification of Metals in Shisha Steam Stones Using ICPMS**; Amberlie Clutterbuck[1]; [1]University of Cincinnati

7 (207) **Comparison of Trace Metals in Ricochet Bullets to Their Corresponding Cartridges and Ricochet Marks**; Victoria Robideau[1], Jason Hamilton[1], Guido Verbeck[1]; [1]University of North Texas

8 (208) **Infrared Multiple Photon Dissociation Action Spectroscopy of Proton-Bound Dimers of Cytosines: Effects of Modifications on Base-Pairing Conformations**; Bo Yang[1], Mary Rodgers[1]; [1]Wayne State University

9 (209) **Imaging the Ion Beam in the Second Vacuum Stage of an ICP-MS Using Planar Laser-Induced Fluorescence**; Alisa J. Edmund[1], Scott D. Bergeson[1, 2], Paul B. Farnsworth[1]; [1]Department of Chemistry and Biochemistry, Brigham Young University, [2]Department of Physics and Astronomy, Brigham Young University

10 (210) **Absolute Number Densities of Helium Metastable Atoms in Helium-Based Discharges Used as Ambient Desorption/Ionization Sources**; Charlotte Reininger[1], Kellie Woodfield[1], Paul B. Farnsworth[1]; [1]Brigham Young University

11 (211) **Infrared Multiple Photon Dissociation Action Spectroscopy of Protonated Nucleosides: Gas Phase Conformations and Energetics**; Mary Rodgers, Ranran Wu[1]; [1]Wayne State University

12 (212) **Hookah Smoking: Which is Worse – the Tobacco or the Charcoal?**; Ryan Saadawi[1], Matt Winfough[1], Traci Hanley[1], Julio Landero[1], Joseph Caruso[1]; [1]University of Cincinnati

13 (213) **Optimization of MALDI-TOF ISD (In-Source Decay) for Protein Analysis**; John McDaniel[1], Amanda Bulman[1]; [1]Bruker Daltonics

14 (214) **Plasma Hydrodynamic Expansion and Relation to fs-LA-ICP-MS Signal Intensities and Elemental Fractionation**; Nicole LaHaye, Prasoon Diwakar[1], Sivanandan Harilal[1], Ahmed Hassanein[1]; [1]Purdue University

15 (215) **Provenance Study of Native Copper using fs-LA-ICP-MS**; Prasoon Diwakar[1], Harold Cooper[1], Sivanandan Harilal[1], Ahmed Hassanein[1]; [1]Center for Materials Under eXtreme Environment, School of Nuclear Engineering Purdue University

16 (216) **Analysis and Discrimination of Inkjet Inks from Different Manufacturers using DART-MS**; Anna Raeva[1], Rhett Williamson[1], José Almirall[1]; [1]Florida International University

17 (217) **Detection of Counterfeit Electronics through Ambient Mass Spectrometry and Chemometrics**; Kevin Pfeuffer[1], Jack Caldwell[2], Steven Ray[1], Gary Hieftje[1]; [1]Indiana University, Department of Chemistry, [2]Naval Surface Warfare Center, Crane

18 (218) **Plasma Sheath Effects in the Sampler and Skimmer Cones of the ICP-MS**; Matthew Zachreson[1], Ross Spencer[1]; [1]Brigham Young University

19 (219) **Desorption Electrospray Ionization Mass Spectrometry Imaging of an Endophytic Penicillium sp. Reveals the Spatial Distribution of Novel Polyhydroxyanthraquinone Constituents**; Alan Jarmusch[1], Mario Figueroa[2, 3], Huzefa Raja[2], Tamam El-Elimat[2], Jeffrey Kavanaugh[4], Alexander Horswill[4], Nadja Cech[2], Nicholas Oberlies[2], R. Graham Cooks[1]; [1]Purdue University, [2]University of North Carolina at Greensboro, [3]Universidad Nacional Autonoma de Mexico, [4]University of Iowa

Pharmaceutical Analysis

Board #

20 (220) **In-Situ Monitoring of Form Change as a Function of Relative Humidity in the Solid State by Vapor Sorption Analysis-Raman Spectroscopy**; Candi Choi[1], Sruthi Janakiraman[1], Denette Murphy[1], Duohai Pan[1], Anisha Patel[1], Roxana Schlam[1], Shawn Yin[1]; [1]Bristol-Myers Squibb

21 (221) **Using Environment Sensitive Fluorescence Probes to Estimate Amorphous Solubility and Characterize Liquid-Liquid Phase Separation Behavior in Highly Supersaturated Solutions of Poorly Soluble Compounds**; Shweta A. Raina[1], David E. Alonzo[1, 3], Yi Gao[1, 2], Geoff G.Z. Zhang[1, 2], Lynne S. Taylor[1]; [1]Purdue University, Department of Industrial and Physical Pharmacy, [2]NCE Formulation - LC, Research and Development, AbbVie Inc., [3]Formulation & Process Development, Gilead Sciences, Inc.

22 (222) **The Effect of Water on NIR Calibrations for Detecting API in Tablets**; Md.Nayeem Hossain[1], Benoît Igne, Carl Anderson, James Drennen[1]; [1]Duquesne University

23 (223) **Development and Implementation of Spectroscopy Methods for Quantitative and Qualitative Analysis of Pharmaceutical Reagents**; Bernard Agyei, John Wasylyk, Ming Huang, Robert Wethman; [1]Bristol-Myers Squibb

24 (224) **Use of Electron Spin Resonance (ESR) for the Identification and Selection of Actives in Fragment based Drug Discovery of Small Molecule Inhibitors of Myeloperoxidase (MPO)**; Balagopalakrishna Chavali[1], Thierry Masquelin[1], Mark Nilges[2], David Timm[1], Stephanie Stout[1], Prabhakar Jadhav[1], William Matter[1], Gary Deng[1]; [1]Eli Lilly and Company, [2]University of Illinois, Champaign

25 (225) **Investigations into the Degradation of Polyquaternium-1**; Carina Gunder[1], Sharon Myers[1], Mary Lee Ciolkowski[1]; [1]Bausch & Lomb, Inc.

26 (226) **Application of Spectroscopy and Multivariate Analysis to Classify Source and Type of Commonly Used Pharmaceutical Excipients**; Ting Wang[1], Ahmed Ibrahim[1, 2], Alan Potts[2, 3], Stephen Hoag[1]; [1]University of Maryland, Baltimore, [2]Misr International University, [3]United States Pharmacopeia

27 (227) **Polarization Dependent Measurements by SHG Microscopy is Able to Detect Kinetically Trapped Meta-Stable Polymorphs of Organic Nano-Crystals**; Azhad Chowdhury[1]; [1]Purdue University

28 (228) **Application of Band Target Entropy Minimization Technique to Extract Eutectic Features from Raman Spectra**; Md Anik Alam[1,2], James Drennen[1, 2], Carl Anderson[1, 2]; [1]Graduate School of Pharmaceutical Sciences, Duquesne University, [2]Duquesne University Center for Pharmaceutical Technology, Duquesne University

29 (229) **Method Development and Validation for Analysis of Pharmaceutical Tablets by Transmission Raman Spectroscopy**; Yi Li[1], Benoît Igne[2], James K. Drennen, III[2], Carl A. Anderson[2]; [1]Graduate School of Pharmaceutical Science,Duquesne University, [2]Duquesne Center of Pharmaceutical Technology,Duquesne University

Board #

30 (230) **Determination of Degradation Pathways of Benzethonium Chloride in a Pharmaceutical Formulation by Accelerated Degradation Studies**; Janet de los Reyes[1], Channa A. Wijesinghe[1], Tristan Walters[1], Mugunthu Dhananjeyan[1], Samuel Molesworth[1]; [1]Hospira, Inc.

31 (231) **Long Wavelength 1064 nm Raman for Finished OTC Pharmaceutical Identification**; Mark Mabry[1], Claire Dentinger[2], Neville Broad[3]; [1]Rigaku Raman Technologies, [2]Rigaku Raman Technologoes, [3]NWB Spectroscopy

32 (232) **A Complete Solution for Sample Prep Technique for New USP**; David Gunn, Arshad Kokardekar; [1]Milestone Inc

RAMAN

33 (233) **Computational Raman Activities for Raman Second Hyperpolarizability Determination and a Comparison with Experiments**; Wei Zhao[1], Anqi He[1, 2], Yizhuang Xu[1, 2]; [1]Department of Chemistry, University of Arkansas at Little Rock, [2]College of Chemistry and Molecular Engineering, Peking University

34 (234) **Evaluation of Transfer Algorithms for Distribution of Spectral Libraries Across Different Instruments**; Jason Rodriguez[1], John Kauffman[1]; [1]Division of Pharmaceutical Analysis, Center for Drug Evaluation and Research, US Food and Drug Administration

35 (235) **Using deep-UV Resonance Raman Spectroscopy to Monitor Protein-Lipid Interactions**; Jian Xiong[1], Rauta Yakubu[1], Michael Eagleburger[1], Jason Cooley[1], Renee JiJi[1]; [1]University of Missouri-Columbia

36 (236) **Orange Carotenoid Protein**; Elizabeth Kish Perrin[1], Diana Kirilovsky[1], Andrew Gall[1], Alberto Mezzetti[1], Riccardo Spezia[1, 2], Bruno Robert[1]; [1]Commissariat à l, [2]Laboratoire analyse et modélisation pour le biologie et environnement

37 (237) **Time Resolved Raman Spectroscopy for Depth Analysis of Multi-Layered Mineral Samples[1]**; Jan-Hein Hooijschuur[1,2], Ingeborg E. Iping Petterson[1], Cees Gooijer[1], Gareth R. Davies[2], Freek Ariese[1]; [1]Department of Biomolecular Spectroscopy, LaserLaB, Vrije Universiteit, [2]Department of Petrology, Vrije Universiteit

38 (238) **Wide Area Standoff Measurements Using a Spatial Heterodyne Raman Spectrometer**; Nirmal Lamsal[1], S. Michael Angel[1]; [1]University of South Carolina

39 (239) **Quantitative Analysis using Raman by a Dummy**; Eunah Lee[1], Andrew Whitley[1]; [1]HORIBA Scientific

40 (240) **Spectroscopic Investigation on the Effect of Naturally Occurring Polyphenolic Compounds on the Structure of the Amyloid-β Peptide**; Brittany Hagenhoff[1], Jian Xiong[1], Renee JiJi[1]; [1]University of Missouri - Columbia

41 (241) **Microfluidic Device for Single Experiment Limit of Detection Assessment**; Antonio Campos[1], Donghyuk Kim[1], Nathan Greeneltch[2], Christy Haynes[1], Richard Van Duyne[2]; [1]University of Minnesota, [2]Northwestern University

42 (242) **Conformational Stability, r0 Structural Parameters, Vibrational Assignment and ab initio Calculations of Ethyldichlorophosphine**; Charles Paquet[1], Ikhlas Darkhalil[1], Mohammad Waqas[1], Todor Gounev[1], James Durig[1]; [1]University of Missouri-Kansas City

Board #

43 (243) **An Aberration Free Spectrograph for Improved Raman Spectroscopy & Imaging**; Brian C. Smith[1]; [1]Princeton Instruments

44 (244) **Plasmon Enhancements using Coherent Anti-Stokes Raman Scattering**; Karen A. Antonio, Lawrence O. Itela[1], Zachary D. Schultz[1]; [1]University of Notre Dame

45 (245) **Quantitative Monitoring of Biphasic Reactions using Flow Systems by Raman Spectroscopy**; Gerald Cairns[1], David Angelone[,2], Shaghayegh Abdolahzadeh[2], Johannes W. de Boer[3], Antoine Varagnat[1], Wesley R. Browne[2]; [1]Andor Technology plc, [2]Centre for Systems Chemistry, Stratingh Institute for Chemistry, University of Groningen, [3]Catexel BV, BioPartner Center Leiden

46 (246) **Raman Spectroscopy Reveals Evidence for Early Bone Changes in Osteoarthritis**; Jemma Kerns[1], Kevin Buckley[, 2], Panagiotis Gikas[1,3], Helen Birch[1], Anthony Parker[, 2], Pavel Matousek[, 2], Allen Goodship[1]; [1]UCL Institute of Orthopaedics, [2]Central Laser Facility, STFC Rutherford Appleton Laboratory, [3]Royal National Orthopaedic Hospital

47 (247) **Nano-Edge Filters Offer Unparalleled Access to Low Wavenumber Raman Modes**; Catherine Aldous[1]; [1]Iridian Spectral Technologies

48 (248) **Novel 1064 nm Dispersive Raman Spectrometer and Raman Microscope for Non-destructive Pigment Analysis**; Lin Chander[1], Jack Qian[1], Owen Wu[1]; [1]BaySpec Inc.

49 (249) **A Study of Varnish Degradation Processes in Art Conservation by Raman Spectroscopy**; Veronica M. Alvarez[1], Anahit M. Campbell[1], Lisa K. Kendhammer[1], Joseph H. Aldstadt[1]; [1]Dept. of Chemistry & Biochemistry, University of Wisconsin-Milwaukee

50 (250) **Monitoring the Fate of Subcutaneously Injected Pharmaceuticals using Raman Spectroscopy**; Oliver Stevens[1]; [1]Bristol University, [2]Bath University

51 (251) **Microwave, Raman and Infrared Spectra, Conformational Stability, r0 Structural Parameters, and Vibrational Assignment of Cyclopentylamine**; Ikhlas D. Darkhalil[1], Nick Nagels[2], Wouter A. Herrebout[2], Benjamin J. van der Veken[2], Ranil M.Gurusinghe[3], Michael J. Tubergen[3], James R. Durig[1]; [1]Department of Chemistry, University of Missouri-Kansas City, [2]Department of Chemistry, Universitair Centrum Antwerpen, [3]Department of Chemistry, Kent State University

52 (252) **Effects of Hypergravity on Crystallinity of Apatite, the Mineral Component of Bone**; Andrew Derry[1], Mary Tecklenburg[1]; [1]Central Michigan University

53 (253) **A Study of the Composition of Varnishes by Raman Spectroscopy and SPME Gas Chromatography**; Lisa K. Kendhammer[1], Sarah K. Patch[, 2], Joseph H. Aldstadt[1]; [1]Dept. of Chemistry & Biochemistry, University of Wisconsin-Milwaukee, [2]Dept. of Physics, University of Wisconsin-Milwaukee

Tuesday Morning, *Room 101A*
ACS-RSC SYMPOSIUM ON SUSTAINABILITY IN MOLECULAR SPECTROSCOPY AND MASS SPECTROMETRY
Organizers: May Copsey and David W. Koppenaal;
Presider: May Copsey

10:20 (254) **Field Detection of Organic Mixtures in Air using Glass Microfabricated Devices**; Alastair Lewis[1], Xiaobing Pang[1], Jacqueline Hamilton[1], Richard Lidster[1], Samuel Edwards[1], Stephen Andrews[1]; [1]Department of Chemistry, University of York

10:40 (255) **Path Forward for Molecular Analysis Using Mass Spectrometry**; Zheng Ouyang[1], Linfan Li[1], Yue Ren[1], Morgan McLuckey[1], Jiangjiang Liu[1], Robert Cooks[1]; [1]Purdue University

11:00 (256) **Ultra-Sensitive Label-Free Detection in Fluids**; Zachary Schultz[1], Steven Asiala[1], Pierre Negri[1], Oluwatosin Dada[1], Kevin Jacobs[1]; [1]University of Notre Dame

11:20 (257) **Digital Microfluidics: A Versatile Platform for Sample Processing and Analysis**; Andrea Kirby[1], Aaron Wheeler[1]; [1]University of Toronto

11:40 (258) **Microscale Spectroscopic Probes**; Francis Esmonde-White[1], Cynthia Cipolla[1], Thitaphat Ngernsutivorakul[1], Michael Morris[1], Robert Kennedy[1]; [1]Dept. of Chemistry, University of Michigan

Tuesday Morning, *Room 101B*
PLANETARY LIBS: GEOLOGICAL AND GEMOLOGICAL APPLICATIONS
Organizers and Presiders: Nancy McMillan and Noureddine Melikechi

10:20 (259) **Searching for Rock Surface Alteration on Mars with the ChemCam Laser-Induced Breakdown Spectroscopy Instrument**; Nina Lanza[1], Samuel Clegg[1], Roger Wiens[1], Richard Léveillé[, 2], Noureddine Melikechi[, 3], Robert Tokar[, 4], Jennifer Blank, Nathan Bridges, Ben Clark, Matthew Deans; [1]Los Alamos National Laboratory, [2]Canadian Space Agency, [3]Delaware State University, [4]Planetary Science Institute

11:00 (260) **Mars Mineralogy at Gale Crater as Measured by the ChemCam LIBS**; M. Darby Dyar[1], Elly Breves[1], Hannah Blau[2], Tommy Boucher[2], Allan Treiman[2, 3], Ryan Anderson[4], Samuel Clegg[4], Nina Lanza[4], Horton Newsom[4], Roger Wiens[4]; [1]Mount Holyoke College, [2]University of Massachusetts, [3]Lunar and Planetary Institute, [4]Los Alamos National Laboratory

11:40 (261) **Cluster Analysis for Provenance Determination of Gemstones: Emerald, a Case Study**; Catherine McManus[1], James Dowe[2], Nancy McMillan[3], Tristan Likes[1]; [1]Materialytics, LLC, [2]Analytical Data Services, [3]New Mexico State University

Tuesday Morning, *Room 101C*
MASS SPECTROMETRY IN FORENSICS
Organizer and Presider: Guido F. Verbeck

10:20 (262) **Metabolomic Analysis of Cocaine Addiction using a Self-Organizing Map-Based Approach**; Cody Goodwin[1,2,3], Christina Marasco[3], Kevin Seale[3], Brian Bachmann[2, 3], John Wikswo, Nicole Schramm-Sapyta[4], John McLean[1, 2, 3]; [1]Vanderbilt University Department of Chemistry, [2]Vanderbilt Institute of Chemical Biology, [3]Vanderbilt Institute for Integrative Biological Research and Education, [4]Duke University Medical Center Department of Psychiatry

10:40 (263) **Validation of UPLC/MS Methods for Trace Analysis of Dyes Extracted from Acrylic, Nylon and Polyester Fibers**; Molly R. Burnip[1], Kaylee R. McDonald[1], Scott J. Hoy[1], Stephen L. Morgan[1]; [1]University of South Carolina

11:00 (264) **Distance-of-Flight Mass Spectrometry with a Matrix-Assisted Laser Desorption Ionization Source: MALDI-DOFMS**; Steven Ray[1], Elise Dennis[1], Alex Graham[1], Christie Enke[1, 3], Charles Barinaga[2], Anthony Carado[2], David Koppenaal[2], Gary Hieftje[1]; [1]Indiana University, [2]Pacific Northwest National Laboratory, [3]Department of Chemistry, University of New Mexico

11:20 (265) **Comparison of Soft-Landed Silver Nanoparticles and Traditional Matrices for Small Molecule MALDI-MS**; Barbara Walton[1], Guido Verbeck[1]; [1]University of North Texas

11:40 (266) **Touch Spray Ambient Ionization for Tissue Disease State Diagnosis by Spot Analysis**; Kevin Kerian[1], Alan Jarmusch[1], Liang Cheng[2], Timothy Masterson[3], Michael Koch[3], Ahmed Hamid[1], Livia Eberlin[1], R. Graham Cooks[1]; [1]Department of Chemistry and Center for Analytical Instrumentation Development, Purdue University, [2]Department of Pathology and Laboratory Medicine, Indiana University School of Medicine, [3]Department of Urology, Indiana University School of Medicine

Tuesday Morning, *Room 102A*
TANDEM MS BIG AND SMALL
Organizer: Ying Ge; Presider: Rachel Loo

10:20 (267) **Top-Down Mass Spectrometry for Characterizing Large Protein Complexes**; Joseph Loo[1], Huilin Li[1], Jiang Zhang[1]; [1]University of California, Los Angeles

10:40 (268) **Enabling Large-Scale Discovery, Characterization and Quantitation of Neuropeptides via Tandem Mass Spectrometry**; Lingjun Li[1], Chenxi Jia[1], Christopher Lietz[1], Qing Yu[1], Robert Sturm[1]; [1]University of Wisconsin

11:00 (269) **Cell Surface Chemoproteomics for Capturing States of Cardiac Differentiation from Pluripotent Stem Cells**; Rebekah Gundry[1]; [1]Medical College of Wisconsin

11:20 (270) **Top-down Identification of Casein Isoforms using a High Performance Benchtop Quadrupole Orbitrap Mass Spectrometer**; David Horn[1], Terry Zhang[1] ; [1]Thermo Fisher Scientific

11:40 (271) **Top-down Electron Capture Dissociation Mass Spectrometry for Deep Sequencing of Phosphoproteins**; Ying Ge[1]; [1]University of Wisconsin-Madison

Tuesday Morning, *Room 102B*
CELL AND ORGANELLE ELECTROPHORESIS
Organizer and Presider: Christopher R. Harrison

10:20 (272) **Electrophoretic Analysis of Individual Autophagosomes**; Edgar Arriaga[1], Chad Satori[1]; [1]University of Minnesota

10:40 (273) **Manipulation of Mitochondria by Insulator-based Dielectrophoresis**; Jinghui Luo[1], Gregory Wolken[, 2], Edgar Arriaga[, 2], Alexandra Ros[1]; [1]Department of Chemistry and Biochemistry, Arizona State University, Tempe, AZ, [2]Department of Chemistry, University of Minnesota, Minneapolis, MN

11:00 (274) **Single cell Capillary Electrophoresis Mass Spectrometry for Studying Neuron Heterogeneity**; Stanislav Rubakhin[1], Jordan Aerts[1], Jonathan Sweedler[1]; [1]University of Illinois at Urbana-Champaign

11:20 (275) **Glutaraldehyde Enhanced Dielectrophoretic Cell Separation**; Zachary Gagnon[1]; [1]Johns Hopkins University

11:40 (276) **Investigation of Erythrocyte Age and Electrophoretic Mobility Correlations**; Christopher Harrison[1], Jack Fang[1]; [1]San Diego State Univeristy

Tuesday Morning, *Room 102C*
ADVANCES IN BIOLOGICAL SERS ANALYSIS
Organizer and Presider: Roy Goodacre

10:20 (277) **Metabolic Profiling of Living Cells by Surface Enhanced Raman Spectroscopy**; Lawrence Ziegler[1]; [1]Boston University

10:40 (278) **Multiplexed and Sensitive Molecular Diagnostics using SERRS**; Karen Faulds[1], Mhairi Harper[1], Kirsten Gracie[1], Duncan Graham[1]; [1]University of Strathclyde

11:00 (279) **Raman Activated Cell Sorting using SERS Technique**; Wei Huang[1]; [1]University of Sheffield

11:20 (280) **Inkjet-Printed Fluidic Paper SERS Devices for Chemical and Biological Analytics**; Ian White[1], Wei Yu[1], Eric Hoppmann[1]; [1]University of Maryland

11:40 (281) **SERS-based Biosensing and Assays**; Sebastian Wachsmann-Hogiu[1], Mehmet Kahraman[1], Zachary Smith[1], Cynthia Pagba[2]; [1]University of California Davis, [2]Georgia Tech

Tuesday Morning, *Room 102D*
THE BIRTH OF CHEMOMETRICS – IN HONOR AND MEMORY OF BRUCE KOWALSKI I
Organizers: Karl Booksh and Barry Lavine;
Presider: Thomas Isenhour

10:20 (282) **Chemometrics and Bruce; Some Fond Memories**; Svante Wold[1]; [1]Inst of Chemistry, Umea University

11:00 (283) **Pattern Recognition Assisted Infrared Spectral Library Searching Applied to Forensic Analysis**; Barry Lavine[1], Ayuba Fasasi[1], Nikhil Mirjankar[1], Mark Sandercock[2]; [1]Department of Chemistry, Oklahoma State University, [2]Royal Canadian Mounted Police Forensic Laboratory

11:20 (284) **Data Analysis Strategies for Comprehensive Two-Dimensional Liquid Chromatography**; Sarah Rutan[1], Robert Allen[1], Hope Bailey[1]; [1]Virginia Commonwealth University

11:40 (285) **Applying Improved Instrument Design with Chemometrics to Difficult Spectroscopy Applications**; Jerome Workman[1]; [1]Unity Scientific

Tuesday Morning, *Room 102E*
FACSS CHARLES MANN AWARD HONORING VOLKER DECKERT
Organizer and Presider: Don Pivonka

10:20 (286) **Raman Spectroscopy of Biological Cells: Potentials and Problems**; Juergen Popp[1,2]; [1]Institut für Photonische Technologien, [2]Institut für Physikalische Chemie and Abbe Center of Photonics, Friedrich-Schiller-Universität Jena

10:40 (287) **Nanoparticle Based Imaging of Cells and Tissue**; Duncan Graham[1], Sarah McAughtrie[1], Derek Craig[1], Karen Faulds[1]; [1]University of Strathclyde

11:00 (288) **Advances in Ultrahigh Vacuum Tip-Enhanced Raman Spectroscopy**; Richard Van Duyne[1]; [1]Northwestern University

11:20 (289) **Spatio-Spectral Vibrational Nano-Imaging of Intermolecular Coupling and Dynamics**; Markus Raschke[1]; [1]University of Colorado

11:40 (290) **Absolute Temperature Determination with Stokes/anti-Stokes Raman Spectroscopy**; Hiro-o Hamaguchi[1]; [1]National Chiao Tung University

Tuesday Morning, *Room 103B*
NANOPARTICLES, METALS, AND MORE: YOUNG INVESTIGATORS IN ATOMIC SPECTROSCOPY
Organizer and Presider: Carsten Engelhard

10:20 (291) **Enhanced Molecular Level Understanding of Nano–TiO_2 Toxicity through Phosphorylated Protein Identification**; Keaton Nahan[1], Joseph Caruso[1]; [1]University of Cincinnati

10:40 (292) **Coupling Micellar Elektrokinetic Chromatography to ICP-MS: New Possibilities for Separation and Characterization of Nanoparticles**; Bastian Franze[1], Carsten Engelhard[2]; [1]University of Muenster, [2]University of Siegen

11:00 (293) **Elemental Mapping of Al-substituted Li7La3Zr2O12 using fs-Laser Induced Breakdown Spectroscopy**; Huaming Hou[1,2], Lei Cheng[1], Joong Sun Park[1], Guoying Chen[1], Thomas Richardson[1], Jordi Cabana[1], Marca Doeff[1], Ronger Zheng[2], Vassilia Zorba[1], Richard E. Russo[1]; [1]Lawrence Berkeley National Laboratory, [2]Optics and Optoelectronics Laboratory, Ocean University of China

11:20 (294) **Development and Fundamental Investigation of Desorption/Ionization Source using High-Power Pulsed Microplasma Jet**; Takahiro Iwai[1], Kensuke Okumura[1], Ken Kakegawa[1], Yoshitaka Utsunomiya[1], Hidekazu Miyahara[1], Akitoshi Okino[1]; [1]Department of Energy Sciences, Tokyo Institute of Technology

11:40 (295) **Metalloproteome of Histoplasma Capsulatum: The Role of Metals in Microbial Growth**; Anna Daigle[1], Julio Landero[1], Kavitha Subramanian[2], George Deepe[2], Joseph Caruso[1]; [1]University of Cincinnati Department of Chemistry, [2]University of Cincinnati College of Medicine

Tuesday Morning, *Room 103C*
FLOW/CONTINUOUS PAT I
Organizer and Presider: Brian Marquardt

10:20 (296) **Has the Flow Changed? From Micro Reactors to Continuous Production**; Paul Watts; [1]NMMU

11:00 (297) **Streamlining Pharmaceutical Processes into Continuous Operations**; Frank Gupton[1]; [1]Virginia Commonwealth University

11:20 (298) **Development of a Process Analytical Sampling System for Real-Time Monitoring of Continuous Flow Reactors**; Michael F Roberto[2], Thomas I Dearing[1], Brian J Marquardt[1]; [1]University of Washington, Applied Physics Laboratory, [2]University of Washington, Department of Chemistry

11:40 (299) **PAT to Enable Continuous Manufacturing at GSK**; Peter Hamilton[1]; [1]GSK

Tuesday Morning, *Room 103D*
SPECTROSCOPY AND SURFACE CHARACTERIZATION OF SEMICONDUCTOR NANOMATERIALS
Organizer and Presider: Song Jin

10:20 (300) **Nanoscale Surface Characterization of Chemically Modified Graphene**; Mark Hersam; [1]Northwestern University

11:00 (301) **Femtosecond Transient Absorption Microscopy of Carrier Dynamics in Single Nanostructures**; Libai Huang[1,2]; [1]University of Notre Dame, [2]Notre Dame Radiation Laboratory

11:20 (302) **Optical Spectroscopy of Novel Two-Dimensional Semiconductors**; Jie Shan[1]; [1]Case Western Reserve University

11:40 (303) **Using Coherent Multidimensional Spectroscopy to Observe Excited State Dynamics of Quantum Confined Structures**; Daniel Kohler[1], Schuyler Kain[1], Andrei Pakoulev[1], John Wright[1]; [1]University of Wisconsin-Madison

Tuesday Afternoon, *Room 101A*
ELECTROPHORESIS AND OMICS
Organizer and Presider: Tzu-Chiao Chao

1:20 (304) **Ambient Imaging Mass Spectrometry with Separations**; Kermit Murray, Sung Gun Park[1], Yonathan Merid[1]; [1]Louisiana State University

1:40 (305) **Digital Microfluidic Sample Preparation for Mass Spectrometry: -Omics and Beyond**; Andrea Kirby[1], Aaron Wheeler[1]; [1]University of Toronto

2:00 (306) **Alignment of Cells under Unidirectional Electric Pulses**; Despina Loufakis[1], Chang Lu[1], Zhenning Cao[1], Sai Ma[1], David Mittelman[1]; [1]Virginia Tech

2:20 (307) **Correlating Neuronal Activity and Neurochemistry: Cytoplasmic Sampling of Selected Cells using Patch Clamp Approach Combined with Capillary Electrophoresis Electrospray Ionization Time of Flight Mass Spectrometry**; Jordan T. Aerts[1], Kathleen R. Louis[1], Shane R. Crandall[1], Gubbi Govindaiah[1], Stanislav S. Rubakhin[1], Charles L. Cox[1], Jonathan V. Sweedler[1]; [1]University of Illinois

2:40 (308) **Capillary Electrophoresis with Post Separation Droplet Formation and Collection**; Christopher Harrison[1], Shay Lin[1]; [1]San Diego State University

Tuesday Afternoon, *Room 101B*
QUANTIFICATION IN LIBS PLASMAS
Organizer and Presider: Ben Smith

1:20 (309) **ChemCam Quantitative Geochemical Analysis on the Mars Curiosity Rover**; Samuel Clegg[1], Olivier Forni[2], Jeremie Jasue[2], Ryan Anderson[3], M. Darby Dyar[4], Steven Bender[1], Robert Tokar[1], Sylvestre Maurice[2], Roger Wiens[1], ChemCam Science Team; [1]Los Alamos National Laboratory, [2]Institut de Recherche en Astrophysique et Planétologie, [3]United States Geological Survey, [4]Mt. Holyoke College

2:00 (310) **Quantitative LIBS Measurements of Silica in Coal Dust Collected on Filters**; Christopher Stipe[1], Arthur Miller[2], Jonathan Brown[1], Susan Bredberg[1], Megan Conville[1]; [1]Seattle University, Seattle, WA, [2]National Institute of Occupational Safety and Health

2:20 (311) **Laser Induced Breakdown Spectroscopy: Application to Slurry Samples**; Jagdish P. Singh[1], Krishna K. Ayyalasomayajula[1], Fang Yu Yueh[1]; [1]Mississippi State University

2:40 (312) **Laser-Induced Breakdown Spectroscopy for Simultaneous Determination of Size and Concentration of Colloidal Solutions of Noble Metal Nanoparticles**; Alessandro De Giacomo[1,2], Marcella Dell[2], Olga De Pascale[2], Remah Elrashedy[1], Rosalba Gaudiuso[1], Can Koral[1]; [1]University of Bari, [2]CNR-IMIP

Tuesday Afternoon, *Room 101C*
DEPARTMENT OF DEFENSE FORENSIC NEEDS AND APPLICATION
Organizer and Presider: David P. Baldwin

1:20 (313) **Forensic Analysis in an Expeditionary Military Environment**; Roman Aranda[1]; [1]Defense Forensic Science Center, [2]Forensic Exploitation Directorate

1:40 (314) **Forensic Analysis in Military Criminal Investigations**; Candice Bridge[1]; [1]Defense Forensic Science Center2:00 (315) **A Nanomanipulation, Probing Station Coupled to Mass Spectrometry for Applications in Expeditionary Laboratories**; Guido Verbeck[1]; [1]University of North Texas

2:20 (316) **STARR: Shortwave-infrared Targeted Agile Raman Robot for the Identification and Confirmation of Emplaced Explosives**; Nathaniel Gomer[1], Oksana Klueva[1], Charles Gardner[1]; [1]ChemImage Corporation

2:40 (317) **Low Frequency/THz-Raman Spectroscopy: Using Structural Information for Material Identification**; James Carriere[1], Frank Havermeyer[1], Randy Heyler[1]; [1]Ondax, Inc.

Tuesday Afternoon, *Room 102A*
SPRAY DESORPTION IONIZATION METHODS
Organizer and Presider: Andre Venter

1:20 (318) **Analysis and Synthesis with Ions: Societal Applications of Mass Spectrometry**; Joshua Wiley[1], R. Graham Cooks[1], Thomas Mueller[1], Xin Yan[1], Xin Li[1], Kevin Kerian[1], Alan Jarmusch[1], Michael Wleklinski[1], Paul Hendricks[1], Zheng Ouyang[1]; [1]Purdue University

1:40 (319) **Intercepting Transient High-Valent Iron-Oxo Catalytic Intermediates Using Desorption Electrospray Ionization Mass Spectrometry**; Richard H. Perry[1], Kevin C. Peters[1], Kevin Parker[1]; [1]University of Illinois Urbana-Champaign

2:00 (320) **Nanospray Desorption Electrospray Ionization Mass Spectrometry: a New Technique for Imaging Lipids, Metabolites and Drugs in Biological Systems**; Ingela Lanekoff[1], Mathew Thomas[2], James Carson[2], Kristin Burnu[2], Allan Konopka[2], Julia Laskin[1]; [1]Physical Sciences Division, PNNL, [2]Biological Sciences Division, PNNL

2:20 (321) **Deconstructing Desorption Electrospray Ionization to Address Protein Analysis**; Kevin Douglass[1], Andre Venter[1]; [1]Western Michigan University

2:40 (322) **Integration of Online Digestion and Electrolytic Reduction with Mass Spectrometry for Rapid Disulfide-Containing Protein Structure Analysis**; Hao Chen[1], Qiuling Zheng[1], Hao Zhang[2]; [1]Ohio Univeristy, [2]Washington University in St Louis

Tuesday Afternoon, *Room 102B*
ANALYTICAL CHEMISTS EASING WORLD POVERTY
Organizer and Presider: Diane Parry

1:20 (323) **Disinfection by-Product Formation and Mitigation Strategies in Point-Of-Use Chlorination of Turbid and Non-Turbid Waters in Western Kenya**; B.C. Blount[1], D. S. Lantagne[2], F. Cardinali[1], R. Quick[2]; [1]Division of Laboratory Sciences, National Center for Environmental Health, U.S. Centers for Disease Control and Prevention, [2]Foodborne and Diarrheal Diseases Branch, U.S. Centers for Disease Control and Prevention

1:40 (324) **World Health Organization, Tobacco Laboratory Network (WHO TobLabNet)**; Ben Blount[1], Rayman Stanelle[1], Maria Damian[1], Megan McGuigan[1], Cliff Watson[1]; [1]U.S. Centers for Disease Control and Prevention

2:00 (325) **Analytical Chemistry towards Enhancing Risk Reduction from Chemicals Exposure and Environmental Protection in Africa and Globally**; Oladele Osibanjo[1,2]; [1]Department of Chemistry, University of Ibadan, [2]Basel Convention Coordinating Centre for Training and Technology Transfer for the African Region in Hazardous Waste Management, University of Ibadan

2:20 (326) **Let's Talk Trash! How Measurement Science Can Enable the Transformation of Waste to Worth**; Jill Boughton[1]; [1]W2Worth Innovations, LLC

2:40 (327) **How Are Analytical Chemists Easing World Poverty?**; Diane Parry[1]; [1]The Procter & Gamble Co.

Tuesday Afternoon, *Room 102C*
LOW FIELD NMR
Organizer and Presider: Fred LaPlant

1:20 (328) **NMR vs. NIR: Instruments, Applications, and Methods**; Fred LaPlant[1]; [1]3M Inc

2:00 (329) **Recent Developments in the Use of Online NMR Reaction Monitoring in the Pharmaceutical Industry**; David Foley[1], Mark Zell[1], Brian Marquez[1]; [1]Pfizer Global Research and Development

2:20 (330) **Application of Low-Field NMR to Quantification of Polymer Composition**; John Battiste[1]; [1]3M

2:40 (331) **Going Further Beyond Conventional NMR: Fast Field Cycling Relaxometry Tools, Method and Applications**; Richard J. Stevens[1], Salvatore Bubici[2], Gianni Ferrante[3], Rebecca Steele[4]; [1]Molecular Specialties, Inc., [2]Stelar, s.r.l., [3]Stelar, s.r.l., [4]Stelar, s.r.l.

Tuesday Afternoon, *Room 102D*
THE BIRTH OF CHEMOMETRICS – IN HONOR AND MEMORY OF BRUCE KOWALSKI II
Organizers: Karl Booksh and Barry Lavine;
Presider: Thomas Isenhour

1:20 (332) **Multivariate Curve Resolution 1990-2012: a Different Way to Examine Chemical Data**; Roma Tauler[1]; [1]IDAEA-CSIC

2:00 (333) **Using Data Fusion to Improve Prediction of Protein Secondary Structure**; Renee JiJi[1], Olayinka Oshokoya[1]; [1]University of Missouri-Columbia

2:20 (334) **Modeling the Impacts of Environmental Chemical Conditions on Microalgal Biomass**; Frank Vogt[1], Lauren White[1], Kendhl Witt[1], David Martin[1]; [1]University of Tennessee - Department of Chemistry

2:40 (335) **Living Bruce's Vision for Industrial Chemometrics at The Dow Chemical Company**; Mary Beth Seasholtz, Randy Pell; [1]The Dow Chemical Company

Tuesday Afternoon, *Room 102E*
COBLENTZ SOCIETY'S CRAVER AWARD SESSION HONORING ROHIT BHARGAVA
Organizers: Jose Almirall and Katherine Bakeev;
Presider: Katherine Bakeev

1:20 (336) **Immobilization of Gold Nanorods onto Electrospun Polymer Nanofibers via Polyelectrolyte Decoration—A Generalized SERS Substrate**; John Rabolt[1], Wenqiong Tang[1], Bruce Chase[1]; [1]University of Delaware

1:40 (337) **Infrared Spectroscopy with 100-nm Spatial Resolution: Applications in Polymers and Life Sciences**; Curtis Marcott[1], Michael Lo[2], Qichi Hu[2], Kevin Kjoller[2], Craig Prater[2]; [1]Light Light Solutions, [2]Anasys Instruments

2:00 (338) **FTIR Spectroscopic Imaging without Optical Aberrations**; Sergei Kazarian[1], Andrew Chan[1]; [1]Imperial College London

2:20 (339) **Multivariate Analyses of NIR Reflectance Hyperspectral Images using a Tunable Laser**; David Haaland[1], Howland Jones[2], Lam Nguyen[2], Gregory Israelson[3], Eli Margalith[2]; [1]Spectral Resolutions, [2]Opotek Inc., [3]Nestle Purina PetCare

2:40 (340) **Structure and Morphology in Triaxial Electrospun Fibers**; Bruce Chase[1], John Rabolt[1], Wenwen Liu[1]; [1]University of Delaware

Tuesday Afternoon, *Room 103B*
CHEMICAL IMAGING IN PHARMACEUTICAL MANUFACTURING
Organizer and Presider: John Bobiak

1:20 (341) **Imaging of Pharmaceutical Systems using Nanoscale Infrared Spectroscopy**; Lynne Taylor, Aaron Harriosn[1], Rajesh Dave[2], Ramani Susarla[2], Steven Beaudoin[1]; [1]Purdue University, [2]New Jersey Institute of Technology

1:40 (342) **Pharmaceutical Blend Characterization Using *In Situ* Near-Infrared Imaging**; Gabor Kemeny[1]; [1]Middleton Research

2:00 (343) **Determination of Spatially Resolved Tablet Density and Hardness using Near-Infrared based Chemical Imaging (NIR-CI) and Micro-Indentation**; Sameer Talwar[1], Rahul Roopwani[1], Ira Buckner[1], James Drennen, III[1], Carl Anderson[1]; [1]Duquesne University

2:20 (344) **Physical Characterization of Drug Product Intermediates using Confocal Raman Imaging and Spectroscopy**; Duohai Pan[1], Shih-Ying Chang[1], Joshua Engstron[1], Daniel Hsieh[1], Chiajen Lai[1], San Kiang[1], Shawn Yin[1]; [1]Bristol-Myers Squibb

2:40 (345) **Terahertz Imaging and Spectroscopy of Small Samples: A Study in Pharmaceutical Beads**; Xiao Hua Zhou[1], Richard McKay[1], Edward King[1], Eiji Kato[2], Mark Sullivan[1], David Heaps[1], Akiyoshi Irisawa[2], Motoki Imamura[2], Richard McKay; [1]Advantest America, Inc., [2]Advantest Corporation

Tuesday Afternoon, *Room 103C*
FLOW/CONTINUOUS PAT II
Organizer and Presider: Brian Marquardt

1:20 (346) **Catalytic Flow Chemistry and Real-time Monitoring Challanges**; D. Tyler McQuade[1,2]; [1]Florida State University, Department of Chemistry and Biochemistry, [2]Max Planck Institute of Colloids and Interfaces, Department of Biomolecular Systems

2:00 (347) **Reaction Characterization and PAT for the Development of Continuous Processes**; Adam McFarland[1]; [1]Eli Lilly and Company

2:20 (348) **Recent Advances in Continuous Flow Chemistry using Real-Time In Situ FTIR (Fourier Transform Infrared Spectroscopy)**; Dominique Hebrault[1]; [1]METTLER TOLEDO

2:40 (349) **Seamless Scale- Up with Corning® Advanced-Flow™ Reactors**; Jeremy Jorda[1], Alessandra Vizza[1], Marc Winter[1]; [1]Corning S.A.S

Tuesday Afternoon, *Room 103D*
CONTRIBUTED PAPERS IN BIO-MEDICAL AND BIO-ANALYTICAL RESEARCH
Organizer: Michael George; Presider: Ioan Notingher

1:20 (350) **Characterization of NMPPAS for Brain Tumor Margining and Related Biosignature**; Sudhir Dahal, Brian Cullum; [1]University of Maryland Baltimore County

1:40 (351) **Infrared Spectroscopic Studies of Cells and Tissues: Triple Helix Proteins as a Potential Biomarker for Tumors**; Allison Stelling[1], Deidre Toher[2], Ortrud Uckermann[3], Jelena Tavkin[1], Elke Leipnitz, Julia Schweizer[1], Holger Cramm[1], Gerald Steiner[1], Kathrin D. Geiger[4], Matthias Kirsch[3]; [1]Clinical Sensing and Monitoring, Faculty of Medicine, Dresden University of Technology, [2]Department of Engineering Design and Mathematics, Faculty of Environment and Technology, University of the West of England, [3]Department of Neurosurgery, Faculty of Medicine and University Hospital, Dresden University of Technology, [4]Department of Neuropathology, Institute of Pathology, Faculty of Medicine and University Hospital, Dresden University of Technology

2:00 (352) **Precision Performance of Raman Spectroscopy in the Assessment of Bone Quality**; Gurjit S. Mandair[1], Jaclynn M. Kreider[2], Steven A. Goldstein[2], Robert R. Recker[3], Michael D. Morris[1]; [1]Department of Chemistry, University of Michigan , [2]Orthopaedic Research Labs, University of Michigan, [3]Osteoporosis Research Center, Creighton University

2:20 (353) **Transcutaneous Measurement of Bone Mineral-To-Collagen Ratio *in vivo* using Spatially Offset Raman Spectroscopy and Various Multivariate Techniques**; Kevin Buckley[1,2], Jemma G. Kerns[2], Anthony W. Parker[1], Allen E. Goodship[2], Pavel Matousek[1], [1]Science & Technology Facilities Council, [2]University College London

2:40 (354) **Characterizing Enzymatic Activity Using NIR Dyes**; Gabor Patonay[1], Maged Henary[1], Garfield Beckford[1], Holly Ellis[2]; [1]Department of Chemistry, Georgia State University, [2]Department of Chemistry and Biochemistry, Auburn University

Tuesday Afternoon, *Room 101A*
NANOSCALE IR
Organizer and Presider: Curtis Marcott

3:50 (355) **Surface Enhanced Photothermal Induced Resonance (SE-PTIR): A New Method to Image near Field Hot Spots and Dark Plasmonic Modes**; Andrea Centrone[1,2]; [1]National Institute of Standard and Technology, [2]University of Maryland

4:10 (356) **Mid-infrared Vibrational Nanospectroscopy via Direct Molecular Force Detection**; Feng Lu[1], Mingzhou Jin[1], Mikhail Belkin[1]; [1]Univ. of Texas at Austin

4:30 (357) **Infrared Nanoscopy Applied to Microbiology and Cellular Biology**; Alexandre Dazzi[1], Ariane Deniset-Besseau[1], Delphine Onidas[1], Marie-Joelle Virolle[2]; [1]LCP, University of Paris-Sud, France, [2]IGM, University of Paris-Sud, France

4:50 (358) **Nano-FTIR: from nano-Spectroscopy to Quantitative Determination of Dielectric Properties and Thickness Profiling**; Alexander Govyadinov[1], Stefan Mastel[1], Martin Schnell[1], Florian Huth[1, 2], Scott Carney[3], Rainer Hillenbrand[1, 4] ; [1]CIC Nanogune Consolider, Donostia-San Sebastian, Spain, [2]Neaspec GmbH, Martinsried, Germany, [3]ECE Dept. and Beckman Institute, U. of Illinois at Urbana-Champaign, Urbana, [4]IKERBASQUE, Basque Foundation for Science

5:10 (359) **Thermal Infrared Near-Field Spectroscopy: Coherence, Heat-Transfer, Optical Forces, and Chemical Nano-Imaging**; Markus Raschke[1]; [1]University of Colorado

5:30 (360) **Expanding Applications for AFM-based Infrared Nanospectroscopy**; Craig Prater[1], Qichi Hu[1], Michael Lo[1], Curtis Marcott[2], Kevin Kjoller[1]; [1]Anasys Instruments, [2]Light Light Solutions

Tuesday Afternoon, *Room 101B*
INDUSTRIAL APPLICATIONS OF LIBS
Organizer and Presider: Greg Lithgow

3:50 (361) **The Things You Learn Deploying LIBS in Heavy Industry**; Arel Weisberg[1], Joseph Craparo[1], Robert De Saro[1]; [1]Energy Research Company

4:10 (362) **Laser-Induced Breakdown Spectroscopy: A Versatile Technique for the Real Time / On-line Analysis of Materials**; Paul Bouchard, Mohamad Sabsabi, François Doucet, André Moreau, René Héon, André Hamel, Francis Boismenu, Lütfü Özcan, Aïssa Harhira; [1]National Research Council Canada

4:30 (363) **LIBS Analyzers in Mining Industry**; Michael Gaft[1], Lev Nagli[1], Yoni Groisman[1]; [1]Laser Distance Spectrometry

4:50 (364) **Application of Laser Induced Breakdown Spectroscopy (LIBS) in Monitoring CO_2 Storage in Deep Saline Formations**; Christian Goueguel[1], Dustin McIntyre[2], Jinesh Jain[2], Jagdish Singh[3], Athanasis Karamalidis[1]; [1]Carngie Mellon University, [2]USDOE National Energy Technology Laboratory, [3]Mississippi State University

5:10 (365) **Towards Optimal Stand-Off LIBS Detection of Various Geochemical Reference Materials at Low Laser Energy**; Soo-Jin Choi[1], Kang-Jae Lee[1], Jack J. Yoh[1]; [1]Seoul National University

Tuesday Afternoon, *Room 101C*
ION CHROMATOGRAPHY
Organizer and Presider: Christopher Harrison

3:50 (366) **Simulating Chromatography with MS Excel™ : An X-ray Vision into a Column : Made into Reality**; Purnendu Dasgupta[1], Brian Stamos[1], Akinde Kadjo[1]; [1]Univ Texas Arlington

4:10 (367) **Advances in High Speed and High Resolution Ion Chromatography**; Charles Lucy[1], M. Farooq Wahab[1]; [1]University of Alberta

4:30 (368) **Amino Acid Containing Column Materials for Transition Metal and Drug Separations**; Roger Harrison[1], Na Li[1], Tayyebeh Panahi[1], Lucy Wang[1], John Lamb[1]; [1]Brigham Young University

4:50 (369) **High-Pressure Ion Chromatography – A New Platform for High Resolution or High Throughput Separations of Ionic Compounds**; Joachim Weiss; [1]Thermo Fisher Scientific GmbH

5:10 (370) **High Performance Ion Exchange Chromatography of Small and Large Molecules using Monolithic Stationary Phases**; Emily Hilder[1], Paul Haddad[1], R. Dario Arrua[1], Mohammad Talebi[1], Nathan Lacher[2] ; [1]University of Tasmania, [2]Pfizer BioTherapeutics Pharmaceutical Sciences

Tuesday Afternoon, *Room 102A*
PHARMACEUTICAL MASS SPECTROMETRY
Organizer and Presider: Peifeng Hu

3:50 (371) **Stable Isotope- and Mass Spectrometry-based Metabolomics as Tools in Drug Metabolism**; Andrew Patterson[1]; [1]The Pennsylvania State University

4:10 (372) **Source Induced Dissociation as a Means for Polymer Structure Characterization and Quantitation**; Peifeng Hu[1], Christopher Jones[1], Liqiong Fang[1]; [1]Baxter Healthcare Corporation

4:30 (373) **High Resolution Mass Spectrometry for Low Level Unknown Identification in Drug Product: from Small Molecules to Large Peptides**; Wendy Zhong[1]; [1]Merck Research Laboratories

4:50 (374) **The Addition of Atmospheric Pressure Chemical Ionization GC-MS to the Structure Elucidation Toolbox**; Christopher Jones[1], Edward Chess[1], Peifeng Hu[1]; [1]Baxter Healthcare Corporation

5:10 (375) **Effects of Nucleobase Identity, the 2′-Hydroxyl Group, and Modifications on Glycosidic Bond Stability: Energy Resolved CID Studies of Protonated Nucleosides**; Mary T. Rodgers[1], Ranran Wu[1], Yanlong Zhu[1], Lin Fan; [1]Wayne State University

Tuesday Afternoon, *Room 102B*
NANO-FACILITATED SENSING
Organizer and Presider: David E. Thompson

3:50 (376) **Hydrophobic Trapping of Molecules in Nanopores**; Lei Geng[1]; [1]University of Iowa

4:10 (377) **Luminescent Probes for High Resolution Chemical Sensing Through Tissue**; Jeffrey Anker[1], Hongyu Chen[1], Fenglin Wang[1]; [1]Clemson University Chemistry Department and Center for Opical Materials Science and Engineering Technology (COMSET)

4:30 (378) **Surface Enhanced Spectroscopy in the Short-Wave IR**; Jon Camden[1]; [1]University of Tennessee

4:50 (379) **Molecular Imprinted Polymers for Raman-based Nanosensors**; Anna Volkert[1], Michael Boller[1], Amanda Haes[1]; [1]University of Iowa

5:10 (380) **Surface Enhanced Spectroscopy on Infrared Transparent Substrates**; David E. Thompson[1], Emily N Miller[1], Dustin C Palm[1], Deepthika De Silva[1], Asish Parbatani[1], Adam R. Meyers[1], Darren L. Williams[1]; [1]Sam Houston State University

Tuesday Afternoon, *Room 102C*
A NEW AGE OF RAMAN IMAGING
Organizers and Presiders: Katsumasa Fujita and Duncan Graham

3:50 (381) **Stable Isotope-labeled Raman Microspectroscopy: Shedding New Light on Cellular Metabolism**; Shinsuke Shigeto[1], Hemanth Nag Noothalapati Venkata[1]; [1]Department of Applied Chemistry, National Chiao Tung University

4:10 (382) **Super-resolution SERS Imaging**; Katherine Willets[1]; [1]University of Texas at Austin

4:30 (383) **Fast and Objective Histopathology by Optical Spectroscopy**; Ioan Notingher[1], Kenny Kong[1], Chris Rowlands[1], Sandeep Varma[3], Ian Leach[3], Alexey Koloydenko[2], Hywel Williams[1]; [1]University of Nottingham, [2]University of London, [3]Nottingham University Hospital NHS Trust

4:50 (384) **Applications of Gold Nanoparticles in SERS Imaging of Fungi**; Kathleen Gough[1], Fatemeh Farazkhorasani[1], Susan Kaminskyj[2]; [1]University of Manitoba, [2]University of Saskatchewan

5:10 (385) **Raman Microscopy in Clinics - What are the Potentials and Limits?**; Juergen Popp[1,2], Petra Roesch[1], Christoph Krafft[2], Karina Weber[1, 2], Dana Cialla[1, 2], Christian Matthaeus[1, 2], Ute Neugebauer[2, 3], Benjamin Dietzek[1,2], Michael Schmitt[1]; [1]Friedrich-Schiller University, Institute of Physical Chemistry and Abbe Center of Photonics, Jena, [2]Institute of Photonic Technology, Jena , [3]Center for Sepsis Control and Care, Jena

Tuesday Afternoon, *Room 102D*
THE BIRTH OF CHEMOMETRICS – IN HONOR AND MEMORY OF BRUCE KOWALSKI III
Organizers: Karl Booksh and Barry Lavine;
Presider: Thomas Isenhour

3:50 (386) **Uncertainties in Clustering and Classification of Multivariate Geochemical Data**; Steven Brown[1], Liyuan Chen[1]; [1]Univ. of Delaware

4:10 (387) **The Errors of My Ways: Maximum Likelihood PCA Seventeen Years after Bruce**; Peter Wentzell; [1]Dalhousie University

4:30 (388) **Are O-PLS Models Really More Interpretable?**; Barry M. Wise[1], Jeremy M. Shaver[1]; [1]Eigenvector Research, Inc.

4:50 (389) **Assessing Multivariate Calibration Trade-Offs to Select Model Tuning Parameters**; John Kalivas[1]; [1]Idaho State University

5:10 (390) **Applying ARSE to Classification and Calibration**; Karl Booksh[1], Josh Ottaway; [1]University of Delaware

Tuesday Afternoon, *Room 102E*
ACS ANALYTICAL CHEMISTRY DIVISION AWARD IN CHEMICAL INSTRUMENTATION HONORING CHARLES WILKINS
Organizer and Presider: Charles Wilkins

3:50 (391) **Hyphenated Instrumentation: Developments to Date and Future Prospects**; Charles Wilkins[1]; [1]University of Arkansas

4:10 (392) **Surface-Enhanced Infrared Absorption Spectroscopy: Arguments against a Plasmonic Origin**; Peter Griffiths[1]; [1]University of Idaho

4:30 (393) **Distance-of-Flight Mass Spectrometry with a Low-Cost Imaging Detector**; Gary Hieftje[1], Alexander Graham[1], Steven Ray[1], Elise Dennis[1], Christie Enke[2], David Koppenaal[3], Charles Barinaga[3]; [1]Indiana University, [2]University of New Mexico, [3]Pacific Northwest National Laboratory

4:50 (394) **Spectroelectrochemistry as a Strategy for Improving Sensor Selectivity**; William Heineman[1], Samuel Bryan[2]; [1]University of Cincinnati, [2]Pacific Northwest National Laboratory

5:10 (395) **Fourier Transform Ion Cyclotron Resonance Mass Spectrometry: 40 Years and Counting**; Alan Marshall[1]; [1]Florida State University

Tuesday Afternoon, *Room 103B*
ADVANCES IN MATERIALS CHARACTERIZATION VIA GLOW DISCHARGE SPECTROMETRY
Organizer and Presider: Gerardo Gamez

3:50 (396) **Capabilities and Limitation of RF-PGD-TOFMS: an Emerging Technique for Near-Surface Analysis**; Jorge Pisonero[1], Cristina González[1], Nicole Tibbetts[2], Katharine Dovidenko[2], Denise Anderson[2], Dustin Ellis[2], Alfredo Sanz-Medel[3], Nerea Bordel[1]; [1]Department of Physics, University of Oviedo, [2]General Electric Global Research, Niskayuna, USA, [3]Department of Physical and Analytical Chemistry, University of Oviedo

4:10 (397) **A Comparative Study of CCD Array Detector and PMT Signals during Thin Layer Compositional Depth Profile Analysis**; Kim Marshall[1], Greg Schilling[1], Scott Chrispell[1]; [1]Leco Corporation

4:30 (398) **Ultrafast Elemental Mapping of High-throughput Screening Samples via Pulsed Glow Discharge Optical Emission Spectroscopy**; Gerardo Gamez[1], Gaurav Mohanty[1], Johann Michler[1]; [1]Swiss Federal Laboratories for Materials Science and Technology, EMP

4:50 (399) **Automatable On-Line Generation of Calibration Curves and Standard Additions with Solution-Cathode Glow Discharge Optical Emission Spectrometry**; Andrew Schwartz[1], Steven Ray[1], Gary Hieftje[1]; [1]Indiana University

5:10 (400) **Investigation of Outgassing of Volatile Compounds in GD-OES**; Arne Bengtson[1], Mats Randelius[1]; [1]Swerea KIMAB AB

Tuesday Afternoon, *Room 103C*
ANALYTICS IN PHARMACEUTICAL COUNTERFEIT DETECTION
Organizer and Presider: Ravi Kalyanaraman

3:50 (401) **Process Patent Protection: Protecting Intellectual Property via Ambient Stable Isotopes**; John Jasper[1], Martin Pavane[2], Dean Eyler[3], Ila Sharma[4], Albert Lee[4]; [1]Nature's Fingerprint®/Molecular Isotope Technologies, LLC, [2]Cozen O'Connor,, [3]Gray Plant Mooty, [4]Chemir Analytical Services

4:10 (402) **Assessment of a Handheld Raman Device in Potential Use to Detect Counterfeit and Substandard Medicines**; Mustapha Hajjou[1]; [1]United States Pharmacopeia

4:30 (403) **Performance Validation of Handheld Raman Spectrometers for Counterfeit Screening**; Robert Brush[1], Robert Green[1], Craig Gardner[1], Wayne Jalenak[1]; [1]Thermo Fisher Scientific

4:50 (404) **The USP Spectal Library Project**; Bei Ma[1]; [1]U.S. Pharmacopeial Convention

5:10 (405) **Don't Always Assume Natural Is Safe: Screening of Supplements for the Presence of Undeclared Drugs**; Connie Gryniewicz-Ruzicka[1], Jamie Dunn[1], Laura Mecker-Pogue[1], Jason Rodriguez[1]; [1]US Food and Drug Administration

Tuesday Afternoon, *Room 103D*
ANALYTICAL CHEMISTRY AS DETECTIVE: CASE STUDIES IN FORENSIC SCIENCE
Organizer and Presider: Brooke Weinger Kammrath

3:50 (406) **Practical Colorant Identification Applied to Forensic Casework**; Christopher Palenik[1], Skip Palenik[1]; [1]Microtrace LLC

4:10 (407) **The Ultimate Challenge For Forensic Science**; John Reffner[1]; [1]John Jay College, CUNY

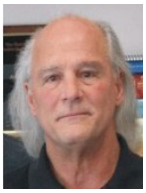
4:30 (408) **Detction of Fuel Fraud by Surface Enhanced Raman Scattering (SERS) Spectroscopy**; Peter White[1], Timothy Wilkinson[1]; [1]DeCipher Pte Ltd

4:50 (409) **Wooden Stick Matches as Evidence in Forensic Casework: Not All matches are 'Equal'**; Marianne Stam[1]; [1]California Criminalistics Institute

5:10 (410) **Revisiting the Elemental Analysis of Bullet Lead**; Peter De Forest[1], Brooke Kammrath[1, 2]; [1]Forensic Consultants, [2]University of New Haven

TECHNICAL PROGRAM – WEDNESDAY
Plenary Lectures, Ballroom A
Presider: Jose Almirall

8:00 am – SAS's Applied Spectroscopy William F. Meggers Award.
(411) A New *in vivo* Raman Probe for Enhanced Applicability to the Body; Paul Pudney[1], Eleanor Bonnist[1], Peter Caspers[2], Jean-Philippe Gorce[1], Chris Marriot[1], Gerwin Puppels[2], Scott Singleton[1], Martin van der Wolf[2]; [1]Unilever Discover, [2]RiverD International



8:30 am – SAS's Lester W. Strock Award.
(412) Isotopic Analysis at Atmospheric Pressure in Laser Plasmas**; Richard Russo**, Lawrence Berkeley National Lab and Applied Spectra, Inc.

Wednesday Poster Session
9:00 – 10:20 am
Ballroom B/C/D

All Wednesday posters should be put up between 7:30 – 8:00 am and removed by 4:00 pm

Atomic

Board #

1 (413) **Inductively Coupled Plasma Gradient Flow Analysis**; Willis Jones[1], George Donati[1], Bradley Jones[1]; [1]Wake Forest University

2 (414) **Development of High-Power Pulsed Microplasma AES System for Analysis of Small Amount Samples**; Kensuke Okumura[1], Takahiro Iwai[1], Ken Kakegawa[1], Hidekazu Miyahara[1], Akitoshi Okino[1]; [1]Department of Energy Sciences, Tokyo Institute of Technology

3 (415) **LA-ICP-oTOF-MS for the Mining Industry : an Investigation**; Andrew Saint[1]; [1]GBC Scientific Equipment Pty. Ltd

4 (416) **An Examination of Matrix Effects of Carbon and Iron Mixtures in LIBS Spectra, Experimental and Numerical Approaches**; Leon Taleh[1], Poopalasingam Sivakumar[1], Yuri Markushin[1], Jeremie Lasue[2, 3, 4], Noureddine Melikechi[1]; [1]Optical Science Center for Applied Research, Department of Physics and Engineering, Delaware State University, [2]Université de Toulouse, [3]ISR, Los Alamos National Laboratory, [4]Lunar and Planetary Institute

5 (417) **Effects of Axial and Transverse Magnetic Fields on Laser Produced Plasmas**; Faisal Odeh[1], Niral Shah[1], Nick Mckenna[1], Prasoon Diwakar[1], Filippo Genco[1], Sivanandan Harilal[1], Ahmed Hassanein[1]; [1]Center for Materials Under Extreme Environment, School of Nuclear Engineering Purdue University, West Lafayette, Indiana

6 (418) **CO_2 Removal Using a Falling-Film Column in the Analysis of Organic Samples with Inductively Coupled Plasmas**; Farzaneh Moradi[1], Helmar Wiltsche[1], Günter Knapp[1]; [1]Graz University of Technology, Institute of Analytical Chemistry and Food Chemistry

7 (419) **Study of S0→S3 Transition for Liquid Benzene and Mono-Substituted Benzenes by Using Far-Ultraviolet Spectroscopy and Quantum Chemical Calculations**; Yuuki Uematsu[1], Yuusuke Morisawa[2], Masahiro Ehara[3], Yukihiro Ozaki[1]; [1]Department of Chemistry, Kwansei Gakuin University, [2]Department of Chemistry, Kinki University, [3]Institute for Molecular Science

8 (420) **The Determination of Si in RM 3475 Silicon Nanoparticles**; Savelas Rabb[1], Vytas Reipa[1]; [1]National Institute of Standards and Technology

Biological, Bioanalytical and Biomedical

Board #

9 (421) **Quantification of the Centimetre-scale Heterogeneity of Human Cortical Bone Composition**; Kevin Buckley[1,2], Jemma G. Kerns[2], Anthony W. Parker[1], Allen E. Goodship[2], Pavel Matousek[1]; [1]Science & Technology Facilities Council, [2]University College London

10 (422) **Use of a Simultaneous Mattauch–Herzog Inductively Coupled Plasma-Mass Spectrometer for Analysis of Cerebrospinal Fluid from Alzheimer's Patients**; Esperanza García-Ruiz[1], Luis Rello[2], Frank Vanhaecke[3], Martín Resano[1]; [1]University of Zaragoza, [2]Hospital Miguel Servet, [3]Ghent University

11 (423) **Integrating Second Harmonic Generation and Two-Photon Ultraviolet Fluorescence into an X-ray Diffraction Beamline for protein Crystal Centering**; Christopher Dettmar[1], Jeremy Madden[1], Justin Newman[1], Scott Toth[1], Michael Becker[2], Robert Fischetti[2], Garth Simpson[1]; [1]Purdue University, [2]GM/CA @ APS, Argonne National Labs

12 (424) **Effects of Local Environment on UV–VIS Spectra of Zinc Porphyrins: Protein & Solvent**; Hannah E. Wagie[1], Jorg C. Woehl[1], Peter Geissinger[1]; [1]University of Wisconsin - Milwaukee

13 (425) **Exploiting Human Fingernail as a Surrogate Marker of Fracture Risk in Postmenopausal Women**; J Renwick Beattie[1], Olive O'Driscoll[2], Niamh Cummins[3], Mark Towler[4]; [1]Crescent Diagnostics Ltd, [2]Cork Institute of Technology, [3]University of Limerick, [4]Ryerson University

14 (426) **Spectral Characterization of Carbonated Apatites and Computation of NMR Spectra**; Mary Tecklenburg[1], Barbara Pavan[1]; [1]Central Michigan University

Chemometrics

15 (427) **Principal Component Analysis of Phenolic Acid Spectra**; Ronald Holser[1]; [1]Russell Research Center

16 (428) **Parallel Factor Analysis of Multi-Excitation UV Resonance Raman Spectra for Protein Secondary Structure Determination**; Olayinka Oshokoya, Renee JiJi[1]; [1]University of Missouri- Columbia

17 (429) **Spectroscopic Discernment of Seed Cotton Trash**; Gary Rayson, Elizabeth Gámez[1], Fengshan Jiang[1], Surja Ghale[1], S. Hughes[2], Dean Anderson[3]; [1]New Mexico State University, [2]USDA-ARS Southwest Cotton Ginning Research Laboratory, [3]USDA-ARS Jornada Experimental Range

Board #

18 (430) **Image Analysis and Machine Learning for the Recognition of Chain-Forming Phytoplankton**; Shawna Tazik[1], Joseph Swanstrom[1], Tammi Richardson[1], Timothy Shaw[1], Michael Myrick[1]; [1]University of South Carolina

19 (431) **Net Analyte Signal Geometry Facilitates Model Selection for Multivariate Calibration with Ridge Regression and Partial Least Squares**; Jonathan Palmer[1], John Kalivas[1]; [1]Idaho State University

20 (432) **Chemometric Assessment of Airborne Silica Dust in Mines by Infrared Spectrometry**; Andrew Weakley[1], Arthur L. Miller[2], Peter R. Griffiths[3], Emanuele G. Cauda[2], Pamela L. Drake[2]; [1]University of Idaho, [2]National Institute of Occupational Safety and Health (NIOSH), [3]Griffiths Spectroscopic Consulting LLC

21 (433) **Applying Multivariate Curve Resolution Analysis Techniques to NIR Reflectance Hyperspectral Images**; Howland Jones[1], Lam Nguyen[1], Eli Margalith[1]; [1]OPOTEK Inc.

22 (434) **Limits of Detection from the Viewpoint of Statistical Hypothesis Testing**; Kaylee R. McDonald[1], Molly R. Burnip[1], Scott J. Hoy[1], Stephen L. Morgan[1]; [1]University of South Carolina

Microscopy, Imaging Spectroscopy, Forensics and Education

23 (435) **Single Molecule Counting in Nanopores**; Yan Hu[1], Lei Geng[1]; [1]University of Iowa

24 (436) **Multi-Modal Imaging Platform for Nanomaterials Characterization**; Emmanuel Leroy[1]; [1]HORIBA Scientific

25 (437) **Identification of Liquids and Solids by Infrared Hyperspectral Imaging**; Sergey Shilov[1], Roland Harig[1], Samer Sabbah[1], René Braun[1], Jörn Gerhard[1], Peter Rusch[1]; [1]Bruker Optics

26 (438) **Individual and Simultaneous Determination of Oxytetracycline and Florfenicol in Salmon Muscle and Skin by Fluorimetry**; M. Ines Toral[1], Patricia Gaete[1], Jose Moncada[1], Patricio Carreño[1], Pablo Richter[1]; [1]University of Chile

27 (439) **Fluorescence Correlation Spectroscopy and Time Resolved Fluorescence Anisotropy Decay Measurements for Structures and Dynamics of Room Temperature Ionic Liquids**; Robert Shaw[1], Jianchang Guo[1], Shannon Mahurin[1], Gary Baker[2], Patrick Hillesheim[1], Sheng Dai[1]; [1]Chemical Sciences Division, Oak Ridge National Laboratory; [2]Department of Chemistry, University of Missouri-Columbia

28 (440) **Emerging Trends in F19 & P31 NMR Spectroscopy**; Abhishek Gupta[1,2]; [1]Indian Institute of Technology, Delhi, India, [2]Daiichi Sankyo India Pharma Pvt.Ltd

29 (441) **Rapid Spectrophotometric Determination of Nitrite across 5 Orders of Magnitude using a Single Set of experimental Conditions**; Mya Porche[1], Benoit Lauly[1], Jonathan Scaffidi[1]; [1]Miami University

30 (442) **A Comparative, Experimental Approach to Teaching Analytical Methods.**; Maury Howard[1]; [1]Virginia Wesleyan College

Board #

31 (443) **3D tomographic FTIR Spectrochemical Imaging for Assessment of Nutrients in Arctic Sea-Ice Diatoms**; Catherine Liao[1], Alexandra Ciapala[1], Peter Trokajlo[1], Julia Sedlmair[3, 4], Carol Hirschmugl[2, 3], C. J. Mundy[1], Kathleen Gough[1]; [1]University of Manitoba, Winnipeg, Manitoba, Canada, [2]University of Wisconsin - Milwaukee, WI, [3]Synchrotron Radiation Center, University of Wisconsin - Madison, WI, [4]USDA Forest Service, Forest Products Laboratory, Madison, WI

32 (444) **Imaging of Nanoparticles and Nano-structual Features Using a Home-built Near-field Scanning Optical Microscope**; Taher Ababneh[1], Jorg Woehl[1]; [1]University of Wisconsin-Milwaukee

33 (445) **Quantitative Imaging of Powder Samples using NIR Reflectance Hyperspectral Imaging with a Tunable Laser**; Howland Jones[1], Lam Nguyen[1], Gregory Israelson[2], Eli Margalith[1]; [1]OPOTEK Inc., [2]Nestle Purina PetCare

34 (446) **Evaluation of the Inhomogeneity of Crystallinity on the Polymer by using Wide Area NIR imaging Camera (Compovision)**; Daitaro Ishikawa[1], Takashi Nishii[1], Fumiaki Mizuno[2], Yukihiro Ozaki[1]; [1]Kwansei Gakuin University, [2]Sumitomo Electric Industries, Ltd.

35 (447) **Applied Brewery Quality Control Curriculum for Analytical Chemistry Course**; Daniel Kool[1], Katie Martin[1], Andrew McDonald[1], Nicholas Rothfus[1], Yuan Yuan[1], Dale LeCaptain[1]; [1]Central Michigan University

36 (448) **Performance of Thermographic Latent Heat Imaging for Forensic Detection of Blood**; Nicholas D. Boltin[1], Brianna M. Cassidy[1], Zhenyu Lu[1], Michael L. Myrick[1], Stephen L. Morgan[1]; [1]University of South Carolina

37 (449) **Greek and Roman Unguentaria: Fingerprinting Ancient Perfumes by ICP-MS and FT-IR**; Jenna Mortensen[1], Bettina Arnold[1], Joseph H. Aldstadt[2]; [1]Dept. of Anthropology, Univ. of Wisconsin-Milwaukee, [2]Dept. of Chemistry & Biochemistry, Univ. of Wisconsin-Milwaukee

RAMAN, SERS and TERS

38 (450) **Selective Fabrication of SERS-active Ag nanoparticles by Near-Field Photo-Reduction and *in situ* AFM Measurement**; Yasutaka Kitahama[1], Takuya Ikemachi[1], Toshiaki Suzuki[1], Yukihiro Ozaki[1]; [1]Kwansei Gakuin University

39 (451) **Plasma-Induced Enhancement of Azo Dye SERS Intensity on ZnO**; Szetsen Lee[1], Chih-Sheng Liu[1], Bing-Han Li[1]; [1]Department of Chemistry, Chung Yuan Christian University

40 (452) **Gold Clusters as SERS Substrates**; M. Fernanda Cardinal[1], Richard P. Van Duyne[1]; [1]Northwestern University

41 (454) **Evaluation of Matrix Effects during SERS-based TNT Determination in Fresh Water**; Marc Wadsworth[1], Benoit Lauly[1], Jon Scaffidi[1]; [1]Miami University

42 (455) **Direct Measurement of Electric Fields from Plasmon Excitation**; James M. Marr[1], Zachary D. Schultz[1]; [1]University of Notre Dame

43 (456) **Simple Approach to Realize Flexible SERS Sensor Platforms on Microfluidic Device**; Donghyuk Kim[1]; [1]University of Minnesota

Board #

44 (457) **Tip-enhanced Raman Scattering (TERS) Study of Local Structure in Ethylene Propylene Diene Terpolymer (EPDM) Rubber/Multiwall Carbon Nanotubes Nanocomposites**; Ryohei Hinaga[1], Toshiaki Suzuki[1], Yukihiro Ozaki[1]; [1]Kwansei Gakuin University

45 (458) **Towards Tip-Enhanced Raman Scattering (TERS) Investigation of Nanoscale Architectures**; Kirsty F. Gibson[1], Jennifer A. Dougan[1], Sergei G. Kazarian[1]; [1]Imperial College London

46 (459) **Self-normalizing SERS-based Determination of Heavy Metals**; Benoit Lauly[1], Jenny DeJesus[1], Jon Scaffidi[1]; [1]Miami University

Wednesday Morning, *Room 101A*
COHERENT TWO-DIMENSIONAL SPECTROSCOPY I
Organizers: Wei Zhao and Junrong Zheng; Presider: Wei Zhao

10:20 (460) **The Multiresonant Family of Coherent Multidimensional Spectroscopy**; John Wright[1]; [1]University of Wisconsin-Madison

11:00 (461) **2DIR and IR Pump-Probe Studies of Ion Dynamics**; Minhaeng Cho[1]; [1]Korea University

11:20 (462) **Moving from 2D Spectroscopy to 3D Spectroscopy: What Are the Potential Advantages of Adding One More Dimension?**; Peter Chen[1]; [1]Spelman College

11:40 (463) **Directly Probing Changes in the Intermolecular Solvent Spectrum during Chemical Reactions**; David Blank[1], Matthew Ammend[1], Benjamin Fitzpatrick[1]; [1]University of Minnesota

Wednesday Morning, *Room 101B*
CHEMOMETRICS FOR LIBS
Organizer and Presider: François R. Doucet

10:20 (464) **Quantitative Analyses for Coal Application using Laser Induced Breakdown Spectroscopy**; Zhe Wang; [1]Tsinghua University

10:40 (465) **Artificial Neural Networks Applied to LIBS Spectra for Both Quantification and Classification of Soil Samples**; Josette El Haddad[1,2], Lionel Canioni[1, 2], Bruno Bousquet[1, 2]; [1]Univ. Bordeaux, [2]CNRS

11:00 (466) **Elemental Analysis (LA-ICP-MS and LIBS) and Multivariate Comparison of Soils: Tape as an Alternative to Pellets for Small Forensic Specimens**; Sarah C. Jantzi[1], José R. Almirall[1]; [1]IFRI, Florida International University

11:20 (467) **Chemometric Analysis of LIBS Based Aluminum Measurements**; Dahu Qi[1], Steven Buckley[1], Chris Stipe[2]; [1]TSI Inc., [2]University of Seattle

11:40 (468) **Application of Laser-Induced Breakdown Spectroscopy for Origin Assessment of Uranium Ore Refining Process Intermediates**; François R. Doucet[1], Paul Bouchard[1], Mohamad Sabsabi[1], Rick Kosierb[2]; [1]National Research Council Canada, Energy, Mining and Environment, [2]Canadian Nuclear Safety Commission, Directorate of Security and Safeguards

Wednesday Morning, *Room 101C*
GEL PERMEATION CHROMATOGRAPHY
Organizer: John McConville: Presiders: Murray Fryman and John McConville

10:20 (469) **Attempts to Overcome Some of the Challenges in Molecular Weight Characterization of Polymers by Gel Permeation Chromatography**; Erick Soto-Cantu[1], David Yarusso[1], Richard Ross[1], Karl Benson[1]; [1]3M Company

10:40 (470) **Bridging the Gap in Polymer Characterization: Single- and Multi-Detector SEC**; Amanda Brewer[1]; [1]Tosoh Bioscience LLC

11:00 (471) **Analyzing Complex Polymers using 2D-Chromatography**; John McConville[1,2], Thorsten Hofe[1], Peter Kilz[1], Peter Montag[1], Derek Lohmann[2]; [1]PSS Polymer Standards Service GmbH, [2]PSS USA Inc.

11:20 (472) **Online Coupling of SEC-MR-NMR**; Derek Lohmann[4], Markus Cudaj[1], Gisela Guthausen[2], John McConville[4], Thorsten Hofe[3], Manfred Wilhelm[1]; [1]Institute for Chemical Technology and Polymer Chemistry, Karlsruhe Institute of Technology (KIT), [2]Institute of Mechanical Process Engineering and Mechanics, SRG10-2, Karlsruhe Institute of Technology (KIT), [3]PSS Polymer Standards Service GmbH, [4]PSS USA-Inc.

11:40 (472B) **Online Polymerization Monitoring with and without GPC**; Wayne Reed, Tulane University

Wednesday Morning, *Room 102A*
ACTIVE NANOCOMPOSITES
Organizer: Jian Chen; Presider: Hongrui Jiang

10:20 (473) **Thermoelectric Fabrics**; David Carroll[1]; [1]Wake Forest University

10:40 (474) **Synthesis and Properties of Nitrogen-doped Carbon Nanotube Cups**; Alexander Star[1]; [1]University of Pittsburgh

11:00 (475) **Nano Materials for Photo-Mechanical Actuators**; Hongrui Jiang[1]; [1]University of Wisconsin - Madison

11:20 (476) **Nanostructured Photovoltaics: Limits and Unique Opportunities**; Richard Lunt[1]; [1]Michigan State University

11:40 (477) **Nanostructured Electrode for Spectroelectrochemistry Studies and Charge Storage**; Shanlin Pan[1]; [1]The University of Alabama

Wednesday Morning, *Room 102B*
APPLICATIONS OF ANALYTICAL SCIENCES IN DIABETES
Organizer and Presider: Michael J. Walsh

10:20 (478) **Histology and Ultrastructure of the Diabetic Kidney**; Suman Setty[1], Vishal Varma[1], Michael Walsh[1], Sanjeev Akkina[1]; [1]University of Illinois at Chicago

10:40 (479) **IR Spectroscopic Imaging for the Monitoring of Diabetic Renal Transplant Patients**; Michael Walsh[1], Vishal Varma[1], Alexandru Susma[1], Sanjeev Akkina[1], Andre Kajdacsy-Balla[1], Suman Setty[1]; [1]University of Illinois at Chicago

11:00 (480) **Raman Spectroscopic Perspective on Long-Term Glycemic Markers**; Narahara Chari Dingari[1], Rishikesh Pandey[1], Jaqueline Soares[1], Gary Horowitz[1], Ramachandra Rao Dasari[1], Ishan Barman[1]; [1]Massachusetts Institute of Technology

11:20 (481) **Fluorescent and Electrochemical Proximity Immunoassays for Quantifying Hormone Secretions in Small Volumes**; Christopher Easley[1], Joonyul Kim[1], Subramaniam Somasundaram[1], Jessica Brooks[1], Kennon Deal[1], Jean Negou[1], Lauren Hoepfner[1], Robert Judd[1]; [1]Auburn University

11:40 (482) **Metabolomics of Diabetic Aorta using Capillary LC-MS**; James Edwards[1]; [1]Saint Louis University

Wednesday Morning, *Room 102C*
SPECTROSCOPIC TECHNIQUES IN FORENSIC INVESTIGATIONS
Organizer and Presider: Mary Miller

10:20 (483) **Spectroscopic Analysis of Consumer Products: A Forensic Approach**; Richard Brown[1], Mary Miller[1]; [1]MVA Scientific Consultants

10:40 (484) **Applications of Micro-Spectroscopy to Forensic Trace Evidence**; John Reffner[1]; [1]John Jay College, CUNY

11:00 (485) **Forensic spectroscopic Chemical Fingerprinting of Fingerprints**; David Wetzel[1], Mark Boatwright[1,2], Jarrod Bechard[2]; [1]Microbeam Molecular Spectroscopy Laboratory, Kansas State University, [2]Department of Biochemistry and Molecular Biophysics, Kansas State University

11:20 (486) **Simultaneous Determination of Geographical Origin and Quality Characteristics of Agricultural Products from the Alpine Area Based on Near Infrared Spectroscopy (NIRS)**; Christian Huck[1], Matthias Schmutzler[1], Oliver Lutz[1], Lorenzo De Benedictis[1]; [1]Institute of Analytical Chemistry and Radiochemistry, CCB – Center for Chemistry and Biomedicine, Leopold-Franzens University, Innsbruck, Austria

11:40 (487) **Profiling Caramel Colour in the Scotch Whisky Industry using Mid-infrared Spectrometry with an Attenuated Total Reflectance Probe**; Megan Holden[1], Alison Nordon[1], David Littlejohn[1], Ian Goodall[2], Craig Owen[2], Walter Johnstone[1], Gary Colquhoun[3]; [1]University of Strathclyde, [2]Scotch Whisky Research Institute, [3]Fibre Photonics

Wednesday Morning, *Room 102D*
HOME MADE EXPLOSIVES
Organizer: Audrey Williams; and Presider: Greg Klunder

10:20 (488) **Detection and Thermal Stability of Home-Made Explosives: A Comprehensive Study of Fuel-Oxidizer Mixtures**; Ilana Goldberg[1], Joseph Kozole[2], Harry Rose[3], Luther Schaeffer[3], Jack Stephenson[4], Jason Stairs[4]; [1]The Johns Hopkins University Applied Physics Laboratory, [2]Dupont, [3]Nova Research, [4]Department of Homeland Security

10:40 (489) **Taming Peroxide Explosive**; Jimmie C. Oxley[1], James L. Smith[1], F. Lucus Steinkamp[1], Joseph Brady, IV[1]; [1]URI

11:20 (490) **Novel Capillary Microextraction Coupled to Gas Chromatography Mass Spectrometry**; Jose Almirall[1], Wen Fan[1]; [1]Florida International University

11:40 (491) **Chemometric Analysis of Multi-Channel Fused Datasets to Improve Source Attribution of Prevalent Homemade Explosives**; Joseph Chipuk[1], Myles Gardner[1], Carolyn Mazzitelli[1], Julie Wilkerson[1], Melissa Reaves[1], Alan Smith[1], Jamie Patterson[1]; [1]Signature Science

Wednesday Morning, *Room 102E*
SAS'S APPLIED SPECTROSCOY MEGGERS AWARD ACCEPTED BY PAUL PUDNEY
Organizer and Presider: Paul Pudney

10:20 (492) **Total Internal Reflection Raman Spectroscopy**; Colin Bain[1]; [1]Durham University

10:40 (493) **Breaking the Mould: Raman Optical Activity as a Structural Tool Beyond Biology**; Christian Johannessen[1]; [1]University of Antwerp

11:00 (494) **MCR Augmented Ordinary Least-Squares Models for Improved *in-vivo* Raman Spectroscopy**; Chunhong Xiao[1,2],Thomas Hancewicz[1], Shuliang Zhang[1], Manoj Misra[1]; [1]Unilever R&D, [2]Perkin-Elmer

11:20 (495) **Applications of Confocal Raman Spectroscopy in Dermal Drug Delivery**; Majella Lane[1]; [1]UCL School of Pharmacy

11:40 (496) **FTIR Spectroscopy and Imaging Studies of Skin and Hair**; David Moore[1]; [1]Rutgers University

Wednesday Morning, *Room 103B*
ADVANCES AND ATYPICAL APPLICATIONS OF NOVEL PLASMAS
Organizer and Presider: Jacob T. Shelley

10:20 (497) **From Explosives to Lipids: Coupling Ambient Ionization to Miniature Mass Spectrometers for *in-situ* Detection and Real-Time Chemical Analysis**; Paul I. Hendricks[1], Jacob T. Shelley[2], Jon K. Dalgleish[1], Jason S. Duncan[1], Matt T. McNicholas[3], Linfan Li[4], Tsung-Chi Chen[4], Chien-hsun Chen[4], Zheng Ouyang[4], R. Graham Cooks[1]; [1]Department of Chemistry, Purdue University, [2]Institute for Inorganic and Analytical Chemistry, University of Muenster, Muenster, Germany, [3]Department of Electrical and Computer Engineering Technology, Purdue University, [4]Weldon School of Biomedical Engineering, Purdue University

10:40 (498) **Enabling Access to Ambient Ionization in a Simpler Mass Spectrometer**; Brian Musselman[1], Joseph Tice[1], Joseph LaPointe[1], Randall Pedder; [1]IonSense, Inc., [2]Ardara Technologies

11:00 (499) **Halo-FAPA, an Angelic Source for Solid, Liquid and Gaseous Sample Volatilization and Ionization**; Kevin P. Pfeuffer[1], J. Niklas Schaper[2], Jacob T. Shelley[3], Steven J. Ray[1], Gary M. Hieftje ; [1]Department of Chemistry, Indiana University, [2]Institute for Inorganic and Analytical Chemistry, Johannes Gutenberg University Mainz, [3]Institute of Inorganic and Analytical Chemistry, University of Munster

11:20 (500) **Compact Laser Ablation - Atmospheric Pressure Glow Discharge System for Elemental Analysis by Optical Spectrometry**; Jhanis Gonzalez[1,3], Benjamin Manard[2], Meirong Dong[1], Arnab Sarkar[1], Jose Chirinos[1], Xianglei Mao[1], Ken Marcus[2], Rick Russo[1,3]; [1]Lawrence Berkeley National Laboratory , [2]Department of Chemistry, Clemson University, [3]Applied Spectra, Inc.

11:40 (501) **Levitated Droplets in Mass Spectrometry**; Jens Riedel[1], Arne Stindt[1], Carsten Warschat[1], Andreas Bierstedt[1], Ulrich Panne[1,2]; [1]BAM Federal Institute for Materials Research and Testing, [2]Humboldt University

Wednesday Morning, *Room 103C*
MACROMOLECULAR BIOPHARMACEUTICALS: RECENT TRENDS AND NEW ANALYTICAL CHALLENGES
Organizer: Rina Dukor; Presider: Laurence A. Nafie

10:20 (502) **Use of Biophysical Testing in Biosimilar Development**; Bryan Bernat[1], Asok Sen[1], Yangshang Wei[1], Jenny Gao[1]; [1]Hospira

10:40 (503) **Denaturation of Therapeutic Proteins Studied by Deep UV Resonance Raman Spectroscopy**; Liwei Yuan[1], Sergey Arzhantsev[1], Vincent Vilker[1], John Kauffman[1]; [1]US Food and Drug Administration

11:00 (504) **Raw Material Characterization for Biopharmaceutical Process Development: Adaptation Drivers and Measurement Approaches**; Maureen Lanan[1], Amr Ali[1], Jessica Mondia[1], Pavel Landsman[1]; [1]Biogen Idec

11:20 (505) **Raman Spectroscopic Characterization of Protein Structure in Lyophilized States**; Yemin Xu[1], Christopher Carpenter[1], Rina Dukor[2], John Carpenter[3], Theodore Randolph[1]; [1]University of Colorado Boulder, [2]BioTools, [3]University of Colorado Denver

11:40 (506) **Probing Higher-Order Structure in Protein Pharmaceuticals using Infrared and Raman Vibrational Optical Activity**; Laurence A Nafie[1,2], Rina K Dukor[2]; [1]Syracuse University, [2]BioTools, Inc.

Wednesday Morning, *Room 103D*
CONTRIBUTED PAPERS IN INSTRUMENT DEVELOPMENT AND SENSOR DESIGN
Organizer: Michael George; Presider: Gurjit Mandair

10:20 (507) **Tunable High-Resolution Atomic and Molecular Spectroscopy Inside and Outside the Laboratory -- at Ranges to 80 km**; Marc Klosner, Andrew Grimes, Gary Chan, Chunbai Wu, John Walling, Donald Heller; [1]Light Age, Inc.

10:40 (508) **Fluorescence Correlation Spectroscopy Used to Study Confinement-Induced Anomalous Macromolecular Transport in Nanochannels**; Dane Grismer[1], Sneha Polisetti[1], Paul Bohn[1]; [1]University of Notre Dame

11:00 (509) **Simultaneous Determination of Concentration and Extinction Coefficient by All-Optical Methods**; David Jonas[1], Byungmoon Cho[1], Vivek Tiwari[1]; [1]University of Colorado at Boulder

11:20 (510) **Cleaning, Replicating and Protecting Diffraction Gratings with First Contact Polymer**; James Hamilton[1]; [1]Photonic Cleaning Technologies

11:40 (511) **A Novel Hydrogen Peroxide Biosensor Based on Adsorption of Horseradish Peroxidase onto a Nanobiomaterial Composite Modified Glassy Carbon Electrode**; Nana Agyei[1], Mambo Moyo[2], Jonathan Okonkwo[2]; [1]University of Limpopo, [2]Tshwane University of Technology

Wednesday Afternoon, *Room 101A*
COHERENT TWO-DIMENSIONAL SPECTROSCOPY II
Organizers: Wei Zhao and Junrong Zheng; Presider: Peter Chen

1:20 (512) **A New Technique for Surfaces and Interfaces: 2D SFG Spectroscopy**; Martin Zanni[1]; [1]University of Wisconsin-Madison

1:40 (513) **Ultrafast Infrared Spectroscopy of Charge Generation, Trapping, and Transport in Emerging Photovoltaic Materials**; John Asbury[1], Ryan Pensack[1], Kwang Jeong[1]; [1]Pennsylvania State University

2:00 (514) **Dual-Frequency Two-Dimensional Infrared Spectroscopy of Conjugated Molecular Vibrations**; Nien-Hui Ge, Hiroaki Maekawa[1], Soohwan Sul[1]; [1]University of California, Irvine

2:20 (515) **Vibrational Energy Transfers in Condensed Phases**; Junrong Zheng[1]; [1]Rice University

2:40 (516) **Fully Coherent Hybrid Raman-IR Multidimensional Spectroscopies**; Erin Boyle[1], Nathan Neff-Mallon[1], Andrei Pakoulev[1], John Wright[1]; [1]UW - Madison

Wednesday Afternoon, *Room 101B*
ANALYTICAL LIBS
Organizer and Presider: Jose Almirall

1:20 (517) **Laser-Induced Breakdown Spectrometry (LIBS) for the Determination of Macro- and Micronutrients in Plants**; Francisco José Krug[1], Dário Santos Jr[2], Lidiane Cristina Nunes[1], Marcelo Guerra[1], Gabriel Carvalho[1], Marcos Gomes[1, 3]; [1]Centro de Energia Nuclear na Agricultura-Universidade de São Paulo, Piracicaba-SP, Brazil, [2]Centro de Ciências Exatas e da Terra-Universidade Federal de São Paulo, Diadema-SP, Brazil, [3]Departamento de Química, Universidade Federal de São Carlos, São Carlos-SP, Brazil

1:40 (518) **Laser Induced Breakdown Spectroscopy for the Quantitative Analysis of Microdrops and Aerosols**; Erica Cahoon[1,2], Jose Almirall.[1]; [1]Florida International University, [2]High Purity Standards

2:00 (519) **Forensic Applications of Laser Induced Breakdown Spectroscopy (LIBS)**; Tatiana Trejos[1], Jose Almirall[1], Kiran Subedi[1]; [1]Florida International University

2:20 (520) **Fundamental Understanding of the Dependence of the LIBS Signal Strength on the Complex Focusing Dynamics of Femtosecond Laser Pulses Either Side of Focus**; Craig Zuhlke[1], John Bruce III[1], Troy Anderson[1], Dennis Alexander[1], Christian Parigger[2]; [1]University of Nebraska-Lincoln, [2]University of Tennessee

2:40 (521) **Sparse Bayesian Inference of LIBS Spectra for Elemental Analysis**; Peter Torrione[1], Leslie Collins[1], Kenneth Morton[1]; [1]Duke University

Wednesday Afternoon, *Room 101C*
FAST LC: HONORING *LCGC* EMERGING LEADER IN CHROMATOGRAPHY AWARD WINNER DAVY GUILLARME
Organizer: Fred LaPlant; Presider: Michael Yurkovich

1:20 (522) **Innovative Strategies for the Analysis of Pharmaceutical Compounds**; Davy Guillarme[1], Szabolcs Fekete[1], Aurelie Periat[1], Alexandre Grand-Guillaume Perrenoud[1], Serge Rudaz[1], Jean-Luc Veuthey[1]; [1]University of Geneva

2:00 (523) **A Novel Optimization Strategy for Multi-Segment Gradient Method Development Based on the One-Segment-Per-Component Strategy**; Gert Desmet[1], Eva Tyteca[1], Kim Vanderlinden[1]; [1]Vrije Universiteit Brussel

2:20 (524) **Technological Improvements Enabling New Levels of Efficiency in UHPLC: 1.3 µm Core-Shell Particles**; Jason Anspach[1], A. Carl Sanchez[1], Tivadar Farkas[1]; [1]Phenomenex

2:40 (525) **Genotoxic Impurities Analysis and Control Strategies in Pharmaceutical Development**; Archana Kumar[1], Kelly Zhang[1], Larry Wigman[1]; [1]Genentech Inc.

TECHNICAL PROGRAM – WEDNESDAY
Orals 1:20 – 3:00 pm

Wednesday Afternoon, *Room 102A*
TERAHERTZ SPECTROSCOPY AND IMAGING
Organizer and Presider: Masahiko Tani

1:20 (526) **Chemical Imaging of Pharmaceutical Cocrystals Using Terahertz Spectroscopy**; Katsuhiro Ajito[1], Jae-Young Kim[1], Danielle M. Charron[1], Yuko Ueno[1]; [1]NTT Microsystem Integration Laboratories

1:40 (527) **Terahertz Spectroscopy on Condensed Phases; Molecular Crystals, Proteins, and Aqueous Solutions**; Keisuke Tominaga[1,2], Ohki Kambara[1,2], Feng Zhang[3], Jun-ichi Nishizawa[1,3], Tetsuo Sasaki[1,4], Houng-Wei Wang[4], Michitoshi Hayashi[1,2,4], Naoki Yamamoto[2], Haruka Iguchi[2], Atsuo Tamura[2]; [1]Shizuoka University, [2]Kobe University, [3]Sophia University, [4]National Taiwan University

2:00 (528) **The Role of Spectrally Resolved Measurements in THz Medical Imaging**; Zachary Taylor[1], Shijun Sung[2], Neha Bajwa[1], James Garritano[1], Bryan Nowroozi[4], Sophie Deng[3], Jean-Pierre Hubschman[3], Erik Dutson[4], Warren Grundfest[1]; [1]UCLA Bioengineering, [2]UCLA Electrical Engineering, [3]UCLA Ophthalmology, [4]UCLA Sugery

2:20 (529) **Investigations of Crystallinity by THz 2D Correlation Spectroscopy and Heterospectral Spectroscopy**; David Heaps[1], Xiao Hua Zhou[1], Richard McKay[1], Mark Sullivan[1], Eiji Kato[1], Edward King[1], Akiyoshi Irisawa[2], Motoki Imamura[2]; [1]Advantest America, Inc., [2]Advantest Corporation

2:40 (530) **Chemometrics as a Tool to Explore Hydration Shell of Molecules with Terahertz Spectroscopy in a Microfluidic Device**; Ludovic Duponchel[1], Simon Laurette[2], Anthony Treizebre[2], Bertrand Bocquet[2]; [1]LASIR, University of Lille, France, [2]IEMN, University of Lille, France

Wednesday Afternoon, *Room 102B*
ANALYTICAL SCIENCE APPLICATIONS IN BURNS, TRAUMA AND WOUND CARE
Organizer and Presider: Nicole J. Crane

1:20 (531) **Battlefield to Bench: Understanding the Role of Technology in Clinical Decision Making**; Eric Elster[1,2]; [1]Uniformed Services University of Health Sciences, [2]Naval Medical Research Center

1:40 (532) **Current Models of Burn Injury and the Development of Novel Characterization Modalities for Burn Wounds**; Jonathan Peterson[1], Katherine Cilwa[2], Francis Esmonde-White[2], Benjamin Levi[1], Stewart Wang[1], Michael Morris[2]; [1]Department of Surgery, University of Michigan Medical School, [2]Department of Chemistry, University of Michigan

2:00 (533) **Toward Non-Invasive Raman Spectroscopy of Pathological Mineralization in Diabetic Foot Wounds**; Karen Esmonde-White[1], Francis Esmonde-White[2], Michael Morris[2], Blake Roessler[1]; [1]University of Michigan Medical School, [2]University of Michigan

2:20 (534) **Optical Spectroscopy Devices for Assessing Wound Healing and Formation**; Joshua Samuels[1], Michael Weingarten[2], Michael Neidrauer[1], Leonid Zubkov[1], Peter Lewin[1]; [1]Drexel University-School of Biomedical Engineering, [2]Drexel University-College of Medicine, Surgery

2:40 (535) **Stand Off Chemical Detection of Contaminated Skin using IR Hyperspectral Imaging**; Oliver Payne[1], Christopher Howle[1], Benjamin Alexander[1], Linda Lee[1], Rhea Clewes[1], Phillippa Spencer[1] [1]DSTL

Wednesday Afternoon, *Room 102C*
SERS – STATE OF THE ART BY THE ARTISTS
Organizer and Presider: Duncan Graham

1:20 (536) **Aptamer-enabled SERS Detection of Staphylococcus Aureus**; Peter Vikesland[1], Weinan Leng[1], Maria Virginia Prieto Riquelme[1], Amy Pruden[1]; [1]Virginia Tech

1:40 (537) **A Quantitative TERS Bioassay for Protein at the Tip of an AFM Cantilever**; Jean-Francois Masson[1], Rita Faid[1], Helene Yockell-Lelievre[1], Felix Lussier[1], Maxime Couture[1], Hugo-Pierre Poirier-Richard[1]; [1]Universite de Montreal

2:00 (538) **Quantification of Xenobiotics and Their Metabolites using SERS**; Roy Goodacre[1], Omar Alharbi[1], Graham Kenyon[1], Samuel Mabbott[1,2], David Cowcher[1], Yun Xu[1], Elon Correa[1]; [1]University of Manchester, [2]University of Strathclyde

2:20 (539) **Dynamic Raman Scattering: Studying Anomalous SERS effects**; Keith Carron[1,2], Brandon Scott[2]; [1]Snowy Range Instruments, [2]University of Wyoming

2:40 (540) **SERS Analysis in Blood**; Christy Haynes[1], Antonio Campos[1]; [1]University of Minnesota

Wednesday Afternoon, *Room 102D*
MAKING THE MOST OF SPECTRAL AND OTHER PROCESS ANALYSIS DATA
Organizer and Presider: Alison Nordon

1:20 (541) **Enhancing Process Understanding in the Pharmaceutical Industry through Chemometric Data Analysis**; Allyson McIntyre[1], Richard Hart[1], Nicholas Pedge[1]; [1]AstraZeneca

1:40 (542) **Monitoring Plutonium Reprocessing Despite Disproportionation and Complexation: uni- and Multivariate Approaches**; Robert Lascola[1], Edward Kyser[1], Patrick O'Rourke[1]; [1]Savannah River National Laboratory

2:00 (543) **Improving Confidence in FT-IR Analysis by Using Multiple Spectral Techniques**; Steve Lowry[1], Garry Ritter[1]; [1]Thermo Fisher Scientific

2:20 (544) **Applying Process Analytical Technology (PAT) Tools to Early Active Pharmaceutical Ingredient (API) Development**; Shelly Li[1], Tasneem Patwa[1], Mengtan Zhang[1], Shane Eisenbeis[1], Michael Coutant[1]; [1]Pfizer Inc

2:40 (545) **Methods for Weighted Outlier Detection**; Mark Dewar, Suresh Thennadil[1], Alison Nordon[1], Craig Herdsman[2], Edo Becker[2]; [1]Strathclyde University, [2]BP Hull

Wednesday Afternoon, *Room 102E*
SAS'S LESTER W. STROCK AWARD HONORING RICHARD RUSSO: ISOTOPE MEASUREMENTS IN LASER PLASMAS
Organizer and Presider: Richard E. Russo

1:20 (546) **High-Resolution Laser Absorption Spectroscopy of Isotopes in Atmospheric-Pressure Laser Induced Plasmas**; Mark Phillips[1], Nicholas Taylor[1]; [1]Pacific Northwest National Laboratory

1:40 (547) **A Computer Simulation Study for Improving Isotopic Determination of Uranium by Atomic Emission Spectrometry**; George Chan[1], Xianglei Mao[1], Inhee Choi[1], Arnab Sarkar[1,2], Richard Russo[1]; [1]Lawrence Berkeley National Laboratory, [2]Bhabha Atomic Research Centre

2:00 (548) **Femtosecond and Nanosecond Laser Ablation Molecular Isotopic Spectrometry of Nuclear Materials**; Igor Jovanovic[1], Phyllis Ko[1], Jessica McNutt[1], Kyle Hartig[1]; [1]Pennsylvania State University

2:20 (549) **Carbon Isotope Separation and Molecular Formation in Laser-Induced Plasmas by Laser Ablation Molecular Isotopic Spectrometry (LAMIS)**; Meirong Dong[1,2], Xianglei Mao[1], George Chan[1], Jhanis Gonzalez[1], Jidong Lu[2], Richard Russo[1]; [1]Lawrence Berkeley National Laboratory, University of California, [2]School of Electric Power, South China University of Technology

2:40 (550) **Laser Ablation Molecular Isotopic Spectrometry for Rare Isotopes of the Light Elements**; Alexander A. Bol'shakov[1], Xianglei Mao[2], Arnab Sarkar[2], Dale L. Perry[2], Richard E. Russo[1, 2]; [1]Applied Spectra , [2]Lawrence Berkeley National Laboratory

Wednesday Afternoon, *Room 103B*
SURFACE ANALYSIS OF ORGANIC AND PHARMACEUTICAL MATERIALS
Organier and Presider: Anna Belu

1:20 (551) **Nanoscale and Surface Characterization of Biomaterials**; Greg Haugstad[1]; [1]University of Minnesota

1:40 (552) **Depth Profiling of OLED Materials by Cluster Ion Beams**; Sankar Raman[1], John Moulder[1], Scott Bryan[1], John Hammond[1], Nicholas Erickson[2], Russell Holmes[3]; [1]Physical Electronics, [2]Department of Electrical and Computer Engineering, University of Minnesota, [3]Department of Materials Science, University of Minnesota

2:00 (553) **A Multi-Technique Analytical Approach to Designing the Surface of a Hydrogel Biomaterial for Ophthalmic Applications**; Daniel Hook[1]; [1]Bausch + Lomb

2:20 (554) **Investigation of Inhalation Ordered Mixtures using Time-of-Flight Secondary Ion Mass Spectrometry (TOF-SIMS)**; Mark Nicholas[1], Marja Savolainen[1], Carl Roos[1], Mats Joseflson[1], Magnus Fransson[1], Kyrre Thalberg[1]; [1]AstraZeneca R&D

2:40 (555) **Application of Surface Characterization Techniques in Pharmaceutical and Biopharmaceutical Development**; Xia Dong; [1]Eli Lilly and Company

Wednesday Afternoon, *Room 103C*
PHARMACEUTICAL APPLICATIONS OF NEAR INFRARED SPECTROSCOPY
Organizers and Presiders: Benoît Igne and Robert Bondi

1:20 (556) **Evaluation of an Ultra-compact NIR Spectrometer for Pharmaceutical Product and Process Monitoring**; Dongsheng Bu[1], Boyong Wan[1], Gary McGeorge[1], Doug Both[1]; [1]Bristol-Myers Squibb

1:40 (557) **Optimization of FT-NIR Instrument Parameters on the Performance of a Content Uniformity Method: A Multivariate Figure of Merit Study**; Zhenqi Shi[1], Greg Doddridge[1]; [1]Eli Lilly and Company

2:00 (558) **Monitoring, Online and in Real Time, the Coating of an Active Solution onto Tablets by Near Infrared Spectroscopy**; Benoit Igne[1], Hiroaki Arai[2], Hanzhou Feng[1], James Drennen[1], Carl Anderson[1]; [1]Duquesne University, [2]Daiichi Sankyo Co., LTD

2:20 (559) **Regulatory View of NIR Implementation in Pharmaceutical Industry**; Bogdan Kurtyka[1]; [1]Food and Drug Administration

2:40 (560) **Finished Product Identity Testing of a Pharmaceutical Dosage Form with API at a Low Concentration Using Reflectance Near Infrared Spectroscopy**; Jerry Jin[1]; [1]Actavis

Wednesday Afternoon, *Room 103D*
VIBRATIONAL SPECTROSCOPY IN PHARMACEUTICAL ANALYSIS
Organizer and Presider: Don Pivonka

1:20 (561) **Towards Stimulated Raman Scattering for Cell Type Differentiation**; Matthew Kole[1], Matthew Schulmerich[1], Sarah Holton[1], Rohit Bhargava[1, 2, 3]; [1]Department of Bioengineering and Beckman Institute for Advanced Science and Technology, University of Illinois at Urbana-Champaign, Urbana, IL, [2]Department of Electrical and Computer Engineering, University of Illinois at Urbana-Champaign, Urbana, IL, [3]University of Illinois Cancer Center, University of Illinois at Urbana-Champaign, Urbana, IL

1:40 (562) **Application of Terahertz Chemical Imaging to Pharmaceutical Coating: Evaluation of a Tableted Immediate Release Dosage**; Thomas Hall[1], Dawn Herrick[1], Kristine Beaulieu[1], Charles Kish[1]; [1]Pfizer Consumer Healthcare

2:00 (563) **Quality by Design and Spectroscopy: A Perfect Match**; John Wasylyk[1], Ming Huang[1], Robert Wethman[1], Daniel Hallow[1], Douglas Mcleod[1]; [1]Bristol-Myers Squibb Co

2:20 (564) **Twists and Turns: VCD Chiral Assignment of Atropisomers in Drug Discovery**; Steven Wesolowski[1], Don Pivonka[2]; [1]AstraZeneca, [2]Incyte

2:40 (565) **Infrared and Raman Analysis of Polymorph Content in Early Development**; Don Pivonka[1], William Rocco[1]; [1]Incyte Corporation

Wednesday Afternoon, *Room 101A*
COHERENT TWO-DIMENSIONAL SPECTROSCOPY III
Oganizers: Wei Zhao and Junrong Zheng; Presider: Junrong Zheng

3:50 (566) **Exciton and Biexciton Dynamics in CdSe/ZnS Nanoparticles by Two-Dimensional Kinetics**; Mark Berg[1], Kalyanasis Sahu[1], Haorui Wu[1]; [1]Department of Chemistry and Biochemistry, University of South Carolina

4:10 (567) **Water on the Edge: Hydrogen Bonding through the Eyes of Vibrational Spectroscopy**; Alexander Benderskii[1]; [1]University of Southern California

4:30 (568) **Ballistic Energy Transport in Oligomers**; Igor Rubtsov[1], Natalia Rubtsova[1], Zhiwei Lin[1]; [1]Tulane University

4:50 (569) **The Effect of Ion Pairing on the Dynamics and Spectroscopy of the Strong Electrolyte Solutions**; Wei Zhuang[1]; [1]Dalian Institute of Chemical Physics

5:10 (570) **Ultrabroadband Two-Dimensional Electronic Spectroscopy of Coupled Semiconducting Carbon Nanotube Thin Films**; Thomas McDonough[1], Randy Mehlenbacher[1], Maksim Grechko[1], Meng-Yin Wu[1], Michael Arnold[1], Martin Zanni[1]; [1]University of Wisconsin-Madison

Wednesday Afternoon, *Room 101B*
LIBS-PLUS
Organizer and Presider: Christopher Stipe

3:50 (571) **Laser Ablation-Laser Induced Breakdown Spectroscopy (LA-LIBS) for the Measurement of Total Elemental Concentration in Soils**; Alejandro Molina[1], Jhon Pareja[1], Sebastian López[1], David W Hahn[2], Daniel Jaramillo[1]; [1]Universidad Nacional de Colombia - Sede Medellín, [2]University of Florida

4:10 (572) **Effect of Solid Substrates on Reproducibility of LIBS Measurements**; Sergey Mozharov[1], Brian Marquardt[1]; [1]University of Washington

4:30 (573) **Comparative Study of Laser Induced Breakdown Spectroscopy (LIBS) and Laser Ablation Molecular Isotopic Spectroscopy (LAMIS)**; Krishna Kanth Ayyalasomayajula[1], Herve Sanghapi[1], Bader Alfarraj[1], Fang Yueh[1], Jagdish Singh[1, 2], Dustin McIntyre[3]; [1]Institute for Clean Energy Technology, Mississippi State University, [2]JPS Advanced Technology LLC , [3]U.S. Department of Energy, National Energy Technology Laboratory

4:50 (574) **Mechanisms Leading to Signal Enhancement in NIR fs-fs and NIR ns-ns Double-Pulse Laser-Induced Breakdown Spectroscopy**; Prasoon Diwakar[1], Sivanandan Harilal[1], Ahmed Hassanein[1]; [1]Center for Materials Under eXtreme Environment, School of Nuclear Engineering, Purdue University

5:10 (575) **Characterization of Single and Double Pulse LIBS with Nd:YAG and CO_2 lasers for Improving Signal-To-Noise Ratio**; Justin Freeman[1], Prasoon Diwakar[1], Sivanandan Harilal[1], Ahmed Hassanein[1]; [1]Purdue University

Wednesday Afternoon, *Room 101C*
UV RAMAN SPECTROSCOPY INSTRUMENTATION DEVELOPMENT AND APPLICATION
Organizer and Presider: Igor K. Lednev

3:50 (576) **UV Resonance Raman (UVRR) Examines the Fibril Structure of a Model Polyglutamine Peptide, D2Q10K2**; Sanford Asher[1], David Punihaole[2], Liqi Feng[1], Jonathan Weisberg[1]; [1]Department of Chemistry, University of Pittsburgh, [2]Molecular Biophysics & Structural Biology Graduate Program, University of Pittsburgh

4:10 (577) **Advanced Instrumentation for Deep UV Raman Spectroscopy and Microscopy**; Vladislav Yakovlev[1], Georgi Petrov[1], Maria Troyanova-Wood[1]; [1]Texas A&M University

4:30 (578) **Resonance Raman Intensity Analysis of $ClNO_2$ in Methanol**; Sophia Hayes[1], Marilena Trimithioti[1]; [1]University of Cyprus

4:50 (579) **Exploring Membrane Protein Structure in the Context of Lipid Type, Protein Sequence and Protein-Protein Interactions by dUVRR**; Jason Cooley[1], Mia Brown[1], Michael Eagleburger[1], Iban Ubarrextena-Bilandia[2], Anna Klass[1], Jian Xiong[1], Renee JiJi[1]; [1]University of Missouri, [2]Icahn Mt. Sinai Medical School

5:10 (580) **UV Raman Spectroscopy as a Probe of Structure and Dynamics of Amyloid Fibrils**; Igor Lednev[1], Dmitry Kurouski[1]; [1]University at Albany, SUNY

Wednesday Afternoon, *Room 102A*
TERAHERTZ SPECTROSCOPY AND IMAGING
Organizer and Presider: Axel Zeitler

3:50 (581) **Terahertz Spectroscopy of Hydrogen-Bonded Glass-Forming Liquids**; Juraj Sibik[1], Axel Zeitler[1]; [1]University of Cambridge

4:10 (582) **Observation of the Structural Evolution of Chemical Compounds using THz-TDS**; Edward Parrott[1], Axel Zeitler[2], Emma Pickwell-MacPherson[1]; [1]Department of Electronic Engineering, The Chinese University of Hong Kong, [2]Department of Chemical Engineering and Biotechnology, University of Cambridge

4:50 (583) **Sweet Things are Made of This**; Philip Taday[1]; [1]TeraView

5:10 (584) **Detecting Early Onset of Crystallization in Pharmaceuticals using a low Frequency High Throughput Raman Spectrometer**; Keith Gordon[1], Sara Fraser[1], Matthew Reish[1], May Mah[1], Clare Strachan[2]; [1]University of Otago, [2]University of Helsinki

Wednesday Afternoon, *Room 102B*
SPECTRAL ANALYSIS OF PATHOGENS
Organizer and Presider: Karen Esmonde-White

3:50 (585) **Advances in Microbiological Identification Technologies**; Bradford Clay[1]; [1]bioMerieux, Inc.

4:10 (586) **Novel Platforms for SERS-Based Sensing of Infectious Disease**; Richard Dluhy[1]; [1]University of Georgia

4:30 (587) **Spectroscopy Characterization of Complex Particles: Applications to Biological Systems**; Luis H. Garcia-Rubio, Debra E. Huffman, Yulia M. Serebrennikova, Jennifer M. Smith; [1]Claro Scientific LLC.

4:50 (588) **Raman Spectroscopy as a Tool for Pathogen Identification in Clinical *in-vitro*-Diagnostics and Environmental Control: Discrimination Power and Robustness**; Denis Leroux[1], Isabelle Espagnon[2], Frédéric Mallard[1], Florian Michel[1], Denis Ostrovskii[1], Brad Clay[1], Charlene Gayrard[1], Pierre Joly[2], Armelle Novelli-Rousseau[1]; [1]bioMérieux S. A., [2]CEA, LIST

5:10 (589) **Approaching Big Data in Biological Research Imaging Spectroscopy with Novel Compression**; Jason Morrison[1], Yixuan Chen[1]; [1]University of Manitoba

Wednesday Afternoon, *Room 102C*
NOVEL RAMAN TECHNIQUES
Organizers and Presiders: Ian R. Lewis, Duncan Graham and Pavel Matousek

3:50 (590) **Scanning Angle Raman Spectroscopy: Measurements of Polymer Film Thickness, Composition and Structure**; Emily A. Smith[1,2], Vy H.T. Nguyen[1, 2], Jonathan Bobbitt[1, 2], Matthew Meyer[1, 2]; [1]U.S. D.O.E., The Ames Laboratory, [2]Iowa State University

4:10 (591) **Overcoming Sampling Limitations in Handheld Raman for Pharmaceutical and Bulk Samples**; Yvette D. Mattley[1], Michael W. Allen[1] ; [1]Ocean Optics, Inc.

4:30 (592) **Novel Accurate Method for Orientation Quantification using Polarized Raman Spectroscopy**; Marie Richard-Lacroix[1], Christian Pellerin[1]; [1]University of Montreal

4:50 (593) **Low-frequency Raman and Terahertz Spectroscopies and Quantum Chemical Calculation Studies on Temperature-Dependent Structural Changes in Nylon 6**; Yukihiro Ozaki[1], Erika Onishi[1], Harumi Sato[2], Shigeki Yamamoto[3], Kummetha Reddy[1], Daitaro Ishikawa[1], Shinya Ishii[4], Hal Suzuki[4], Hiromichi Hoshina[4], Yusuke Morisawa; [1]Kwansei Gakuin University, [2]Kobe University, [3]Osaka University, [4]RIKEN

5:10 (594) **Detection of Chemical Nerve Agent Simulants using Flexible, Porous SERS-active Substrates**; Aaron D. Strickland[1], Robert Diaz-Morales[1], Michael J. Canfield[1]; [1]iFyber

Wednesday Afternoon, *Room 102D*
CONTRIBUTED PAPERS IN RAMAN SPECTROSCOPY
Organzier: Michael George; Presider: Paul Pudney

3:50 (595) **Portable Ultra-High Resolution, Dynamic SERS Imaging System**; Eric Languirand, John Kiser[1], Brian Cullum[1]; [1]University of Maryland

4:10 (596) **Observation of Reaction Kinetics in Self-Assembled Monolayers using Surface- and Tip-Enhanced Raman Spectroscopy**; Evelien van Schrojenstein Lantman[1], Arjan Mank[4], Tanja Deckert-Gaudig[3], Onno Gijzeman[1], Volker Deckert[2, 3], Bert Weckhuysen[1]; [1]Utrecht University , [2]Friedrich-Schiller University Jena, [3]Institute of Photonic Technology, [4]Philips Innovation Services

4:30 (597) **Effect of Ionization of Thiophenol on the Mechanism of Heterogeneous Adsorption on Gold Substrates by Surface-Enhanced Raman Spectroscopy**; Ashish Tripathi[1], Erik Emmons[1], Steven Christesen[2], Augustus Fountain[2], Jason Guicheteau[2]; [1]Science Applications International Corporation, [2]USA RDECOM Edgewood Chemical Biological Center

4:50 (598) **Tracing the Extent of Chemical Warfare Agent Decontamination Reactions Using Raman Spectroscopy**; Emmons Erik[1], Ashish Tripathi[1], Michael Ellzy[2], Jason Guicheteau[2], Ai Sohrabi[2], Steven Christesen[2]; [1]Science Applications International Corporation, Gunpowder Branch, [2]USA RDECOM Edgewood Chemical Biological Center

5:10 (599) **Terahertz Raman of Nano Metal Oxides and Chalcogenides**; James Hamilton[1], Jorge Camacho[1], Neelanjan Bhattacharya[1], Ethan Becker[1]; [1]University of Wisconsin-Platteville

5:30 (600) **Transmission Raman Spectroscopy and Low-Frequency Option: Development of Applications**; Renata Lewandowska[1], Vincent Larat[1], Ophelie Lancry[1], Catalina David[1]; [1]HORIBA Scientific

Wednesday Afternoon, *Room 102E*
REAL-WORLD APPLICATIONS OF SURFACE ANALYSIS
Organizer and Presider: Anna Belu

3:50 (601) **Chemical Imaging of Surface Chemistry in an Industrial Environment**; Michaeleen Pacholski[1]; [1]The Dow Chemical Company

4:10 (602) **Selected Industrial Applications of X-Ray Photoelectron Spectroscopy**; Derrick Poirier[1]; [1]3M

4:30 (603) **Secondary Ion Mass Spectrometry (SIMS) as a Practical, Applied Surface Analysis Method**; Paul Vlasak[1], Steven Pachuta[1]; [1]3M Company

4:50 (604) **Nanomechanical Testing: Tools, Techniques, and Real-World Applications**; Jeffrey Schirer[1]; [1]Hysitron, Inc.

5:10 (605) **Closing the Loop on Catalyst Design – XPS as a Tool to Probe Catalyst Tuning in Ionic Liquids**; Peter Licence[1]; [1]University of Nottingham

Wednesday Afternoon, *Room 103B*
NEW INSTRUMENTATION AND NEW APPROACHES AT THE FRONTIER OF ATOMIC SPECTROSCOPY
Organizer and Presider: Carsten Engelhard

3:50 (606) **Towards an Expert System for Inductively Coupled Plasma-Atomic Emission Spectrometry: An Automated Statistical Protocol for Flagging Matrix Interferences**; George Chan[1], Gary Hieftje[1]; [1]Department of Chemistry, Indiana University

4:10 (607) **Microwave Induced Plasma Source for Optical Emission and Mass Spectroscopy**; Jovan Jevtic[1], Ashok Menon[2], Velibor Pikelja[2]; [1]Milwaukee School of Engineering, [2]Radom Corporation

4:30 (608) **Spatially Resolved Fully Simultaneous Determination of Large Numbers of Isotope Concentrations and Isotope Ratios by LA-MH-ICP-MS**; Willi Barger, Dirk Ardelt[1], Maurice Reijnen[1], Oliver Primm[1]; [1]SPECTRO Analytical Instruments GmbH

4:30 (609) **The Liquid Sampling-Atmospheric Pressure Glow Dicharge-More Than Just a Toy**; R, Kenneth Marcus[1], Benjamin T. Manard[1], Richard E. Russo[2], Jhanis Gonzalez[2], David W. Koppenaal[3]; [1]Clemson University, [2]Lawrence Berekely National Laboratory, [3]Pacific Northwest National Laboratory

5:10 (610) **From Sample Dilution to Matrix Removal and Purification: Automating Sample Preparation for ICPOES, ICPMS and MC-ICPMS**; Paul Field[1], Patrick Sullivan[1]; [1]Elemental Scientific, Inc

Wednesday Afternoon; *Room 103C*
INDUSTRIAL APPLICATIONS OF SPECTROSCOPY
Organizer and Presider: Gloria Story

3:50 (611) **Optimization and Application of Sensitivity-Enhanced Transmission Raman Spectroscopy**; Michael Pelletier; [1]Pfizer

4:10 (612) **Vibrational Spectroscopy in the Field**; Luisa T.M. Profeta[1], Corrie L. Carnes[1], Jon D. Onstot[1]; [1]MRIGlobal

4:30 (613) **Handheld Spectrometers: the State of the Art**; Richard Crocombe[1]; [1]Thermo Fisher Scientific

4:50 (614) ***In-Vivo* Optical Spectroscopy in Skin and Cosmetic Research**; Tom Cambron[1], Joe Kaczvinsky[1]; [1]The Procter and Gamble Co.

5:10 (615) **Near Infrared Hyper-spectral Imaging for Controlling the Quality of Large Scale Transdermal Drug Manufacturing**; Benoit Igne[1], Carl Anderson[1], James Drennen[1]; [1]Duquesne University

Wednesday Afternoon, *Room 103D*
BIOANALYTICAL APPLICATIONS OF PLASMONICS
Organizer: Jean-Francois Masson; Presider: Amanda Haes

3:50 (616) **Calcinated Gold Particle Nanofilms for Surface Enhanced Optical Sensing and MS Analysis**; Quan Cheng[1], Chih-yuan Chen[1], Sam Hinman[1]; [1]University of California Riverside

4:10 (617) **Plasmonic Nanorings for Biosensing and Materials Applications**; Kyunghee (Mike) Cho[1], Mana Toma[1], Gabriel Loget[1], Jennifer Wood[1], Aaron Halpern[1], Robert Corn[1]; [1]UC Irvine

4:30 (618) **Plasmonic Interaction with a Single Nanoparticle and-a Nanohole Array**; Karl Booksh[1], Laurel Kegel[1]; [1]University of Delaware

4:50 (619) **Metallic Nanoparticles and Surfaces for Surface Enhanced Raman Scattering**; Duncan Graham[1], David Thompson[1], Sam Mabbot[1], Sathkumara Mudalige[1]; [1]University of Strathclyde

5:10 (620) **Nanoparticle-based Competition Immunoassay for Methotrexate Detection in Serum Sample of Chemotherapy Patients**; Jean-Francois Masson[1], Sandy Shuo Zhao[1], Helene Yockell-Lelievre[1], Natalia Bukar[1], Joelle N. Pelletier[1]; [1]Universite de Montreal

TECHNICAL PROGRAM – THURSDAY
Plenary Lectures, Ballroom A
Presider: Jose Almirall

8:00 am – ANACHEM Award
(621) Capillary Electrophoresis for High Throughput Proteomics; **Norman Dovichi**[1], Liangliang Sun[1], Guijie Zhu, Xiaojing Yan[1]; [1]University of Notre Dame

8:30 am – *LCGC* Chromatography Award.
(622) Two-Dimensional Liquid Chromatography. The Future of HPLC; **Peter Carr**, University of Minnesota

THURSDAY POSTER SESSION
9:00 – 10:20 am
102 Foyer

All Thursday posters should be put up between 7:30 – 8:00 am and removed by 5:30 pm

Biological and Bioanalytical Applications

Board #

1 (623) **Improved Breast Cancer Detection from High-Resolution Fourier Transform Infrared (FT-IR) Spectroscopic Imaging**; Rohith Reddy[1], David Mayerich[1], Rohit Bhargava[1]; [1]University of Illinois at Urbana Champaign

2 (624) **CAP-LC and QQQ-ICPMS, for Detecting Phosphorus and Sulfur in DNA-Protein Cross-Links**; Jiawei Gong, Julio Figueroa[1], Morwena Solivio[1]; [1]University of Cincinnati

3 (625) **Mass Spectrometry Based Label-Free Multiplex Mutation Site Genotyping Method by Allele Specific Ligation and Probe Amplification**; Jung Hun Park[1], Ye Lim Jung[1]; [1]KAIST, Republic of Korea

4 (626) **ToF-SIMS as a Tool for Probing Lipid Saturation in Acute Myeloid Leukaemia Cells Treated with a Novel Combination Therapy**; Joanna Denbigh[1], Andrew Southam[2], Farhat Khanim[2], Roy Goodacre[1], Nick Lockyer[1]; [1]Manchester Institute of Biotechnology, University of Manchester, [2]School of Biosciences, University of Birmingham

5 (627) **Using Attenuated Total Reflectance Fourier Transform Infrared Spectroscopy to Optimize Surfaces for the Immobilization of Nanolipoprotein Particles**; Jessica Moore[1], Elyse Towns[1], Craig Blanchette[2], Don Land[1]; [1]UC Davis, [2]Lawrence Livermore National Laboratory

6 (628) **The Automated FADU-Assay to Quantify Formation and Repair of DNA Strand Breaks -A Rapid and Meaningful Genotoxicity Quantification**; Miriam Unger[1], Marcel Pilartz[1], Maria Moreno-Villanueva[2]; [1]CETICS Healthcare Technologies GmbH, Esslingen am Neckar, Germany, [2]Department of Biology, University of Konstanz

7 (629) **Nonlinear Optical (NLO) imaging Approaches for Protein Crystal Detection and Crystal Quality Assessment**; Emma DeWalt[1], Victoria Begue[1], Judith Ronau[1], Shane Sullivan[1], Ryan Muir[1], Chittaranjan Das[1], Garth Simpson[1]; [1]Purdue University

8 (630) **Analysis of the Surface Aggregation of Phospholipids using Attenuated Total Reflectance Fourier Transform Infrared Spectroscopy**; Elyse Towns[1], Donald Land[1], Donald Land[1]; [1]University of California, Davis

Board #

9 (631) **Material and Biological Properties Controlling the Interaction of Bacterial Cells with Nanomaterials**; Ian Gunsolus[1], William Chrisler[2], Dehong Hu[2], Cosmin Mihai[2], Galya Orr[2], Christy Haynes[1], Christy Haynes[1]; [1]University of Minnesota, [2]Pacific Northwest National Laboratory, [3]University of Wisconsin-Madison

Chromatography, Microfluidics and Separation Science

10 (632) **Novel On-Chip Capacitively Coupled Contactless Conductivity Detection using Injected Metal Electrodes**; Leigh D. Thredgold[1], Dmitriy Khodakov[1], Amanda V. Ellis[1], Claire E. Lenehan[2]; [1]Flinders Centre for NanoScale Science and Technology, Flinders University, GPO Adelaide, [2]School of Chemical and Physical Sciences, Flinders University, Adelaide

11 (633) **Screening Method for Oxytetracycline in Muscle and Skin Salmon by derivative Spectroscopy and Its Comparison with Chromatographic Method**; M. Ines Toral[1], Tamara Sabay[1], Pablo Richter[1]; [1]University of Chile

12 (634) **A Response Surface Experimental Design Approach for Optimizing the Analysis of Glyphosate in Aqueous Solutions using Fluorenylmethyloxycarbonyl Chloride (FMOC-Cl) Derivatization and Liquid Chromatography Tandem Mass Spetcrometry (LC-MS/MS**; Misjudeen Raji[1]; [1]King Abdullah University of Science and Technology

13 (635) **Analysis of Wheatgrass Endophytes**; Kimberly Clapp[1], Christine MacTaylor[1]; [1]Salem State University

14 (636) **Determination of Glyoxal, Methylglyoxal and Diacetyl at physiological Concentrations in Urine by HPLC with Fluorimetric Detection, using 4-metoxi-phenylenediamine for Derivatization.**; Armando Gomez[1], Katarzyna Wrobel[1], Alma Corrales[1], Ma. Eugenia Garay Sevilla[1], Kazimierz Wrobel[1]; [1]University of Guanajuato

15 (637) **An Integrated Microfluidic Device for Trapping**; Alaknanda Amin[1], Christine Carlson[1], Jörg Woehl[1]; [1]University of Wisconsin-Milwaukee

16 (638) **Room-Temperature Ionic Liquids: Tunable Solvents for the Removal of Dyestuffs from Aqueous Waste Streams**; Sarah Oplawski[1], Mark Dietz[1]; [1]University of Wisconsin-Milwaukee

17 (639) **Chemical Analysis of Major and Minor Components in Fuel and Hydrocarbon Liquids**; Josef Simeonsson[1], Vamshi Inumula[1], Eric Kennehan[1], Ashley Frazzini[1]; [1]Youngstown State University

Molecular Spectroscopy

Board #

18 (640) **ATR Spectra of Polyethylene Films - Orientation and Crystallinity**; Chris Lynch[1,2], Richard Spragg[1], Ben Perston[1]; [1]PerkinElmer ASLS, Seer Green, HP9 2FX, UK, [2]PerkinElmer Inc., Shelton, CT

19 (641) **AFM-based Chemical and Mechanical Property Characterization of Interconnects in Semiconductors**; Michael Lo[1], Sean King[2], Eoghan Dillon[1], Qichi Hu[1], Roshan Shetty[1], Craig Prater[1]; [1]Anasys Instruments, [2]Intel Corporation

20 (642) **Temperature and Consentration Dependence of Far Ultraviolet Spectra in Alcohol-Hexane Solution ~ Alternation of Hydrogen bonding~**; Yusuke Morisawa[1], Yukihiro Teramoto[1], Yukihiro Ozaki[2]; [1]Kinki University, [2]Kwansei Gakuin University

21 (643) **A Simple Method to Obtain Absorption Spectra at Sub-Micrometer Spatial Resolution using a Transmission Grating Spectrograph**; Dharmendar Kumar Sharma[1], Arindam Chowdhury[1]; [1]Indian Institute of Technology Bombay

22 (644) **Use of Raman and Infrared Spectroscopy to Study the "Fuzzy Chemistry" of the Formation of Iron (III) Hydroxide Polymorphs**; Dale L Perry[1], Nicolaza Pariona[2], Karla I Camacho[2], Arturo I Martinez[2]; [1]Lawrence Berkeley National Laboratory, University of California, Berkeley, [2]Center for Research and Advanced Studies of the National Polytechnic Institute, Cinvestav - Saltillo

23 (645) **Evaluating a Modified NDIR Approach for Measuring Silica on Filter Samples of Coal Dust**; Art Miller[1], Thomas Grant[2], Grant King[1], Tim Nicholes[2], Brett Bollier[2]; [1]CDC/NIOSH, [2]Gonzaga University

24 (646) **Variable-Pathlength Cavity Spectroscopy: Development of a Real-Time Monitoring System**; Ryan A. Schmeling[1], Peter Geissinger[1], Joseph H. Aldstadt[1]; [1]Dept. of Chemistry & Biochemistry, University of Wisconsin-Milwaukee

25 (647) **A Spectroscopy Study of the Transformation of Ferrihydrite to Hematite**; Dale L Perry[3], N. Pariona[1], J. Quispe-Marcatoma[2], U.D. Chacón Hernández[2], W. T. Herrera[2], E. Baggio-Saitovitch[2], Dale L Perry[3], Arturo I. Martinez[1]; [1]Center for Research and Advanced Studies of the National Polytechnic Institute, Cinvestav-Saltillo, [2]Centro Brasileiro de Pesquisas Físicas, Rio de Janeiro, Brazil, [3]Lawrence Berkeley National Laboratory, University of California, Berkeley

26 (648) **Recent Advances in Broadly Tunable & Narrow Linewidth Mid-IR Lasers - Addressing the Varied Needs of Molecular Spectroscopy**; Robert Shine Jr[1], David Arnone[1], Leigh Bromley[1], David Caffey[1], William Chapman[1], Vince Cook[1], Timothy Day[1], Allen Priest[1], Michael Pushkarsky[1]; [1]Daylight Solutions, Inc

27 (649) **Recent Advances in Glow Discharge Optical Spectrometry for the Characterization of Materials**; Patrick Chapon[1], Christophe Morin[1], Philippe Hunault[1]; [1]HORIBA Scientific

Nanotechnology and Materials Characterization

28 (650) **Fabrication of Silver-Mesoporous Silica Core-Shell Nanomaterials and Evaluation of Silver Dissolution: Effects of Different Core Morphologies**; Ashish Datt[1], Ian Gunsolus[1], Maral Mousavi[1], Carlos Perez De Jesus[1], Philippe Buhlmann[1], Christy Haynes[1]; [1]University of Minnesota

Board #

29 (651) **Evaluating the Kinetics of Nanoparticle-Molecular Interactions for Spectroscopy**; Binaya Shrestha[1], Thomas Heiderscheit[1], Amanda Haes[1]; [1]University of Iowa

30 (652) **Measurement of Particulate Carbon Using Laser-induced and Spark Plasma Emission Spectroscopy: Application to Measurement of Airborne Carbon Nanomaterials**; Pramod Kulkarni[1], Lina Zheng[1], M. Eileen Birch[1], Gregory Deye[1], Dionysios Dionysiou[1]; [1]Centers for Disease Control and Prevention

31 (653) **Modeling Heat Transfer through Multiple Interfaces of Differing Phase for Predictive Temperature Cycling Regulation**; Bradley M. Moran[1], Peter Geissinger[1], Jorg C. Woehl[1]; [1]University of Wisconsin-Milwaukee

32 (654) **Immobilizing a DNA Molecule within an Electrostatic Corral**; Xavier Udad[1], Alaknanda Amin-Patel[1], Christine Carlson[1], Jorg Woehl[1]; [1]University of Wisconsin-Milwaukee

33 (655) **Silver Speciation in Commercially Marketed Products Containing Silver Nanoparticles**; Traci Hanley[1], Ryan Saadawi[1], Julio Julio Landero-Figueroa[1], Peng Zhang[1], Joseph Caruso[1]; [1]University of Cincinnati, Department of Chemistry, Cincinnati, OH

34 (656) **Single Molecule Confocal Fluorescence Lifetime Correlation Spectroscopy for Accurate Nanoparticle Size Determination**; Bonghwan Chon[1], Kimberly Briggman[1], Jeeseong Hwang[1]; [1]National Institute of Standards and Technology

Thursday Morning, *Room 101A*
CONTRIBUTED PAPERS IN MOLECULAR SPECTROSCOPY

Organizer: Michael George; Presider: Linda Kidder

10:20 (657) **Standoff Material Characterization by Mid-Infrared Quantum Cascade Laser Reflection Spectroscopy**; Mark Norman[1], John Coates[2]; [1]Block Engineering, [2]Coates Consulting

10:40 (658) **Effects of Particle Size on Infrared Reflectance Spectra**; Tanya Myers[1], Yin-Fong Su[1], Carolyn Brauer[1], Thomas Blake[1], Timothy Johnson[1]; [1]Pacific Northwest National Laboratory

11:00 (659) **Flexible Probes for Process-Spectroscopy**; Viacheslav Artyushenko[1], Alexey Bocharnikov[1], Joachim Mannhardt[1], Tatiana Sakharova[2] ; [1]art photonics GmbH, [2]General Physics Institute of RAN

11:20 (660) **Rapid, Nondestructive Estimation of surface Polymer Layer Thickness using ATR FTIR Spectroscopy and Synthetic Spectra Derived from Optical Principles**; B. Andre Weinstock[1], Christopher Loose[1]; [1]Semprus BioSciences Inc.

11:40 (661) **Electron Solvation Process Examined with Multi-Channel Femtosecond Time-Resolved Near-IR Spectroscopy at 1.0 to 1.5 Micrometer**; Koichi Iwata[1], Setsuka Arii[1], Tomohisa Takaya[1]; [1]Gakushuin University

Thursday Morning, *Room 101B*
THE NEXT FRONTIER: THE FUTURE OF LIBS

Organizers and Presiders: David J. Cremers and Amy J. Bauer

10:20 (662) **Deep Ocean LIBS: Calibration Issues**; Stanley Angel[1], Joseph Bonvallet[1]; [1]Department of Chemistry and Biochemistry, The University of South Carolina

10:40 (663) **Planetary Geochemical Investigations by Raman-LIBS Spectroscopy (RLS)**; Samuel Clegg[1], Roger Wiens[1], Anupam Misra[2], Shiv Sharma[2], Steven Bender[1], Raymond Newell[1], James Lambert[3], Sue Smrekar[3], M. Darby Dyar[1], Sylvestre Maurice[4]; [1]Los Alamos National Laboratory, [2]University of Hawaii, [3]Jet Propulsion Laboratory, [4]Institut de Recherche en Astrophysique et Planétologie

11:00 (664) **Incorporating Laser-Induced Breakdown Spectroscopy (LIBS) into Undergraduate Education**; Daniel Kwasniewski[1,2], Rosemarie Chinni[1]; [1]Alvernia University, [2]University of Southern California

11:20 (665) **Modeling of Trace Elements (Li, Ba, Sr, and Rb) using Curiosity's ChemCam and Early Results for Gale Crater, Mars**; Ann Ollila[1], Horton Newsom[1], Agnes Cousin[2], Roger Wiens[2], Sylvestre Maurice[3], Olivier Gasnault[2], Olivier Forni[3], Jeremie Lasue[3], Anya Rosengooding[4]; [1]University of New Mexico, [2]Los Alamos National Laboratory, [3]Institut de Recherches en Astrophysique et Planétologie, [4]Albuquerque Public High School

11:40 (666) **Analysis of Calcium in CO_2-laden Brine (NaCl-$CaCl_2$) by Laser-induced Breakdown Spectroscopy (LIBS)**; Christian Goueguel, Dustin McIntyre[2], Jinesh Jain[2], Jagdish Singh[3], Athanasis Karamalidis[1]; [1]Carngie Mellon University, [2]USDOE National Energy Technology Laboratory, [3]Mississippi State University

Thursday Morning, *Room 101C*
NANOMATERIALS FOR PLASMONICS I
Organizer and Presider: Jean-Francois Masson

10:20 (667) **Localized Surface Plasmon Resonance Biosensing: Multiplexed Arrays and Single Nanoparticle Tracking**; Richard Van Duyne[1], Julia Ruemmele[1], W. Paige Hall[1], Laura Ruvuna[1], Laura Sagle[1], Julia Bingham[1], Chunming Liu[2], Paul Cremer[2]; [1]Northwestern University, [2]Texas A&M University

10:40 (668) **Bacterial Detection through Combined Siderophore-Based Molecular Recognition and Second-Generation Plasmonics**; Paul W. Bohn[1,2], Yang Yang[1], Sean P. Branagan[1], Cheng Ji[2], Marvin J. Miller[2]; [1]Department of Chemical & Biomolecular Engineering, University of Notre Dame , [2]Department of Chemistry & Biochemistry, University of Notre Dame

11:00 (669) **Location Dependent Localized Surface Plasmon Resonance and Surface Enhanced Raman Spectropy of Gold Nanoplates at the Single Particle Level**; Francis Zamborini[1], Aiqin Fang[1], Lanlan Bao[1], Srinivas Beeram[1]; [1]University of Louisville

11:20 (670) **Plasmonic Metal@Silica Fluorescent Nanoprobes for Biosensing Applications**; Denis Boudreau[1]; [1]Université Laval

11:40 (671) **Detecting Plasmon Resonance Energy Transfer with Differential Interference Contrast (DIC) Microscopy**; Ashley Augspurger[1], Anthony Stender[1], Rui Han[1], Ning Fang[1]; [1]Iowa State University

Thursday Morning, *Room 101D*
WOMEN IN SCIENCE
Organizer and Presider: Ingeborg Iping Petterson

10:20 (672) **Why are Women Underrepresented in Science? Evidence for and against 5 Common Hypotheses**; Karla S. McCain[1]; [1]Austin College

11:00 (673) **A Spectroscopist's Perspective on Working in Government Laboratories**; Nicole Crane[1,2]; [1]Naval Medical Research Center, [2]Uniformed Services University of Health Sciences

11:20 (674) **Building a Successful Spectroscopy Career via a Non-Traditional Path**; Gloria Story[1]; [1]The Procter & Gamble Company

11:40 (675) **How Taking a Risk Changed my Future**; Anna Tisinger[1]; [1]Agilent Technologies

Thursday Morning, *Room 102A*
A SPECTROSCOPIC SLANT ON LAB-ON-CHIP DIAGNOSTICS
Organizers and Presiders: Ishan Barman and Narahara Chari Dingari

10:20 (676) **Computational Microscopy, Sensing and Diagnostics for Telemedicine and Global Health Applications**; Aydogan Ozcan[1]; [1]University of California, Los Angeles

10:40 (677) **Novel on-Chip Biophotonics for Trapping and Imaging**; Kishan Dholakia[1]; [1]University of St Andrews

11:00 (678) **Digital Microfluidic Magnetic Separation for Particle-based Immunoassays**; Alphonsus Ng[1], Kihwan Choi[2], Ryan Fobel[1], Aaron Wheeler[1]; [1]Institute of Biomaterials and Biomedical Engineering, University of Toronto, [2]Department of Chemistry, University of Toronto

11:20 (679) **Ultrasensitive Detection of Dyes and Proteins by Surface-Enhanced Raman Spectroscopy (SERS) in Capillary Electrophoresis (CE)**; Pierre Negri[1], Zachary Schultz[1]; [1]University of Notre Dame

11:40 (680) **SPRi: A Flexible Platform for Diagnostic Signatures in Blood**; Stephen Vance[1], Marinella Sandros[1]; [1]University of North Carolina at Greensboro

Thursday Morning, *Room 102B*
CONTRIBUTED PAPERS IN LIBS AND ATOMIC SPECTROSCOPY
Organizer: Michael George; Presider: Steve Ray

10:20 (681) **Advancement in Low Pressure LIBS Detection of Laser-Induced Confined Plasma**; Soo-Jin Choi[1], Kang-jae Lee[1], Jack Yoh[1]; [1]Seoul National University

10:40 (682) **LIBS: Carbon Swan Plasma Emission Spectroscopy**; Michael Witte[1], Christian Parigger[1]; [1]University of Tennessee Space Institute

11:00 (683) **Direct Analysis of Biodiesel Fuel to Simultaneously Determine Na and K by Tungsten Coil Atomic Emission Spectrometry**; George L. Donati[1], Stacia E. Dancsak[1], Sidnei Silva[2], Joaquim A. Nobrega[2], Bradley T. Jones[1]; [1]Wake Forest University, [2]Federal University of Sao Carlos,

11:20 (684) **Simultaneous Atomic Absorption and Atomic Fluorescence Spectrophotometery for Mercury Determination in Water Samples**; Sumedh Phatak[1,2], David Gunn[1]; [1]Milestone Inc.

11:40 (685) **LIBS: Aluminum Monoxide Emission Measurements**; David Surmick[1], Christian Parigger[1]; [1]University of Tennessee Space Institute

Thursday Morning, *Room 102C*
RAMAN IN BIOCHEMICAL ANALYSIS
Organizers and Presiders: Ian R. Lewis, Duncan Graham and Pavel Matousek

10:20 (686) ***In Vivo* Validation for Transcutaneous Raman Spectroscopy of Bone in Humans**; Francis Esmonde-White[1], Karen Esmonde-White[2], Michael Morris[1]; [1]Dept. of Chemistry, University of Michigan, [2]Dept. of Internal Medecine, University of Michigan Medical School

10:40 (687) **Devising and Comparing the Assessment of Raman Spectroscopic Classification Models for Lesion Discrimination in Freshly Excised Stereotactic Breast Biopsies with Microcalcifications**; Narahara Chari Dingari[1], Ishan Barman[1], Jaqueline Soares[1], Anushree Saha[2], Sasha McGee[2, 4], Wendy Liu[2, 3], Donna Plecha[2, 3], Nina Klein[2,3], Ramachandra Rao Dasari[1], Maryann Fitzmaurice[2]; [1]Massachusetts Institute of Technology, [2]Case Western Reserve University, [3]University Hospitals Case Medical Center , [4]Current Address: University of North Carolina at Chapel Hill

11:00 (688) **Label-free Time-Course Study of Human Embryonic Stem Cells Differentiation by Raman Micro-Spectroscopy**; Flavius C. Pascut[1], Adrian Ghita[1], Spandan Karla[1], Virginie Sottile[1], Chris Denning[1], Ioan Notingher[1]; [1]The University of Nottingham

11:20 (689) **Differentiating Healthy and Cancer Cells Using Surface-Enhanced Raman Scattering**; Mustafa Culha[1], Sevda Mert[1]; [1]Yeditepe University

11:40 (690) **Intermolecular Interaction in Transparent Surfactant Gels Examined Using a Low-wavenumber Raman Microspectrometer**; Ashok Zachariah Samuel[1], Koichi Iwata[1]; [1]Gakushuin University

Thursday Morning, *Room 102D*
THE DIGITAL CRYSTAL BALL
Organizer and Presider: Robert A. Lodder

10:20 (691) **Peering Into the Digital Crystal Ball with Hyperspectral Imaging**; Robert Lodder[1]; [1]University of Kentucky

10:40 (692) **An ApoE Model in Mathematica for BSN272 Metabolism**; Jarrod Williams[1,2]; [1]Biospherics.net, [2]University of Kentucky

11:00 (693) **Some Processes R BEST Modeled in Higher Dimensions**; Andrew Brooks[1]; [1]0trak, [2]University of Kentucky

11:20 (694) **When Does a Nanotechnology Device Become a Drug?**; Jarrod Williams[1]; [1]Biospherics.net, [2]University of Kentucky

11:40 (695) **What Would Turing Say?**; Robert Lodder[1]; [1]University of Kentucky

Thursday Morning, *Room 102E*
2D HPLC: HONORING *LCGC* LIFETIME ACHIEVEMENT AWARD WINNER PETER CARR
Organizer and Presider: Dwight R. Stoll

10:20 (696) **Two-Dimensional Liquid Chromatography: The Future of HPLC?**; Peter Carr[1]; [1]University of Minnesota

11:00 (697) **Characterization of Carbon Nanomaterial Modified Silicas for Use in Two-Dimensional High Performance Liquid Chromatography**; Dwight Stoll[1], Tuan Tran[1], Ian Gibbs-Hall[1], Paul Young[1], John Danforth[1], Jonathan Thompson[2]; [1]Gustavus Adolphus College, [2]United Science, LLC

11:20 (698) **Development and Application of Two Dimensional HPLC for Small Molecule Pharmaceutical Analysis**; Todd Maloney[1], Mark Argentine[1], Brian Scherer[1]; [1]Eli Lilly and Company

11:40 (699) **Use of Two-Dimensional HPLC in a Contract Lab Environment for MS Analysis of Unknown Analytes in Mobile Phases Containing Non-Volatile Modifiers**; David Sherlock[1]; [1]PPD

Thursday Morning, *Room 103B*
METALLOMICS: THE VIBRANT ROLE OF METALS IN BIOLOGY, DISEASE, AND TREATMENT
Organizer and Presider: Joseph Caruso

10:20 (700) **New Tools for Metallomics**; Gary Hieftje[1], Steven Ray[1], Alexander Graham[1], Elise Dennis[1], Christie Enke[2], David Koppenaal[3], Charles Barinaga[3]; [1]Indiana University, [2]University of New Mexico, [3]Pacific Northwest National Laboratory

10:40 (701) **Our Metallomics Picture Correct? Consequences of Solvent Composition and analytical Sample Preparation Methods**; R. Kenneth Marcus[1], Derrick Quarles[1], Benjamin Manard[1], Carolyn Burdette[1]; [1]Clemson University

11:00 (702) **Study of Protein/DNA binding via Phosphorus and Sulfur Detection via Triple Quadrupole ICP-MS A Study of Protein/DNA binding via Phosphorus and Sulfur Detection.**; Julio Landero-Figueroa[1], Morwena Solvio[1], Jiawei Gong[1], Edward Merino[1], Joseph Caruso[1]; [1]University of Cincinnati

11:20 (703) **Metallomics in Microbiology**; David W. Koppenaal[1]; [1]Pacific Northwest National Laboratory

11:40 (704) **Metallomics Studies for Fungal Disease Remission via Zn Deprivation – an Emphasis on Free Metal Imaging**; Joseph Caruso[1], Julio A. Landero-Figueroa[1], Kavitha Subramanian-Vignesh[1], George Deepe[1]; [1]University of Cincinnati

Thursday Morning, *Room 103C*
TRANSLATION AND COMMERCIALIZATION IN BIOMEDICAL APPLICATION
Organizer and Presider: Karen Esmonde-White

10:20 (705) **The Business of Commercializing Analytical Technologies**; Mark Druy[1]; [1]Physical Sciences Inc.

10:40 (706) **Stories from the Front Lines - Technology Transfer Terrors and Triumphs**; Jeremy Shaver[1], Barry Wise[1]; [1]Eigenvector Research

11:00 (707) **Steps for Commercializing Spectroscopic Devices in a Regulated Industry**; Bradford Clay[1]; [1]bioMerieux, Inc.

11:20 (708) **From an Academic Invention to a Commercial Product: Steps Taken to Translate a New Analytical Took into a Marketable Device**; Martin Zanni; [1]University of Wisconsin-Madison

11:40 **Audience Q&A - Speaker Roundtable**

Thursday Afternoon, *Room 101A*
IRENI – SYNCHROTRON BASED WIDEFIELD INFRARED MICROSPECTROSCOPY
Organizer and Presider: Carol Hirschmugl

1:20 (709) **Utilising the IRENI Beamline to Provide an Enhanced Understanding of Human Breast Calcifications and Their Association with Diseased Tissue**; Nick Stone[1,2], Marleen Kerssens[2, 3], Catherine Kendall[1, 2, 3]; [1]University of Exeter, [2]Gloucestershire Hospitals NHS Foundation Trust, [3]Cranfield University

1:40 (710) **FT-Infrared (FT-IR) Spectroscopic Tomography: Development of a 3D mid-IR Spectral Imaging Technique**; Miriam Unger[1,2], Julia Sedlmair[3], Michael Martin[4], Carol Hirschmugl[1]; [1]Department of Physics, University of Wisconsin-Milwaukee, Milwaukee, USA., [2]CETICS Healthcare Technologies GmbH, Esslingen am Neckar, Germany, [3]Synchrotron Radiation Center, University of Wisconsin-Madison, Stoughton, WI, [4]Advanced Light Source Division, Lawrence Berkeley National Laboratory, Berkeley, CA

2:00 (711) **FTIR Spectrochemical Imaging at the Diffraction Limit**; Kathleen Gough[1], Catherine Liao[1], Alexandra Ciapala[1], Peter Trokajlo[1], Benedict Albensi[1], CJ Mundy[1], Julia Sedlmair[3, 4], Carol Hirschmugl[2]; [1]University of Manitoba, [2]University of Wisconsin-Milwaukee, [3]US Forest Service, Forest Products Laboratory, Madison WI, [4]Synchrotron Radiation Center, University of Wisconsin-Madison, Stoughton, WI

2:20 (712) **Using Synchrotron Light for Integrated Spectroscopic Studies of Disturbed Energy Metabolism and Oxidative Stress within the Brain**; Mark Hackett[1], Ferenc Borondics[2], Carol Hirschmugl[3], Phyllis Paterson[1], Helen Nichol[1], Ingrid Pickering[1], Graham George[1]; [1]University of Saskatchewan, [2]Canadian Light Source, [3]University of Wisconsin

2:40 (713) **Probing Bonding and Dynamics at Adsorbate/Graphene Interfaces**; Eric Mattson[1], Kanupriya Pande[1], Miriam Unger[1, 3], Shumao Cui[2], Marija Gajdardziska-Josifovska[1], Michael Weinert[1], Junhong Chen[2], Carol Hirschmugl[1]; [1]University of Wisconsin-Milwaukee, Physics Dept., [2]University of Wisconsin-Milwaukee, Mechanical Engineering Dept., [3]Synchrotron Radiation Center

Thursday Afternoon, *Room 101B*
NEW APPLICATIONS OF LIBS
Organizer and Presider: Richard E. Russo

1:20 (714) **Ultrafast Laser Induced Breakdown Spectroscopy for 3-Dimensional Chemical Imaging**; Vassilia Zorba[1]; [1]Lawrence Berkeley National Laboratory

1:40 (715) **The Application of LIBS in the Failure Prediction of Hear Transfer Surface in Boilers**; Jidong Lu[1], Shunchun Yao[1], Jun Li[1], Meirong Yao[1], Bo Zhang[1]; [1]School of Electric Power, South China University of Technology

2:00 (716) **Use of Laser Induced Breakdown Spectroscopy for the Analysis of Poultry Products**; Gary Gamble[1]; [1]USDA-ARS

2:20 (717) **Challenges and Advantages of Extraterrestrial LIBS**; Ryan Anderson[1], Jeremie Lasue[2], Sam Clegg[3], Roger Wiens[3], Ann Ollila[4], Olivier Forni[2], Sylvestre Maurice[2], Steve Bender[3], Alissa Mezzacappa, Nourredine Melikechi; [1]U.S. Geological Survey, [2]Institut de Recherche en Astrophysique et Planétologie, [3]Los Alamos National Laboratory, [4]University of New Mexico

2:40 (718) **Laser Induced Breakdown Spectroscopy (LIBS) for Monitoring of Carbon Sequestration**; Jinesh Jain[1,2], Dustin McIntyre[1], Christian Goueguel[1], Barbara Kutchko[1], Brian Strazisar[1]; [1]USDOE-National Energy Technology Laboratory, [2]URS Corporation

Thursday Afternoon, *Room 101C*
SUPERCRITICAL FLUID CHROMATOGRAPHY
Organizer and Presider: Donald P. Poe

1:20 (719) **Past Present and Future Applications of Supercritical Fluid Chromatography (SFC)**; Terry Berger[1]; [1]SFC Solutions, Inc.

1:40 (720) **Efficiency of SFC Columns in Different Thermal Conditions**; Donald Poe[1], Krzysztof Kaczmarski[2], Abhijit Tarafder[3], Georges Guiochon[3]; [1]University of Minnesota Duluth, [2]Rzeszow University of Technology Poland, [3]University of Tennessee Knoxville

2:00 (721) **Determination of Equilibrium Isotherms in Supercritical Fluid Chromatography**; Georges Guiochon[1], Fabrice Gritti[1], Abhijit Tarafder[2], Fahimeh Kamarei[1], Peter Vajda[1]; [1]University of Tennessee, Knoxville, TN, [2]Waters Corporation, Milford, MA

2:20 (722) **The Marriage of SFC and Mass Spectrometry: An Old Romance Rekindled**; John Van Antwerp[1]; [1]Waters

2:40 (723) **Application of SFC in Process Analytical Chemistry**; Yanqun Zhao, Wayne Pritts[1]; [1]AbbVie, Inc

Thursday Afternoon, *Room 101D*
CONTRIBUTED PAPERS IN RAMAN IMAGING
Organizer: Michael George; Presider: Keith Gordon

1:20 (724) **Hyperspectral Chemical Sensing and Imaging using Optimized Binary Compressive Detection**; Owen Rehrauer[1], David Wilcox[1], Bharat Mankani[1], Dor Ben-Amotz[1]; [1]Purdue University

1:40 (725) **Confocal Raman Microscopy for in-situ Measurement of Octanol Water Partition Coefficients in Single Femtoliter-Volume Particles**; Jay Kitt[1], Joel Harris[1]; [1]University of Utah

2:00 (726) **Resolution in 3D Confocal Raman Imaging: The Contribution of Physics, Instrumentation, and Sample**; Jianyong Yang[2], Wei Liu[2], Thomas Dieing[1], Klaus Weishaupt[1], Ute Schmidt[1]; [1]WITec GmbH, Ulm Germany, [2]WITec Intruments Corp. Knoxville, Tennessee

2:20 (727) **HTVS Enhanced Hyperspectral Imagers for Process Analytics and Security Threat Detection**; Jeffrey Meade[1], Andrew Cenko[1], Bradford Behr[1], Arsen Hajian[1]; [1]Tornado Spectral Systems

2:40 (728) **Evaluation of Crystalline Content in Poly-L-lactide Using Raman Hyperspectral Imaging**; Venkata N K Rao Bobba[1], John F. Turner II[1]; [1]Cleveland State University

Thursday Afternoon, *Room 102A*
TOBACCO ANALYSIS BY MS
Organizer and Presider: Christina Young

1:20 (729) **FDA's New Authority to Regulate Tobacco Products**; Christina Young[1]; [1]U.S. Food and Drug Administration (FDA), Center for Tobacco Products, Office of Science

1:40 (730) **Quantitative Analysis of Volatile Organic Constituents in Mainstream Cigarette Smoke**; Clifford Watson[1]; [1]Centers for Diease Control and Pevention

2:00 (731) **Selected Aromatic Amines by Gas Chromatography Mass Spectrometry: Challenges of Mainstream Cigarette Smoke**; Alexandra Martin[1]; [1]Arista Laboratories, Inc.

2:20 (732) **Some Real-Time and Batch Sample Analysis Mass Spectrometry-Based Techniques to Inform Tobacco Product Regulation**; Marielle Brinkman[1], Sydney Gordon[1], Stephanie Buehler[1], Kandice Cross[1], Robyn Kroeger[1], Hyoshin Kim[1], Ian MacGregor[1], Douglas Turner[1], Theodore Klupinski[1], Erich Strozier[1]; [1]Battelle Memorial Institute Tobacco Exposure Research Laboratory

2:40 (733) **Determination of Carbonyl Compounds in Tobacco Products by Gas Chromatography Mass Spectrometry**; Peter Joza[1], Mingliang Bao[1], Andrew Masters[1]; [1]Labstat International ULC

Thursday Afternoon, *Room 102B*
MEDICAL APPLICATIONS
Organizer and Presider: Karen Esmonde-White

1:20 (734) **Process Optimization for Shake Flask Bio-treatment of Disperse Yellow 9 Textile Dye with White-rot Fungi and their Enzymes**; Muhammad Ramzan[1], Muhammad Asgher[1], Raymond Legge[2]; [1]University of Agriculture Faisalabad, [2]University of Waterloo

1:40 (735) **Imaging Mass Spectrometry of Three-Dimensional Cell Culture Systems**; Eric Weaver[1], Amanda Hummon[1]; [1]University of Notre Dame

2:00 (736) **Targeted Imaging of Biomolecules by Tip Enhanced Raman Spectroscopy**; Hao Wang[1], Zachary Schultz[1]; [1]University of Notre Dame

2:20 (737) **Raman Spectroscopy Paired with Dynamic Light Scattering: Probing Higher-order Structure of Pprotein Biotherapeutics**; Linda H Kidder[1], Wei Qi[1], Kevin Dahl[1], Kenneth S. Haber[1], E. Neil Lewis; [1]Malvern Instruments

2:40 (738) **Proteins Dielectrophoresis: A Promising Purification Method**; Fernanda Camacho-Alanis[1], Asuka Nakano[1], Alexandra Ros[1]; [1]Arizona State University[4]

Thursday Afternoon, *Room 102C*
EARLY CAREER SCIENTISTS IN RAMAN SPECTROSCOPY
Organizers and Presiders: Ian R. Lewis, Duncan Graham and Pavel Matousek

1:20 (739) **Raman Spectroscopy and Translational Research: Application in Diagnosis and Characterization of Heterotopic Ossification**; Katherine E. Cilwa[1], Jonathan R. Peterson[, 2], Benjamin Levi[, 2], Stewart C. Wang[, 2], Michael D. Morris[1]; [1]Department of Chemistry, University of Michigan, [2]Department of Surgery, University of Michigan Medical School

1:40 (740) **Non-invasive *in vivo* Collection of Biochemical Information from Human Bone using Spatially Offset Raman Spectroscopy; Developing Methodology for Clinical Investigation**; Jemma Kerns[1], Kevin Buckley[2], Helen Birch[1], Anthony Parker[2], Pavel Matouse[2], Richard Keen[3], Allen Goodship[1]; [1]Institute of Orthopaedics and Musculoskeletal Science, University College London, [2]Laser Facility, STFC Rutherford Appleton Laboratory., [3]Royal National Orthopaedic Hospital.

2:00 (741) **Tip-enhanced Raman Spectroscopic Study of Epitaxial Graphene on SiC Silicon Face and SiC Carbon Face**; Toshiaki Suzuki[1], Satoshi Minami[1], Yasunori Kutsuma[1], Koji Ashida[1], Tadaaki Kaneko[1], Yusuke Morisawa[2], Tamitake Itoh[3], Takeshi Miura[4], Yukihiro Ozaki[1]; [1]Kansei Gakuin University, [2]Kinki University, [3]National Institute of Advanced Industrial Science and Technology (AIST), [4]Unisoku

2:20 (742) **Toward Surface Enhanced Raman Correlation Spectroscopy (SERCoS)**; Steven M. Asiala[1], Zachary D. Schultz[1]; [1]University of Notre Dame

2:40 (743) **Label-Free Electrochemical SERS-based Assay for DNA Analysis Based on the Use of DNA Intercalators**; Evanthia Papadopoulou[1], Nittaya Gale[1], Sarah, A Goodchild[2], Simon Weller[2], David W Cleary[2], Tom Brown[1], Philip N Bartlett[1]; [1]School of Chemistry, University of Southampton, [2]DSTL, Porton Down

Thursday Afternoon, *Room 102D*
NANOMATERIALS FOR PLASMONICS II
Organizer and Presider: Jean-Francois Masson

1:20 (744) **Gold Nanorods - Surface Modification for SERS**; Amanda Haes[1]; [1]University of Iowa

1:40 (745) **Role of Plasmonic Interactions and Other Factors in Nanoparticle-based Immunoassays**; Marc Porter[1], China Lim[1], Nicholas Owens[1], Jennifer Granger[1]; [1]University of Utah

2:00 (746) **Probing the Optical Near Field Behavior of Asymmetric Plasmonic Nanoantennas**; Jennifer S. Shumaker-Parry[1]; [1]University of Utah

2:20 (747) **Hydration Effects on Plasmonic Coupling in a Gold Nanoparticle Enabled SERS Immunoassay**; Jeremy Driskell[1]; [1]Illinois State University

2:40 (748) **High Fidelity Polydopamine Surface Attachment Chemistries for SPR Imaging Applications of Biopolymer Microarrays, Nanostructured Surfaces and Biofunctionalized Nanoparticles**; Jennifer Wood[1], Gabriel Loget[1], Kyunghee Cho[1], Mana Toma[1], Aaron Halpern[1], Robert Corn[1]; [1]University of California, Irvine

Thursday Afternoon, *Room 102E*
ANACHEM AWARD HONORING NORMAN DOVICHI
Organizer and Presider: Keith L. Olson

1:20 (749) **Multi-segment Injection-Capillary Electrophoresis-Mass Spectrometry for Biomarker Discovery in Metabolomics**; Philip Britz-McKibbin[1], Naomi Kuehnbaum[1], Aleisha Kormendi[1], Jenna Gillen[2], Martin Gibala[2]; [1]Department of Chemistry and Chemical Biology, McMaster University, [2]Department of Kinesiology, McMaster University

1:40 (750) **New Ways of Using Capillary Electrophoresis to Study Proteins**; Robert Kennedy[1]; [1]University of Michigan

2:00 (751) **Bioanalysis for Biocatalysis: Multiplexed Capillary Electrophoresis–Mass Spectrometry Assay for Aminotransferase Substrate Discovery and Specificity Profiling**; Maxim V. Berezovski[1], Gleb G. Mironov[1], Antony D. St.-Jacques[1], Alexander Mungham[1], Matthew G. Eason[1], Roberto A. Chica[1]; [1]University of Ottawa

2:20 (752) **Punctuated Microgradients in Bioanalysis**; Mark A. Hayes[1]; [1]Arizona State University

2:40 (753) **Mechanistic Insight into the Improvements in Proteome Coverage and Low Abundance Protein Quantitation through Digestion and Depletion**; Bryan Fonslow[1], Mark Hixon[, 2], John Yates III[1]; [1]The Scripps Research Institute, [2]Takeda San Diego, Inc.

TECHNICAL PROGRAM – THURSDAY
Orals 1:20 – 3:00 pm and 3:50 – 5:30 pm

Thursday Afternoon, *Room 103B*
INNOVATIVE APPLICATIONS OF MID- AND NEAR-IR SPECTROSCOPY
Organizer: Michael George; Presider: Martyn Poliakoff

1:20 (754) **Optical Sensors via Infrared Absorption Spectroscopy for the Detection of Homemade Explosives**; Kevin Major[1], Kenneth Ewing[2], Rajendra Joshi[1], Menelaos Poutous[1], Catalin Florea[3], Jasbinder Sanghera[2], Ishwar Aggarwal[1]; [1]UNC Charlotte, [2]Naval Research Laboratory, [3]Sotera Defense Solutions

1:40 (755) **Comparison of Vibrational Spectroscopic Techniques with Powder X-ray Diffraction for the Quantitative Measurement of Crystalline/Amorphous Content in Pharmaceutical Solids**; Mark Sullivan[1], David Heaps[1], Richard McKay[1], Xiao Hua Zhou[1], Edward King[1], Ajit Narang[2], Benjamin Wong[2]; [1]Advantest America, Inc., [2]Bristol Myers Squibb

2:00 (756) **Node Attenuation to Enhance Apparent Spectral Fine Features**; Isao Noda[1]; [1]University of Delaware

2:20 (757) **Distribution Analysis for Quality Evaluation of Pharmaceutical Tablet by using a Newly Portable NIR Imaging Device (D-NIRs)**; Daitaro Ishikawa[1], Kodai Murayama[2], Takuma Genkawa[3], Mkoto Komiyama[2], Yukihiro Ozaki[1]; [1]Kwansei Gakuin University, [2]Yokogawa Electric Co., [3]University of Tsukuba

2:40 (758) **Near Infrared Imaging Enables Chemical Analysis of Milled Wheat Fractions Physically Separated by Particle Size**; Mark Boatwright[1,2], David Wetzel[2], Jeffrey Gwirtz[3], Elieser Posner[4]; [1]Department of Biochemistry and Molecular Biophysics, Kansas State University, [2]Microbeam Molecular Spectroscopy Laboratory, Kansas State University, [3]JAG Services, Inc, [4]ESP International

Thursday Afternoon, *Room 103C*
WHAT IS THE STATE OF PROCESS ANALYTICAL TECHNOLOGY? A TECHNICAL PANEL
Organizer and Presider: James W. Rydzak

1:20 (759) **Application of Process Analytical Technology (PAT) in Pharmaceutical Manufacturing - FDA Perspective**; Bogdan Kurtyka[1]; [1]FDA

1:40 (760) **The Development and Application of PAT Tools to Achieve Process Understanding**; Brian Marquardt[1], Mel Koch[1]; [1]University of Washington

2:00 (761) **PAT – Past, Present & Future – A Personal Perspective**; John Richmond[1]; [1]Bruker Optics Inc.

2:20 **Technical Panel – Panel Discusson of PAT**

Thursday Afternoon, *Room 102C*
FACSS INNOVATION AWARDS
Organizer: Jose Almirall; Presider: Michael George

3:50 (762) **Imaging Quantum Effects in Biological Systems**; Gregory S. Engel[1]; [1]The University of Chicago

4:10 (763) **Ultra-compact LIBS Systems: Utilizing Microchip Laser Engines to Enable New Applications and Markets for LIBS**; Jason Eichenholz[1], Scott Buchter[2]; [1]Open Photonics Inc., [2]Lasersec

4:30 (764) **Biometrics from the Stable Isotope Analysis of Amino Acids in Human Hair**; Glen Jackson[1,2], Yan An[3], Kateryna Konstantynova[2]; [1]Forensic & Investigatice Science, WVU, [2]C. Eugene Bennett Department of Chemistry, WVU, [3]Department of Chemistry and Biochemistry, Ohio University

4:50 (765) **Portable Spectrometry: Making Good Use of CMOS Detectors**; Alexander Scheeline[1], Thu Anh Bui[1, 2]; [1]SpectroClick Inc., [2]Vietnam National University Hanoi

5:10 (766) **2D FT Electronic Spectroscopy of Quantum Dots in the Short-Wave Infrared**; David Jonas[1], Samuel Park[1], Dmitry Baranov[1], Byungmoon Cho[1]; [1]University of Colorado at Boulder

Friday Morning, *Room Regency A/B – Hyatt Hotel*

SPECIAL PLENARY SESSION: WELCOMING A NEW MEMBER ORGANIZATION INTO FACSS AND MUCH MORE….

Organizer and Presider: Michael George

8:00 (767) **FACSS and Its Annual Conference – 40 and Fabulous. The Good, the Bad, and the Innovative or Origin, Analysis, and Future Directions**; Ian R. Lewis[1]; [1]FACSS

8:30 (768) **A Year is a Long Time in Publishing**; May Copsey[1]; [1]Royal Society of Chemistry

9:00 (769) **What Does a Seventeenth Century Academy Have to Offer to Science Today?**; Martyn Poliakoff[1]; [1]University of Nottingham

9:30 (770) **The Lawyer Ate My Paper: Can Industry do Science in the Age of Litigation?**; Fred LaPlant[1]; [1]3M

10:00 (771) **What Does the IRDG Have to Offer FACSS?;** Michael George[1], [1]University of Nottingham

10:30 **Welcome to SciX 2014;** Luisa Profeta and Jose Almirall

SciX 2014, Grand Sierra Resort, Reno-Tahoe, NV; September 28 – October 3

SciX 2015, Rhode Island Convention Center, Providence, RI; September 27 – October 2

GET INVOLVED

Would you like to be involved with a SciX Conference or the FACSS Organization?
Wondering who to talk to or how you might be able to help?

START HERE!

Opportunities Include

Program Suggestions
Program Section Organization
Employment Center
General On-site Volunteer
Photography
Workshops
Social Media
Advertising / PR
Marketing
International Ambassadors

Future SciX / FACSS Leadership Roles

Talk to us in Milwaukee or send us an email.

SciX 2014 Chairs – Reno-Tahoe

General Chair
Luisa Profeta
MRIGlobal
lprofeta@mriglobal.org

Program Chair
Jose Almirall
Florida International University
almirall@fiu.edu

FACSS 2014/2015 Chairs

FACSS
Governing Board Chair
Greg Klunder
LLNL
klunder@llnl.gov

FACSS
Marketing Chair
John Wasylyk
Bristol-Myers Squibb
john.wasylyk@bms.com

SciX 2015 Chairs – Providence, RI

General Chair
Edita Botonjic-Sehic
Morpho Detection, Inc.
edita.botonjic-sehic
@morphodetection.com

Program Chair
Glen Jackson
West Virginia University
glen.jackson@mail.wvu.edu

ABSTRACTS

(1) **From TestTube to YouTube**

Martyn Poliakoff[1]; [1]University of Nottingham

This lecture tells two interwoven stories. First, it explains how I became involved by chance in taking Green Chemistry, cleaner approaches to making and using chemicals, to sub-Saharan Africa, in particular Ethiopia.[1] Secondly, it describes how my participation in making some videos for the University of Nottingham's YouTube channel, www.test-tube.org.uk led to my collaborating with a very talented video-journalist Brady Haran, www.bradyharan.com and the creation of the YouTube channel, The Periodic Table of Videos, www.periodicvideos.com. This began as a collection of 120 videos (one for each of the 118 elements of the Periodic Table, plus an introduction and a trailer).[2] Quickly, it gathered momentum[3] and now (11pm on 30th July 2013) it has 470 uploaded videos with 292,702 YouTube subscribers and a total >45 M views in over 200 countries.[4] In this lecture, I explain how the two stories are united by a passion for chemistry and a desire to communicate that passion to the wider community.

1. "Collaborations - Empowering Green Chemists in Ethiopia. (N. Asfaw, P. Licence, T. Engida, and M. Poliakoff) Science (2007) 316, 1849-1850.
2. "Elements Achieve Internet Stardom" (S. K. Ritter) C & E News (September 15, 2008) 86, No 37, 42-43
3. "YouTube in its Element." (M. Poliakoff and B. Haran) tce (2009) 812, 36-37.
4. "The Periodic Table of Videos" SPORE Essay - Science Prize for Online Resources for Education (B Haran and M. Poliakoff) Science (2011) 332, 1046-1047.
5. "How to Measure the Impact of Chemistry on the Small Screen." (B. Haran and M. Poliakoff) Nature Chem. (2011) 3, 180-182.

(2) **Future Challenges in Green Chemistry;**

Paul Anastas[1]; [1]Yale University

We live on this planet in a way that is far from sustainable. Our population already exceeds 7 billion and there is an increasing demand for chemical products and materials. At the same time, we are squandering some of the planet's chemical riches. Every modern cell phone contains more than 30 or 40 different chemical elements, some of which are already in short supply. Yet nearly half a million phones are discarded each day in the USA alone! As is sometimes said, "If we continue in the present direction, we will end up where we are heading." So we need to change. Green Chemistry aims to help us make that change by letting us exploit chemistry in a more sustainable and environmentally way. It is best defined as 'Carrying out chemical activities (design, manufacture, use and disposal) such that hazardous substances will not be used or generated.' Clearly, such an aspiration requires a set of metrics against which you can evaluate a particular chemical process or product. Our first attempt was the 12 Principles of Green Chemistry [1] which have stood the test of time remarkably well. Some of the Principles are relatively prescriptive; for example, Principle No1 "It is better to prevent waste than to treat or clean up waste after it is formed" or Principle No. 6"Energy requirements should be recognized for their environmental and economic impacts and should be minimized." However, from the point of view of this conference, the key Principle is No. 11. "Analytical methodologies need to be developed further to allow for real-time in-process monitoring and control prior to the formation of hazardous substances." In this lecture, I will set out the need for Green Chemistry, illustrate the use of the Principles, and explain why the 11th Principle is so important to the future success of Green Chemistry.

1."Green Chemistry: Theory and Practice" P T Anastas and J C Warner, Oxford University Press, Oxford 1998.

(3) **Protonation-Deprotonation Processes of 2-(4'-pyridyl)benzimidazole in Its Inclusion Complex with cucurbit[n]uril**

Vijay Kant[1], Uma Nudurupati[1], Sohidul Mondal[1], Anindya Datta[1]; [1]Indian Institute of Technolohy Bombay

In the present study, we report the modulation of the ground- and excited state proton transfer processes of 2-(4'-pyridyl)benzimidazole (4PBI) in aqueous solutions by CB5, CB6, CB7 and CB8 in acidic and alkaline media and in order to examine if the protonation-deprotonation equilibria involving different forms of 4PBI are affected by inclusion in macrocyclic hosts of this class. Given a choice between a cation, anion and a neutral it is known that CB would selectively stabilize the cation, but the question we have addressed here concerns the choice between two monocations of the same molecule. 2-(4' Pyridyl)benzimidazole (4PBI) guest comprising two binding sites, one benzimidazole group and one pyridyl group, proved could form inclusion complexes with cucurbit[n]uril (CB[n]) in aqueous solution. The binding in to the hydrophobic cavity and at the portals of cucurbit[n]uril of guest, absorption and fluorescent response of a guest could be dramatically changed, so by the steady state and time resolved fluorescence spectroscopy, it very easy to demonstrate that the 2-(4'-Pyridyl)benzimidazole could be interact with both cavity and portal. 1H NMR spectroscopy and DFT calculations is also proving information about the formation of inclusion complexes. 1H NMR of both the guest and the host indicates that guest enters in CB[n] from the benzimidazole side in hydrophobic cavity.

(4) **Monitoring the Uniformity of α-Helices in Lipophilic Environments**

Anahita Zare[1], Jian Xiong[1], Jason Cooley[1], Renee Jiji[1]; [1]University of Missouri-Columbia

It is known that membrane embedded α-helices are more uniform structurally than their aqueous counterparts. Despite this uniformity, protein dynamics are thought to be common in these proteins in order for them to conduct their cellular tasks. However, how amino acid sequence facilitate these dynamics remains unknown as methods for investigating structural heterogeneity in transmembrane proteins are limited. Circular dichroism (CD) is often used to characterize the secondary structure of the protein, but its sensitivity to specific non-helical structural configurations is low. Deep-ultraviolet resonance Raman spectroscopy (DUVRR) is a structurally sensitive spectroscopy technique emerging for analyzing membrane protein structures. A set of *de novo* designed peptides have been constructed that contain varying contents of helix breaking residues (HBR) in order to test their role helical instability in lipophilic environments. The secondary structure of each peptide was monitored through the measured by DUVRR spectroscopy, where the Amide I mode was used to monitor relative lipid versus aqueous solvation. Furthermore, changes in the Amide III and S modes indicate helices do not necessarily become less uniform in membrane environments with incorporation of HBRs, but that HBRs actually cause the "unwinding" or the helix when solubilized in detergent environments. This observation has implications towards the role of water presentation in membrane protein dynamics.

(5) **Secondary Structure of Poly-L-Alanine in Solution Studied by Raman and ROA with Quantum Chemical Computation**

Tatsuya Furukawa[1], Shigeki Yamamoto[2], Yukihiro Ozaki[1]; [1]Department of Chemistry, Graduate School of Science and Technology, Kwansei Gakuin University; [2]Department of Chemistry, Graduate School of Science, Osaka University

Raman optical activity (ROA) spectroscopy is a sensitive technique to explore solvated secondary structures of peptides and proteins in solutions. The extended amide III ROA bands at ~1340 cm^{-1} and

~1300 cm^{-1} of proteins have been empirically assigned to characteristics of the "hydrated α-helix" and the "hydrophobic α-helix" structures, respectively[1]. Intensity ratio of these two bands varies depending on solvent. We have examined which factors, dielectric constants of the solvents and/or torsional angles of the peptide backbone, can influence on the ROA intensities of poly-L-alanine (PLA). These two conditions were independently changed in quantum mechanical calculations of ROA spectra of PLA with a molecular fragmentation method[2].ROA spectra of the α-helical $(Ala)_{18}$ were calculated under vacuum with the two peptide dihedral angles, (φ, ψ) = (-66°, -41°) and (φ, ψ) = (-59°, -44°). The experimental bands at ~1340 cm^{-1} and ~1300 cm^{-1} can be assigned to the calculated peaks at ~1360 cm^{-1} (δ (CαH) along the CαC axis) and ~1330 cm^{-1} (δ (CαH) along the NCα axis). The experimental intensity ratios of these bands (1340 cm^{-1}/1300 cm^{-1}) were experimentally observed as 1.05 in dichloroacetic/chloroform = 30/70 (ε = 5.72 (calc.)) and 1.26 in dichloroacetic acid (ε = 8.08)[3]. The calculations with the peptide dihedral angles of (φ, ψ) = (-66°, -41°) reproduced well this experimental tendency, but not the dihedral angles of (φ, ψ) = (-59°, -44°). The calculated intensity ratios increased as the dielectric constant of the solvent model increased, as 0.79 under vacuum, 1.31 under the conductor-like polarizable continuum model (CPCM) of chloroform (ε = 4.71), and 1.52 under the CPCM of dichloroethane (ε = 9.20). We concluded that the relative intensity of the two extended amide III ROA bands at ~1340 cm^{-1} and ~1300 cm^{-1} of PLA would be determined the dielectric constant of the surrounding solvent.

[1]Iain H. McColl, et al., *J. Am. Chem*. Soc. 2004, 126, 8181-8188.
[2] Bouř, P. et al., *J. Comput. Chem*. 1997, 18, 646-659.
[3]Schellman, J. A., Schellman, C., *The Proteins*, Second Edition; Neurath, H., Ed.; Academic Press: New York, 1964,1-132.

(6) **Rapid Dialysis within Microfluidic Channels: Spatiotemporal Control of Solution Micro-environment using Hydrogel Membrane Microwindows**

Joel Paustian, Todd Squires[1]; [1]University of California, Santa Barbara

We have developed a simple technique to synthesize hydrogel membranes locally within microfluidic channels, with high precision and resolution. Using a standard fluorescence microscope, we photopolymerize thin (W=10-25μm) hydrogel membrane 'microwindows' (HMMs) between microfluidic channels. The hydrogels have a pore size large enough to admit solute and solvent diffusion, yet small enough to prevent significant fluid flow. Constant-concentration 'reservoir' channels may thus be maintained or rapidly switched on one side of the HMM by flowing solutions, provoking changes in solution composition on the other (sample-containing) side without mechanical disturbances often associated with convective delivery. The thin width of the hydrogel allows fast diffusion times across the membrane, and the composite permeable/impermeable channel walls allow local gradients to be rapidly established within seconds and steadily maintained.

Here, we demonstrate applications of HMMs for local dialysis in microfluidic channels. Dynamics of salt transport are investigated by quickly switching reservoir solutions and visualizing the HMM and sample channel response. Fast switching is demonstrated by complete switching of salt solutions (0 to 250 mM NaCl) in a flow-free microfluidic channel in under 6 seconds. Local gradients of solute and solvent are applied to investigate the phoretic motion of suspended colloids. Finally, the hydrogel's permeability properties are investigated by varying the effective pore size within the hydrogel network and visualizing the diffusive flux of solute.

(7) **Human Red Blood Cell Deformation and Crenation under High Frequency Spatial AC Field**

Ran An[1], Adrienne Minerick[1]; [1]Michigan Technological University

Dielectrophoretic (DEP) cell manipulations are the result of frequency-dependent polarization differences between the cell and the surrounding medium, whose properties are traditionally treated as a uniform quantity. Human red blood cells (RBC) are observed to crenate over 10 minute experiments in perpendicularly configured electrode microdevices under non-uniform AC electric fields. Cell crenation magnitude is examined in nonuniform AC electric fields as functions of frequency from 250 kHz to 1 MHz and peak to peak potential from 10 Vpp to 17.5 Vpp over the 100 μm electrode gap. Experimental results show higher peak to peak potential and lower frequency lead to greater cell volume crenation up to a maximum volume loss of 20%. These cell deformations are attributed to hypertonicity induced by ion propagation and local increases in ion concentration in the spatially nonuniform AC DEP electric field. A series of experiments are conducted to elucidate the physical mechanism inducing crenation. Nonuniform and uniform electrode systems are compared and illustrate minor (4% volume change) when DEP inducing field gradients are not present. Other factors with the potential to impact cell crenation are examined including cell AC electroporation, system temperature, rapid temperature changes and medium pH, but none can account for the crenation behaviors observed. AC electroosmotic (ACEO) and AC electrothermal (ACET) factors that compromise the ability to observe pure DEP behaviors were also quantified. Fluorescent latex beads were used to detect flows generated in the system at 15V peak-to-peak potentials and 250kHz - 50MHz frequencies. All contributing mechanisms are quantified and concluded cell crenation is induced by local increases in ion concentration as a result of electric field nonuniformity induced migration of ions.

(8) **Determination and Quantification of Water-Soluble and Fat-Soluble Vitamins in Human Biofluids with HPLC/MS**

Maryam Khaksari[1], Chunhai Ruan[2], Peng Song[2], Neil Hershey[2], Robert Kennedy[2], Mark Burns[2], Dave Burke[2], Adrienne Minerick[1]; [1]Michigan Technological University; [2]University of Michigan

Nutritional deficiencies in children are currently clinically diagnosed based on recognition of symptoms. The weakness of this approach is that symptoms-presentation substantially lags the deficiency, since tissue damage has already occurred. It would be more powerful to ascertain deficiencies well in advance of overt symptoms. Vitamins are convenient indicators of nutritional health because they are not manufactured by the body and, consequently, reflect the available food sources. Currently, determination of vitamin levels requires milliliters of blood serum, which are outsourced to medical laboratories. Reducing the logistical barriers to vitamin assays would speed deficiency diagnoses. Thus, we have developed protocols to assay vitamin levels in alternative biofluids to correlate levels with blood serum. Here we introduce two sensitive sample preparation and high performance liquid chromatography (HPLC) mass spectrometry (MS) methods, one for simultaneous determination of 9 water-soluble vitamins and another for simultaneous detection of 4 fat-soluble vitamins. Total analysis time with controls from vitamin standards to minimize elution time was 18 min for elution of all water-soluble vitamins and 25 min for 4 fat-soluble vitamins. Acetic acid and ammonium formate were added as additives in the mobile phases to enhance species ionization to the protonated ion, [M+H]+, respectively for water-soluble and fat-soluble vitamins. Quantification of vitamins was done under MS/MS condition with isolating the most intense precursor ion for each analyte. This method is currently being used to examine vitamin levels in human biofluids and blood plasma, the clinical standard, to ascertain the viability of using alternative biofluids to assess vitamin levels.

(9) **High Sensitive Detection of Antigen-Antibody Reaction using Quantum Crystal SERS Substrate**

Daichi Araki[1], Yuuki Hasegawa[2], Katsuyuki Hasegawa[2], Yuko S. Yamamoto[3], Tamitake Itoh[3], Yasutaka Kitahama[1], Yukihiro Ozaki[1]; [1]Kwansei Gakuin University; [2]Mytech Corporation; [3]AIST

Surface-enhanced Raman scattering (SERS) is a technique to detect a small amount of molecules the enhanced electromagnetic field between metal nano-particles. Recently, its application to detection of various biomolecules has been tried. In this study, we measured SERS spectra before and after antigen-antibody reaction by using a quantum crystal substrate. We dropped silver complex solution onto metal alloy and blew off the solution after 3 minutes. Then, many silver nanoparticle aggregates were formed on the metal alloy [1]. Here, we call them on the substrate "quantum crystal". First, SERS substrate was formed from a mix of the silver complex solution and antibody (Immunoglobulin G, IgG) on the alloy. Then, we measured SERS spectrum from an antigen solution on the substrate. New peak appeared around at 1310cm^{-1}. By using the antigen with different dyes (TRITC and FITC), the new peak was observed at the same position. By using different antibody (IgE) also the new peak appeared at the same position (1310cm^{-1}) as the former results. On the other hand, we tried biotin and avidin. In general, biotin is bound by avidin strongly. By the similar method, a new peak was observed around at 930cm^{-1}. Next, a new peak was observed around at 900cm^{-1} in the case of gelation of limulus amebocyte lysate (LAL) due to endotoxin. In summary, the SERS peak for the antigen-antibody reaction was observed at the same position, although antigents with different dyes were used for the detection. However, the SERS peaks for antigen-antibody reaction, avidin-biotin binding, and LAL test appeared at different positions.

[1] Y. S. Yamamoto, K. Hasegawa, Y. Hasegawa, N. Takahashi, Y. Kitahama, S.
Fukuoka, N. Murase, Y. Baba, Y. Ozakid and T. Itoh, Phys. Chem. Chem. Phys.,
2013, DOI: 10.1039/c3cp52564c.

(10) **Powder XRD of Pharmaceutical Ingredients with PPM Detection Limits**

Scott Toth[1], Matthew Jackson[2], Justin Newman[1], Christopher Dettmar[1], Michael Becker[3], Robert Fischetti[3], Lynne Taylor[2], Garth Simpson[1]; [1]Purdue University, Department of Chemistry, West Lafayette, IN; [2]Purdue University, Department of Industrial and Physical Pharmacy, West Lafayette, IN; [3]GM/CA@APS, Advanced Photon Source, Argonne National Laboratory, Argonne, IL

The limits of detection for benchtop X-ray diffractometers are on the order of a few percent. Second harmonic generation (SHG) microscopy in combination with two-photon excited ultraviolet fluorescence (TPE-UVF) is an attractive alternative for the determination of percent crystallinity of a sample. In previous studies, calibration curves were prepared to quantitatively assess the viability of SHG-based crystallinity detection, and were found to be in good agreement with typical techniques such as powder X-ray diffraction (XRD). However, SHG provides little direct structural information about the crystal lattice/composition, but the combination of SHG with synchrotron XRD can allow for the elucidation of structural information, while allowing for substantially lower limits of detection. The incorporation of a nonlinear optical instrument, combining SHG and TPE-UVF, with a synchrotron X-ray source, allows for the potential to substantially decrease XRD limits of detection. Pharmaceutical samples with a 0.01% w/w API loading were examined, resulting in strong agreement with SHG and X-ray raster scanned diffraction. The combination of second harmonic generation microscopy, two-photon excited ultraviolet fluorescence, and mini-beam collimation of a synchrotron beam with area detection of the diffracted X-rays, has the potential to identify crystal forms at ppm or ppb levels.

(11) **Chemometrics Applied to Terahertz Spectroscopy**

Josette EL Haddad[1,2], Frédérick De Miollis[1, 2], Bruno Bousquet[1, 2], Lionel Canioni[1, 2], Patrick Mounaix[1, 2]; [1]Univ. Bordeaux, Loma, UMR, Talence, France; [2]CNRS, LOMA, UMR Talence, France

Terahertz radiation has become more and more attractive in the framework of quality control and sensing, especially because of its ability to penetrate through packaging materials. Moreover, terahertz responses depend not only on the molecules nature but also on their environment. Terahertz spectroscopy is consequently particularly well suited to address the question of chirality and potentially allows identifying different polymorphs. Typical terahertz spectra are performed over a very wide spectral window from 100GHz up to 4THz and then contain thousands of values. Spectral absorption related to a molecule/environment is usually spread over broad spectral bands. Multivariate analysis or chemometrics offers the possibility to simultaneously take into account many wavelengths in order to enhance the analytical performance of terahertz spectroscopy. In the present work, chemometrics was applied to analyze the THz spectra of a series of samples specially synthetized in order to demonstrate the potentiality of the technique. The samples were prepared as pressed pellets of 400 mg total weight with 80% in weight of Polyethylene (PE) as binder and 20% in weight of one, two or three molecular compounds, namely D-(-) Fructose, Citric acid monohydrate and α-Lactose monohydrate. The experiments were carried on a TPS spectra 3000 system from Teraview providing terahertz spectra ranging from 0.1 to 4 THz. All the measurements were obtained under dry air conditions and averaged over 1000 repetitions. Pertinent parameters are than extracted and analyzed. Different types of chemometric methods were compared. First, two methods dedicated to the classification of samples, namely principal component analysis (PCA) and PLS discriminant analysis (PLS-DA) were discussed. In addition to classification, semi-quantitative analyses of unknown samples were performed by retrieving the right ratios of the three products. For quantitative analysis, a 3-layer artificial neural network (ANN) was built and optimized and finally compared to the more common partial least squares regression (PLS). In order to assess these two methods, the experimental data were split into three sets for calibration, validation and test. The results about classification, semi-quantitative and quantitative approaches will be discussed in terms of figures of merit and statistical tests commonly applied in chemometrics.

(12) **Microwave and Infrared Spectral Studies of Cyclobutylcarboxylic Acid Chloride**

Joshua J. Klaassen[1], Peter Groner[1], James R. Durig[1]; [1]University of Missouri Kansas City

The FT-microwave spectrum of cyclobutylcarboxylic acid chloride, c-$C_4H_7C(O)Cl$, has been recorded and 153 transitions for the ^{35}Cl and ^{37}Cl isotopologues have been assigned for the gauche-equatorial(g-Eq) conformation. The ground state rotational constants were determined for ^{35}Cl [^{37}Cl]: A = 4349.8429(25) [4322.0555(56)], B = 1414.8032(25) [1384.5058(25)], and C = 1148.2411(25) [1126.3546(25)] MHz. From these rotational constants and ab initio predicted parameters, adjusted r_0 parameters are reported with distances (Å): rC_α-C = 1.491(4), rC=O = 1.193(3), rC_α-C_β = 1.553(4), rC_α-$C_{\beta'}$ = 1.540(4), rC_γ-C_β = 1.547(4), rC_γ-$C_{\beta'}$ = 1.546(4), rC-Cl = 1.801(3) and angles (^{o}) $C_\gamma C_\beta C_{\beta'} C_\alpha$ = 30.9(5). Variable temperature (-70 to -100^{o}C) infrared spectra (4000 to 400 cm^{-1}) were recorded in liquid xenon and the g-Eq conformer was determined the most stable form; with enthalpy differences of 91 ± 9 cm^{-1} (1.09 ± 0.05 kJ/mol) for the gauche-axial(g-Ax) form and 173 ± 17 cm^{-1} (2.07 ± 0.04 kJ/mol) for the trans-equatorial(t-Eq) conformer. The relative

amounts at ambient temperature are 54% g-Eq, 35 ± 1% g-Ax and 12 ± 1% t-Eq forms. Vibrational assignments have been provided for the three conformers and theoretical calculations were carried out. The results are discussed and compared to corresponding properties of related molecules.

(13) **Heterodyne Electro-Optic Sampling of THz Pulsed Waves**

Masahiko Tani[1], Tetsuya Kinoshita[1], Tomohiro Nagase[1], Shinpei Ozawa[1], Shogo Azuma[1], Satoshi Tsuzuki[1], Daiki Takeshima[1], Tatsuya Joja[1], Atsushi Iwamae[1], Stefan Funkner[1]; [1]Research Center for Development of Far-Infrared Region, University of Fukui; [2]University of Philippines Diliman, Philippines; [3]Faculty of Education and Regional Stduies, Uiversity of Fukui; [4]University of Nizhny Novgorod, Russia

A newly developed "heterodyne electro-optic (EO) sampling" technique for detection of pulsed terahertz (THz) waves is demonstrated and its detection characteristics are discussed in comparison with other techniques. The heterodyne EO sampling is based on Cherenkov phase-matching, which circumvents the detrimental effects of the large mismatch in the optical and THz frequency refractive indices of an EO crystal, such as LiNbO3 (LN). This technique can be used for any optical probe wavelength since the phase matching is achieved by adjusting the relative angle between the optical probe pulse and the terahertz wave to be detected. Furthermore, in the heterodyne EO sampling, no polarization optics is necessary since the signal originates from the direct intensity modulation by the EO effect. An improvement of the heterodyne EOS signal can be achieved by balanced detection of the two signals originating from difference frequency mixing and sum frequency mixing between the THz wave and the optical sampling wave. In addition, heterodyne EO sampling makes frequency-selective detection achievable. Because of the angle dependent difference frequency and sum frequency mixing processes in the EO crystal, it is possible to obtain frequency resolved EO sampling signal by selecting a particular cross sectional region of the sampling beam. It is also shown that metallic parallel plate waveguide structures are useful to enhance the EO signal. An enhancement of THz EO signal by a factor of 20 has been successfully demonstrated by using a parallel plate waveguide with a Si-prism/LN structure.

(14) **The Determination of Silicon Concentration on Hair Tresses Using FTIR**

Alex Augatis[1], Eugene Oldham[1], Chi-san Wu[1], Musa Osama[1], Courtney Usher[1], Bret Clark[1]; [1]Ashland Specialty Ingredients

The deposition of silicone on hair enables the hair to exhibit numerous performance attributes desirable in the Personal Care Markets. As such, it is desirable to measure the amount of silicone present on hair as it is related to performance. In addition, it is also crucial to monitor the level of silicone after hair is exposed to typical external forces (washing, rinsing, heat treatment, etc). Therefore, identification of an analytical technique that can determine silicone at low levels is desirable. In this study, a quantitative method is presented using Fourier Transform Infrared Spectroscopy (FTIR) to monitor silicone deposition on hair down to ppm levels. Monitoring the intensity of the Si-CH3 stretching absorbance at 1260 cm-1, a linear calibration curve was established with R2 = 0.9969. From this curve, silicone extracted from hair was measured and reported. Further, this study will also demonstrate the validity of this spectroscopic method by a correlation to values obtained chromatographically and by ICP-AES.

(15) **Detection Limits for Blood on Four Fabric Types Using Infrared Diffuse Reflection Spectroscopy in Mid-- and Near--Infrared Spectral Windows**

Stephanie A. DeJong[1], Stephen L. Morgan[1], Michael L. Myrick[1]; [1]University of South Carolina

Infrared spectroscopy provides a non-destructive method for detecting stains of forensic interest on various substrates. In this study, detection limits (DLs) for blood on four fabrics were estimated using infrared diffuse reflection spectroscopy. Samples were prepared by dip-coating acrylic, cotton, nylon, and polyester from solutions of rat blood diluted with water by factors of 25, 50, 100, and 200. Because different ranges of optical frequencies in the mid- and near-infrared spectral regions may provide differential sensitivity, penetration depth, and interference from thermal radiation, four different wavelength regions were compared: long-wave mid-infrared (600-2000 cm-1), short-wave mid-infrared (2000-3800 cm-1), long-wave near-infrared (3800-5000 cm-1), and short-wave near-infrared (5000-7000 cm-1). DLs were estimated in these wavelength regions by the application of partial least squares (PLS) calibration with fourth derivative spectral pretreatment. Selection of the appropriate gap size and the estimated DLs are presented here. DLs range from a dilution factor of 280 (0.11% w/w blood) for nylon to a dilution factor of 4800 (0.009% w/w blood) for acrylic.

(16) **Electrochemical Cell Developed to Measure Heating at an Electrode Surface During Cyclic Voltammetry**

Stephanie A. DeJong[1], Donna Chen[1], John Monnier[1], John Weidner[1]; [1]University of South Carolina

Understanding the processes of oxidation and reduction at electrode surfaces is important for the evaluation of new catalysts. An electrochemical cell has been developed to measure the heating at an electrode surface as a function of current and voltage using a thermal infrared camera. This cell uses an optically reflective thin layer electrode (ORTLE) as the working electrode. The ORTLE comprises a gold-coated layer of porous alumina on an infrared transparent window. The gold coating is optically reflective, allowing selective investigation of the solution within the pores, which instantaneously equilibrate with the solution at the electrode surface. As the current/voltage is systematically varied, the heating at the electrode surface is recorded by the infrared camera monitoring the solution of the pores and so the solution at the electrode surface without interference of the bulk solution.

(17) ***In situ*** **Infrared Spectroscopy of Polystyrene Brush Growth by ATRP Grafted From Initiator on Au Shows Two Kinetic Regimes**

Richard Osibanjo[1], Arrash Yasovolian[1], Taylor Brickey[1], Kaye Caburnay[1], Tonya Kuhl[1], Donald Land[1]; [1]University of California Davis

Growth of well-controlled polymer brushes by living polymerization from surfaces in solution has a wide range of potential applications. In this study, the entire process, from initiator deposition through polymerization, is followed using *in situ* monitoring of several distinct absorption bands for various species by attenuated total reflectance Fourier transform Infrared (ATR-FTIR) spectroscopy. Specifically, atom transfer radical polymerization (ATRP) is used to polymerize styrene at 50ºC from 11-mercaptoundecyl bromoisobutyrate self-assembled on nanoparticle gold electrolessly deposited on germanium substrates. The loss of the initiator film, growth of polystyrene, and loss of styrene monomer as a function of time are followed. All three processes show a rapid initial rate during the first hour, then a much slower rate that persists for hours. The rates of monomer consumption and polymer formation are similar in both regimes. Initial loss of initiator is much faster than the

polymerization reaction, but becomes comparable in the later, slow regime.

(18) **Examining the Structure and Formation of Varying Length Alkyl Silane Monolayers on TiO2 Nanoparticles using *in situ* Attenuated Total Reflectance Infrared Spectroscopy**

Catherine G. McKenas[1], Karla S. McCain[1]; [1]Austin College

Preparing stable monolayers on TiO_2 nanoparticles is important for their use in many applications including dye sensitized solar cells. Alkyl silanes form stable covalent bonds with TiO_2 at room temperature and without the need for an acid or base catalyst. Monolayers were formed with alkyl groups ranging from propyl to octadecyl and bands associated with the monolayers can be seen growing in over time using *in situ* attenuated total reflectance infrared spectroscopy. The structures of the monolayers were analyzed by examining the CH_2 stretching bands and show that monolayers became more ordered as the alkyl group length increased. By working with micromolar concentrations, the kinetics of the reaction can be slowed enough to be measured on a time scale of minutes and were fit to find first order rate constants.

(19) **Rapid Characterization and Quality Control of Cell Proliferation -SPECCs Shedding Light on Culture Media Solutions**

Miriam Unger[1], Inka Pfitzner[2]; [1]CETICS Healthcare Technologies GmbH, Esslingen am Neckar, Germany; [2]BioTeSys GmbH, Esslingen am Neckar, Germany

Cell culture has become one of the major tools used in life science today. In addition to the study of cell functions for fundamental research, the uses of cell lines for the production of pharmaceutical substances or the applications of cells for the assessment of cytotoxicity of materials are of great importance. Thus, quality control and standardization have become indispensable tools in cell culture laboratories. Evaluating the general health or "happiness" of a cell culture is usually based on different cell characteristics: morphology, growth rate and expression of special functions. However, in order to determine if a proposed cell line is suitable for a typical biological assay, reliable and robust analytical techniques are necessary. FT-Infrared (FT-IR) spectroscopy in combination with chemometric methods proves to be highly advantages for this purpose. In this context, it will shown that an especially constructed FT-IR spectroscopic instrument (called SPECCs) is a simple, rapid and cost-effective solution for the characterization of cell quality based on the culture media solutions. The instrument is based on the mid-IR spectral range, the centerpiece is a patent-registered flow-through transmission cell, consisting of a path length of approx. 7 µm and therefore optimized for the measurement of aqueous solutions. Furthermore, the presented study demonstrates that by using well-established chemometric methods like PCA in conjunction with infrared spectroscopy one can generate a simple and effective identification and quality assessment methodology for the complex constituents of different cell media solutions and therefore monitor the status of cell quality.

(20) **Improved Detection of Trace Elements for a Microwave Plasma Atomic Emission Spectrometer (MP-AES) Coupled with an Ultrasonic Nebulizer**

Fred Smith[1], Steve Wall[2]; [1]CETAC Technologies; [2]Agilent Technologies

A new commercial atomic emission spectrometer is equipped with a magnetically excited microwave plasma as the emission source. This source is sustained with nitrogen gas, avoiding the need for more expensive flammable and oxidizing gases used with traditional flame atomic absorption (AA) spectrometers. In addition, the new spectrometer is a scanning type with a CCD detector for multielement measurements, providing sub-microgram/liter detection limits for many elements. This poster will examine the coupling of an ultrasonic nebulizer (USN) to a microwave plasma atomic emission spectrometer (MP-AES). The USN is commonly used with argon-based ICP-AES (inductively coupled plasma atomic emission spectrometer) instruments for enhanced detection limits versus conventional pneumatic nebulizers. As the MP-AES is supplied with a standard pneumatic nebulizer, improved trace element detection should also be possible with the ultrasonic nebulizer. Figures of merit will include calibration and instrument detection limits (IDLs). Of particular interest is improved detection of more difficult elements such as arsenic and selenium and platinum group elements (PGEs) such as platinum, palladium, and gold.

(21) **Qualitative and Quantitative Elemental Analysis using a Tandem System that Combines Laser-Induced Breakdown Spectroscopy (LIBS) and Laser Ablation Inductively Coupled Plasma Spectrometry (LA-ICP-MS)**

Jhanis Gonzalez[1,3], José Chirinos[2], Dayana Oropeza[1], Meirong Dong[1], Richard Russo[1, 3]; [1]Lawrence Berkeley National Laboratory; [2]Escuela de Quimica, Universidad Central de Venezuela; [3]Applied Spectra, Inc.

A system that combined the capabilities and analytical benefits of LIBS and LA-ICP-MS was evaluated for the analysis of a wide range of samples matrices. The ablation system consisted on a Nd:YAG laser operated at 213 nm. Czerny-turner spectrograph with ICCD detection and Time-Of-Flight based mass spectrometer were selected for LIBS and ICP-MS detection, respectively. This tandem system allows simultaneous determination of major elements such Si, Ca, Mg, C, Al using LIBS, while trace elements (i.e REE's) information can be obtained by ICP-TOF-MS. The samples consisted on reference materials used in industries as metallurgic (i.e. Zn, Cu, Fe-based alloys), geochemistry (minerals), and mining (i.e. coal samples). This work focused on calibration strategies, specifically univariate and multivariate calibration. Results shows correlation between data obtained with ICP-MS and LIBS. Also is shown that multivariate calibration can be used in some cases to reduce interferences encountered during the analysis of complex matrices such as coal.

(22) **Differential Laser Absorption Spectroscopy in an Atmospheric Pressure Laser-Induced Plasma: Measurement of Fundamental Uranium Parameters**

Nicholas Taylor[1], Mark C. Phillips[1]; [1]Pacific Northwest National Laboratory

Active probing of laser-induced plasmas using tunable diode laser absorption spectroscopy provides an attractive method of measuring fundamental parameters of atomic and ionic species in the plasma with high spectral and temporal resolution. However, the ablation process for certain samples produces non-resonant amplitude fluctuations in the transient absorbance signal which degrades the signal-to-noise ratio of the method. We present a two-beam differential laser absorption method where two laser beams, a probe beam and reference beam, are spatially combined and used to interrogate the plasma. The probe laser is frequency tuned across a selected uranium transition in discrete frequency steps while the reference laser remains static and detuned from the uranium transition. By measuring the difference in absorption between the probe laser and reference laser, we reduce effects of noise from pulse-to-pulse plasma fluctuations and non-resonant scattering. The method allows us to measure accurate and precise absorption spectra in the plasma, even for weak absorption features.

The differential absorption method was used to perform an experimental characterization of temporally-resolved absorption linewidths of selected atomic and ionic transitions for uranium in

laser-induced plasmas. The increase in measurement sensitivity allowed use of low-concentration uranium-doped glass samples. Uranium absorption spectra were measured in cover gases of argon, helium, nitrogen, and dry air at pressures between 2 and 760 Torr. From Voigt profile fits to the measured high-resolution absorption spectra we separate the time-dependent line-broadening contributions. In particular, we determine pressure-broadening coefficients for uranium in argon, helium, nitrogen, and dry air, as well as an absorption full width at half maximum linewidth for the uranium neutral transition at 861 nm of 2.2 GHz (5.4 pm) in air at atmospheric pressure. Although the current work focuses on uranium, the technique can easily be applied to a wide range of elements and transitions. The results from this work will be valuable both for understanding the fundamental spectroscopy of uranium, and for improving the precision and accuracy of laser-induced plasma spectroscopy measurements including laser-induced breakdown spectroscopy (LIBS).

(23) **LIBS: Hydrogen Balmer Series Plasma Spectroscopy in Air**

Lauren Swafford[1], Christian Parigger[1]; [1]University of Tennessee Space Institute

Time-resolved laser spectroscopy techniques are employed in the study of laser-induced optical breakdown. We utilize Nd:YAG Q-switched laser radiation at a wavelength of 1.064 micrometer to generate a micro-plasma in air that is recorded with a spectrometer and an intensified, linear diode array coupled to an optical multichannel analyzer. The primary objective is to determine the electron density and temperature from the time-resolved spectra for the hydrogen-alpha and hydrogen-beta lines. Stark broadening tables allow us to infer the electron density for various time delays. Due to the presence of species such as nitrogen and oxygen in laboratory air, the hydrogen-alpha line evolves from the free electron background at a time delay of 0.4 microseconds and it is measured for time delays up to 30 microseconds after optical breakdown. The hydrogen-beta line becomes discernible 1.7 microseconds after optical breakdown The electron temperature is inferred from Boltzmann plots, provided that the Balmer series lines are well developed. Current results for air-plasma are compared with previous measurements in pure hydrogen. We also address self-absorption in our experimental studies of the hydrogen Balmer alpha and beta lines in laser-generated micro-plasma. This review includes time-resolved spectroscopy measurements with a gated CCD camera for the purpose of characterizing the plasma's spatial and temporal evolution.

(24) **Manifold Regression of LIBS Data from Geological Samples for Application to ChemCam on Mars**

M. Darby Dyar[1], Thomas Boucher[2], Marco Carmosino[2], Sridhar Mahadevan[2], Samuel Clegg[3], Roger Wiens[3]; [1]Mount Holyoke College; [2]University of Massachusetts Amherst; [3]Los Alamos National Laboratory

ChemCam is a Laser-Induced Breakdown Spectroscopy (LIBS) instrument on board the Mars Science Laboratory rover Curiosity. From distances up to 7m from the target, ChemCam pulses its target, creating a plasma that is recorded over 6,144 channels representing wavelengths from the UV to near-IR. To predict elemental abundances in the rocks, soils, and minerals probed, raw responses are preprocessed and then their compositions are predicted using multinomial regression models (currently PLS) developed by the ChemCam team. To suggest possible alternatives for future models, we used a previously well-studied dataset of spectra from 100 geological samples acquired at Los Alamos National Laboratory using a LIBS instrument designed to simulate ChemCam under Mars-like conditions. Using this dataset for training models, the current best performing regression models are sparse partial-least square (SPLS) models and l_1/l_2-regularized least squares (RLS) models. In this study, we use *locally-linear embeddings* in combination with the best current models to improve the overall prediction accuracy of both SPLS and RLS. Locally-linear embedding is an unsupervised machine learning algorithm that provides a non-linear, low dimensional embedding of high dimensional data. By maintaining local neighborhood distances and discarding large global geodesic distances in the embedding, the algorithm attempts to discover the underlying low dimensional latent manifold of the model's explanatory variables. By using manifold learning techniques, we are both regressing on the intrinsic geometry of the data and removing noisy features. To train and evaluate the models, the dataset was divided into training and test sets with approximately the same elemental compositions. On the training set, 10-fold cross validation was used to fit the weights of the model and grid-search with a one-standard error heuristic was used to tune the hyperparameters. All model evaluation was performed on the held out test set. Using the 100-sample dataset and our new *manifold regression* model, we show a statistically significant improvement in the prediction accuracy of certain principle elements.

(25) **On the Effects of Distance between a Laser and Its Target in LIBS Measurements**

Alissa Mezzacappa[1], Noureddine Melikechi[1], Agnes Cousin[2], Nina Lanza[2], Sam Clegg[2], Gilles Berger[3], Steve Bender[2], Jeremie Lasue[3], Roger Wiens[2], Sylvestre Maurice[3]; [1]Delaware State University; [2]Los Alamos National Laboratory; [3]Institut de Recherche en Astrophysique et Planetologie (IRAP)

The ChemCam instrument focuses its excitation laser through a telescope. While this configuration allows the tremendous advantage of LIBS observations at many distances, it also changes the spot size of the focused beam on its target . Changing spot size impacts irradiance, ablation crater size, and analytical signals. To address the impact of the variable geometry of ChemCam observations, we define an internal standard using dust which is discriminated from 1st shot observations. We generate a model for selected emissions' behaviors from the standard. We test the accuracy with which this model corrects for variable distance for each individual emission selected using the thermal vacuum data set taken at LANL with the ChemCam flight model. We verify that corrected signals match measured signals within 5%-20% for Mg, Si, Al, Ca & K and ~30% and ~40% respectively for Fe and Na. Generating PCA with original and corrected spectra yield non-trivial differences in principle components on the order of ~10%. We conclude from applying our method to the TVAC dataset that distance correction using the first laser shot yields improvements in TVAC data in terms of reproducibility from one distance to another. From the PCA results we extrapolate that varying distance conditions has impacts on higher-level multivariate analyses.

(26) **Advancing the Analytical Capabilities of Laser Ablation Molecular Isotopic Spectrometry (LAMIS) for Boron Isotopic Analysis**

Arnab Sarkar[1,2], Xianglei Mao[1], Meirong Dong[1], Richard Russo[1]; [1]Lawrence Berkeley National Laboratory, Berkeley, California; [2]Fuel Chemistry Division, Bhabha Atomic Research Centre, Mumbai, India

Isotopic analysis is a critical component of material characterization for the nuclear industry and nuclear forensic. From fuel preparation to waste storage, each stage requires isotopic ratio determination. Russo *et al.* demonstrated that LIBS can be extended to study molecular emission in addition to atomic or ionic, thereby expanding the analytical capability to include isotopic analysis. The technique is called **Laser Ablation Molecular Isotopic Spectroscopy** (**LAMIS**). The method has been successfully applied for isotopic studies of C, H, B and Sr. The precision of the method in the initial reported study was 25 - 40‰. Although these values are impressive for a new technology, they are less than ICP-OES (~1-10‰), ICP-MS (~10-

30‰), GFAAS(5-50‰) and TIMS(<0.01-0.1‰). The aim of this work was to investigate the effect of different spectral region, data pre-treatment and degree of spectral accumulation on the precision of the LAMIS method for B isotopic measurement. BO has a rich molecular spectrum consisting of week B- X (~255 nm) and strong A- X (300-700nm) vibrational bands. B_2O_3 isotopic standards prepared by mixing pure $^{1}B_2O_3$ and pure $^{10}B_2O_3$ on weight basis were used for this study. An in house Labview based PLSR algorithm has been used for this study. PLSR calibration curves were constructed for four strong emission regions and compared using different statistical parameters (Standard error of calibration, Standard error of Prediction and Relative error of Prediction). The 503-571 nm region consisting of 0-2 band was the best region in terms of statistical parameters. Using this region the precision improved to ~17‰ from ~35‰. Different normalization procedures viz, normalization with respect to maximum, minimum standard deviation, norm etc. were carried out as a part of data pretreatment before analysis by PLSR. By applying this procedure the precision further improved to ~13‰. Spectral accumulation is known to increase the signal to noise ratio thereby decreasing the noise contribution in spectra. By increasing the accumulation number of laser ablation pulses per spectra to 1000 precision of ~5‰ was achieved. Extrapolation the number of pulses to 105 provides a precision <1‰.

(27) **Boron Isotopic Compositional Mapping by Laser Ablation Molecular Isotopic Spectrometry (LAMIS)**

Arnab Sarkar[1,2], Jose R. Chirinos[1], Dayana D. Oropeza[1], James K. Wu[1], Jhanis J. Gonzalez[1], Meirong Dong[1], Xianglei Mao[1], Richard E. Russo[1]; [1]Lawrence Berkeley National Laboratory, Berkeley, California; [2]Fuel Chemistry Division, Bhabha Atomic Research Centre, Mumbai, India

In the water cooled and/or moderated thermal neutron nuclear power reactors like pressurized heavy water reactor (PHWR), boron in form of boron carbide (B_4C) is the most commonly used material in control rod for neutron absorption during the control and the shut-down of the reactor. In the reactor, after a long time exposer of neutron radiation inhomogeneous radial burnout of B in the B_4C pellet can occur. Mapping of this radial burn-up of boron is very important to understand the neutron flux history of the reactor. Models which allow one to estimate this radial burnout are typically validated by TIMS analysis of a previously dissolved fraction of the material, resulting area-averaged analytical burnout values. SIMS has been also applied for this study, but it is a very time consuming and also not cost effective method. The Laser Ablation Molecular Isotopic Spectroscopy (LAMIS) method developed by Russo et al. is an optical detection system and has the capability to doing real time, on-line, *in situ* isotopic analysis in hazardous environment such as in nuclear reactor. The method has been successfully applied for isotopic study of C, H, B and Sr. In the present work, the LAMIS technology has been applied for mapping a B_2O_3 pellet having different isotopic composition in the axial direction. The isotopic composition was varied from 20% ^{10}B to 80%^{10}B. Keeping in mind the goal of mapping, the number of laser shot was kept as minimum as possible but not degrading the analytical precision by more than 2%. 30 laser shot spectral accumulation in the 503-571 nm region consisting of 0-2 band was found to the optimum with an analytical precision of ~1.6%. Using this condition a 7.3 X 7.3 mm area was mapped with 11x11 pixel resolution. The obtained map was found to be in good agreement with the map obtained from LA-ICP-MS mapping analysis.

(28) **Oscillator Strength Measurements in Lanthanides and Transition Metals Using Laser-Induced Breakdown Spectroscopy**

Russell Putnam[1], Caleb Ryder[2], Steven Rehse[1]; [1]Department of Physics - University of Windsor; [2]National Superconducting Laboratory - Michigan State University

Models for stellar nucleosynthesis, age determinations for stars in the Milky Way's galactic halo, and stellar chemical abundance determinations are dependent upon accurate atomic spectroscopic data to allow the correct interpretation of stellar absorption and emission spectra. It is well known that calculations of many astrophysically important atomic parameters are limited due to line blending, insufficient spectral resolution of some key spectral lines, and also the complicated electronic structure of the important heavy elements. Astrophysicists have therefore looked to laboratory astrophysics experiments to provide accurate atomic data to help resolve these limiting issues. In this set of experiments, laser-induced breakdown spectroscopy (LIBS) has been employed for the rapid and convenient production of a high-temperature plasma to act as a source of excited atoms and ions. Emission from the LIBS plasma, when dispersed in a high-resolution Echelle spectrometer, is used to measure all the emission lines from numerous excited energy levels simultaneously. Branching ratios from over 1,000 highly-excited energy levels in astrophysically relevant lanthanides (gadolinium, neodymium, praseodymium and samarium) and transition metals (copper and iron) were measured in order to calculate emission oscillator strengths (gA values or log gf values). In this poster we will present our most recent results and compare them to previous experimental measurements and calculations.

(29) **Atomic Emission Lifetimes of Quiescent Air, AP and AN from ns Laser Induced Plasma Plume vis-à-vis Laser Induced Breakdown Spectroscopy**

Manoj Kumar G[1], Leela Ch[1], Suman Bagchi[2], Sreedhar S[1], Ashwin Kumar M[1], Prem Kiran P[1]; [1]ACRHEM, University of Hyderabad, Hyderabad, India; [2]Raja Ramanna Centre for Advanced Technology, Indore, M. P, India

We compare the atomic emission lifetimes of quiescent air, Ammonium Perchlorate (AP) and Ammonium Nitrate (AN) measured by high-speed time resolved imaging of ns laser (Nd:YAG, 532nm, 7 ns) induced plasma plumes with that of the lifetimes obtained using Laser induced breakdown spectroscopy (LIBS) technique. High-speed imaging is performed by capturing spatio-temporal evolution of various species from expanding laser plasma plume using an ICCD camera (ANDOR, DH-734). A tunable filter in the visible spectral region (VARISPEC VIS-07-20-STD, 10 nm bandwidth) was used to capture the emission line of interest. Specific line emissions H_β (486 nm), N^+ (568 nm) and O (720 nm) from air and H (656nm), NaI (589nm) and NaII (635nm) from AP & AN were measured and compared. The captured images were processed using MATLAB to extract the integrated photon count and lifetimes, generating the emission profile from prominent lines of air, AP and AN. Atomic line emissions from LIBS data was collected using a combination of Mechelle spectrograph (ME-5000) and an ICCD camera (DH-734, ANDOR). AP and AN were taken in the form of a pellets. Of the emission lines studied, the line at 656 nm (H) was found to be closely matching with the lifetime estimated using LIBS spectrograph, though the spectral bandwidth of the diagnostics used is drastically different. The anomaly between the different diagnostics is due to the presence of different emission lines within the allowed spectral width (10nm) of the filter in the case of time resolved imaging, while the LIBS spectrograph has a spectral resolution of 0.05nm at 254nm. By narrowing down the spectral range of the imaged light to that of a specific line, this method can be extended to the study of reaction kinetics and has a potential application in the pollution monitoring during the combustion process.

(30) **Temporal Characterization of Nanosecond Pulsed Laser Initiated Breakdown Threshold in Liquid Water**

Bhamidipati Sitalakshmi[1], Sunku Sreedhar[2], Ashoka Vudayagiri[1, 2]; [1]University of Hyderabad; [2]ACRHEM

Powerful pulsed lasers has been used for creating breakdown in solids,liquids and gasses. Dominating mechanism of creating critical density of electrons during breakdown process with short and ultrashort pulses is multiphoton ionization (MI). During breakdown initiation with nanosecond and longer pulsed laser, cascade ionization also contributes to the free electron generation along with the MI. Cascade ionization is a statistical process as it needs numerous collisions for collisional ionization and also for electrons to get energized through inverse bremsstrahlung absorption. These statistical process makes the initiation process probabilistic and more so in liquids because of their amorphous nature. We propose here a spectroscopic method for defining the breakdown initiation time in nanoseconds for the phase transition of liquid water into plasma using an enhanced stimulated Raman signal (SRS). Since Raman modes in water molecule are enormously ampli ed due to the presence of solvated electrons, this signal is a very intense and can be measured with a fast rise time photodetector. The emitted SRS has pulse width shorter than the incident exciting laser, 7 nanosecond laser pulse in our case and decays down before the critical density of plasma is reached. These solvated electrons are generated by the nanosecond pulse when the threshold intensity for ionization is just reached and these initial first electrons induce strong electric field. As water molecules are polar, a local nonlinear polarizability is induced very close to these charges. Our spectroscopic de nition allows a measurement of onset of breakdown. Though this does not remove the uncertainty in the threshold level for plasma initiation, it can nevertheless gives a signal in nanoseconds to picoseconds before the critical density of plasma is reached within the focal volume during the time scales when the nanosecond pulse is present. The spatial extent of the plasma can also be computed using the spatial extent of the laser beam pulse and the `Moving breakdown model'. Results of this calculation will be presented for different incident laser energies.

(31) **Spectral Analysis of RF Emissions from Laser Produced Plasma of Atmospheric Air and Metals**

Manoj Kumar[1], Vinoth Kumar L[1], Manikanta Elle[1], Leela Chelikani[1], Prem Kiran Pathuri[1]; [1]Advanced Centre of Research in High Energy Materials (ACRHEM), University of Hyderabad

Laser produced plasma (LPP) of target materials (solids, gases etc) are used to generate electromagnetic (em) radiation over a wide range of frequencies in the em spectrum. The low frequency region of the em spectrum (RF and micro waves) from LPP has potential applications such as laser ground penetrating radar (LGPR), standoff materials detection and characterization etc. The RF and micro wave spectra emitted by the nanosecond LPP of atmospheric air and metal (aluminum and copper) targets were detected using antennas of different frequency ranges (30MHz-18GHz) and were monitored using a spectrum analyzer (3Hz-50GHz). The characteristics of these low frequency em waves were studied. With different target materials, for a particular laser and antenna polarization, the dominant emission lines corresponding to the oscillations of the induced dipoles were observed to fall in different frequency ranges within the detection limit. Besides, continuum background, which is due to the acceleration/deceleration of the electrons in the plasma, was observed. The RF emissions from the LPP of metals, with linearly polarized input laser beam, were observed to be lesser than that of air, which is a mixture of different elements. The emissions from the LPP of copper were in the higher frequency range (100-200 MHz) than that of aluminum (30-100 MHz). This may be due to the higher value of electron density, which contributes to the plasma conductivity, in the LPP of copper. From the LPP of atmospheric air, the RF output was found to be increasing with the input laser energy up to certain value, beyond which almost no emission was observed in the detection range. This effect can be attributed to the modification in the net induced dipole moment due to the multiple plasma sources in the LPP at higher input laser energies. For all the materials studied, the RF emissions, in 0.03-1GHz range was found to be greater than that in 1-18GHz range by three orders of magnitude. The detected radiation was observed to be dependent on laser and antenna polarization. Detailed studies may lead to an efficient technique for material identification from the RF characteristic peaks.

(32) **A Reinterpretation of Depth Profiling Data Using LIBS**

Carlos Montoya[1], Nancy Mcmillian[1], Warren Chesner[2]; [1]New Mexico State University; [2]Chesner Engineering

Current methods of providing depth profiles using LIBS have been hampered by poor depth resolution of sharp boundaries. Instead of rapid changes in elemental intensities with depth, intensities change gradually over 10s to 100s of laser pulses. This study proposes a physical model for this phenomenon. In this study a Big Sky Nd-YAG laser operated at its fundamental wavelength of 1064 nm at a laser power of 121.4 mJ. A steel coupon coated with a layer of Acrolon 218 HS acrylic polyurethane gloss over a layer of Macropoxy 920 per-primer over Zinc Clad III HS epoxy primer that overlies a base surface of steel was used. Five locations on each coating surface were analyzed using the drilling method. Spectra from laser pulses at depth are contaminated by material from the upper layers. For example, Ca intensities start fairly high in Acrolon and decrease smoothly with depth even when the laser has reached steel. The presence of significant Ca peaks in steel suggests contamination from the overlaying Acrolon and primer layers. Similarly, Zn intensities continue to increase after the laser has reached steel. We interpret this trend as a result of the Gaussian shape of the laser pulse and catastrophic ablation of material, which produces an irregularly shaped drill hole whose edges are ablated with each pulse. This phenomenon has been observed in geologic materials such as Mn oxide and caliche coatings in desert environments.

(33) **Calibration Issues in Deep-Ocean LIBS: The Use of H and O as Internal Standards**

Joseph Bonvallet[1], S. Michael Angel[1]; [1]University of South Carolina

The development of *in situ* chemical sensors that can provide real time, multi-elemental sensing capability would be a significant advance over current oceanographic technology. To this end, laser induced breakdown spectroscopy (LIBS) has been used to carry out a wide range of laboratory measurements to validate the use of LIBS in aqueous solutions under realistic oceanic pressures, with a long-range goal of deploying a LIBS system on Alvin or other deep-ocean submersibles to measure the elemental composition of deep-ocean hydrothermal vent fluids. The results of our studies indicate an ability to measure the alkali and alkaline metals at ppm levels at pressures up to 3 × 10E7 Pa (~2800 m water depth equivalent), and that matrix effects produced by interactions between elements in mixtures (such as seawater) are virtually nonexistent. However, an ongoing issue using LIBS in bulk aqueous solution is variability in the intensity of the LIBS emission. A current study to improve precision in LIBS measurements is to use an element of known or fixed concentration in water as an internal standard. The use of O and H as internal standards for high pressure LIBS measurements in water looks promising. In this talk, the results of our latest studies using O, H, and other elements as internal standards to improve the precision of LIBS measurements of Na, Li, K, Ca, and Mn will be presented.

(34) **Dynamics of Ultrafast Laser Ablation Plumes in the Presence of Gases: Implications to LA-ICP-MS and LIBS**

Prasoon Diwakar[1], Sivanandan Harilal[1], Ahmed Hassanein[1]; [1]Center for Materials Under eXtreme Environment, School of Nuclear Engineering Purdue University, West Lafayette, Indiana

Laser produced plasmas (LPP) are an important source for various applications including pulsed laser deposition, nanoparticle production, cluster formation, laser induced breakdown spectroscopy (LIBS), and laser-ablation inductively coupled plasma (LA-ICP-MS). Understanding plasma plume dynamics is key for these applications. Evolution of plasma plume is transient in nature and is influenced by laser parameters such as laser wavelength, pulse duration, spot size, irradiance, target properties, and ambient background pressure and composition of gas. The processes are more complex in fs LPP and are not clearly understood and needs further investigation.

In this study, expansion dynamics and internal plume structure of fs laser ablated brass plasma in Ar and He at different pressures ranging from vacuum to atmospheric was studied using time resolved and time integrated 2-dimensional imaging. A brass target consisting of roughly 70% copper and 30% zinc was used for plasma creation. Plasma creation was accomplished using a Ti: Sapphire laser system to produce 40 fs laser pulses, measured using an autocorrelator, at a wavelength of 800 nm. Fast photography was performed using an intensified CCD camera placed orthogonal to the laser beam. Visible radiation from a wavelength range of 350–900 nm was recorded integrally from the plasma. The images were obtained using monochromatic line filters to separate out emission from Cu and Zn species in brass plume with the aim of understating spatial distribution of Cu and Zn species in brass plume. Brass target is subject to elemental fractionation in ns plasma sources owing to huge differences in their thermal properties resulting in matrix and fractionation effect which affects LIBS and LA-ICP-MS quantitative measurements. Femtosecond LA is known to reduce such fractionation effects. In this study, we report spatial distribution of Cu and Zn species in fs LPP and the observations are discussed. Plume confinement and fractionation effects were observed at higher pressures for both He and Ar with the effect being more prominent for He ambient environment.

(35) **Isomer Identification Using Laser Induced Breakdown Spectroscopy**

Manoj Kumar Gundawar[1], Ashwin Kumar Myakalwar[1], Shiv Kumar Anubham[1], Ishan Barman[2], Narahara Chari[2]; [1]University of Hyderabad; [2]Massachusetts Institute of Technology

Isomer identification is crucial in reactions where the product molecule can exist in different isomer forms. Various techniques, like Nuclear Magnetic Resonance, high resolution mass spectroscopy, are presently employed to distinguish one isomer from another or to tag a given compound as being a particular isomer. The present methodologies require elaborate sample preparation protocols and the instrumentation is costly. We propose a simple and cost effective method based on laser induced breakdown spectroscopy (LIBS) for isomer identification. LIBS signal consists of atomic emission from the plasma created by a laser focused on to the sample. Isomers produce LIBS signal with similar signatures but exhibit subtle, reproducible variations that maybe potentially useful for classification. The implementation of multivariate chemometrics makes it possible to build an algorithm based on training set of data that can identify a prospective sample, whose particular isomer status is not known a priori by the model. In this paper we present the results on two sets of isomers of sugars and pyrojoles. LIBS spectra were acquired using a home-made setup consisting of a Nd :YAG laser and a Michelle spectrogram coupled to an ICCD. In both cases, apart from the atomic signatures of carbon, oxygen, nitrogen and hydrogen, molecular emissions of CN were observed. The application of Partial least squares resulted in a score plot with very well separated clusters. An average sensitivity and specificity in excess of 0.80 was obtained in both the cases using the raw data. The results are encouraging and it can expected that with the appropriate data preprocessing, outlier removal and feature selection the sensitivity and specificity can be further enhanced, which will presented in this paper.

(36) **Discrimination Analysis of Nitroimidazoles Studied with Femtosecond Laser Induced Breakdown Spectroscopy**

Manoj Kumar Gundawar[1], Nageswara Rao Epuru[1], Sreedhar Sunku[1], Venugopal Rao Soma[1]; [1]ACRHEM, University of Hyderabad, India.

Though LIBS technique has been successfully employed in various fields there are a number of challenges to be addressed before it can be successfully implemented for explosives detection. We reported some of our results of LIBS spectra of different nitro group explosives such as Imidazole, 4-nitroimidazole, 1,4-dinitrimidazole, 2,4-dinitroimidazole, 1-methyl-4-nitroimidazole, 2-methyl-4(5)-nitroimidazole and 1-methyl-2,4-dinitroimidazole recorded with femtosecond pulses. 25 LIBS spectra were collected in argon atmosphere and used for discrimination analysis and four spectra in ambient air atmosphere with input laser energy of ~1 mJ. Our experiments utilized a gate delay of 100 ns and a gate width of 800 ns for ratiometric analysis. We studied the features in the spectral range of C2 swan system with Δv=-1,0 and +1 (460-475 nm, 510-520 nm and 550-565 nm) and CN violet system with Δv=-1,0 and +1 (357-360 nm, 384-389 nm and 414-423 nm) along with elemental (C, H, N, O) features. The CN violet band was most intense in nitrogen atmosphere than air and argon atmosphere. The C2 swan band was intense in argon atmosphere compared to nitrogen and argon atmospheres. We investigated the several intensity ratios of molecular CN, C2 to atomic C, H, O and N intensity ratios were O/N, O/H, N/H, O/C, H/C N/C and CN/C2, CN/C, C2/C, (C2+C)/CN, CN (total at Δv=-1,0,+1)/C, C2 (total at Δv=-1,0,+1)/C. The intensity ratios of O/H and H/C are about matched according to the molecular formula for all nitroimidazoles except the 1methyl-2,4-dinitroimidazole and 2,4-dinitroimidazole. The effect of number of nitro groups on the atomic and molecular emission and signature of high energy materials has been evaluated.

(37) **Fast Steel Analysis Using Laser-Induced Breakdown Spectroscopy**

Markus Gaelli[1]; [1]TSI Incorporated

Laser-induced Breakdown Spectroscopy (LIBS) is a fast method to quantitatively measure components in steel as well as for classification of different steel types. LIBS works by creating a laser-induced plasma at the surface of an untreated sample, and the resulting emission spectra are collected in milliseconds, allowing for fast elemental analysis. These capabilities have a wide field of application, such as QA/QC in steel manufacturing, sorting of scrap metal, incoming material inspection, and many others. In this work, we will present results on steel identification using the new TSI ChemReveal Desktop LIBS analyzer. Different grades of steel were sampled and the resulting LIBS spectra were analyzed using both univariate and multivariate methods. Quantitative determination of concentrations of several elements in the steel samples will be compared between univariate calibration, using TSIs ChemLytics software, and a commercial multivariate approach. In addition, different grades of steel were classified using the SIMCA (Soft Independent Modelling of Class Analogies) algorithm, which sorts samples based on similarities and differences in spectra using Principal Component Analysis (PCA). Results will be compared to measurements made with a commercial Arc/Spark-OES instrument. The LIBS system offers a number of advantages for the applications described here, such as simultaneous quantification of many elements, fast analysis (both measurement and data analysis), little or no sample preparation, ability to measure irregular shapes of

material, and capabilities for surface mapping and depth profiling. LIBS can therefore be used to test for sample homogeneity (e.g. inclusions), both on a surface and throughout the sample, providing a very comprehensive assessment of an unknown metal sample.

(38) **Elemental Analysis of Thin Cu(In,Ga)Se2 Solar Cell Films Using Femtosecond Laser-Induced Breakdown Spectroscopy**

Seokhee Lee[1,2], Jhanis Gonzalez[2, 3], Jong Yoo[3], Xianglei Mao[2], Richard Russo[2, 3], Sungho Jeong[1]; [1]School of Mechatronics, Gwangju Institute of Science and Technology; [2]Lawrence Berkeley National Laboratory; [3]Applied Spectra Inc.

In this work, the analysis of elemental composition of thin $Cu(In,Ga)Se_2$ (CIGS) solar cell films (1~2 μm thickness) by femtosecond laser induced breakdown spectroscopy (fs-LIBS) is reported. A third harmonic fs laser (wavelength = 343 nm, pulse width = 500 fs) was used for the ablation of CIGS films with a spot diameter of 20 μm at the sample surface and the emission spectra were detected with an intensified charge coupled device (ICCD) spectrometer. The optimal laser pulse energy (0.1 mJ, 31.83 J/cm^2) and ICCD detector parameters such as gate delay (40 ns) and gate width (300 ns) were determined at the conditions of highest signal-to-background ratios of Ga and In emission lines because the concentrations of these elements are closely related to the efficiency of CIGS solar cells. The calibration curves for LIBS signal intensity ratios of Ga/Cu, In /Cu, and Ga/In were generated with respect to the concentration ratios measured by inductively coupled plasma optical emission spectrometry (ICP-OES). Also, the correlation of fs-LIBS intensity ratios with those from fs laser ablation inductively coupled plasma mass spectrometry (fs-LA-ICP-MS) and nanosecond (ns) LIBS was examined. The results showed that the fs-LIBS results had a high linearity with fs-LA-ICP-MS and ICP-OES results, whereas ns-LIBS results showed nonlinear change.

(39) **Spatially Resolved vs. Spatially Integrated Measurements of Parameters of Laser Induced Plasma**

Igor Gornushkin[1], Alexandr Demidov[1], Ulrich Panne[1, 2], Ebo Ewusi-Annan[3], Ben Smith[3], Nicolo Omenetto[3]; [1]Federal Institute for Materials Research and Testing (BAM); [2]Humboldt-Universität zu Berlin, Department of Chemistry; [3]Department of Chemistry, University of Florida

It is common to assume that laser induced plasma (LIP) is under local thermodynamic equilibrium (LTE), is spatially homogeneous and stationary. Considering that LIP is a transient event, these assumptions may or may not be justified. Uncertainties in plasma parameters (e.g. temperature and number density of species) coming from spatially integrated measurements can be large. In this work, we compare spatially resolved and spatially integrated diagnostics of LIP. We use the spectral matching method developed by us earlier which is performed on spatially resolved plasma emissivities and spatially integrated plasma intensities. In order to obtain spatially resolved distribution of plasma emissivity, we measure spectra emitted by narrow horizontal slices of the plasma and perform Abel inversion on them. The spectral matching method is based on generation of synthetic spectra and fitting them to experimental spectra. This is done by the iteration of plasma parameters, i.e. plasma temperature and concentrations of species. We assume LTE for generation of spectra.

The analysis is done for LIPs ignited in argon and on aluminum alloy and on carbon samples in atmospheric air. In the latter case we measured not only atomic but also molecular emission that allowed us to detect vibro-rotational plasma temperature. The plasma evolution is monitored on the μs time scale for the light integrated within several tens of ns. We show how the plasma temperature and species number densities differ for measurements with spatially resolved emissivities and spatially integrated intensities at different delay times with respect to plasma initiation.

(40) **Absorption Laser-Induced Breakdown Spectroscopy**

Igor Gornushkin[1], Michael Asgill[1], Ulrich Panne[2]; [1]Optical Spectroscopy Working Group, Federal Institute for Materials Research and Testing, Berlin, Germany; [2]Humboldt-Universität zu Berlin, Department of Chemistry, Berlin, Germany

Absorption Laser-Induced Breakdown Spectroscopy (Absorption LIBS) is a technique that aims at combined atomic emission and absorption measurements to improve the capabilities of traditional LIBS. The technique involves using a high repetition rate laser to ablate the sample. While the luminous early plasma is used for traditional atomic emission LIBS, the late plasma is used for absorption LIBS. After the plasma has cooled, the non-luminous cold atomic vapor cloud is illuminated by a broadband light source. The source is either a second laser-induced plasma induced in the vicinity of the vapor cloud or a high intensity broadband continuum lamp. The light passed through the absorbing cloud is coupled to a high resolution spectrometer in order to perform High-Resolution Continuum Source Atomic Absorption Spectroscopy (HR-CS-AAS) [1]. Since the absorption signal is directly proportional to the number of absorbers, calibration-free analysis can be attempted. By simultaneously processing the emission and absorption spectra, the accuracy and precision of LIBS is further improved. Also, while using a second laser-induced plasma as the line light source, the study explores line source absorption LIBS (LS Absorption LIBS). In this technique, the two laser pulses and the collection are timed such that the atomic emission from the illuminating plasma serves as the line source for the absorption by the cold vapor cloud. Preliminary results on iron and copper are presented using an Energetiq EQ-99 Laser Driven Light Source as the broadband continuum lamp, a LaserTechnik Berlin Aryelle Butterfly high resolution echelle spectrometer and a Teem Photonics PowerChip Diode Pumped Solid State laser operating at 1000 Hz to create the vapor cloud.

[1] B. Welz, H. Becker-Ross, S. Florek, U. Heitmann, High-Resolution Continuum Source AAS: The Better Way to Do Atomic Absorption Spectrometry, Wiley-VCH Verlag GmbH & Co. KGaA, Weinheim, Germany, 2005.

(41) **Concepts of Operation for LIBS-based Exploratory Geochemistry and Chemostratigraphy**

Pablo Sobron[1,2]; [1]SETI Institute; [2]MalaUva Labs

Laser-induced breakdown spectroscopy (LIBS) is an emerging tool in exploratory geochemistry owing to its capability to obtain chemical information from a large variety of targets in both close-up and stand-off configurations. In this paper we demonstrate two concepts of operation of the LIBS technique to characterize the chemostratigraphy, i.e. variations in major and trace element abundances and its correlation with layering in (i) meter-scale outcrops comprising sedimentary layers, and (ii) sub-millimeter coatings in altered rocks.

Our results prove that semiquantitative chemical stratigraphy can be very rapidly obtained by performing stand-off LIBS measurements on visually distinct layers within outcrops. Such semiquantitative chemical stratigraphy provides critical information on the distribution of elements across the layers, which can be used for tactical operation purposes such as preliminary characterization or identification of specific layers for more detailed sampling and analysis with close-up instrumentation. In addition, our results show that close-up LIBS can be used to rapidly differentiate coatings based on their chemical composition and to quantify layer-to-layer chemical transitions in alteration coatings on rocks. This characterization provides insight on the formation of those deposits and the chemical composition of fluids in the multiple episodes of mineral deposition. LIBS signature of coatings is also a powerful tool that provides tactical advantages in in-situ geochemical exploration as the signature can effectively be used to rapidly identify potential targets for further sampling or detailed analysis.

(42) **Study of Plasma Dynamics for Dicarboxylic Acids Induced by NDYAG- CO2 Enhanced Dual Laser Pulses**

Staci Brown[1,2,3], Charlemagne Akpovo[1, 2, 3], Jorge Martinez[1, 2, 3], Lewis Johnson[1, 2, 3]; [1]Florida A & M University; [2]Physics Department; [3]Center for Plasma Science and Technology

Laser Induced Breakdown Spectroscopy (LIBS) was used as a method to monitor the evolution of carbon, hydrogen-alpha, nitrogen, carbon-carbon and carbon-nitrogen spectral emissions from atmospheric recombination in a specific set of organic materials. Ablated samples were composed of a series of linear chain dicarboxylic acids with two to seven carbon atoms. Accumulated pulses of a focused Nd:YAG Q-Switched laser beam operated at 532nm generate a plasma in air at the sample surface. A comparative study was conducted by enhancing the nanosecond LIBS plasma with CO2 laser pulses with an operating wavelength of 10.6μm. Preliminary results with nanosecond pulses indicate that (1) the carboxylic functional group, -COOH, does not contribute to the production of C2 emissions; (2) C2 emission intensity increased with increasing number of non-functional carbon; (3) the presence of a chiral carbon inhibits the production of C2 emissions; (4) CN emissions tend to split the group of samples into two sets within which the CN emission intensity increased with increasing number of carbon. Through a time-resolved analysis, we demonstrated the correlation between selected emissions signal strength and the number of carbon in the linear chain. We also, illustrate the effects that these constraints, along with the presence that a chiral carbon in the chain, have on the peak intensities of the individual lines with respect to each other and plasma temperature through showing the increase or nonexistence of certain spectral lines as we increase the number of carbon in the linear chain. Molecular temperature calculations were done by applying a spectral fit to molecular spectra.

(43) **Multivariate Optimization and Sample Preparation for Analysis of Fertilizers by Laser Induced Breakdown Spectroscopy**

Lidiane Cristina Nunes, Edenir Rodrigues Pereira-Filho[2], Francisco José Krug[1]; [1]Center for Nuclear Energy in Agriculture (CENA-USP); [2]Federal University of São Carlos (UFSCar)

The suitability of quantitative analysis by LIBS combines features of grinding for appropriate homogenization, and sampling. In addition, experimental variables may affect instrumental data and the quality of the results. In this contribution a LIBS procedure is proposed for the direct analysis of fertilizers. The strategy was to optimize LIBS operational conditions for the simultaneous determination of Cd, Cr, Pb, and Ni in two groups of samples: phosphate fertilizers and sources of micronutrients. Delay time, lens-to-sample distance (LTSD), laser energy, and number of accumulated pulses were optimized through Doehlert design and desirability function approach. The experimental setup was designed with a Q-switch Nd:YAG laser (5 ns, 10 Hz, 1064 nm) and the emission signals were collected by lenses into an optical fiber coupled to spectrometer furnished with an Echelle optics and equipped with an ICCD detector. Test samples (pellets) were prepared after laboratory samples comminution in a cryogenic mill with a self-container liquid nitrogen bath, or by using a planetary ball milling with tungsten carbide components (jars and balls). Pellets were prepared by transferring 0.80 g of powdered material to a 15 mm diameter set and applying 8.0 ton cm-2 during 5 min. The effects of laser-pellets interaction will be shown through SEM images. As expected, the resulting emission signals of Cd, Cr, Pb, and Ni varied as a function of particle size distributions that, in turn, depend on grinding time and the grinding method. All tested variables were significant based on the factorial experimental design. For each group of fertilizers a single LIBS working conditions, that maximize emission intensities of all elements simultaneously, is recommended. It is also demonstrated that the proposed approach can be a suitable and useful tool for the optimization of complex matrix dependent analytical problems.

Acknowledgments: Processo nº 2010/17158-8, São Paulo Research Foundation (FAPESP) and CNPq (140926/2009-7, 305913/2009-3, 578728/2008-7) for fellowships, grants and financial support.

(44) **New Applications of Quantum Cascade Lasers in Analytical Chemistry**

Bernhard Lendl[1], Markus Brandstetter[1], Christoph Reidl-Leuthner[1], Georg Ramer[1], Johannes Waclawek[1], Harald Moser[1]; [1]Vienna University of Technology

Mid-IR quantum cascade lasers can be considered an enabling technology for the development of novel applications of mid-infrared spectroscopy for the analytical sciences. This presentation will highlight recent advances in the analysis of liquids for biomedical diagnostics and trace gas analysis using open-path as well as photo-acoustic spectroscopy. Finally, results on the hyphenation of quantum cascade lasers with atomic force microscopy for infrared imaging on the nano-scale will be shown as well.

(45) **Quantum Cascade Laser Arrays for Integrated Optics**

Mathieu Carras[1], Sergio NIcoletti[2], Mickael Brun[2], Gregory Maisons[1], Fahem Boulila[1], Pierre Labeye[2], Pierre Barritault[2]; [1]III-V Lab; [2]CEA-LETI

In optical spectroscopy applications, Quantum Cascade Lasers (QCL) have become one of the main candidate for easy to integrate, cheap, high power, high beam quality emission sources. Distributed feedback version of this semiconductor lasers has brought narrow spectral line width enabling high selectivity at the molecule detection level. However, the limited number of available wavelengths is still a break in the take-off of the technology. We present here a approach in which a laser array comprising tenth of lasers act has a continuously tunable source with a single output facet thanks to the use of an AWG (arrayed waveguide) made of silicon. The AWG presented in the paper covers 100cm-1, with 30 channels. It is configured to target specific molecules (CO, CO2 and N2O). The final device is composed of the two elements, actively aligned and glued. The power consumption of the device is the same as the single DFB, as lasers are switched on one at a time. The spectral quality of the source is of course the same as for a DFB. In order to achieve such an integrated device, we have developed a new MIR Si based waveguide structure with SiGe core and Si cladding structure able to cover 3 to 9 μm. We also have developed as QCL technology suitable for a control of the wavelength below 1 cm-1 in order to cope with the multiplexor, namely the AWG, entries.

Such a source enables to address many gases with a unique devices or more complex molecules with wide signatures and gives spectral coverage for niche applications molecule for which no wavelengths can be specially developed.

(46) **Monolithic Tuning of Quantum Cascade Lasers for Compact Infrared Spectroscopy**

Christian Pfluegl[1], Mark Witinski[1], Laurent Diehl[1]; [1]Eos Photonics Inc.

We will present our recent developments on widely tunable quantum cascade laser arrays for spectroscopic applications. Our QCL array approach is based on proprietary technology and inventions pioneered by the group of Prof. Federico Capasso at Harvard University and further developed by Eos Photonics. Each element of the array is individually addressable and emits by design at a slightly different wavelength. Our array technology is also a very promising candidate for high power applications. Combining the output power of all array emitters with our beam combining solutions allows for power scaling without degrading beam quality.

(47) **Mid-infrared Microspectroscopic Imaging with a Quantum Cascade Laser**

Kevin Yeh[1], Matthew Schulmerich[1], Rohit Bhargava[1]; [1]University of Illinois at Urbana-Champaign, Urbana

Conventional mid-infrared (mid-IR) Fourier transform infrared (FT-IR) spectroscopic imaging systems employ an incoherent globar source and achieve spectral contrast through interferometry. While this approach is suitable for many general applications, recent advancements in broadly tunable external cavity Quantum Cascade Lasers (QCL) offer new approaches to and new possibilities for mid-IR micro-spectroscopic imaging. While QCL-based devices have yet to achieve the wide spectral range generally employed by spectroscopists for molecular analyses, they are starting to be used for microscopy at discrete frequencies. Here, we present a discrete frequency IR (DFIR) microscope based on a QCL source and explore its utility for mid-IR imaging. In our prototype instrument, spectral contrast is achieved by tuning the QCL to bands in a narrow spectral region of interest. We demonstrate wide-field imaging employing a 128x128 pixel liquid nitrogen cooled mercury cadmium telluride (MCT) focal plane array (FPA) detector. The resulting images demonstrate successful imaging as well as several unique features due to coherence effects from the laser source. Here we discuss the effects of this coherence and compare our instrument to conventional mid-IR imaging instrumentation.

(48) **Broadly-tunable Room Temperature Terahertz Quantum Cascade Laser Sources: Devices and Applications**

Mikhail Belkin[1], Yifan Jiang[1], Karun Vijayraghavan[1], Frederic Demmerle[2], Gerhard Boehm[2], Markus-Christian Amann[2]; [1]Department of Electrical and Computer Engineering, The University of Texas at Austin; [2]Walter Schottky Institute, Technical University of Munich

Room temperature, broadly-tunable, electrically-pumped semiconductor sources in the terahertz spectral range similar in operation simplicity to diode lasers and mid-infrared quantum cascade lasers are highly desired for applications. Here we report world's first room-temperature external-cavity terahertz quantum cascade laser sources. Tuning range over 1.5-5.5 THz range is demonstrated from a single device operated in pulsed mode at room temperature with peak power output varying between 5 and 100 microwatts depending on emission frequency. First spectroscopic applications results using these sources will be presented.

(49) **Design and Performance of a Person-Portable LIBS Instrument for the Detection of RNE Threats**

David Cremers[1], Melissa Bostian[1], Gary Smith[1], C. Randy Jones[1], Rosalie Multari[1], James Barefield II[2], Beth Judge[2], John Berg[2], Leonardo Trujillo[2]; [1]Applied Research Associates, Inc.; [2]Los Alamos National Laboratory

The ability to rapidly identify in-the-field RNE (radiological, nuclear, and explosive) threats will greatly enhance the capabilities of inspection teams to determine and verify facility operational status. One facility of interest is a gas centrifuge enrichment plant (GCEP). One inspection goal is to verify that enrichment of nuclear materials (uranium in particular) does not exceed that characteristic of fuel grade material (i.e. 4-5% 235U). Higher enrichments indicate weapons development. We have developed a series of person-portable LIBS instruments for this application and other inspection operations. These instruments are undergoing evaluation and testing for the detection of RNE materials. The basic unit consists of a handheld probe connected to a backpack. The probe, when combined with a high resolution spectrometer, also permits detection of uranium isotopes. Software has been developed to immediately analyze the LIBS spectrum and report results to the user within seconds. Capabilities include the identification of elements and, through the use of chemometric algorithms, the ability to identify a range of explosives. The design of the instruments will be described and performance for RNE detection will be summarized. Using a LIBS computational model, element signals expected from the instruments have been predicted and these agree closely with observed signals after radiometric calibration of instrument response. The LIBS model along with the capabilities of the LIBS instruments have been programmed into a gaming exercise aimed at training inspection teams in GCEP surveillance.

(50) **Design and Application of a New LIBS Desktop Analyzer**

Phillip Tan[1], Dan Jensen[1], Gregg Lithgow[1], Kregg Philpott[1], Markus Gaelli[1], Robert Robinsky[1]; [1]TSI Inc

A new Laser Induced Breakdown Spectroscopy (LIBS) system for rapid analysis of solid materials has been developed and will be described (TSI ChemReveal LIBS Desktop Analyzer). This LIBS system was designed for applications demanding high repeatability, robustness under constant use, and high performance. Data will be presented showing test results from multiple instruments, demonstrating high reproducibility. This LIBS system is also integrated with new advanced software for sample imaging, sample manipulation and calibration model creation. Data will be presented showing univariate elemental quantification of solid samples in seconds. This new LIBS system represents the first ISO 9001:2008 quality assured and quality controlled LIBS instrument offered in the marketplace.

(51) **In Search of Robust Multivariate Classification Method for Identification of High Energy Materials Using Laser Induced Breakdown Spectroscopy**

Manoj Kumar Gundawar[1], Ashwin Kumar Myakalwar[1], Shiv Kumar Anubham[1], Narahara Chari Dingari[2], Ishan Barman[2]; [1]University of Hyderabad; [2]Massachusetts Institute of Technology

Identification and detection of hazardous materials, particularly High Energy Materials (HEMs) has become important in the recent years. One of the important challenges here is to perform a standoff detection. Laser Induced Breakdown Spectroscopy (LIBS) has been shown to be promising technology in this endeavor by several researchers. Inspite of its standoff detection capability and other advantages, identification of HEMs poses a challenge in the form of very similar composition of the compounds. Most of the HEMs of interest show very similar LIBS spectra as they primarily consist of carbon, hydrogen, nitrogen and oxygen. Multivariate chemometrics has been successfully adopted to deal with similar problems in other spectroscopic domains. However, there are many different types of chemometrics tools available and there has been little work in comparing or constructing a roboust and hybrid approach to deal with the identification of HEMs. In this paper, we compare the performance of several chemometrics techniques such as Principal component analysis (PCA), K-nearest neighbors (KNN), Soft independent modeling by class analogy (SIMCA), artificial neural network (ANN), Partial least squares Discriminant Analysis (PLSDA) and Support vector machines (SVM) for the identification of HEMs. Multiple LIBS spectra of HEMs such as NTO, RDX and PETN have been collected. Our initial result shows that SVM and ANN project a better recognition rate than SIMCA and KNN. SIMCA performs overall recognition rate on LIBS of HEM about 58%, KNN upto 87% and ANN ~89% while SVM perform upto ~ 93%. To the best of our knowledge, the potential of SVM has not yet been utilized for LIBS based identification of HEMs. Being a nonlinear technique SVM can be a potential solution in this field. Further, compared to whole spectrum as an input, considering only select peaks lead to a significant enhancement of the classification. A comprehensive performance comparison of all the techniques, considering feature selection and outlier removal, will be presented.

(52) **Application of Laser-Induced Breakdown Spectroscopy for Quality Assessment of Pharmaceutical Products**

Sergey Arzhantsev[1], Gang Li[1], John Kauffman[1]; [1]US Food and Drug Administration

Impending changes to standards for elemental impurities in pharmaceuticals will require instrumental methods of metal analysis in place of the current wet chemical compendia. Inductively coupled plasma mass spectrometry (ICPMS) and ICP atomic emission spectrometry (ICPAES) are being widely developed for this application. During the last decade laser-induced breakdown spectroscopy (LIBS) has also attracted the attention of atomic spectroscopists in several fields of application. LIBS is an attractive alternative to ICP based methods because is relatively simple, low cost and requires little sample preparation. The sensitivity of current instrumentation is on order of part per million for toxic metals. X-ray fluorescence spectrometry (XRF) is another well-developed technology that may be useful for analysis of elemental impurities in pharmaceuticals. In this presentation we will compare the capabilities of LIBS, ICP-MS and XRF for determination of elemental impurities in pharmaceutical products. The advantages and limitations of each technique will be presented.

(53) **LIBS: Plasma Containing Titanium as a Probe for Temperature**

Alexander Woods[1], Christian Parigger[1], James Hornkohl[2]; [1]University of Tennessee Space Institute

The behavior of titanium particles in plasma gathers research efforts ranging from the modeling of stellar atmospheres to the enhancement of thin film production via pulsed laser deposition. Current efforts involving laser-induced breakdown spectroscopy investigate titanium monoxide (TiO) transitions, inferring temperature for various delay times following laser-induced breakdown. A titanium sample resting in laboratory air is repeatedly exposed to nanosecond, pulsed radiation generated by a Nd:YAG laser. Temperature inferences are accomplished by fitting synthetic spectra of varying micro-plasma parameters to the gathered spectra utilizing a Nelder-Mead algorithm. When imaging certain areas of the ablation plume, these inferences provide a temperature versus time profile containing a local minimum, as a slight increase occurs in the inferred temperature at later delay times. This phenomenon, possibly due to combustion, is investigated by analyzing signal to noise ratios with respect to their effect on the inferred temperature of diatomic molecular transitions. This is facilitated by the use of Monte Carlo type simulations adjusting both the background the TiO spectra are superposed upon and providing noise throughout the measured data. Atomic Ti structure, detectable at early as well as later delay times, is also addressed. Computation of predicted TiO spectra for various isotopomers is discussed with regards to application in stellar environments.

(54) **Sensing More with LessNew Strategies for Assays with Quantum Dots**

Russ Algar[1]; [1]University of British Columbia

Semiconductor quantum dots (QDs) are one of the most promising nanomaterials for bioanalysis and bioimaging. Compared to conventional fluorescent dyes, the unique, size-dependent optical properties of QDs and their ability to serve as tailorable nanoscale scaffolds for the multivalent assembly of biomolecular probes add extra value in bioanalyses. This presentation will address three aspects of the design, characterization, and application of QD-peptide conjugates for sensing proteolytic enzyme activity. First, using thrombin as a model protease, we will describe how QD surface chemistry can affect proteolytic activity and thus alter the sensitivity and selectivity of an assay. Next, we will show how non-traditional combinations of QDs and Förster resonance energy transfer (FRET) can permit multiplexed sensing of proteolysis with a single color of QD. Such configurations break with the current state-of-the-art of using N colors of QD for N analytes and are well suited for real-time tracking of coupled biochemical processes. Finally, we will discuss how QDs can be used with simple, low-cost optical readout systems for potential point-of-care diagnostic applications. Cellulose paper substrates can be modified with QD probes and exhibit 4-fold enhanced rates of FRET compared to QD probes in bulk solution. These paper assays can be interrogated using a low-power violet light emitting diode (LED) and the QD and FRET-sensitized dye emission can be measured using portable, low-cost CMOS devices such as a cell phone camera or webcam. The built-in color filters in these cameras permit spectrally resolved detection of QD and dye emission and, using a red/green color ratio, enable quantitative analysis down to ~1 nM trypsin protease. Moreover, the built-in color filters of a cell phone camera can be combined with QD probes for multiplexed homogeneous assays of the activity of three different proteases. Overall, the physical and optical properties of QDs are very promising for developing point-of-care diagnostics and cellular probes.

(55) **Energy Transfer Based Biosensing with Luminescent Semiconductor Quantum Dots**

Igor Medintz[1]; [1]U.S. Naval Research Laboratory

The unique photophysical properties of luminescent semiconductor nanocrystals or quantum dots (QDs) have made them useful within a number of different biological labeling, sensing and imaging applications. QDs are typically characterized by high quantum yields, narrow-symmetrical photoluminescent emission spectra that can be tuned as a function of the core size, absorption spectra that increase towards the blue which provide for large effective Stokes shifts, and remarkable resistance to both chemical and photodegradation. Further, the ability to exploit the non-trivial QD surface area and controllably decorate the QDs with both labeled biomolecules and a variety of energy transfer donors, or acceptors, allows them to act as both a central nanoscaffold and to actively participate in Förster resonance energy transfer or electron transfer-based processes. This talk will provide an overview of the different types of energy transfer that QDs can engage in with a specific focus on targeted biosensing as highlighted by some of our research in this area. In particular, the benefits of using QDs as Förster resonance energy transfer (FRET) donors will be a focus along with an overview of their capabilities as FRET acceptors. Recent work showing that QDs can also be used in biosensing configurations as a charge transfer donor or acceptor will also be highlighted within the context of *in vitro* biosensing assays or within live cells.

Center for Bio/Molecular Science and Engineering Code 6900

(56) **From Nanobodies to Antibodies: Time-Resolved Long-Lifetime FRET for Homogeneous Immunoassays**

Niko Hildebrandt[1]; [1]Université Paris-Sud

Quantum dot (QD) biosensors provide many photophysical advantages over conventional fluorophores. However, lack of reproducible, stable and robust immunoassays using easily-prepared QD-antibody conjugates have so far prevented QDs from being used as standard fluorescent reagents in clinical diagnostics. In this contribution we present ratiometric homogeneous FRET immunoassay with multiplexing capability using long photoluminescence lifetime Tb donors and QD acceptors. Antibody engineering using IgG, F(ab`)2, F(ab) and single-domain antibodies (or nanobodies) allows for high flexibility in conjugation ratios and Tb-donor to QD-acceptor distances. The homogeneous sandwich immunoassays are very stable and can be carried out in small-volume serum samples without any washing or separation steps (mix and measure). High sensitivity in clinically relevant concentration ranges is demonstrated by sub-nanomolar detection limits for the important cancer biomarkers prostate specific antigen (PSA, ca. 1 ng/mL) and

epidermal growth factor receptor (EGFR, ca. 30 ng/mL) by using time-gated photoluminescence detection and two different QD colors. We will present the photophysical analysis of the time-resolved FRET immunoassay systems and their use on a clinical fluorescence plate reader for in-vitro diagnostics. Our results show that Tb-to-QD FRET systems and careful design of antibody conjugation concepts can provide very efficient homogeneous immunoassays that offer high sensitivity, multiplexing capability and a facile integration into real-life clinical diagnostics for biomarker detection in low-volume serum samples.

(57) **Nanoparticles in Theranostics: The Good the Bad and the Predictable**

David Cramb; University of Calgary

Nanoparticles are increasingly used in medical applications such as drug delivery, imaging and biodiagnostics, particularly for cancer. The design of nanoparticles for tumor delivery has been largely empirical, owing to a lack of quantitative data on angiogenic tissue sequestration. Using fluorescence correlation spectroscopy, we have determined the deposition rate constants of nanoparticles into angiogenic blood vessel tissue. We show that deposition is dependent on surface charge. Moreover, the size dependency strongly suggests that nanoparticles are taken up by a passive mechanism that depends largely on geometry. These findings imply that it is possible to tune nanoparticle pharmacokinetics simply by adjusting nanoparticle size.

(58) **Reactions of Iron and Iron Oxide Clusters with Carbon Monoxide Using Guided Ion Beam Tandem Mass Spectrometry**

Peter Armentrout[1], Christopher McNary[1], Oscar Wheeler[1]; [1]Department of Chemistry, University of Utah

An efficient catalyst for the oxidation of carbon monoxide to carbon dioxide would be an important technological advance of great utility for processing harmful CO gas. Finding inexpensive transition metal catalysts that might effect this reaction would be particularly beneficial. Castleman and coworkers have shown that small iron oxide clusters undergo this process at room temperature, but the energetics of these processes are not well characterized. Using guided ion beam tandem mass spectrometry, we have investigated two aspects of this process. First, what are the binding energies of CO to iron clusters and how does this compare to surface thermodynamics. Second, how efficient is the oxidation of CO by iron oxide cluster cations and what are the thermodynamics of these processes. In this talk, we discuss our ongoing work in both areas.

(59) **Collision-induced Dissociation Energetics of Gly-Gly-Gly and Gly-Gly-Gly-NH2 Explored Using Tandem Mass Spectrometry and Theoretical Calculations**

Michael Van Stipdonk[1,2], Allison Williams[2], Benjamin Bythell[3], Abhigya Mookherjee[4], Peter Armentrout[4]; [1]Duquesne University; [2]Lawrence University; [3]University of Missouri-St. Louis/National High Magnetic Field Laboratory, Florida State University; [4]University of Utah

The "pathways in competition" model has significantly improved our understanding of peptide fragmentation reactions, and allows prediction of activation barriers for generation of key sequence ions for small model peptides. In this study, variable time and energy ion trap collision-induced dissociation (CID) experiments and threshold CID measurements on a guided ion beam instrument were used to study in detail the fragmentation of the protonated tripeptides Gly-Gly-Gly (GGG) and Gly-Gly-Gly-NH_2 (GGG-NH_2). Ion trap CID was performed using a ThermoFinnigan LCQ-Deca mass spectrometer with He as the bath/collision gas. A custom guided ion beam tandem mass spectrometer was used to measure kinetic-energy-dependent cross sections for CID of the same peptides. Density functional theory (DFT) calculations were used to predict structures and energies for relevant minima, including reaction intermediates, post-reaction complexes, and proton-bound dimers; and for transition states. Under the low-energy conditions of ion trap CID, fragmentation of protonated GGG leads nearly exclusively to b_2^+. A more diverse group of products were observed in the TCID experiments. The threshold measured for generation b_2^+ is lower by ~ 1 eV (center of mass frame) compared to other products such as b_3^+ and y_2^+, consistent with the lower energy (multiple collision) ion trap CID experiments and with the relative energies for products predicted by DFT calculations. DFT calculations predict that the formation of b_3^+ from GGG-NH_2 should be favored over formation of b_2^+, unlike the situation observed for the free-acid version of the peptide. Loss of H_2O is also a major fragmentation channel from GGG-NH_2. DFT calculations indicate a complex multistep rearrangement leads to formation of a protonated imidazole-4-one product. Formation of this product is energetically (~45 kJ/mol) and entropically less favorable for the more conventional free-acid GGG.

(60) **Guided Ion Beam Studies of Proton-Bound Dimers of Cytosines: Determination of Hydrogen-Bond Stabilization Energies and Relative Proton Affinities**

Bo Yang[1], Mary Rodgers[1]; [1]Wayne State University

The DNA *i* motif conformation was discovered in $(CCG)_n$•$(CGG)_n$ trinucleotide repeats, which are associated with fragile-X syndrome. The *i*-motif DNA secondary structure involves proton-bound dimers of cytosine. It has been found that methylation of cytosine results in silencing of the FMR1 gene and a deficiency of its protein product, fragile X mental retardation protein, leading to the fragile-X syndrome. Previous infrared multiple photon dissociation action spectroscopy studies of proton-bound dimers of cytosine and 5-substitituted cytosines have shown that methylation or halogenation at the C5 position does not alter the preferred base-pairing interactions. However, quantitative determination of the strength of the hydrogen-bond stabilization energies (HBSEs) in the ground-state proton-bound dimers remains elusive. In order to understand the influence of various modifications of cytosine on the strengths of the base-pairing interactions in the *i*-motif and the relative proton affinities (PAs) of the nucleobases, a comprehensive study has been taken here. Experimentally, HBSEs of the proton-bound dimers of cytosine and modified cytosines generated by electrospray ionization are determined using threshold collision-induced dissociation techniques in a guided ion beam tandem mass spectrometer. Relative N3 PAs of the modified cytosines were also extracted from experimental data for the proton-bound heterodimers. Geometry optimizations and frequency analyses are performed at the B3LYP level of theory using the 6-31G* and def2-TZVPPD basis sets to obtain structures and molecular constants of the neutral and protonated forms of cytosine and the modified cytosines as well as the proton-bound dimers, which are necessary for thermodynamic analysis of the experimental data. Single point energy calculations are performed at the B3LYP and MP2(full) levels of theory using 6-311+G(2d,2p) and def2-TZVPPD basis sets to obtain theoretical estimates for the measured HBSEs and relative N3 PAs. The measured values are compared with theoretical results calculated at the B3LYP and MP2(full) levels of theory to validate the ability of each level of theory for predicting accurate energetics.

(61) **Computational Studies of Ion-neutral Reactions of Astrochemical Relevance**

Zhibo Yang[1]; [1]University of Oklahoma

Aromatic hydrocarbons (AHs) and their derivatives have been suggested as the building blocks of interstellar dust grains and are responsible for the evolution of astrobiological molecules via surface reactions in space. Gas-phase studies of molecules and ions known to exist in space are crucial to understand relevant ion-molecule reactions and the generation of new species. Reactions catalyzed by large species such as AHs remain relatively unexplored. Our

computational studies focus on the energetics and reaction mechanisms of the formation of representative molecules (i.e., hydrogen peroxide and amino acetonitrile) that are critical for the origin of water and amino acids in the universe. Calculations have been carried out using Gaussian 09. Geometry optimization and frequency calculation were performed at the B3LYP/aug-cc-pVDZ level of theory to obtain the optimized structure and zero-point energy (ZPE). Final energies for reactants, transition states, and products were calculated at the CCSD(T)/aug-cc-pVDZ level of theory including the ZPE correction. Potential energy curves of reactions were constructed based on the relative energies, and reaction mechanisms were investigated.

Species involved in the computational studies include benzene (C_6H_6), naphthalene ($C_{10}H8$), acetonitrile (CH_3CN), amino acetonitrile (NH_2CH_2CN), ammonia (NH_3), O_2, and hydrogen atom. Except for naphthalene, all species have been identified in the interstellar medium (ISM; the material filling in the space between stars in a galaxy) and the circumstellar envelope (the material around a star but not gravitationally bound to the star core) in the galaxy. Although naphthalene have not been detected in the space, there are strong evidences that large species, such as polycyclic aromatic hydrocarbons (PAHs) are very likely to exist. Due the photoionization of neutral species readily occurs in some stellar regions due to the existing radiation (UV, X-ray, γ-ray, etc.), ions are formed and involved in astrochemical reactions. Structures and energies were calculated for reactants, transition states, and products of systems of interest. The potential energy curves of reactions leading to the formation of hydrogen peroxide (H_2O_2) and amino acetonitrile (NH_2CH2CN) were investigated. The preliminary results suggest that there are energetically accessible reaction pathways leading to the formation H_2O_2 and NH_2CH_2CN through species has been discovered in the ISM. The ionized benzene and PAHs can act as catalysts to facilitate the formation of astromolecules. The proposed studies will enhance our understanding of ion-molecule reactions that are relevant to the formation of important astromolecules in the gas phase, and provide a new way to investigate the formation of polyatomic molecules on surfaces of dust grains such as large PAHs. Mass spectrometry experiments will be carried out in the future studies using for the selected model systems.

(62) **Structure and Reactivity of Gas-Phase Peptide Radical Ions**

Victor Ryzhov[1]; [1]Northern Illinois University

Gas-phase radical ions of amino acids and peptides have generated substantial interest recently. Distonic, captodative, and canonical structures have been generated at most relevant amino acid positions and studied by various experimental and theoretical methods. In this work, we generate and study the gas-phase properties of radical ions based at cysteine and tryptophan residues. We use collision-induced dissociation (CID), ion-molecule reactions, infrared multiple photon dissociation (IRMPD) spectroscopy, and theoretical calculations to characterize these species. To regiospecifically generate thiyl cysteine or indolyl tryptophan radicals, we used nitrosylation of peptides in solution followed by electrospray ionization and S-NO (N-NO) bond homolysis via CID. Tryptophan-based aromatic (canonical) radical ions were generated by CID of ternary copper complexes. The reactivity of these radical species in the gas-phase strongly depends on the position of the radical - thiyl radical react with typical radical "sponges" like allyl iodide and dimethyl sulfide, tryptophan-based aromatic radicals are less reactive but abstract hydrogen from thiols, and tryptophan indolyl distonic radical ions are even less reactive. Thus, all of these species can be distinguished by their gas-phase reactivity. Intramolecular radical transfer was studied by CID and ion-molecule reactions, with some of the results confirmed by IRMPD spectroscopy. For instance, sulfur-based radicals tend to rearrange to a captodative alpha-carbon species. Ion-molecule reactions shed light on thermal or near-thermal radical migration while CID allows access to more energy-demanding processes.

(63) **Electrokinetic Transport of Single DNA Molecules through Nanochannel Networks**

J. Michael Ramsey[1], Laurent D. Menard[1], Jinsheng Zhou[1]; [1]University of North Carolina at Chapel Hill

Large DNA molecules assume extended conformations upon their insertion into nanofluidic channels. This confinement-induced extension can be used to increase the spatial resolution with which the molecule can be sized, probe locations mapped, or nucleotide sequence decoded. Greater extension, and spatial resolution, can be achieved by decreasing the critical dimensions (width and depth) of nanochannels. This, however, imposes stricter requirements on fabrication methods and creates new challenges for device operation. For example, as nanochannel dimensions decrease, the entropic barrier to DNA threading into the channels increases. As a result, larger applied forces (e.g., pressure or electrostatic) are required to drive DNA threading into and transport through nanochannels and faster DNA transport is observed. This makes characterization of the confined DNA difficult when using detection methods having limited bandwidth or sensitivity. In order to maximize control over both DNA extension and transport velocity, fluidic devices are required that allow greater control over transport dynamics. We report on the development and operation of devices with components such as three-dimensional nanofunnels. The use of such structures lowers the threshold force needed to drive transport and thus provides greater control over transport dynamics. It is therefore possible to characterize a molecule when it first enters a nanochannel and trigger a command to the device. With electrokinetically-driven DNA transport, for example, the molecule can be sorted or its transport halted, slowed, or reversed by adjusting the on-chip voltages. We also report on the development of an all-fluidic device for the detection of DNA during its transport through a nanochannel. This is achieved by intersecting a long transport channel with a shorter orthogonal nanochannel. The ionic conductance of this transverse nanochannel is monitored while DNA is electrokinetically driven through the transport channel. When DNA passes the intersection, the transverse conductance is altered, resulting in a transient current response.

(64) **Coupling Electrokinetic Flow to Spectroelectrochemistry in Low-Dimensional Nanostructures for Chemical and Biochemical Sensing**

Paul W. Bohn[1,2], Jing Zhao[1], Nicholas M. Contento[1], Dane A. Grismer[1], Lawrence P. Zaino[2], Sneha Polisetti[1]; [1]Department of Chemical & Biomolecular Engineering, University of Notre Dame, Notre Dame, IN; [2]Department of Chemistry & Biochemistry, University of Notre Dame, Notre Dame, IN

We are interested in fabricating nanostructured architectures so that molecular transport (analyte/reagent delivery), chemical sensing (optical or electrochemical) and subsequent chemical conversion can all be coupled in the same physical construct. The ultimate goal of these experiments is to produce chemical reagents *in situ* and consume them directly at a proximal reaction site, so that chemical transformations may be realized with optimal efficiency. To realize this goal we are developing sensing strategies that efficiently match electron transfer and spectroscopic probing to low-dimensional, *i.e.* zero- and one-dimensional nanostructures.

In one version of the experiment vertically-oriented nanopores provide fluidic communication in nanocapillary array membranes supporting embedded annular nanoband electrodes (EANEs) fabricated on the interior of the nanopores. In these structures, electroosmotic flow (EOF) is used to enhance the delivery of electroactive species to the EANE, and the same potential used to drive EOF also provides for electron transfer. Because transport and

electron transfer are intimately coupled, high efficiency electrochemical conversions can be achieved. Conversion efficiency is improved by approximately 10-fold compared to a comparable microfluidic structure.

In a different experiment, we exploit the localization of optical fields to reduce spectroscopic background signals and enable studies of single electroactive fluorophores. Zero-mode waveguides (ZMWs) strongly confine optical fields to zeptoliter volumes and can be coupled with fluorescence microscopy to study the dynamics of single enzyme molecules, due to their excellent optical confinement, precise positioning, and massive parallelism. The redox enzyme, monomeric sarcosine oxidase (MSOX) contains a covalently bound flavin adenine dinucleotide (FAD) cofactor which is highly fluorescent in the oxidized state and dark in the reduced state, thus producing a characteristic on-off fluorescence signal synchronous with transitions between oxidation states. Furthermore, the electron transfer can occur between solution-phase substrate and immobilized enzyme, or, if redox species are immobilized on the metallic sidewalls of the ZMW, it is possible to observe the single molecule fluorescence signatures resulting from direct heterogeneous electron transfer from metallic electrodes to single redox-active molecules. We have prepared ZMW arrays with a significant number of single FAD chromophores bound to the Au sidewalls. Experiments to illustrate potential control over electron transfer to single FAD molecules in ZMWs suggest that the transition rates between luminescent (oxidized, FAD^{+}) and dark (reduced, $FADH_2$) states can be modulated with electrochemical potential.

(65) **Bioanalytical Measurement with Scanning Ion Conductance Microscopy**

Lane Baker[1], Chiao-Chen Chen[1], Yi Zhou[1], Jianghui Hou[2], Beth Yuilli[1], Anumita Saha[1], Alicia Friedman[1], Steve Ray[1]; [1]Indiana University; [2]Washington University

Scanning Ion Conductance Microscopy (SICM) has been developed originally for high-resolution imaging of topographic features. Here, we extend the capabilities of SICM in two unique applications, measurement of transmembrane conductance and as a sampling device for mass spectrometric measuremetns. We have described a hybrid voltage scanning mode of SICM, termed Potentiometric-SICM (P-SICM) for recording transmembrane ionic conductance at specific nanostructures of synthetic and biological interfaces. With this technique, paracellular conductance through tight junctions – a subcellular structure that has been difficult to interrogate previously – has been realized. The unique combination of voltage scanning and topographic imaging enables P-SICM to capture paracellular conductance within a nominal radius of several hundred nm. In a second application, SICM is used as a sampling device to interrogate biological samples with mass spectrometry. These techniques are amenable to utilization with both electrospray and matrix assisted laser desorption ionization techniques.

(66) **Using Super-Resolution Optical Microscopy to Study Molecular Diffusion on Interfaces and in Nanopores**

Gufeng Wang[1], Luyang Zhao[1], Fang Chen[1], Bhanu Neupane[1]; [1]North Carolina State University

Molecular transport, i.e., adsorption/desorption, diffusion and migration, near a liquid-solid interface is the key process in both fundamental sciences and many advanced applications. In this study, we investigate nanometer-sized particles diffusion near a liquid-solid interface and inside straight nanopores using 3D super localization microscopy and single particle confocal fluorescence microscopy. By studying carboxylated polystyrene particles diffusing in unmodified 200 nm alumina pores, we show that the axial diffusion of the nanoparticles in the pores is 10~15 times slower than that in the bulk solution. While the reason for the slow diffusion is under investigation, we are able to exclude the possibility of millisecond time scale adsorptions by using a collection temporal resolution of 0.5~1.0 ms. Super-localization experiments suggest that the particles are being trapped near the surface through long-range interactions. This view may shed new light on particle-surface interactions and the targeted binding of nano-particular objects to a solid surface. This study is supported by NCSU startup fund and NCSU FRPD award.

(67) **Nanofluidic Circuits for Monitoring Single Virus Particles and Their Assembly**

Stephen C. Jacobson[1], Zachary Harms[1], Andrew Kneller[1], Lisa Selzer[1], Adam Zlotnick[1]; [1]Indiana University

We are developing label-free, nondestructive techniques for rapid sensing, characterization, and sorting of virus particles. To sense and characterize individual virus capsids, we use resistive-pulse sensing to measure changes in ion current from the transit of particles through an electrically biased nanopore filled with electrolyte. Each in-plane device contains microchannels that are machined into the glass substrate by standard photolithography and wet chemical etching. Nanochannels are then milled into the glass substrate with a focused ion beam and bridge the gaps between the microchannels. For resistive-pulse sensing of the virus particles, we use nanochannels with one, two, or three pores to track individual particles and measure their physical properties, e.g., electrophoretic mobility. In other designs, we have integrated mixing on-chip and are able to monitor the assembly of single hepatitis B virus particles in real time and at biologically relevant concentrations.

(68) **Monitoring of Continuous Crystallization Using Non-Invasive Raman and Acoustic Emission Spectroscopies**

Laura Palmer[1], David Littlejohn[1], Alison Nordon[1], Jan Sefcik[1], Alastair Florence[1]; [1]University of Strathclyde

Conventional crystallization processes often result in poor quality, inconsistent products, high levels of rejected batches and problems with scale up. For these reasons, interest in continuous manufacturing is growing due to the potential ability to control crystal properties. In this study, batch and continuous oscillatory baffled reactors obtained from NiTech Solutions have been compared for the crystallization of both L-glutamic acid and Mannitol. Different analytical techniques were evaluated for monitoring the crystallization process. In this work, non-invasive Raman spectroscopy was investigated for process monitoring in each of the reactors. The effects of different process conditions on crystal formation and polymorph transformation have been studied using measurements with a Kaiser Raman PhAT probe. In addition, acoustic emission spectroscopy was considered as a supplementary technique to provide information on particle properties including size. Off-line analysis by XRD and particle sizing techniques provided additional information on the crystal properties.

The results show that varying the operating conditions in the batch and continuous OBR impacts the properties of the particles obtained including the particle size, particle size distribution and polymorphic composition. Non-invasive Raman measurements provided useful information on the difference in nucleation temperature when different conditions and reactors were used which helped to explain the differences in the particle size distributions and polymorph of the final product. Acoustic emission measurements provided information on the effect of operating conditions on the particle size during the crystallization and proved to be an effective complementary technique to use alongside Raman spectroscopy.

(69) **Raman Spectroscopy in Biopharmaceutical Manufacturing: Measuring the Media.**

Alan Ryder[1], Boyan Li[1], Bridget Kissane[1], Amandine Calvet[1]; [1]Nanoscale Biophotonics Laboratory, School of Chemistry, National University of Ireland Galway.

Cell culture media (CCM) are an intrinsically vital element in cell culture and the quality of the media is fundamental to the effective growth of healthy cells. In an industrial context the quality and reproducibility of the CCM determines process productivity and as such it has gained enormous importance with the growth in biological active pharmaceutical ingredients. CCM are nearly always complex (or very complex) mixtures of materials which span a wide range of concentrations from the ppm level up to 10-20% w/w. The analytical challenge is thus to develop rapid and cost-effective methods for both qualitative and quantitative assessment of CCM quality in terms of variance and stability. This has to be implemented for both the solid state and when produced as dilute aqueous solutions ready for use. Standard chromatographic based methods are generally too slow and time-consuming for rapid screening of these complex mixtures. Vibrational spectroscopy like Raman and NIR are very useful in this context because they offer rapid, non-contact, non-destructive methods of analysis, that in case of the Raman also offers a high chemical specificity. However, CCM materials pose some interesting challenges in terms of compositional complexity (e.g. biogenically derived CCM like yeast extracts), fluorescence interference, and strong water signals. These issues coupled with the need for quantification require the use of extensive chemometric data analysis and careful experimental design. We show how we applied both 785 and 993 nm based Raman systems to analyze these complex materials, and how these can be implemented in biopharmaceutical manufacturing. Finally we demonstrate how Surface Enhanced Raman Scattering (SERS) spectroscopy could be utilized for the assessment of CCM changes induced by various environmental factors [3,4]. SERS can show very subtle changes in CCM composition which otherwise are not observable by conventional Raman spectroscopy or by fluorescence spectroscopy [5].

References:

1) A.G. Ryder, J. De Vencentis, et al. J. Raman Spectrosc., 41, 1266, (2010).
2) B. Li, P.W. Ryan, et al. Biotechnol.Bioeng.,107, 290, (2010).
3) B. Ray, A.G. Ryder, J. Raman Spectrosc., 43, 1074, (2012).
4) A. Calvet, A.G. Ryder, in preparation.
5) A. Calvet, B. Li, A.G. Ryder, submitted

(70) **Pharmaceutical Tablet Matrix Effects in Quantitative Transmission Raman Spectroscopy**

Anders Sparén[1], Olof Svensson[1], Madeleine Hartman[2], Magnus Fransson[1], Jonas Johansson[1]; [1]AstraZeneca R&D Mölndal, Sweden; [2]Uppsala University, Sweden

Raman spectroscopy can be an alternative to near-infrared spectroscopy (NIR) for non-destructive quantitative analysis of solid pharmaceutical formulations. Compared with NIR spectra, Raman spectra have much better selectivity, which may simplify data evaluation.

The main drawback with Raman spectroscopy for quantitative assessment has been sub-sampling, which leads to higher than necessary prediction errors. Raman spectroscopy in transmission mode has reduced the sub-sampling problem, since a large volume the sample is measured. Because of the improved sampling, transmission Raman spectroscopy is a good alternative for non-destructive quantitative analysis of assay, uniformity of content and polymorphs in solid pharmaceutical formulations. In recent years, however, it has been discovered that matrix effects, such as particle size of the active pharmaceutical ingredient can affect the Raman signal. In this work, matrix effects in transmission NIR and Raman spectroscopy were investigated for a solid pharmaceutical formulation. Tablets were manufactured according to a full factorial design, varying the factors particle size of the Drug Substance (DS), particle size of the filler, compression force during compaction and DS content. All factors were varied at two levels plus centre point, except the DS content that was varied at five levels. Six tablets from each experimental point were measured with transmission NIR and Raman spectroscopy and the assay of the DS was determined for a third of those tablets. Principal component analysis of NIR and Raman spectra showed that, apart from the DS content, also the particle size of the DS, the particle size of the filler and the compression force affected both NIR and Raman spectra. For quantitative assessment, orthogonal partial least squares regression was applied. All factors varied in the experimental design influenced the prediction of the DS content to some extent, both for NIR and Raman spectroscopy, the particle size of the filler having the largest effect. When all matrix variations were included in the multivariate calibrations, however, good predictions of all types of tablets were obtained, both for NIR and Raman spectroscopy. The prediction error using transmission Raman spectroscopy was about 30 % lower than that obtained with transmission NIR spectroscopy.

(71) **Tablet Assay of Acetaminophen by Transmission Raman**

Carl A. Anderson[1], Benoît Igne[1], MD Nayeem Hossain[1], James K. Drennen[1]; [1]Duquesne University Center for Pharmaceutical Technology

Rapid assay of acetaminophen in an immediate release solid oral dosage form was demonstrated using transmission Raman spectroscopy. An analytical method suitable for at-line or off-line analysis was demonstrated to be linear, accurate, and precise when compared to a reference HPLC method. Tablets composed of acetaminophen, lactose (intra- and extra- granular), and magnesium stearate were manufactured using pilot and laboratory scale equipment. A Full-factorial design of experiments was utilized across acetaminophen (5 levels), and excipients ratio (3 levels) to generate tablets for calibration. Acetaminophen content was determined by a stability indicating HPLC method after collecting transmission Raman spectra of the tablets. The capabilities of the transmission Raman method were demonstrated using HPLC results as reference values for acetaminophen content. Model tranferability between laboratory and pilot scale tablets is addressed.

(72) **Portable Spectrometers: The First step in Pharmaceutical Counterfeit Investigation**

Ravi Kalyanaraman[1]; [1]Bristol-Myers Squibb

Pharmaceutical counterfeiting has become a major issue in the recent decade in developing countries. It has also placed a significant pressure on the assurance of supply chain integrity in developed countries due to increasing international trade due to globalization and sales via the internet. The recent incident of counterfeit Avastin in the United States shows the vulnerability of the supply chain even in developed countries. Several technologies are currently available to detect counterfeit drugs and these include covert and overt features added to the packaging material and to the drug product itself, and authenticating the suspect drug for these features. In addition to these covert and overt features, Bristol-Myers Squibb (BMS) has been using Infrared (mid and NIR) and Raman spectral techniques, which are complimentary in nature, to detect counterfeit drugs more rapidly. Both techniques are nonintrusive and nondestructive that can be used for the analysis of many classes of pharmaceutical dosage forms. The nonintrusive nature of both techniques makes it feasible to analyze a drug product directly through the packaging, such as bottles or blisters, and through capsule shells for encapsulated products. Portable versions of Infrared (mid and NIR) and Raman spectrometers have paved the way to take the 'lab' closer to where

the counterfeit activities are taking place, such as deceitful manufacturing facilities and pharmacies. These portable spectrometers are accurate, precise and easy to use and are becoming increasing important as the first analytical technique to be used even in the lab for counterfeit investigation. This talk will feature examples of using portable spectrometers as the first line of defense in screening counterfeit drugs and also in aiding further investigation using other techniques, such as chromatography and other spectroscopic techniques such as Nuclear Magnetic Resonance (NMR) and Mass spectrometry (MS).

(73) **Laser-Induced Breakdown Spectroscopy for Real-Time Nuclear Forensics**

François R. Doucet[1], Paul Bouchard[1], Mohamad Sabsabi[1], Rick Kosierb[2]; [1]National Research Council Canada, Energy, Mining and Environment; [2]Canadian Nuclear Safety Commission, Directorate of Security and Safeguards

The International Atomic Energy Agency (IAEA) has the mandate to safeguard the use of uranium, plutonium and thorium worldwide, as nuclear fuel for civil uses, avoiding their diversion use in weapons of mass destruction or explosive devices. Terrorist and proliferation activists are employing more sophisticated means than those used in the past to achieve their objectives. Border security services, first responders and regulators need to adapt to this challenge and to seek technologies that can provide quick and accurate information, in order to prevent clandestine activities or initiate rapid responses to them. Laser-Induced Breakdown Spectroscopy (LIBS) technique has several advantages, the most relevant are real-time measurement, contact with the sample is not necessary, and analysis can be made at a distance avoiding contamination by radioactive materials. LIBS and different combination of chemometric techniques were integrated in a portable autonomous system that can perform real-time measurement. In addition, this portable LIBS instrument can be operated by a person that does not required an extensive knowledge of neither spectroscopy nor chemometrics. The present paper describes different applications that are or in the integration process in the portable LIBS unit. In particular, the possibility of analyzing isotope ratio using LIBS, assessment of yellow cake origin as well as discriminating the different compounds found in the uranium ore refining process. The performance obtained with such a LIBS sensor will be discussed for nuclear forensics. The results obtained with the transportable LIBS unit clearly show the usefulness of this approach for real-time onsite nuclear forensics.

(74) **The Analysis of Special Nuclear Materials using Laser-Induced Breakdown Spectroscopy (LIBS)**

Elizabeth J. Judge[1], James E. Barefield II[1], John M. Berg[1], Stephen P. Willson[1], Loan A. Le[1], Leon N. Lopez[1], Leonardo Trujillo[1]; [1]Los Alamos National Laboratory

The identification and assignments of complex atomic emission spectra of mixed actinide oxides using laser-induced plasma spectroscopy or laser-induced breakdown spectroscopy (LIBS) are reported here. Results of LIBS measurements on samples of: (1) UO_2 / ThO_2 in a stearic acid binder, (2) UO_2 / PuO_2 / AmO_2 / NpO_2 in simulated fuel pellets (or mixed actinide oxide sample), (3) UO_2 / PuO_2, (4) preliminary single shot measurements of depleted uranium, and (5) a vitrified glass bead sample are reported and discussed. Over 800 spectral lines (transitions) have been identified and assigned for the pressed and simulated fuel pellet samples thus far. The identification and assignments of spectral emission transitions for Th, U, Pu, and Am are consistent with wavelength data from the literature. However, only a few transitions have been assigned with a high degree of confidence for Np when compared to available atomic emission data from the literature. We also indicate where atomic emission transitions for curium (Cm) would most likely appear in the displayed spectral regions shown. This work clearly indicates that a LIBS system with a resolving power of approximately 20,000 is adequate for analyzing complex mixtures of actinide elements within the same sample.

(75) **High Spatial Resolution Surface Analysis via Femtosecond Laser Ablation-Multi-Collector-Inductively Coupled Plasma Mass Spectrometry**

Greg Eiden[1], Andrew Duffin[1], Jesse Ward[1], Kellen WE Springer[1], Albert J. Fahey[1], John W. Robinson[1]; [1]Pacific Northwest National Laboratory

Femtosecond laser ablation multicollector inductively coupled mass spectrometry (fs-LA-MC-ICPMS) is a powerful technique for direct analysis of solid samples. We are developing this method for high spatial resolution analysis of surfaces and have reported results for the analysis of standard reference material glasses (ScieX 2012 presentation 540; JRNC). In this presentation, we extend the previous NIST glass results to isotope ratio measurement performance at lower ablation and ablation of other materials.

(76) **Surrogate Nuclear Explosion Debris (SNED): New Materials for Testing, Evaluation, and Research**

Greg Eiden[1], April Carman[1], Scott Harvey[1], Martin Liezers[1], Albert Fahey[1], Janet Cloutier[1]; [1]Pacific Northwest National Laboratory

Laboratory methods for creating materials that mimic key features of nuclear explosion debris are described. Results to date have focused on two approaches directed at two broad types of fallout material: fallout which is homogeneous with respect to the distribution of radioactive species within a particle and fallout in which the radioactive species occur as a coating on an environmental particle.

(77) **Infrared and Near Infrared Spectroscopy of Uranium Ore Concentrates for Nuclear Forensic Analysis**

Gregory Klunder[1], Paul Spackman[1], Patrick Grant[1], Ian Hutcheon[1]; [1]Lawrence Livermore National Laboratory

One of the first steps in uranium production is the mining and processing of uranium ore to produce uranium ore concentrates (UOC). Nuclear forensic analysis of UOC samples relies on a number of different analytical techniques to provide information about the samples to identify the process, materials, and origin. Elemental and isotopic analysis can be used to trace materials back to the source; however, this requires a lengthy process of digestion and dissolution of the sample. Non-destructive spectroscopic methods have been recently demonstrated to provide molecular, process, and provenance information about UOC samples. Varga et al. analyzed several types UOC materials using transmission FT-IR spectroscopy on KBr pressed samples with classification chemometric analysis. Plaue et al. recently demonstrated the use of near-infrared (NIR) spectroscopy to provide molecular and process information. In addition to vibrational overtone and combination bands of C-H, O-H, and N-H detected in the spectral range from 1000 – 2500 nm, the phase and crystal field can contribute to unique spectral features of uranium based compounds. Due to complex nature of the samples from contaminants and different uranium species, employing multiple spectroscopic techniques can provide more discriminating information for nuclear forensic interests.

In this study, we compare spectra obtained using attenuated total reflectance (ATR) FT-IR and diffuse reflectance NIR spectroscopy for the analysis of UOC materials produced from different processes. In addition, electronic transitions from various uranium oxide species, U_3O_8, UO_2, UO_3 and UO_4 have been identified. We have measured spectra from a number of different UOC samples whose major phases have been identified by x-ray diffraction. The results of this study and the applicability of this technique for UOC characterization will be discussed.

Z. Varga, B. Öztürk, M. Meppen, K. Mayer, M. Wallenius, C. Apostolidis, . "Characterization and classification of uranium ore concentrates (yellow cakes) using infrared spectrometry". Radiochim. Acta. 2011. 99(12):807-813.
J.W. Plaue, G.L. Klunder, I.D. Hutcheon, K.R. Czerwinski. "Near Infrared reflectance spectroscopy as a process signature in uranium oxides". J Radioanal Nucl Chem. 2013. 296(1): 551-555.
This work performed under the auspices of the U.S. Department of Energy by Lawrence Livermore National Laboratory under Contract DE-AC52-07NA27344.

(78) **Mass Spectrometry As an Indispensable Tool to Build and Maintain a Sustainable Future**

Jacob Shelley[1], Christopher Kuhlmann[1], Joshua Wiley[2], R. Graham Cooks[2], Carsten Engelhard[1]; [1]Institute for Inorganic and Analytical Chemistry, University of Muenster; [2]Department of Chemistry, Purdue University

The road to a healthy, prosperous future for humankind and nature as a whole is dependent scientific discovery to understand negative human impact and to develop approaches to reverse these effects. At the heart of these discoveries is the need for powerful analytical instrumentation to gauge the human impact of past and to project the path of the future. The ideal analytical tool is one that would quickly provide a comprehensive assessment of species in a sample *in situ*. While this ideal seems far from reality, efforts in the design and application of ionization sources for mass spectrometry have demonstrated many of these attributes to be achievable. In such ambient mass spectrometry experiments, as they are often called, the source removes molecules from a sample surface in its native environment, softly ionizes the species, and transfers these ions into a mass spectrometer. The separation power and sensitivity of the mass spectrometer is used to resolve individual components in a complex mixture. This presentation will focus on the utility of mass spectrometry and, in particular, direct, remote analyses through ambient desorption/ionization mass spectrometry in understanding the past, present, and future of human impact on the environment. Specifically, the power of plasma-based ambient ionization sources will be demonstrated through the direct detection of species known to have a negative impact on the environment. In addition, the construction and utility of a portable, backpack mass spectrometer combined with a plasma-based ambient ionization source will be shown. This instrument houses the compact pumping system and control electronics in a backpack, while the mass analyzer and integrated coaxial LTP/MS-inlet, for geometry independent sampling, are contained in a hand-held unit connected to the backpack via flexible vacuum tubing. This instrument is also capable of detecting both positively and negatively charged ions and allows tandem MS to improve the selectivity and S/N. Furthermore, the in-house designed software autonomously controls the system. The design and performance characteristics of the instrument will be presented, as well as applications, such as the detection of illicit drugs and chemical warfare simulants at nanogram levels from non-standard surfaces, such as human skin.

(79) **Towards the Development of Greener Methods Using Direct Solid Sampling**

Martin Resano[1], Esperanza Garcia-Ruiz[1], Miguel A. Belarra[1]; [1]University of Zaragoza

Owing to the increasing public awareness on the importance of environmental issues, there is a firm and growing tendency to evaluate the environmental impact of every human activity. Of course, Chemistry is particularly sensitive with this situation. In this regard, the concept of Green Chemistry was established in the last decade of the last century, concept that has continued evolving in order to develop suitable patterns that permit carrying out different chemical processes, and particularly those related with synthesis and production, in a more environmentally-friendly way [1,2]. Obviously, the environmental impact of analytical labs is expected to be much lower than those related with the synthesis and production of large amounts of chemicals, but that does not excuse analytical chemists to try to adapt their methodologies to the main basic principles of Green Chemistry, which seems a priori a feasible goal. In this regard, the response of the analytical community has been positive, since the number of publications dealing with Green Analytical Chemistry has increased steadily during the last fifteen years. When the goal is to analyze solid samples, the major breakthrough would consist in not needing any sample pretreatment at all, since it is during these pretreatment processes where the majority of hazardous substances are used. It is the main aim of this work to discuss the current potential of some solid sampling techniques that, according to advances reported in the literature during the last decade, offer possibilities to implement greener strategies in atomic spectrometry. Several examples (e.g., direct determination of PGMs in NiS buttons, direct analysis of silicon) will be discussed in detail, together with some strategies (e.g., development of screening methods) that seem particularly compatible with the philosophy behind Green Analytical Chemistry.

1. Anastas, P.T. and Warner, J.C. (1998) Green Chemistry: Theory and Practice, Oxford University Press, New York.
2. Clark, J.H. (1999) Green Chemistry: challenges and opportunities, Green Chem., 1, 1–8.

(80) **Novel Calibration Strategies for Quantitative Iron Imaging of Soft Tissues using Laser Ablation with ICPMS**

Jennifer O'Reilly[1], Liuxing Feng[2], Wang Jun[2], Heidi Goenaga-Infante[1]; [1]LGC Limited, Queens Road, Teddington, Middlesex, United Kingdom; [2]Division of Metrology in Chemistry, National Institute of Metrology, Beijing, China

Clinical diagnosis and treatment of neurodegenerative diseases such as Alzheimer's disease are of increasing importance to society[1]. In order to understand their pathogenesis and potential treatments, traceable methods for the determination of total metal concentrations, as well as the regional spatial distribution (quantitative imaging), in diseased tissues compared to normal tissues are urgently needed. There have been numerous publications outlining potential calibration strategies for quantitative imaging of trace elements in biological tissues. However, validation of these approaches remains a challenge due to the lack of suitable certified reference materials and of primary methods for quantitative elemental imaging. This lecture will discuss the advantages and limitations of a newly developed calibration strategy for quantitative imaging of Fe in brain tissues using laser ablation (LA) coupled to ICP-MS and internal standardisation. It involves the use of a simple and straightforward approach for preparation of matrix matched calibration standards, which can be re-used for multiple batch analyses. Using the developed strategy, an appropriate internal standard can be equally added to standards and sample without altering the original iron distribution of the sample. Efforts were made to validate this calibration approach, intended for use in routine elemental imaging analysis, by μ-XRF analysis of the same sample; the XRF data was in good agreement with the LA-ICPMS data. Finally, the lecture will discuss the feasibility and applicability of reference methodology based on LA-ID ICPMS for the characterisation of the in-house prepared calibrants and for accurate quantitative Fe imaging of biological tissues.

[1] So PW, Kalber T, Hunt D, Farquharson M, Al-Ebraheem A, Parkes HG, Simon R, Bell JD, 2010, Cell Transplantation, 19: 410-29.

(81) **Laser Ablation for Chemical Analysis: Contribution to Sustainability of Atomic Spectroscopy**

Jhanis Gonzalez[1,2], Jose Chirinos[1], Dayana Oropeza[1], Meirong Dong[1], Huaming Hou[1], Vassilia Zorba[1], Xianglei Mao[1], Rick Russo[1,2]; [1]Lawrence Berkeley National Laboratory, Berkeley, CA; [2]Applied Spectra, Inc. Fremont CA

The word "Sustainability" implies reconciliation of environmental, social equity and economic demands – in recent years each of these categories has forced drastic changes in the way we think about and do chemical analysis. For example, environmental and economic demands have driven the scientific and commercial community to design (or redesign in some cases) compact analytical instruments with low operating costs. The low operating cost of these instruments is primarily associated with low consumption of consumables i.e. working gases, power demands, and cooling water. Low costs and miniaturized instrumentation offer the prospect for field portability, as well as the possibility of accessing these technologies to people in regions with limited resources, which in time can transform improvements in the standard of living in undeveloped countries. Additionally to changes in instrument design driven by sustainability, some current challenges in atomic spectroscopy compel analytical techniques with high spectral and spatial resolution, high sample throughput, ultra-sensitive analysis, as well as reduction in waste generation. In this context, laser ablation for sampling or as a standalone technique nicely addresses the concept of sustainability for chemical analysis. In this presentation we will highlight some of the contributions of our research group regarding chemical mapping, high repetition rate sampling, compact tandem instrumentation, and the ability to measure isotopes at atmospheric pressure from laser induced plasmas.

(82) **Sustainability & Analytical Chemistry: Developing Greener Methods in the Mass Spectrometry Laboratory**

Carsten Engelhard[1,2], Anastasia Albert[2], Britta Vortmann[2], Wolfgang Buscher[2], Christopher Kuhlmann[2], Sascha Nowak[2], Jacob T. Shelley[2]; [1]University of Siegen; [2]University of Muenster

Sustainability and greener methods in analytical chemistry are important from an environmental, social, and economic point of view. For example, using less resources, high-purity gases, and chemicals in the laboratory translates to reduced direct operating cost, but also to less shipping traffic and reduced exhaust emissions. Instrument manufactures and scientists should therefore always strive for improved and greener methods. In this presentation, past and future research examples will be given that aim at the development of greener methods in the mass spectrometry laboratory. Different roads can be taken, but saving gas and chemicals as well as reducing the amount of waste produced are certainly key factors in the analytical chemistry laboratory. First, it will be discussed how conventional inductively coupled plasma mass spectrometer (ICP-MS) and optical emission spectrometer (ICP-OES), respectively, can be modified to save 95% argon during operation. Here, an ICP torch geometry will be discussed that is cooled by pressurized air and operates with less than one liter argon per minute.

Second, the development of mass spectrometry methods for direct analysis with new desorption/ionization sources enables us to skip a preceding chromatography run if high mass resolution is available at the detector. This, in turn, significantly reduces the amount of solvents required per analysis. Consequently, we have applied this method to lithium-ion-battery (LIB) research. Battery research is important for the next generation of electric vehicles and LIBs are currently a major focus of research. However, battery lifetime heavily depends on degradation processes that are occurring in the battery and not fully understood to date. Degradation processes of model LIB electrolytes *in situ* were studied and first results will be presented.

(83) **X-ray Spectroscopy and Imaging of Painted Works of Art: From the Nanometer to the Meter Scale**

Koen Janssens[1], Matthias Alfeld[1], Geert Van der Snickt[1], Joris Dik[2], Letizia Monico[1, 3], Jo Verbeeck[1]; [1]University of Antwerp; [2]Delft University of Technology; [3]University of Perugia

Paintings from different historic periods (from the Antique era upto the time when photography was introduced) are considered to be valuable windows on the past. Via the Pompeian frescoes, we have a detailed view on how Roman society functioned. The paintings of Breugel show the life of ordinary citizens in the 15th Century Low Countries while those Rubens and Rembrandt depict many aspects of society in the Golden age. Hidden below the surface of many works of art overpainted representations are present that provide additional information on the painter, painting or its (preservation) history. Traditionally, a combination of X-ray radiography (XRR) and Infra-red reflectography (IRR) are used to examine the interior parts of paintings. We have recently developed a more powerful analytical method to vizualize these hidden layers that is based on X-ray fluorescence (XRF) analysis, called macroscopic XRF (MA-XRF). In this presentation, recent MA-XRF results obtained from paintings by Memling, Rembrandt, Flinck and Rubens will be discussed. For example in a 16th C. altar piece by Memling, made for a weatlhy family of Bruges, Belgium, the gradual expansion of the family and how this was reflected in the painting are revealed, as well as more subtle changes in the occupation and outlook of some of the family members. In addition, the possibility exists to employ submicroscopic X-ray beams to describe and understand better the changes in speciation that may cause some painters' pigments to gradually lose their color. A combination of microbeam XRF, diffraction and absorption spectroscopy are very useful, especially in combination with synchrotron radiation. As one of the examples, the factors determining the transformation process of chrome yellow, a pigment frequently used by Vincent Van Gogh, will be discussed. Next to the wavelength distribution and dose of the light falling on the painting, also the crystal structure and composition of the lead chromate determines its tendency towards browning. In this context, the use of the high resolution TEM-based methods of speciation can lead to an increasing level of insight into the reaction mechanisms of the alteration.

(84) **Chemical Characterization of Pegmatite Quartz Quarries in the Churchill River Basin using SIMS**

Rachel ten Bruggencate[1], Mostafa Fayek[1], Brooke Milne[1], Kevin Brownlee[2], Scott Hamilton[3]; [1]University of Manitoba; [2]Manitoba Museum; [3]Lakehead University

Identifying raw material sources used by stone tool makers can provide insight into the relationships between social and environmental factors and the organization of stone tool technology. SIMS quantification of trace element (Ti, U, Th) concentrations and Pb isotope ratios was used to characterize sources of pegmatite quartz exploited by toolmakers in the Churchill River basin of northern Manitoba and Saskatchewan. The same technique was applied to a sample of chipped quartz tools from northern Manitoba to determine the contribution of characterized sources to toolkits in the area. The results of this analysis indicate that 1) characterized pegmatite quartz sources played a significant role in quartz economies in northern Manitoba, 2) toolmakers in the study area had large procurement ranges, and 3) lithic resource stress contributed to the selection of technological strategies in the Churchill River basin.

(85) **Spectroscopic Examination of First Pyramidal Hypogeum Found in Etruria and Italy**

Mary Kate Donais[1], David George[2]; [1]Saint Anselm College Department of Chemistry; [2]Saint Anselm College Department of Classics

The excavation of a pyramidal hypogeum of Archaic Etruscan date was begun in summer 2012. The structure, located beneath the city of Orvieto (Italy), measures 5.5 m x 5.5 m at its lowest excavated level as of the end of the 2012 excavation season. Items recovered thus far from the site include animal bones, fragments of braziers, bucchero vessels, fragments of Red figure pottery, and fragments of Attic Black figure pottery. The walls are well dressed and show no evidence of hydraulic mortar. These are the first such structures found in either Etruria or Italy. Recent work at the site has led the research team to conclude that it is a sanctuary. For the first time at this site, portable spectroscopic instrumentation including x-ray fluorescence spectrometry and Raman spectroscopy were utilized during the 2013 excavation to aid in the archaeological study of this structure. Through analyses of artifacts and construction materials and the subsequent statistical, graphical, and chemometric evaluation of the resulting spectral data, the research team is able to better understand the site and the people that occupied it. Spectral data and results will be presented.

(86) **Using Non-Destructive Portable X-Ray Fluorescence Spectrometers on Archaeological Material in Museums: The Good and the Bad for Analyzing Stone, Ceramics, Metals, and Other Materials**

Robert Tykot[1]; [1]University of South Florida

Many methods of elemental analysis have been successfully used on archaeological materials to address their overall composition or specific elements to identify the source of their geological components. These include optical emission spectroscopy (OES), atomic absorption spectroscopy (AAS), neutron activation analysis (INAA), electron microprobe (EPMA), scanning electron microscope (SEM), X-ray fluorescence spectrometry (XRF; both energy- and wavelength-dispersive), inductively coupled plasma - optical emission spectroscopy (ICP-OES), and ICP mass spectrometry (usually with laser ablation). For many studies, having access to instrumentation, and the destructive nature and per-sample time and cost of analysis have limited the number and/or size of archaeological artifacts tested. Over the last several years, however, portable XRF instruments have become widely popular, allowing non-destructive analyses to be conducted in museums, on virtually any size artifact, producing data for up to several hundred samples per day. Presented here are the advantages and disadvantages of the pXRF, based on my usage for over six years on thousands of obsidian, ceramic, metal, and other artifacts from around the world.

Major issues have been raised about the sensitivity, precision and accuracy of these devices, and how to compare pXRF data from different models as well as with other analytical methods. This largely involves the analytical settings chosen, the use of standard reference materials, and the calibration software utilized. My research has included direct trace element data comparison, for the same obsidian geological samples, between pXRF and INAA, ICP-MS, microprobe, and ED-XRF. One limitation of XRF is performing surface analysis on potentially heterogeneous materials like ceramics, and especially with the pXRF not having the ability to focus on tiny spots. My research on ceramics without painted or glazed surfaces has been quite successful however, with multiple analyses performed on inside and outside surfaces, and on broken edges. One resolvable issue is that the producers of these instruments have seriously lagged in providing calibration software necessary for the bulk composition of archaeological materials such as metal alloys. Yet overall, the use of pXRF by educated consumers has greatly expanded our archaeological datasets, in many cases where elemental analysis simply was not previously possible.

(87) **Authenticating Art With Raman Spectroscopy: An Undergraduate Instrumental Analysis Laboratory Experiment**

Sara Nielsen[1], Ellen Yezierski[1], Jonathan Scaffidi[1]; [1]Miami University

Raman spectroscopy is commonly used to analyze archaeological artifacts and artwork as well as to detect forgeries. In this student-centered laboratory experiment, undergraduate instrumental analysis students used Raman spectroscopy to differentiate between two visually identical paintings and determine which is “authentic” and which is “forged.” Students learned how to safely use Raman instrumentation, the theory underlying Raman spectroscopy, and the value of this technique to scientists, art historians, archaeologists, and museum curators. The majority of students were able to successfully identify the forgery in addition to support their conclusions in journal-style articles.

(88) **To Hyternity and Beyond**

Fabien Chauchard[1], Richard Escott[1], Audrey Zilliox[2], Charles Ghommidh[3]; [1]INDATECH; [2]GSK; [3]Joint Research Unit Agropolymer Engineering and Emmerging Technologies

Pharmaceutical and petrochemical products are often produced by several sequential liquid or solid processes. They can involve complex liquid transformationss, such as crystallsations with particles in suspension or biotechnology processes. Complex solid processes include fluidised bed drying, blending and compaction. NIR spectroscopy has been widely used in these areas but appears to have several limitations due to significant changes in the physical structure of the product:

- It is often sensitive to physical aspects of the sample but is not able to accurately predict them (weight, shape, density, particles size, homogeneity, etc..)
- Detection of small chemical anomolies is sometimes not possible (eg API agglomerate, contaminant, ..)
- Separation of information is often difficult (e.g for particles in suspension within a liquid : the technique provides the spectra of the particle and also the spectra of liquid)

These issues rely on several variables and in order to overcome them it is necessary to develop an industrial methology based on multipoint VIS-NIR measurement. A global solution named Hy-Ternity (Hyperspectral Terminal for NIR Spectroscopy), able to provide hyperspectral images, Spatially resolved spectroscopy and multipoint NIR measurements, has been developed. Two industrial application case studies will be presented :

- Biotechnology based with measurements at different angles in order to control both physical (turbidity, number of cells, cell decay etc) and chemical parameters.
- Pharmaceutical tableting control for high speed sorting illustrating detection of cracks, API concentration, density, coating thickness, humidity …etc.

(89) **Development of Real Time Assurance for Oligonucleotide Synthesis**

James Rydzak[1], David White[1], Christian Airiau[1], Don Clancy[1]; [1]GlaxoSmithKline Pharmaceuticals

The synthesis of oligonucleotides is currently done using automated, flow synthesis that takes place on solid support in a packed column. The synthesis is a cycle of recurring steps that add different nucleotide bases onto the growing compound in sequence. The steps in the synthesis occur quickly and are controlled via programming and accurate dispensing pumps. We have used mid-IR, Raman and UV to monitor the synthesis of a model oligonucleotide. To assure the synthesis, we have developed calibration models for the input reagents as a means to detect accidental contamination, mix-ups of

solutions or concentration errors, ensuring the feed solution inputs are correct. Other sources of errors in the synthesis could come from water absorbed into materials, pump or valve malfunctions, and other unanticipated errors. In order to monitor and potentially control the synthesis, we are developing an MSPC model that provides real time monitoring of the parameters controlling the synthesis This presentation will talk about the development of techniques to assure the quality of the oligonucleotide synthesis.

(90) **Development of a Control Strategy for Real Time Release Testing of Ciprofloxacin HCl Controlled Release Multiparticulate Beads**

Stephen W. Hoag[1]; [1]University of Maryland, Baltimore

The development of a system for real time release testing (RTRT) requires process understanding and a comprehensive system for controlling all the sources of variability from raw materials to processing conditions for each of the different unit operations needed to make the multiparticulate beads. One of the most important critical quality attributes to control is the dissolution rate, which will be discussed in this presentation. To obtain a consistent and reproducible drug release profile for controlled release multiparticulate beads, a constant amount of polymer deposition in the fluid bed system must be achieved, and this is directly related to the process efficiency. In addition for pseudolatex films, uniform and reproducible film formation is essential for product quality, and controlling the dissolution rate in particular. The phenomenon of film formation happens in three stages; 1) evaporation of the water and ordering of the particles 2) particle deformation and 3) pseudolatex particle coalescence via the inter diffusion of polymer chains across particle boundaries. This process is often called curing, and it is essential to adequately cure the coat to ensure the desired dissolution rate, even with the correct coat thickness. To develop a RTRT system for dissolution we must ensure that we have the proper coating efficiency and extent of curing. Thus, we will talk about developing models for predicting these two attributes using NIR data. Finally, we will talk about developing a model for the dissolution rate using NIR and environmental data such as temperature and humidity.

(91) **Spectral Imaging for Real Time Release**

Rudolf Kessler[1]; [1]Process Analysis and Technology, Reutlingen Research Institute, Reutlingen University, Reutlingen

Real time release (RTR) and real time release testing (RTRT) is still more a concept rather than reality in industry. The European Medicine Agency and the FDA defines RTRT as the set of in-process controls that "may provide greater assurance of product quality than end-product testing." RTRT along with product knowledge and enhanced process understanding enables RTR. When chromatography is used as the tool for e.g. measuring content uniformity, the entire tablet is dissolved and all the API molecules will be detected. But the number of samples which can be controlled within a limited time frame is small, usually about 5 – 15 samples out of e.g. 100 000 hourly produced tablets. When the same tablets are measured by spectroscopic techniques, neither all photons in reflectance nor in transmittance can interact with all API-molecules. The reason is that the photons will be scattered in both optical arrangements back and forth and also deflected. But a a 100 % inline control can be realized. Pushbroom imaging technology can provide the technological basis due to its high speed and its multiplexing ability. Furthermore, not only the contents of the components are measured but also the distribution and texture of the particles can be used for charcterization. A pushbroom imager is a line scanning system and acquires the full spectral information for all lateral x-coordinates simultaneously in a single line, often of several thousand pixels. Depending on the camera set up and the selected wavelength ranges of the spectrograph, a high speed data acquisition is possible especially in the short NIR-range. This wavelength range also provides high penetration depths due to the low absorption coefficients of the third overtone. It is also possible to attach up to 100 glass fibers in front of the entrance slit of a pushbroom imager. Thereby the imager becomes a multi information system. This allows also a tremendous cost reduction as a single pushbroom imager can now be used in parallel at different production lines.

(92) **Can Calibrations Based on Light Propagation Theories Lead to Better Performance for Real Time Monitoring?**

Suresh Thennadil[1], Yi-Chieh Chen[1], Nicolau Dehanov[1]; [1]University of Strathclyde

Real time estimation of chemical properties of particulate systems such as fermentation broth and polymer latex suspensions using NIR spectroscopy is difficult due to the presence of multiple scattering effects. Empirical scatter correction methods are commonly used to remove spectral variation resulting from non-chemical effects by using additive and multiplicative or more complex terms. However in most cases a satifactory solution to the problem has not been achieved. The calibration models are usually not sufficiently robust to changes in light scattering effects due to variations across batches in particle size, shape and particle concentrations which lead to highly nonlinear variations in the spectra. It is possible to effectively decouple the absorption and scattering effects using the underlying physics of light propagation. This approach would be preferrable since robust calibration models can be built on the "scatter-free" absorption spectra resulting from the decoupling step. An approach based on the exact solution of the radiative transfer equation (RTE) to decouple the two effects has in theory the potential to provide significant improvements in model performance. The decoupling step however involves the inversion of the RTE which is computationally intensive and also prone to errors due to convergence issues making it difficult for the method to be used as a tool for real time assurance. In order to make the approach practical, the computational time and the need for operator interventions to address convergence issues have to be reduced. To address these issues approximate formulas based on the Kubelka-Munk (K-M) theory are considered in this work. The approximate approaches are tested using two systems. The first data set is based on a model system system that mimics optical properties of many biological fluids such as tissue, blood or cell cultures. The system consists of intralipid (fat emulsion) as light scatterer, glucose as the target analyte, and urea as the interference component to break the correlation between glucose and other components in the system. The second data set is based on the emulsion polymerisation of styrene with samples collected over the course of the reaction with the aim of building calibration models for monitoring the conversion of monomer and the mean particle size. Using the exact solution of the RTT as the benchmark approach for the decoupling step, we compare the performance of multivariate calibration models built using the Kubelka-Munk (KM) theory as well as empirical pre-processing techniques. Analysis of these 2 data sets show that the simpler KM based method which is fast and does not exhibit significant convergence problems can provide better model performance and has the potential to be applied for real time characterisation of particulate systems.

(93) **Extending the Dynamic Range of Photon Counting Using Digital Filters Designed by Linear Discriminant Analysis (LDA).**

Garth Simpson[1]; [1]Purdue University

We report a general approach for optimizing the design of digital filters for deconvolution by casting the filter design as a linear discriminant analysis (LDA) problem in a space defined by the dimensions of the filter, and subsequently apply the method to extend the dynamic range of photon counting. Photon-counting and ion-counting yield signal to noise ratios approaching the theoretical shot-noise limit, but suffer from "paralysis" at high flux. Bias from paralysis arises when the time between photon or ion induced voltage

transients is shorter than the ring-down time of the detector, such that multiple-photon events still result in a single measured count when using a discriminator. In this work, the dynamic range of photon counting has been extended through development of a digital filter optimized to recover an impulse response, effectively removing the convolution with the impulse response function of the detector. In brief, the LDA filter is trained by defining two classes: time-coincident traces corresponding to voltage transients initiated at the center of the filter, and time-offset traces generated by introducing a random temporal offset. LDA identifies the direction in the filter-space that maximizes the resolution between the two classes (coincident and offset). Subsequent convolution of the raw data with the LDA-derived digital filter recovers impulses for the coincident events optimally resolved from offset events. The post-filtered output can then be subjected to conventional photon counting algorithms. Analysis of the pre- and post-filtered time traces yields an order of magnitude extension in the dynamic range for photon counting of the filtered data before the onset of significant measurement bias in the counting results. Assessment of the capabilities and limitations of the LDA-derived digital filter will be critically reviewed based on analysis of both simulations and experimental results. Extensions of LDA-derived digital filters to other deconvolution problems will also be considered.

(94) **Evaluation of a Calibration Matrix for Heavily Overlapped Ultra-Violet Spectra by Target Factor Analysis**

Huggins Z. Msimanga[1], Newsha Tavakoli[1]; [1]Kennesaw State University

Children's Dime Tap (CDT) a cough medicine readily available over the counter, contains brompheniramine, dextromethorphan, and phenylephrine as active ingredients, all of which are UV-active. Additional UV-active compounds, identified by high-performance liquid chromatography using a photodiode array detector (HPLC/PDA), included sodium benzoate, FD&C Blue #1, and FD&C Red #40. Spectra of all six components span the whole UV region, making it very difficult to design a calibration matrix for quantifying the actives. A successful prediction model requires that all the compounds responding to the detector must be included in the calibration matrix, appropriate concentration ranges of the actives must be established prior to designing the calibration matrix, and a window inclusive of the actives where there is minimum interference must be established. Sorting out all the compounds that are UV-active is a daunting task and time-consuming. In this study, a spiking technique was used to eliminate the need to determine all the UV-actives. The technique involves adding varying amounts of the active ingredient to a fixed volume of the sample solution. Percent recoveries are calculated over the entire UV range. From a plot of percent recoveries, versus analyte concentrations, suitable concentration ranges of the actives as well as an appropriate analytical window for all actives were determined. Concentration ranges that gave close to 100 % recoveries were used to design the calibration matrix. A predictor model, calculated by target factor analysis (TFA), was used to determine concentrations of the actives in CDT. Using this approach, predicted concentrations were 968 ppm dextromethorphan, 477 ppm phenylephrine, and 220 ppm brompheniramine, with % relative errors of 3, 4, and 10, based on the manufacturer's claims of 1000 ppm, 500 ppm, and 200 ppm respectively.

(95) **Development of a Data Abstraction Strategy to Model Critical Properties of Navy Mobility Fuels from Mass Spectral Data**

Jeffrey Cramer[1], Robert Morris[1], Mark Hammond[1]; [1]U.S. Naval Research Laboratory

The relationships between the chemical constituencies of fuels and their effects on fuel properties and performance are being explored for the purposes of comprehensive fit-for-purpose (FFP) fuel modeling. Our research has previously been focused on the development of chemometric modeling strategies to define the significance of various fuel constituents or classes of constituents with respect to critical performance parameters. The current approach presented here is based on a data abstraction procedure that produces a metaspectal array that can be subjected to chemometric analysis. A compositional definition of FFP addresses the limitations of traditional property specification-based fuel assessment methodologies. It also provides a framework for determining the FFP characteristics, and thus the applicability of any petroleum fuel, alternative fuel or mixtures thereof for use. This strategy is based on compound-level analyses to circumvent the challenges associated with the introduction of uncalibrated emerging fuels that contain both calibrated and uncalibrated constituents. It will be shown that those compounds and compound classes known to be significant to various fuel properties are, in fact, maintained by the metaspectral modeling procedure. However, there are limits in how simple the compositional complexity of a material can be, with respect to petroleum fuels, before mass spectral property prediction models become unacceptably error-prone. Results will be shown that indicate how "sparse" the composition of a fuel can be and what can be done to minimize these errors.

(96) **Raman Spectroscopy to Explore the Chemical Structure of Hypomineralised Teeth and Monitor Treatment with Dental Resins**

Sara Fraser[1], Arun Natarajan[2], Bernadette Drummond[2], Keith Gordon[1]; [1]MacDiarmid Institute of Advanced Materials and Nanotechnology, Department of Chemistry, University of Otago, Dunedin, New Zealand; [2]Oral Sciences, Faculty of Dentistry, University of Otago, Dunedin, New Zealand

Hypomineralised regions of human tooth enamel are known to be significantly weaker than typical enamel. The decreased hardness has been found to correspond with lower crystallinity, lower mineral density of the hypomineralised region, a higher protein content and a more porous structure. [1,2] Issues associated with hypomineralised enamel include fracture of enamel, hypersensitivity to cold and increased need for treatments. Resins have been suggested as a potential infiltration and sealing method to decrease sensitivity, increase hardness and decrease porosity. Raman micro-spectroscopy was used to map and probe hypomineralised human tooth enamel before and after resin treatment. The hypomineralised tooth spectra were analysed using peak ratios and principal component analysis (PCA). PCA maps and associated loadings plots were used to observe and assign chemical differences across the hypomineralised tooth section. Both peak ratios and PCA maps showed increased protein to hydroxyapatite levels in the hypomineralised region compared with healthy enamel. Differences in the hydroxyapatite matrix were observed in interfaces between different regions of the mapped hypomineralised tooth sections. These differences indicated differing order and substitution in the hydroxyapatite matrix. [3] The resin treatment was found to intermittently penetrate slightly into the tooth matrix at low levels.

[1] Fagrell, T. G.; Dietz, W.; Jalevik, B.; Noren, J. G. Acta Odontologica Scandinavica 2010, 68, 215.
[2] Farah, R. A.; Swain, M. V.; Drummond, B. K.; Cook, R.; Atieh, M. Journal of Dentistry 2010, 38, 50.
[3] Thomas, D. B.; McGoverin, C. M.; Fordyce, R. E.; Frew, R. D.; Gordon, K. C. Palaeogeography Palaeoclimatology Palaeoecology 2011, 310, 62.

(97) **Predicting Rheological Behavior of Wheat Dough Based on Machine Learning and Front-Face Fluorescence Spectroscopy on Wheat Flour**

Lyes Lakhal[1], Larbi Rhazi[1], Jean-Paul Bonhoure[1], Thierry Aussenac[1]; [1]Institut Polytechnique LaSalle Beauvais

The milling and baking quality of wheat dough is commonly measured by its rheological properties assed using internationally accepted standard rheological techniques such Farinographs, Mixoraphs, Extensographs and Alveographs. The drawback of these measurement methods is that they are time consuming and costly. Hence, there is a global thrust towards the development of more time and cost efficient methodologies for rapid and accurate determination of wheat flour dough and final products qualities. Front-face fluorescence spectroscopy provides a good alternative as it is rapid, timely, less expensive, non-destructive and straightforward. The aim of this work is to develop a fast and reliable devise for wheat and flour quality control. Rheological quality of wheat dough prepared from 130 cultivars wheat flour samples was assessed with Alveograph indices (W, P, L, P/L and G). Unsupervised fuzzy C-means clustering algorithm is then used to classify alveographic indexes data into four rheological groups based on similarities among the individual data items. Fluorescence excitation and emission spectra of all samples were measured on Horiba Jobin Yvon spectrofluorometer. Using a pattern recognition technique, MOLMAP approach coupled with Bi-Directional Kohonen network, rheological groups were predicted. Despite the small number of available training samples, the estimated correct classification rates were 67 %, 81% and 87 % when the samples were divided into four, three and two rheological groups respectively.

(98) **Analysis with XRF and Raman Spectroscopies of 18th Century Böttger Red Stonewares: Unraveling Chemistry, Technology and Possible Provenance**

Francesca Casadio[2], Gulsu Simsek[1], Philippe Colomban[1], Ludovic Bellot-Gurlet[1], Katherine Faber[3], Ghenete Zelleke[2], Veronique Milande[4]; [1]Ladir, Universite Pierre et Marie Curie, Paris; [2]Art Institute of Chicago, Chicago, IL; [3]Northwestern University, Chicago, IL; [4]Cité de la Céramique, Place de la Manufacture, Sèvres, France

Stoneware was first produced in China approximately 4000 years ago. In the early 18th century (1706-08 are the dates more frequently cited) stoneware was re-discovered and produced in the West by Böttger at Meissen. Other centers of European production were The Netherlands (17th C, Ary de Milde, Delft); England (Elers Brothers, Wedgwood, 19th C.) and Plaue (Germany, 18th C.).Stonewares of various hues and depths of color (from brick red to dark rust to a rusty brown) were based on mixtures of clay, quartz, feldspar, lime (or gypsum in the case of Böttger) and iron oxide in various ratios. They were typically fired above 1200^{o}C. In this work, in-situ, non-invasive analysis was conducted with XRF and Raman spectroscopy of 68 red stonewares from different collections (Musée National de Céramique, Sèvres, France; Art Institute of Chicago, USA; Private Collection, USA). The stonewares had been assigned to Böttger (Meissen, Saxony), China , Delft, or suspected modern production based on documentation and/or connoisseurship. The objects displayed a variety of dimensions and representative range of surface finish including unpolished, polished, or black glaze decoration with unfired colors. Statistical treatment of the XRF data and careful evaluation of the ratios of major (Si, Al), minor (K, Ca, Fe) and trace element (Ti, Mn, Zr, Rb, Sr) content highlighted the possibility of grouping the different artifacts as a function of their production technology and raw materials. Additionally, Raman spectroscopy provided complementary phase identification of the unglazed ceramic bodies, as well as a detailed characterization of the glassy matrix for the dark glaze. The materials fingerprint thus obtained provided valuable clues to assist art historians and connoisseurs in making determinations about different production centers, and also distinguish genuine objects from modern replicas.

(99) **Chemical Insights on Modern Art Paintings**

Colombini Maria Perla[1]; [1]University of Pisa

Modern art is widespread in the world. Differently from most ancient paintings, which are kept in museum and collections, modern art is widespread also in small private collections and private houses. Although individual countries are actively engaged in conservation of their paintings collections, the degradation of modern painting is still an open issue. Modern paint media used by artists in the 20th century have expanded far beyond the traditional binders, by the introduction of industrially processed drying and semidrying oils, of synthetic materials and newly processed traditional natural binders. The range of phenomena and compositional features able to influence ageing processes and degradations is thus more complex than traditional binders. In modern paintings a wide range of organic and inorganic new pigments, developed both for economic and health safeguard reasons, is available, much wider in respect to pigments encountered in traditional oil paints present in artworks dating before 20th century. The paint formulations, the exposed paint surface in combination with environmental factors such as light, changes in relative humidity and noxious gases, may have had an effect on specific degradation of the paints. In addition, artists' specific experimentation with material mixing and application may have played a role. The lecture will focus on the update chemical description of acrylic, alkyd and oil paint binders and their behavior under ageing by using analytical procedures based on Py-GC/MS, DE-MS, GC/MS and HPLC-ESI-MS. Specifically, it will be shown the development of an integrated methodology for the diagnosis of degradation phenomena in modern paintings, for an in depth, reliable understanding of typical conservation issues. Applications to some paintings by Munch, Kiefer and Haring will be shown

(100) **Raman Spectroscopy for the Characterization of Ceramic and Stone Pottery**

Danilo Bersani[1]; [1]University of Parma, Department of Physics and Earth Sciences

Pots and dishes made of ceramics or stone (e.g. soapstone) are one of the most important classes of archaeological findings. They are very complex objects, consisting in a ceramic or stone body and an external decorated layer which could contain, in turn, a paint layer and an ingobe or a glaze. Crystalline and amorphous, inorganic and, sometimes, organic phases have to be identified. A complete characterization requires the use of many different experimental techniques. Raman spectroscopy can play a very important role in the analysis of this kind of materials thanks to some specific capabilities. Raman spectroscopy is non-invasive; it is possible to analyze the archaeological objects without any sampling. Unmovable artistic objects preserved in museums could be studied by portable Raman equipment. It is possible to analyze both crystalline and amorphous phases. In the analysis of ceramic or stone bodies, the high space resolution of Raman spectroscopy allows the identification of minor phases, useful for provenance study. Raman is a "point" technique, and so the coupling with a diffraction technique (X-ray or neutrons) is very effective to obtain a quantitative determination of the different phases. Raman spectroscopy is an invaluable tool for the analysis of the inorganic or organic pigments, in-glaze or under-glaze. The only exception is when the colors are obtained by metal ions dispersed in the glaze. In that case, the best combination is with an elemental technique. Some particular aspects of the Raman analysis of ceramics and stone artefatcs is discussed: the use of titanium oxides for thermometry; the hematite to magnetite ratio for the characterization of the heating atmosphere; the mistakes induced by the high difference in Raman cross-sections of the various phases. In the particular case of soapstone pots, it is possible to have detailed

information on the composition of the crystalline phases: the case of garnets and olivines is shown. The use of Raman mapping to obtain the microscopic distribution of the different phases and their orientation is reported.

(101) **Mobile Raman Spectroscopy in Art Analysis: Pros and Cons**

Peter Vandenabeele[1]; [1]Ghent University

Raman spectroscopy is a molecular spectroscopic technique that is becomming increasinglymore popular in archaeometry. The technique has quite some favourable properties, including the ability to obtain molecular information of micrometer-sized particles, and the possibilty to record spectra of inorganic as well as organic molecules. Materials can easily be identified by comparing their Raman spectrum agains a reference collection of spectra of well-defined samples. Degrading materials and deterioration processes can be studied by monitoring changes in the molecular spectra. Recently, increasdingly more mobile Raman spectrometers appear on the market. Using this instrumentation in art analysis has inherently some serious advantages: as the technique is non-destructive, provided the laser power is kept sufficiently low, using mobile Raman instrumentation allows us to record spectra of art objects, without causing them any damage: sampling is not needed. However, as many mobile Raman instruments are available on the market, it is important toe evaluate their potential and to evaluate what characteristics are especially important when using this type of mobile spectrometers. It will be shown how mobile spectrometers can be evaluated and practical applications of art analysis using an EnWave Dual laser mobile Raman spectrometer will be presented.

(102) **Novel Sampling Strategies for Trace Element Quantification in Ancient Copper Artifacts using LA-ICP-MS**

Marcel Burger[1], Reto Glaus[1], Vera Hubert[2], Samuel van Willigen[2], Marie Wörle-Soares[2], Detlef Günther[1]; [1]ETH Zürich, Laboratory of Inorganic Chemistry; [2]Swiss National Museum

Laser ablation inductively coupled plasma mass spectrometry (LA-ICP-MS) is a very versatile and powerful technique for elemental and isotopic analysis of solid samples in a quasi-nondestructive manner. It allows for quantification of major, minor and trace element concentrations with low or minimum sample preparation. In order to make large or immovable objects (e.g. archeological artifacts) accessible to LA-ICP-MS, it is desirable to allow the sampling process outside the laboratory or to develop a strategy that allows the analysis of solids independent of size and geometry of an ablation cell. This work aims establishing an analytical method for the determination of trace element concentrations in ancient copper artifacts not accessible via conventional LA-ICP-MS setup. The sampling step is performed in ambient atmospheric conditions using a portable nanosecond laser device (pLA, λ=532 nm) and fiber optics to ablate the solid sample. The generated aerosol is either directly guided into the ICP via a gas exchange device (GED) or collected on polycarbonate membrane filters which are subsequently analyzed in a laboratory based ns-LA-ICP-MS (λ=213 nm) setup. The use of an external standard allows for trace element quantification in both cases. Both analytical approaches were used to quantify trace element concentrations in various copper reference materials. The laboratory based, but ablation cell independent pLA-GED-ICP-MS analysis yielded results comparable to those obtained via conventional LA-ICP-MS setup (±10%). Good performances (±30%) were also obtained when the offline-LA LA-ICP-MS approach was applied. Although more accurate results and lower limits of detection can be reached when an online-LA-ICP-MS setup is used, the attempt at offline laser ablation sampling and subsequent LA-ICP-MS analysis is most promising for trace element quantification in samples that cannot be transported to the laboratory. Following their characterization, these two approaches were applied to quantify trace element concentrations in archeological copper artifacts.

(103) **Precise Cranial Surgery With Femtosecond Laser Ablation, Laser Induced Breakdown Spectroscopy and Second Harmonic Generation.**

Philbert Tsai, Diana Jeong[1], David Kleinfeld[1]; [1]University of California, San Diego

Precise removal of bone is required in several surgical procedures performed in both clinical and laboratory settings. Notably, in the case of head and neck surgeries, the close proximity of bone to delicate neural tissue presents specific challenges for the removal of bone while minimizing collateral damage to nearby soft tissue. To address these challenges, we demonstrate femtosecond pulse laser ablation of cranial bone in conjunction with Laser Induced Breakdown Spectroscopy (LIBS) and Second Harmonic Generation (SHG) to monitor and guide the bone cutting process. In particular LIBS allows us to distinguish bone from soft tissue, while SHG is an effective tool for range-finding. Ablation is performed in a flowing aqueous environment, to prevent the accumulation of blood and debris at the surgical site. A double-pulsed ablation scheme is utilized to optimize the breakdown spectral emission obtained in a submerged environment. The preliminary goal of our work is to automate the surgical removal of bone to provide optical access to the mouse brain for two-photon laser scanning microscopy of neuronal and neurovascular dynamics. We utilize an amplified Ti:Sapphire laser system to perform femtosecond pulse ablation of the skull. We demonstrate real-time monitoring of the material composition at the ablation focus using LIBS, along with iterative determination of the remaining skull thickness using SHG between ablation passes. Using these techniques, we ablate along the surface contour of the skull to produce a thinned skull cranial window in a mouse. Post-ablation two photon imaging of cerebral blood flow was performed through the laser-manufactured cranial window. Post-mortem histology of the neuronal tissue underlying the cranial window was used to verify the lack of collateral soft-tissue damage by this feedback-guided ablation process. We further demonstrate the potential for our techniques to produce precise guide holes for the insertion of micro-electrodes, particularly multi-electrode arrays, through the skull and into the brain with minimal damage to cranial bone, in order to maintain the long-term integrity of underlying neural tissue.

(104) **Healing Humanity One Spark at a Time: Medical Applications of LIBS**

Steven Rehse[1]; [1]University of Windsor

The range of activities to which LIBS has been applied continues to grow rapidly. One very interesting area of research has been its use in the field of medicine and the health sciences. Although showing great promise, this recent flurry of activity has yielded mostly laboratory-type demonstrations, while genuine interest from the world of clinical medicine has been elusive. To date no wide-spread clinical applications have been implemented. Nonetheless, the scope of the various medical applications that have been demonstrated around the world are impressive. Broadly speaking, these can be divided into two categories: assays which aim to quantify or monitor specific elemental concentrations in medical specimens and diagnostics that use unique elemental compositions to rapidly identify or classify specimens. In this talk, I will review the recent progress in the application of LIBS in several classes of medical assays including: the analysis of hard/calcified tissues such as tooth enamel, stones and calculi, and fingernails; the analysis of soft tissues such as organs, cancerous/malignant tissues, and hair/skin; and the characterization of medical specimens like blood and proteins. Diagnostic tests that aim to rapidly identify/classify microbial agents causing human disease such as bacteria, molds, yeasts, and viruses

will be reviewed as will the development of rapid screening tests for conditions of human pathology including drug-addiction, doping, and poisoning.

Lastly, it is significant that although photoablation procedures are common in laser medicine, the real-time feedback that LIBS could provide via an optical analysis of the ablation event is not currently utilized or exploited. It is this real-time control of the medical procedure, or the ability to immediately obtain diagnostic information, that is the greatest advantage that LIBS could bring to the practice of medicine, and ideas for its implementation will be discussed.

(105) **Quantitative Analysis with LIBS at Low Ablative Energies**

M.A. Meneses-Nava[1], V. Contreras[1], O. Barbosa-Garcia[1], J.L. Maldonado[1], G. Ramos-Ortiz[1]; [1]Centro de Investigaciones en Optica A.C.

Laser-induced breakdown spectroscopy (LIBS) represents a powerful tool for qualitative analysis and can achieve quantitative results with acceptable accuracy and precision. However, LIBS still presents some drawbacks to be accepted as a universal analytical technique in elemental analysis, such as a high detection limit and the use of calibration curves for quantification. To solve the detection limit inconvenience without losing LIBS advantages, Double Pulse LIBS (DP-LIBS) has been used which is an attractive approach to increase LIBS sensitivity. In DP-LIBS the addition of a second pulse increases the analytical performance of conventional LIBS through a better coupling between the laser pulse energy and the ablated matter. An alternative approach for quantitative analysis without the use of calibration curves is the Calibration Free LIBS (CF-LIBS). With these two techniques acceptable results have been obtained, but with the inconvenience that they have been applied independently from each other. In this work it is demonstrated for the first time to the best of our knowledge, that CF-LIBS can be successfully applied to spectral lines obtained from orthogonal DP-LIBS configuration. The improvement in atomic emission, signal-to-noise ratio (SNR) and reproducibility offered by DP-LIBS has been tested in CF-LIBS in order to reduce the use of high energies. As a consequence, when CF-LIBS is applied to DP-LIBS instead of conventional LIBS, the mass removed by laser ablation is reduced by a factor of 13 without losing signal intensity. This remarkable finding can be exploited in critical applications where sample damage represents a drawback. Two examples for quantification, anti-diabetic tablets and steel samples, are discussed.

(106) **Chemometric Data Analysis Strategies for Optimizing Pathogen Discrimination and Classification Using Laser-Induced Breakdown Spectroscopy (LIBS) Emission Spectra**

Russell Putnam[1], Khadija Sheikh[1, 2], Andrew Daabous[1], Steven Rehse[1]; [1]Department of Physics - University of Windsor

Laser-induced breakdown spectroscopy (LIBS) is currently undergoing a period of rapid growth as reflected by both the variety of applications to which it has been applied and the number of peer-reviewed articles that have appeared describing the advances in the field. The speed, portability, ruggedness, sensitivity, and selectivity of the technique all suggest that LIBS can provide a rapid point-of-care bacterial diagnostic technology for clinical, military, environmental, or civilian applications. The potential significance of such a technology is global in scale and encompasses almost every aspect of human health and safety. For bacterial identification, the intensities of many atomic emission lines within the LIBS plasma spectrum (mostly from trace inorganic elements such as calcium, magnesium, phosphorus, potassium, etc.) provide an immediate and unique spectral atomic emission "fingerprint" which positively identifies the bacteria. Statistical signal-processing techniques (known broadly as chemometrics) allow an unknown LIBS spectral fingerprint to be almost immediately classified against a reference library of pre-existing fingerprints. We have investigated a number of strategies for optimizing these chemometric algorithms to allow the efficient discrimination and rapid classification of pathogenic and non-pathogenic bacteria from their LIBS spectra. The use of individual atomic emission lines as well as various combinations of ratios of those lines as independent predictor variables will be presented. Also, a direct comparison of discriminant function analysis (DFA) and partial least squares discriminant analysis (PLS-DA) was performed.

(107) **Femtosecond Laser-Induced Breakdown Spectroscopy (fs-LIBS) of Electrode/Electrolyte Interfaces**

Sid Ahmed Beldjilali[1,2], Ulrike Vogl[1, 3], Simon Lux[1], Jaroslaw Syzdek[1], Huaming Hou[1], Xianglei Mao[1], Vassilia Zorba[1], Martin Winter[3], Robert Kostecki[1], Richard E. Russo[1]; [1]Environmental Energy Technologies Division, Lawrence Berkeley National Laboratory, Berkeley, CA; [2]LPPMCA, USTOMB - Université des Sciences et de la Technologie d'Oran, Oran, Algeria; [3]MEET - Münster Electrochemical Energy Technology, Institute of Physical Chemistry, University of Muenster, Münster, Germany

Li-ion batteries are the most widely used energy storage devices in consumer electronics and main technology for powering electric vehicles. Direct chemical analysis of electrode/electrolyte interfaces can provide critical information on surface phenomena that define and control the performance, life-time and safety of Li-based battery systems. In this work, ex situ femtosecond (fs) Laser-Induced Breakdown Spectroscopy (LIBS) is used to probe compositional variations within the Solid Electrolyte Interphase (SEI) layer. The distribution of elements as a function of depth is studied for SEI layers grown on Highly Oriented Pyrolytic Graphite (HOPG) and single-crystalline Si electrodes in organic carbonate-based electrolytes. These results demonstrate that fs-LIBS is a promising tool for direct depth-resolved chemical analysis of interfacial layers in electrochemical energy storage systems.

(108) **Ultra-Low Frequency Raman Spectroscopy: A New Technique for Polymorph Characterization of Pharmacuetical Drug Substances**

Peter Larkin[1], Marta Dabros[1], Beth Sarsfield[1], James Carriere[2], Brian Smith[3]; [1]Bristol Myers Squibb; [2]Ondax; [3]Princeton Instruments

Polymorph detection, identification, and quantitation in crystalline materials is a matter of great importance in the pharmaceutical industry. Vibrational spectroscopic techniques used for this purpose in the pharmaceutical industry include mid-infrared (FT-IR), near-infrared (FT-NIR), Raman spectroscopy and THz (far-IR) spectroscopy. Typically, high frequency Raman spectroscopy and mid-infrared are used to indirectly monitor long range order of molecular crystals. However, ultra-low frequency vibrational spectroscopy provides access to the lattice vibrations of molecular crystals and hence the potential to more directly probe the intermolecular interactions of molecules in the solid state. Recent advances in filter technology enable high-quality ultra-low frequency Raman spectra to be acquired using a single stage spectrograph. This innovation enables cost-effective collection of high quality Raman spectra in the range of 10-200 cm^{-1} region. We demonstrate the potential of ultra-low frequency Raman spectroscopy for polymorphic characterization of pharmaceutical drug substances. Advantages include: ease and flexibility of sampling, intense Raman bands, rich and complex band structures, and discrimination between different crystalline forms. Future growth of the technique will require understanding the relationship between the crystalline structure and the spectral characteristics.

(109) **Raman Spectroscopy of Oil Shale**

David Tuschel[1]; [1]HORIBA Scientific

This presentation will cover the application of Raman spectroscopy for the characterization of oil shale, particularly black shale, which consists of kerogen (fossilized organic matter) trapped in sedimentary rock consisting of clays, calcites, silicates, and titanium dioxides among other inorganic minerals. We show that Raman spectroscopy is useful for characterizing the varieties of kerogen structure (chemical bonding and solid state), differentiating shales with different relative amounts of kerogen to inorganic mineral, and differentiating polymorphs of naturally occurring inorganic oxides.

(110) **Nanoscale Chemical and Thermal Identification of Inclusions in Polymers and Engineered Thermoplastic Blends using AFM Coupled to IR Spectroscopy, Thermal and Mechanical Analysis**

Anne M. Simon[1], Nancy L. Jestel[1], Bing Zhou[1], Michael Lo[2]; [1]SABIC; [2]Anasys Instruments, Inc

Inclusions in polymer samples can reduce material quality, both aesthetically and functionally. Degraded polymer, foreign species, and air pockets are known examples of inclusions in polymers. We will discuss our investigation of inclusions in polycarbonate samples with atomic force microscopy (AFM) coupled to IR spectroscopy (AFM-IR) and combined with nanoscale thermal and mechanical measurements. In one example, the IR spectra of the inclusion and the bulk polycarbonate matrix were indistinguishable, but the thermal measurements revealed that the inclusion had a higher onset melting point than the main or bulk material. This suggests that the inclusion may arise from a higher degree of cross-linking. A significant advantage of this instrument configuration over traditional methods, such as IR and Raman microscopy or micro x-ray fluorescence (XRF), is the ability to generate diverse types of data (chemical, thermal, and physical) without reconfiguring the instrument or removing the sample. Additionally, even though the inclusion's size might be sub-micrometer, the nanometer-scale resolution of the instrument means that multiple sampling points can be interrogated on a given inclusion, increasing statistical confidence in the results. Frequently, the results obtained by conventional methods are inconclusive, while the higher level of certainty with this instrument will aide in the ability to recommend corrective actions to improve polymer quality.

(111) **Assessing Intermediate Degrees of Acylation of Starch Granules via Infrared Microspectroscopy**

Mark Boatwright[1,2], Meng Xue[3], Yongcheng Shi[3], David Wetzel[23]; [1]Department of Biochemistry and Molecular Biophysics, Kansas State University, Manhattan, KS; [2]Microbeam Molecular Spectroscopy Laboratory, Kansas State University, Manhattan, KS; [3]Department of Grain Science, Kansas State University, Manhattan, KS

The use of starch derivatives is widespread, and the degree of substitution is a matter of concern in manufacturing and application. Infrared microspectroscopy (IMS) is used to track esterification of starch on a granular level via the appearance of substituted carbonyl stretching bands, and the disappearance of the -OH bending vibrations. IMS is an alternative to proton NMR for determining the degree of substitution. It requires smaller quantities and can be performed on a granular level without dissolution of starch in deuterated solvent. Data is presented that was obtained from acylated starch granules flattened on an infrared reflecting glass surface to obtain spectra in transmission reflection transmission mode. Only granules in the diameter range of 20-30 µm as observed under the microscope were scanned. The changes of carbonyl absorption at 1740 cm-1, and of -OH deformation absorption at 1094 cm-1 were expressed by the band ratios, and were plotted against the degree of substitution results determined by proton NMR. Starch derivatives are receiving increasing attention due to their application in time release medicinal encapsulation, biodegradable coatings and films as an alternative to petroleum based polymers. IMS provides a convenient, alternative way to determine the degree of substitution of starch derivatives in place of conventional wet chemistry or NMR methods.

(112) **Infrared Microspectroscopic Assessment of Hydrophilic Surface Treatment of Polydimethylsiloxane (PDMS) for Use in Microfluidics**

David Wetzel[1,3], Mark Boatwright[2, 3], Christopher Culbertson[1], Makund Koirala[1, 3]; [1]Department of Chemistry, Kansas State University, Manhattan, KS; [2]Department of Biochemistry and Molecular Biophysics, Kansas State University, Manhattan, KS; [3]Microbeam Molecular Spectroscoy Laboratory, Kansas State University, Manhattan, KS

Polydimethylsiloxane (PDMS) is popular material for the fabrication of microfluidic devices based on its ease of fabrication, transparency, and cost. For aqueous solutions, however, the small channels are difficult to wet. Modification of the nonpolar surfaces of the channel is often necessary to impart hydrophilic character and reduce the adhesion and adsorption of hydrophobic analytes. Infrared microspectroscopy enables monitoring of the substitution of methyl groups with hydrophilic groups. Prior to separation, the vibrational microspectroscopic technique provides a way to measure the relative amount of substitution during the preparation of microfluidics devices based on the appearance of absorption bands unique to the modifying group. This microsampling technique allows the use of infrared microspectroscopy to verify adequate modification in advance of testing the separation performance of the microchip. The depth of modification of the channel is assessed and durability with use is studied. Spectra are presented to demonstrate the utility of this highly localized analytical technique.

(113) **Threat Specific Spectral Searches in the Detection of Explosives**

Kevin Judge[1], Greger Andersson[1]; [1]Smiths Detection

Spectral library searches are commonly performed to assist in the identification of an unknown substance. In many field-based applications, the primary objective is to detect the presence or absence of specific chemical threats, such as explosives. The term "threat check" will be described as a targeted search focused on specific chemicals. It has the advantage of reduced analysis time while providing the user with the necessary information to make actionable decisions in the field. It is essential that an independent threat check be sensitive enough to alarm when the chemical is present in a mixture, but also specific to avoid false positives. Spectral regions associated with the threat are selected in an effort to achieve this desired balance. The current variable selection approach begins with an initial set of spectral features found in the target spectrum. This list can be reduced based on a frequency distribution of a larger library, assuming the more unique regions are likely the most useful in discriminating the threat of interest. An iterative process involving the removal of individual regions is employed to further identify expendable features. This computationally-expensive process is executed on an external computer, with only the outputs being applied to the instrument search routine. Ideally, this functionality could be implemented directly into the instrument software, requiring a more efficient method. This presentation includes an overview of the algorithm concept, along with experimental evidence to support the effectiveness of an explosives threat check.

(114) **A Modified Exponential Gaussian Hybrid Function and Its Application to Processing the Data Obtained by Ultra-high Resolution TOFMS Coupled with Chromatography**

Jihong Wang[1], Peter M Willis[1]; [1]LECO Corporation

Fitting a chromatographic concentration profile with mathematical models has been widely explored. For processing the large data sets produced by Ultra High-Resolution TOFMS (UHR-TOFMS) instruments, a high speed algorithm is a priority for profile fitting and deconvolution. In this work, a new peak shape model is developed based on the exponential Gaussian hybrid function. The presented model provides several advantages in UHR-TOFMS signal processing: [1] The model fits asymmetrical peak shapes well; [2] The model has fast convergence. For UHR-TOFMS signal processing the above features are extremely helpful when fitting a large number of peaks with low residual.

(115) **Muscle Oxygenation Measurement in Humans by Noninvasive Optical Spectroscopy and Locally Weighted Regression**

Lorilee Arakaki[1], Kenneth Schenkman[1], Wayne Ciesielski[1], Jeremy Shaver[2]; [1]University of Washington; [2]Eigenvector Research, Inc.

Shock is a medical condition characterized by low blood perfusion of tissues. Early recognition of shock is critical to timely treatment that would help to prevent the cascade of events leading to long-term hospitalizations and/or death by multiple organ failure. We have developed a reflectance optical system that measures muscle oxygenation (Mox) from the surface of the skin in the visible-NIR region. Low Mox measured from an extremity like the hand can identify low tissue perfusion early since during shock, blood is shunted from the extremities to preferentially perfuse and oxygenate core internal organs (e.g., heart, lungs, and liver) and the brain. The physical and biological differences between human subjects present a complicated problem when predicting Mox, a measure of the relative amounts of oxygenated and deoxygenated hemoglobin and myoglobin in the muscle. We used Multivariate Curve Resolution to predict Mox from healthy controls subjected to 15 min of arm ischemia and used those values in a Locally Weighted Regression/Partial Least Squares (LWR/PLS) model. The resulting LWR/PLS model allowed accurate predictions of Mox from test set subjects, despite the complexities caused by differences in body mass index and skin color in the test subject population.

(116) **Multivariate Models for Rapid Identification with Handheld Spectrometers**

Katherine Bakeev[1], Dawn Yang[1]; [1]B&W Tek, Inc

Multivariate Classification methods are well known with spectroscopic and other data, and are growing in use as rapid identification methods for material, counterfeits, explosives and other materials abound. In developing models for use in such scenarios, it is desired to have a system that can be used without need for extensive chemometric analysis and expertise by the end-user. A challenge is to develop systems that guide a user in collection of quality data, and also enable the development of methods with little user intervention. We will present information on PCA-based modeling of Raman data with handheld instrumentation, along with data checks done to ensure integrity of the data and consistency before a model is created.

(117) **A Chemometric Algorithm for Detection of Lipid Core Coronary Plaques Using Intravascular Near-Infrared Spectroscopy**

Huwei Tan, Craig Gardner, Stephen Sum[1], Sean Madden[1], Chunsheng Jiang, Zhehua He[1], Tianchen Shi, Edward Hull, Jay Caplan, James Muller[1]; [1]InfraReDx Inc.

Infraredx® intracoronary near infrared spectroscopy (NIRS) system is a novel method for the characterization of an important property in coronary plaque composition - lipid cores - a property associated with heart attacks. A novel chemometric algorithm constitutes a key component in detection of the lipid core plaques (LCP). The algorithm utilizes multivariate models to account for spectral variation over patients, instruments, catheters, blood, pullbacks and rotation angles, following detection of LCP by the core classifier. The models were calibrated and validated from 84 autopsy hearts against histology. A description of the autopsy experimental setup, histological reference, model development and validation will be discussed. The prospectively validated models were found to identify LCP with an area under the receiver-operating characteristic curve of 0.80 (95% confidence interval: 0.76 to 0.85). These models have been approved by the FDA and integrated into the Infraredx® true vessel characterization (TVC) imaging system. The system has now been used in over 3,000 patients in 11 countries. The accurate detection of lipid core coronary plaques provides doctors with a unique parameter to better inform the treatment of patients with coronary artery disease.

(118) **Solvo-, Chemi-, Diffusio- and Electro-phoretic Migration: New Techniques to Measure Exotic Phoretic Mobilities and Characterize Colloidal Surfaces**

Todd Squires, Joel Paustian[1], Rodrigo Nery-Azevedo[1]; [1]University of California, Santa Barbara

The electrophoretic mobility of a colloid encodes the properties of its surface, and is so widely-used for material characterization that advanced instruments for electrophoresis measurements have become routine laboratory tools. This electrophoretic migration is driven by applied gradients in the electrostatic potential in the surrounding electrolyte. Other gradients also drive phoretic migration of colloids: gradients in ionic strength (or solute concentration more generally) drive diffusiophoretic and chemiphoretic motion, and gradients in solvent composition drive solvophoresis. While such phenomena have been known to occur for a half-century, and have been exploited industrially (e.g. in the manufacture of films and coatings), it has proven difficult to measure such lesser-known phoretic mobilities directly. The difficulties in establishing gradients that are strong enough to drive measurable migration, yet stable against convective fluid motion, have necessitated indirect methods. Here we describe a generalized framework to understand these phenomena, and introduce new techniques we are developed to measure the phoretic migration of colloids under a variety of imposed gradients. We describe methods for designing, imposing, and maintaining strong, stable and steady gradients of solute and/or solvent, while tracking the phoretic migration of suspended colloids. Additionally, we describe measurements of dynamic electrophoresis, where we change the surrounding chemical environment in real time, to probe the dynamics of the colloidal surface in response to its changing environment.

(119) **Moving Charges to Order Particles: The Disorder-Order Transition for Dielectrophoretic Colloidal Assembly**

Eric Furst[1]; [1]University of Delaware

The self-assembly of colloidal building blocks into ordered, periodic structures using directing electric fields is a rapid, highly scalable, and potentially low-cost route for manufacturing functional nanomaterials and devices. The dielectrophoretic assembly of colloidal suspensions into crystalline arrays follows a master scaling that collapses the disorder-order transition as a function of field strength, frequency and particle size. This master scaling has been verified for particle diameters ranging from $2a = 200$ nm to 3 μm by light scattering (Lumsdon et al., Langmuir 20, 2108-2116, 2004; McMullan and Wagner, Langmuir 28, 4123-4130, 2012), laser tweezer pair interaction measurements (Mittal et al., J. Chem. Phys. 129, 064513, 2008) and small-angle neutron scattering (McMullan and Wagner, Soft Matter 6, 5443-5450, 2010). In this work, we

reconcile the established empirical phase diagram with direct measurements of the colloid polarizability using dielectric spectroscopy. By varying volume fraction, particle size and ionic strength, we confirm the disorder-to-crystal electric field assembly phase diagram. This represents an alternative means to search for optimal self-assembly conditions that is not limited by particle size, shape, chemistry or solvent characteristics.

(120) **Fluid and Ion Transport at the Nanoscales: Application to Osmotic Energy Harvesting**

Lyderic Bocquet[1,2]; [1]ILM - University of Lyon; [2]MIT

« There is plenty of room at the bottom ». This visionary foresight of R. Feynman, introduced during a lecture at Caltech in 1959, was at the root of numerous scientific and technological developments, taking benefit of the "strange phenomena" occuring at the smallest scales. There remains however a lot to explore, in particular in the context of fluids at the nanoscales and their specific transport properties. The great efficiency of biological nanopores, such as aquaporins, in terms of permeability or selectivity is definitely a great motivation to foster research in this direction. How to reach such efficiency in artificial nano-systems, and build new devices taking benefit of the strange transport behavior of fluids at nanoscales is still an open question. In this talk, I will discuss some theoretical and experimental results obtained in our group on the fluid transport at the nanoscales, in particular inside nanopores, nanochannels and nanotubes. More specifically, I will focus on the study of transport inside a single Boron-Nitribe nanotube, obtained in a specifically developped trans-membrane nanofluidic device. Experiments show unprecedented energy conversion from salt concentration gradients. Applications in the field of osmotic energy harvesting will be discussed.

References:

« Giant osmotic energy conversion measured in a single transmembrane boron-nitride nanotube », A. Siria, P. Poncharal, A.-L. Biance, R. Fulcrand, X. Blase, S. Purcell, and L. Bocquet, Nature 494 455-458 (2013)

« Soft nanofluidic transport in a soap film », O. Bonhomme, O. Liot, A.-L. Biance, and L. Bocquet, Phys. Rev. Lett. 110 054102 (2013)

« Nanofluidics, from bulk to interfaces», L. Bocquet , E. Charlaix, Chemical Society Reviews 39, 1073 - 1095 (2010)

(121) **Ion Correlation and Ion Steric Effects on Electrophoresis of a Colloidal Particle**

Aditya Khair[1], Robert Stout[1]; [1]Department of Chemical Engineering, Carnegie Mellon University

For over a hundred years the Poisson-Nernst-Planck (PNP) equations have been employed as the de facto theoretical model of electrokinetic phenomena. However, the assumption of non-interacting, point-sized ions inherent to the PNP model can lead to impossibly large concentrations at moderate voltages. Moreover, the PNP model does not account for electrostatic correlations between ions, which are of importance in concentrated, multivalent electrolytes and room temperature ionic liquids. Here, we revisit the classic problem of electrophoresis of a spherical colloid, using modified PNP equations that account for: (i) steric repulsion between finite sized ions through Bikerman's model [1]; and (ii) electrostatic correlations between ions via a modified Poisson equation recently proposed by Bazant et al. [2]. At low particle zeta potentials (< 25mV) we derive an analytical formula for the electrophoretic mobility accounting for ion correlations, which predicts mobility reversals at sufficiently large ion correlation lengths. Next, following Khair and Squires (J. Fluid Mech. 2009) we develop an asymptotic scheme for thin Debye layers to compute the mobility for larger zeta potentials, where ion steric effects impose a limit on the counter-ion density in the diffuse Debye layer. In both cases, our calculations are compared to existing experiments on electrophoresis in concentrated multivalent electrolytes, which exhibit a mobility reversal.

[1] J. J. Bikerman, Philos. Mag. 33, 384 (1942)

[2] M. Z. Bazant, B. D. Storey, and A. A. Kornyshev, Phys. Rev. Lett. 106, 046102 (2011).

(122) **Ultrafast Plasmonics: Surface-Enhanced Femtosecond Stimulated Raman Spectroscopy**

Richard Van Duyne, Renee Frontiera[1], Natalie Gruenke[1], Anne-Isabelle Henry[1]; [1]Northwestern University

We have developed a new ultrafast SERS technique to study chemical reactions of molecules in plasmonic hotspots on the femtosecond timescale of molecular motion. With the first demonstration of surface-enhanced femtosecond stimulated Raman Spectrsocopy (SE-FSRS), we have created a coherent vibrational technique capable of obtaining complete vibrational spectra with ultrafast temporal resolution. SE-FSRS combines the high plasmonic enhancements of surface-enhanced Raman spectroscopy (SERS) with the high spectral and temporal resolution of femtosecond stimulated Raman spectroscopy (FSRS). This technique is an important step towards studying chemical reactions of a small subset of molecules on the femtosecond timescale of nuclear motion. We have examined the molecule-plasmon coupling that leads to the Fano-like lineshapes observed in SE-FSRS, providing important insights into the ultrafast dynamics of molecule-plasmon coupled systems. Currently we are exploring a number of substrate systems to further characterize this new technique and to expand the types of molecular systems we can study with SE-FSRS.

(123) **Raman Microscopy for Imaging Cellular Dynamics**

Katsumasa Fujita[1]; [1]Osaka University

Raman spectroscopy offers the detailed analysis of sample molecules with the capability of detecting molecular vibrations and has emerged as a tool for investigation of intracellular molecules. However, 1) the small cross-section of Raman scattering and 2) the spectral overlap from various molecular species hinder Raman spectroscopic investigation of intracellular molecules with high spatial and temporal resolution. To tackle these issues, we have developed a Raman microscope system in which the image acquisition speed was improved by parallel detection of Raman spectra from multiple points in a sample. The microscope can obtain a Raman image of cells with the diffraction-limited resolution in several to a few tens of minutes, allowing us to trace molecular dynamics in cellular events, such as cell division and apoptosis. We have also developed a tiny tag using alkyne to highlight small molecules that are too small to be labelled by fluorescence molecules. Alkyne gives a Raman peak at the wavenumber region where endogenous molecules do not have Raman peaks, allowing for separation of the tagged molecules from others. By designing alkyne tags with strong Raman scattering, the simultaneous observation of two different small molecules, nucleoside and ubiquinone, was successfully performed. For improving the sensitivity in molecular detection by Raman scattering, we introduced gold nanoparticles into a living cell and detected the enhanced Raman scattering from the vicinity of the nanoparticle. Tracking of nanoparticle position simultaneous with Raman detection allows us to obtain a Raman spectra with 50 msec temporal resolution and 60 nm spatial accuracy. With the developed system, we imaged the pathway of the nanoparticle transportation within sub-micron region in the cell by Raman scattering.

(124) **Investigation of Nanostructure Dynamics by Femtosecond Time-Resolved Spectroscopy with Nanometer Spatial Resolution**

Arnulf Materny[1]; [1]Jacobs University Bremen

Structural and electronic properties change if samples are prepared on a nanometer scale. This is also reflected in their molecular dynamics. Organic electronics has become a very promising approach to build

cheap and versatile electronic devices. Examples are organic field effect transistors or organic solar cells where nanostructures play an important role. Also there, the behavior is expected to be different from that observed in bulk material influencing the properties of the electronic devices. Since averaging over the volume defined by the optical focus (Abbé limit) will only give very limited access to the size-dependent information, a spectroscopic investigation with high spatial resolution would be desirable also for the investigation of the organic semiconductor devices. In order to study organic semiconductor nanostructures, we have used nonlinear spectroscopic techniques in combination with scanning near-field optical microscopy (SNOM). Femtosecond CARS and pump-probe spectroscopy with spatial resolution down to approximately 50 nm has been successfully applied. Results of this exciting research will be presented. Newest results have been obtained for 3,4,9,10-Perylenetetracarboxylic dianhydride (PTCDA) crystallites and Poly(3-hexylthiophen-2,5-diyl) nanostructures (P3HT). Vibrational selectivity helps to differentiate between components of the semiconductor (e.g. solar cell) in time-resolved CARS experiments. Excited state exciton dynamics has been measured as a function of crystallite size and laser power. It could be demonstrated that the SNOM technique does not only allow for a selection of single nanostructures, but also for the measurement with well-defined light-excitation powers.

(125) **Quantitative Raman Spectroscopy in Turbid Matter: Reflection or Transmission Mode?**

Rudolf Kessler[1], Dieter Oelkrug[2], Edwin Ostertag,[1]; [1]Process Analysis and Technology, Reutlingen Research Institute, Reutlingen University, Reutlingen; [2]Institute of Physical and Theoretical Chemistry, University of Tübingen, Tübingen

There is an increasing demand for analytical techniques based on Raman radiation generated in the volume of a multiple scattering sample. Areas of application are in-line process monitoring with fast quality control e.g. in pharmaceutical manufacturing, in-situ characterization of surface reactions on supported catalysts or counterfeit detection of pharmaceutical products through the packaging, just to name a few. Several approaches to quantify active pharmaceutical ingredients (API) in pharmaceutical mixtures by transmission Raman spectroscopy in combination with multivariate data analysis have been published. In this paper we compare collimated and diffuse irradiation of opaque systems and calculate the transmitted and reflected Raman intensities as a function of the layer thickness, absorption coefficient, and scattering coefficient. Starting from theoretical calculations based on random walk simulations and analytical approaches the results are then verified by experiments. We also emphasize composite layers and describe methods how to enhance the fractions of the desired intensities in forward and backward directions, respectively. For non-absorbing layers the Raman reflection and transmission intensities rise steadily with the layer thickness. In absorbing materials the reflected Raman signal saturates at levels that depend strongly on the absorption and scattering coefficients. The transmitted Raman intensity passes through a maximum and decreases then exponentially with increasing layer thickness to zero. The radial spreads of the emitted Raman signals are determined and critically confronted with the limited aperture of the detection system. The calculated results are experimentally tested with organic polymers and basic materials for pharmaceutical tablets. From the calculated radial intensity spreads follows that quantitative transmission Raman spectroscopy requires diameters of the detected sample areas that should be significantly larger than the sample thickness. In stratified systems, Raman transmission allows deep probing even of small quantities in buried layers. However with a special set up, it is also possible to monitor the whole depth of a multiple scattering sample with equal statistical weight in reflectance. This may be a favorable approach for inline Raman spectroscopy in process analytical technology.

(126) **Investigating the Degradation of Stored Red Blood Cells Using Raman Spectroscopy**

Chad Atkins[1,2], H. Georg Schulze[2], Deborah Chen[3], Peter Schubert[3,4], Katherine Serrano[3,4], Dana Devine[3,4], Michael Blades[1], Robin Turner[1,2]; [1]University of British Columbia, Chemistry Department; [2]Michael Smith Laboratories; [3]University of British Columbia, Centre for Blood Research; [4]Canadian Blood Services

The first approach for measuring cellular degradation of stored red blood cells (RBCs) using Raman spectroscopy is described. When stored using standard protocols, RBCs are considered to be viable for 42 days. However, this timeframe is based on averages from conventional assays that are costly and time-consuming; in reality, blood from different patients will degrade at significantly different rates. This degradation is called 'storage lesion' and refers to a multitude of chemical, physiological, and morphological changes that occur in the stored units over time. Clinical evidence exists which suggests these variations are responsible for a variety of post-transfusion illnesses. It would therefore be advantageous to assess the state of stored blood rapidly and accurately without needing to sample the contents of the bag.

Many of the age-related compositional changes associated with RBC storage are expected to be reflected in their Raman signatures (e.g., denatured hemoglobin, cell membrane changes, loss of metabolic regulators, etc.). Progress toward the identification of specific spectral features that can be designated as indicators of the progression of storage lesion is presented. Proof-of-principle measurements were made with a commercial Raman microspectrometer, using near-infrared excitation at 785 nm. A blood storage bag is essentially a closed system and the composition of the liquid fraction changes over time, reflecting changes in the physiology and integrity of the cells. Samples of RBCs from several donors at various stages of storage (0-49 days) were obtained and the supernatant of the storage mixture was investigated and compared between donors. From data obtained thus far, the most obvious spectroscopic feature that could function as an indicator of RBC quality is related to a phosphate vibrational mode assigned to either ATP or 2,3-DPG. Currently, quantification efforts using biochemical assays are underway to understand how these components change over the period of storage and how these changes correlate with the observed spectral changes.

(127) **Worker Exposure Assessment in Developing Countries**

Kevin Ashley[1]; [1]Centers for Disease Control and Prevention, National Institute for Occupational Safety and Health (CDC / NIOSH)

Hazardous industrial processes are often carried out in developing countries, and they are frequently located near residences in communities where the population education level and socio-economic status are low and unemployment is high, factors which contribute to ignorance or acceptance of hazardous exposures. In some cases, process emission controls are not installed or maintained because they are seen as unnecessary, resulting in high exposures. Health concerns underscore a need for quantitative exposure evaluations of workers in developing countries, although government capacity to conduct such studies is often lagging behind industrial development. Several cases in Latin America illustrate how the Centers for Disease Control and Prevention, National Institute for Occupational Safety and Health (CDC / NIOSH) has assisted other governments, intergovernmental organizations and industries to evaluate worker exposures and improve occupational health capacity. Examples include studies of worker exposures at a lead smelter in Peru and at a battery manufacturing and recycling facility in El Salvador; and teaching and field demonstration activities in Peru, El

Salvador and Mexico. In Peru, bio-monitoring methods were used to assess worker exposures to lead, with a goal of evaluating a field-portable lead-in-blood monitoring device. In El Salvador, airborne exposure monitoring was performed in order to estimate worker exposures to lead in workplace air. In Peru and Mexico, short courses were presented which included hands-on instruction using industrial hygiene sampling equipment and portable analytical devices. Standardized sampling and analytical methods are key tools used for capacity-building activities in developing countries worldwide.

(128) **Vaccine Adjuvant Development for Neglected Diseases: An Analytical Approach**

Christopher Fox[1], Steven Reed[1]; [1]IDRI

Adjuvant formulations are critical components of modern vaccines based on purified recombinant antigens. However, adjuvant development has historically been largely empirical in nature. Today, there are still only a few adjuvants (all of them aluminum-salt based) employed in FDA-approved vaccines. Access to adjuvant development and characterization know-how is limited, especially for institutions in developing countries, even though they suffer disproportionately from complex diseases such as malaria and tuberculosis that will likely require potent adjuvants in order to develop effective vaccines against them. We have developed a series of well-defined adjuvant formulations based on synthetic immunomodulatory ligands and particulate vehicles, including aluminum salts, liposomes, and oil-in-water emulsions, for application with a number of vaccine antigens of global health importance, including malaria, tuberculosis, leishmaniasis, and pandemic influenza. In a series of case studies, we describe the importance of analytical characterization in the development and manufacture of adjuvant formulations, including assessment of interactions between adjuvant and vaccine antigen, employing a suite of methods including HPLC with charged aerosol detection, dynamic light scattering, nanoparticle tracking analysis, cryo-transmission electron microscopy, fluorescence spectroscopy, laser scattering optical profiling, and zeta potential measurement. Finally, we describe the successful technology transfer of manufacturing and analytics to resource-poor areas around the globe, and discuss lessons learned to help promote similar projects designed to empower developing country vaccine manufacturers.

(129) **Developing Analytical Centers for Excellence at Local Universities in Africa**

Aloysius Ike Ononye[1]; [1]Procter and Gamble

n partnership with the Royal Society of Chemistry, two local analytical centers of excellence have been initiated at two universities in Nigeria with a donation of Agilent 6890 GC-FID to each institution. Further support by way of installation, training, and maintenance was provided to enable utilization of the systems. This work illustrates a successful way of growing effective analytical capability in Africa. Full details of the work and partnership with the Royal Society of Chemistry will be discussed.

(130) **Improving Global Nutrition and Medical Care with Inexpensive Paper Analytical Devices**

Marya Lieberman[1], Nicholas Myers[1]; [1]University of Notre Dame

Iodine fortification of salt safeguards people in almost every country in the world against cognitive impairment of infants and children and iodine deficiency disorders in adults. Maintaining the quality of the iodized salt, which is often produced in small factories and distributed through inefficient supply chains, and assessing whether people in all regions are actually consuming high-quality iodized salt is a continuing analytical chemistry challenge. We designed paper analytical devices to carry out two of the most common iodine analysis tasks: iodometric titration to determine 0-60 ppm iodine concentrations in salt, and analysis of urine samples to determine 25-300 ppb iodide concentrations in urine. The tests are designed for rapid and scalable implementation in developing countries. They can be fabricated by a combination of printing (eg Whitesides type wax printing) and stamping technologies. The tests do not require electrical power, weighing or handling of reagents, or any instrument other than a camera-enabled cell phone, and they are designed to be read with the aid of an image processing program. In this talk I will focus on the adaptations necessary to translate the solution chemistry to stable paper devices, the preparation of samples without lab equipment, the analytical metrics of the tests, and methods to deal with interferences under field conditions. Where the rubber really meets the road is in field testing; I will discuss preliminary results from collaborations with salt programs in Haiti and India.

(131) **Establishing Innovative Sustainable Pharmaceutical Quality Assessment Capacity in Resource Constrained Settings**

Thomas Layloff[1], Eliangiringa Kaale[2], David Jenkins[3], S. Michael Hope[4]; [1]Supply Chain Management System; [2]Muhimbili University of Health and Allied Sciences; [3]FHI 360; [4]United States Agency for International Development

In the developing countries, assessment technologies, such as diode array detection systems, must be robust and sustainable. Power outages can be frequent and non-interruptible power supplies are expensive. Thus, technologies must have a rapid recovery to usable condition after power is restored and data recovery should be facile. Repairs to HPLC pumps or valve systems can be expensive and not timely since part importation may require customs clearance and technical assistance often requires extensive travel. These limitations make HPLC assessment technologies out of reach for routine applications. To mitigate these challenges, we have focused on using HPTLC with auto-sample application and densitometry readout to obtain assessments with excellent precision. HPTLC development is off-line and does not require power and densitometer assessments can be easily reinitiated in the event of power failure. By using the same relatively inexpensive and non-toxic solvents used in the Global Pharma Health Fund “Minilab®”, those TLC methods can be readily escalated to HPTLC.

Additionally, the over 500 Minilabs established in developing countries have produced a large cadre of individuals knowledgeable in basic planar chromatography applications. We additionally are using reflectance spectra technologies as a screening tool to assess consistency of manufacture to reduce the number of material lots submitted for HPTLC assessments.

However, some assessments are out of reach with these technologies and HPLC may be required as a referral method of last resort for some of the products. The applications of HPTLC and reflectance spectroscopy technologies have markedly reduced product quality assessment costs which are helping to improve the marketplace and access to better healthcare.

These developments and future challenges will be discussed.

(132) **Glow Discharge Mass Spectrometry and Its Application to Determination of Purity to Support Global Traceability of Chemical Measurements**

Ralph Sturgeon, Bradley Methven, Scott Willie; [1]National Research Council of Canada

Managers of analytical laboratories have recognized the advantages that arise from having their facilities accredited to ISO/IEC 17025. Under the umbrella of the International Laboratory Accreditation Cooperation (ILAC), which oversees compliance of all national accrediting bodies, the system fosters confidence in analytical data throughout both space and time when measurements are linked to the common SI system of units. One of the cornerstones of technical accreditation is the concept of traceability, as it permits a rigorous calculation of uncertainty associated with a measurement result. This

parameter is often the weakest link in the traceability chain of measurements and is frequently unavailable or too difficult to establish and for that reason it is generally overlooked. Glow discharge mass spectrometry is one of the most comprehensive and sensitive techniques available for the analysis of solids, providing coverage across the Periodic Table and typically at levels of sub-ng/g detectability of impurities. Moreover, a fit for purpose calibration is achieved based on available certified reference materials to yield purity assessments on high-purity calibrants that are traceable to the SI. This presentation briefly reviews the concept of traceability and activity fostered by the BIPM to promote international comparability of measurement capabilities as well as illustrates how GD-MS may be used to globally underpin purity evaluation of primary inorganic calibrants. The program to achieve this at the National Research Council of Canada will illustrate how this measurement technique has been validated over the past decade through activities of the Consultative Committee on the Amount of Substance (CCQM) at the BIPM.

(133) **Amerithrax: The Most Complex Investigation in the FBI's History Explained in 20 minutes**

Vahid Majidi[1]; [1]TASC

This talk is an abridged account of the challenges faced by the FBI during the investigation of anthrax mailings in 2001. Over the past twelve years, I have had a series of opportunities that allowed me to work on this case from three separate and vastly different positions; each providing a unique piece to this monumental puzzle. In the fall of 2001, the Bacillus anthraces letters killed five people and infected 17 individuals. Agents from the Federal Bureau of Investigation (FBI) and the United States Postal Inspection Service formed a Task Force and, for the next eight years, they tirelessly investigated this crime. Developments in forensic tools and the resulting case findings will be discussed.

(134) **What Jim Taught Me in Graduate School that Helped My Career in the Semiconductor Industry. P.S. It Wasn't the Academics**

Chris Sparks[1]; [1]Air Liquide Electronics US - Balazs NanoAnalysis

The semiconductor industry is well known for its "significant if not dramatic cyclical swings" (Wikipedia). Fortunately, for this analytical chemist, the time spent in Jim Holcombe's research group helped prepare me for this wild ride. While the academics and training in the scientific method were practical, the other concepts I learned were also beneficial. This presentation will highlight a few of those concepts. Some examples are, science is not an insular undertaking, a chemist can fix (build) anything, an atomic spectroscopist can learn new tricks, and that one can always dig more out of the data.

(135) **Chemical Investigation of Novel Psychoactive Substances Sold in the UK**

Jacqueline L. Stair[1], Sulaf Assi[1], Kathryn Kellet[1], Suzanne Fergus[1], Sheelagh Halsey[2]; [1]University of Hertfordshire; [2]Thermo Fisher Scientific

The identification of novel psychoactive substances (NPS) presents a significant challenge for analysts. NPS products often differ markedly from their labelled ingredients and contain a variety of impurities and/or adulterants. Aminoindanes are a class of abused NPS that have become popular in the UK, yet chemical characterisation of these products has been limited. Products claiming to contain an aminoindan analogue were purchased from on-line retailers and characterised for both molecular and elemental constituents using a range of handheld spectrometers and lab-based techniques. Of the handheld spectrometers tested, the Raman spectrometer was most successful in identifying 2-aminoindan in model mixtures with caffeine (i.e., down to 20% m/m); however, identification of purchased products was variable for each spectrometer based upon the aminoindan analogue and adulterants present. Further analyses using gas chromatography mass spectrometry and ultra high-performance liquid chromatography showed that 80% of the products tested contained an aminoindan analogue, but only 55% contained the aminoindan stated on the product label. Adulterants found included caffeine and methylphenidate. Trace elemental analysis identified a variety of elements present in purchased products, most notably Ni and Pb, with concentrations up to 230 and 3.9 ppm, respectively. More work is needed to quantify both molecular and elemental species in NPS products to aid in the development of novel detection methods.

(136) **Pearls of Wisdom from a Proteomic Chemist: Passed Down from Father to Daughter to You**

Brook Nunn[1]; [1]University of Washington

Avoiding all opportunities of becoming my dad, I have successfully steered myself away from atomic spectroscopy and am in a completely different career path: proteomic mass spectrometry. No doubt my fame has arisen from the pearls of wisdom I was fed at every opportunity that my dad, Dr. Holcombe, saw fit. For those of you who have not received pearls of wisdom from Dr. Holcombe I will review some of the key points, so please bring a notebook. Pearl of Wisdom No. 1: *"Don't pigeonhole yourself."* One of the 'Holy Grails' in environmental ecology is a biochemical snapshot that allows researchers to examine community responses and adaptations to a specific set of conditions. Because proteomes are dynamic, frequently changing within minutes of a perturbation, profiling the proteins present at the time of collection can provide an abundance of information on communities living in unique, or extreme, conditions. Most proteomic techniques used to identify biological functions in complex samples rely on protein databases translated from genomic-level information and although there has been a recent explosion of environmental genomic sequencing it is rare to have a complete meta-genome from the environmental sample of interest. For the past 10 years we have been evaluating different techniques of correlating tens of thousands of peptide tandem mass spectra to the millions of protein sequences available from the marine environment. Pearl of Wisdom No. 2: *"If the problem is too complex, simplify the answer."* Here, we present a unique search strategy utilizing the fundamental theory that successful biochemistry is passed down from organism to organism. We utilize the conserved domain database of protein function in order to confidently identify protein functions from unknown mixed microbial communities from unique places such as hydrothermal vents, open ocean bacteria, Arctic-dwelling sea ice bacteria, phytoplankton and sediments.

(137) **Kinetics-Based Reaction Monitoring Using In-Line Raman Spectroscopy**

Ming Huang[1], Robert Wethman[1], John Wasylyk[1]; [1]Bristol-Myers Squibb

In-line Raman spectroscopy has been used successfully for reaction monitoring as an in-process control (IPC) technique for determining the end of reaction in the plant, particularly where the reactions were carried out at elevated temperature and operated at near-saturated concentration, making sampling a difficult task. In-line Raman spectroscopy can often be used to quantitatively determine the reaction profile and end-point. When low Raman signal intensity prohibits accurate end-point determination, a kinetic approach can be applied to project the end of reaction. The kinetics model can be established for many first-order or pseudo first-order reactions by plotting the rate constant against the temperature. This approach was successfully implemented during the recent multi-batch campaign in the plant setting. The addition of kinetic modeling greatly expands the feasibility of using in-line Raman spectroscopy for general reaction monitoring in the lab and plant. Multiple lab-scale reactions

were conducted and pooled together to establish the calibration model. The establishment of the calibration set, the development of the Raman model and the results of the in-line Raman techniques as applied to the lab reactions and glass plant campaigns will be presented.

(138) **On-line Application of NIRS for Monitoring of PPM level Water in Manufacturing-scale Distillation Process**

Zhenqi Shi[1], Gordon Lambertus[1], Robert Forbes[1], Steven Doherty[1], James Hermiller[1], Norma Scully[1], Sze Wing Wong[1], Mark LaPack[1]; [1]Eli Lilly and Company

An analytical method based on transmission Near-infrared spectroscopy (NIRS) for quantitative determination of water (ppm levels) has been developed and applied to the manufacture of a pharmaceutically relevant intermediate at the end of distillation of a toluene/product solution prior to use in a Grignard reaction. Calibration models for water analysis, built at the development site and applied at the manufacturing site, were successfully demonstrated during six manufacturing runs at 250-gal scale. The water measurements is planned to be used as forward processing criteria in the next GMP campaign. An innovative approach was used to determine the limit of detection around 60ppm for this NIRS-based water method. The most significant impact of using this NIRS-based Process Analytical Technology (PAT) to replace offline measurements is the significant reduction in risks to operator exposure through elimination of sampling to this severely lachrymatory and mutagenic compound. The work outlined in this report illustrates the development effort from proof-of-concept phase to manufacturing implementation.

(139) **Infrared Calibration Life-Cycle Management of the Active Content of an Oral Dosage Form**

Benoit Igne[1], Md. Nayeem Hossain[1], Carl Anderson[1], James Drennen[1]; [1]Duquesne University

A multivariate process analytical technology method lifecycle is characterized by the model conception, validation, and long term management. While method development and validation have been the primary center of attention, method management is becoming more critical as pharmaceutical companies implement multivariate PAT models. In regulatory filings, sponsors propose the strategy they will be implementing when a particular method requires updating (changing raw materials or material attributes, instrument failure, etc.). However, limited work has been performed on model management specifically on testing and updating of models. Using near infrared spectroscopy, the lifecycle of a calibration model used to predict the distribution of active ingredient in tablets will be investigated. Considerations with respect to a comparability protocol will be provided as a mechanism for regulatory compliance.

(140) **Quantitative Predictions of Nifedipine Polymorphic Transitions Using In-Line Raman Spectroscopy, Principle Component Analysis and Multivariate Curve Resolution**

Shweta Raina, David E. Alonzo[3], Yi Gao[2], Geoff g. Z. Zhang[2], Lynne S. Taylor[1]; [1]Purdue University, Department of Industrial and Physical Pharmacy, West Lafayette, IN; [2]NCE Formulation - LC, Research and Development, AbbVie, Inc., North Chjcago IL; [3]Formulation & Process Development, Gilead Sciences, Inc., Foster City, CA

Objective: Quantitative evaluation of crystallization kinetics of amorphous systems using spectroscopy typically requires a set of calibration standards. This enables an estimate of percent (%) of a given form as a function of time. However, when working with an active pharmaceutical ingredient (API) which can transform into multiple polymorphs, creating such calibration curves is problematic. The purpose of this study was to employ chemometrics and use principal component analysis (PCA) and multivariate curve resolution (MCR) as an alternative quantitative approach to study crystallization kinetics of amorphous systems. Materials and Methods: Nifedipine was used as a model drug. Polymers used in the study included PVP (polyvinylpyrrolidone), HPMC (hydroxypropylmethyl cellulose) and HPMCAS (hydroxypropylmethyl cellulose acetate succinate). Amorphous nifedipine was prepared using melt quench technique or solvent evaporation followed by cryomilling. The amorphous powder was suspended in a buffered solution in the absence or presence of polymers at 1 mg/mL. Raman spectroscopy was used to monitor crystallization kinetics in the slurries of amorphous drug and solid dispersions. PCA and MCR were carried out using the software (Unscrambler X 10.1, CAMO software AS, Oslo, Japan). Standard normal variate or peak normalization with baseline offset corrections were carried out to minimize fluctuations in spectral intensity. Results**:** PCA analysis of the Raman spectroscopy data established the presence of three forms, namely glass (g), γ- and α-polymorph. The loadings plots for PC-1 and 2 highlight two wavenumbers of 1205 and 1224 cm^{-1} corresponding to α- and γ-polymorph peaks in the Raman spectra. A comprehensive analysis of the loadings, variance and influence plots in tandem with the Raman spectra suggests that PC-1 accounts for ~80% variance i.e. the complete conversion from glass to γ-polymorph and to some extent the conversion of γ-polymorph to the α-form. PC-2 accounts for the remaining ~20% transformation of γ- to α-polymorph. Good correlation was obtained between manual spectroscopic evaluation and kinetic profiles as predicted by MCR. Conclusions**:** PCA and MCR were found to be useful tools in deconvoluting complex polymorphic transitions and quantitatively predicting crystallization kinetics in solution. They are particularly valuable when dealing with transformations to multiple solid state forms.

(141) **In-process Monitoring of API Dissolution in Softgel Capsule Manufacturing using ATR-UV and Raman Spectroscopy**

Boyong Wan[1], Christopher Zordan[1], Xujin Lu[1], Gary McGeorge[1]; [1]Bristol-Myers Squibb Co.

In manufacturing of softgel capsule product it is important to analyze the API potency within the vehicle and to ensure complete dissolution of API material in vessel. Traditionally, this was done by frequent manual sampling during dissolution followed by HPLC assay, which is labor intensive and time-consuming. To improve process understanding and better control, both on-line UV and Raman spectroscopic methods were investigated for the API dissolution monitoring. On-line UV measurements were performed using a UV spectrometer equipped with an attenuated total reflectance (ATR) probe and fiber optics (FO). Raman data were collected using a hybrid Kaiser Raman spectrometer with an immersion FO probe. ATR-UV and Raman probes were deployed simultaneously to monitor API dissolution processes for batches manufactured with API of different physical properties and under different operation conditions. Both online ATR-UV and Raman were proven to be feasible for modeling the API dissolution profile and API potency determination. UV absorbance even at a single wavelength can clearly demonstrate the dissolution trending profiles. However, it was found that ATR-UV absorbance can be sensitive to temperature variations, which may be due to the change of refractive index of solution with temperature. In combination with various spectral preprocessing strategies, multivariate calibration analysis method was evaluated in an attempt to minimize such temperature effects. On the other hand, with proper spectral processing procedures and simple univariate/multivariate calibration, Raman method can give very accurate and robust online prediction. It was shown that the method was very robust against process perturbations like temperature variations or to changes of stirring speed, which may normally happen during large-scale manufacturing. Algorithms can

be established for end-point determination based on dissolution profile.

(142) **Extreme Spatial and Temporal Resolution in Tip-Enhanced Raman Spectroscopy**

Norihiko Hayazawa[1,2], Chi Chen[1], Kentaro Furusawa[1, 4], Satoshi Kawata[1, 3]; [1]RIKEN; [2]Tokyo Institute of Technology; [3]Osaka University; [4]Tohoku University

The desire to see the invisibly small world has triggered the development of all kinds of microscopy techniques, including optical microscopy, electron microscopy, and scanning probe microscopy covering the length scale from mm to nm. On one hand, scientists are still trying to improve the spatial resolution of each technique. On the other hand, it is equally important to develop spectroscopic method to distinguish different chemical species. Recently, the surface morphology of materials is routinely analyzed by atomic force microscopy (AFM) and scanning tunneling microscopy (STM) down to sub-nanometer resolution. However, it is still difficult to simultaneously distinguish chemical species simply based on topography or limited STM and AFM based spectroscopy methods in low temperature and ultra high vacuum environment. While optical spectroscopy method provides various chemical information, the spatial resolution has been very poor due to diffraction limit of light as compared to electron microscopy, AFM, and STM. However, with the innovation of tip-enhanced spectroscopy, it soon becomes a potential tool in nanoscale chemical analysis and imaging with high resolution beyond the diffraction limit. However the reported spatial resolution so far is in the order of 10 nm, which is still one to two order larger than intrinsic AFM and STM's resolution in ambient. In this contribution, we report an extremely high spatial resolution down to 1 nm in tip-enhanced Raman spectroscopy and imaging on single walled carbon nanotubes (SWNTs). While developing the optical microscope with high spatial resolution, a natural question subsequently arises as to how short excitation is possible with such extremely high spatial resolution since one of the virtues of optical excitations is its high temporal resolution that is not attainable by any other techniques. We demonstrate a generation of extreme spatio-temporally confined nano-light source exhibiting 10 fs in time. The mechanism is based on degenerated four-wave mixing (FWM) at a sharp metallic tip induced by an ultra-short broadband pulse. We will discuss the potential applications of tip-enhanced Raman and nonlinear Raman spectroscopy and microscopy based on our extreme spatial and temporal resolution.

(143) **Confocal Raman Microscopy to Investigate the Chemistry of Silane Ligands Immobilized on Porous Silica Particles**

Natascha Knowlton[1], Jay Kitt[1], Joel Harris[1]; [1]University of Utah

The modification of porous oxide surfaces, such as silica and alumina, with silane reagents is crucial for development of materials for chemical separations, sensing, and catalysis. Currently, there are few analytical techniques that allow *in situ* detection and characterization of functionalized monolayers on these oxide surfaces. Raman spectroscopy is capable of acquiring vibrational spectra of molecules within porous oxide materials, with little interference arising from the oxide substrate providing both quantitative and structural information about molecules immobilized on the surface. While Raman scattering is a very weak effect, sub-monolayers of molecules bound to porous silica substrates can be readily detected due to the high specific surface area of the material. The influence of the particle packing density on quantitative results and interferences from solution between particles can be overcome by examining the interior of a *single silica particle* through the use of confocal Raman microscopy. In this work, confocal Raman microscopy is used *in situ* to investigate the kinetics of silane functionalization reactions within single porous silica particles. Due to the high surface area of porous silica, the local concentration of bound molecules within the confocal probe volume increases over the course of the immobilization reaction, allowing the reaction kinetics to be monitored over time. This method was employed to determine the kinetics of benzyldimethyl¬chlorosilane functionalization of porous chromatographic silica by quantifying the peak intensities of Raman active modes of the silane reagent as it binds and fitting the results to a Langmuir kinetic model. This methodology can be extended to studying the reactions of immobilized ligands with other molecules in solution to expand the range of immobilized ligands and to develop insight into chromatographic retention mechanisms.

(144) **Polarized Raman Spectroscopy of Individual Electrospun Nanofibers**

Christian Pellerin[1], Marie Richard-Lacroix[1]; [1]University of Montreal

Electrospinning is widely used for producing nanofibers that may be used in tissue engineering, selective filtration, etc. However, their practical application is limited by an inadequate control of their properties, in part because most characterization techniques can only provide bundle-averaged information about their structure and orientation. We have recently demonstrated that polarized confocal Raman microscopy is a powerful tool for the characterization of individual electrospun nanofibers using poly(ethylene terephthalate) (PET) as a model system. A large distribution of orientation was observed from fiber to fiber, associated with the formation of a highly oriented mesomorphic phase. In this presentation, we will report our recent work on using polarized Raman spectroscopy to study nanofibers of PET and other polymers. The impact of electrospinning conditions, such as the solvent and type of collector, will be described. *In situ* temperature-controlled studies were also conducted to probe the impact of annealing on the polymer microstructure, in particular the evolution of the mesomorphic phase.

(145) **Spectrophotometric Determination of Sn (IV) in Solutions for Electrodeposition of Sn and Sn alloys**

Jingjing Wang[1], Chuannai Bai[1], Eugene Shalyt[1]; [1]ECI Technology

Sn and Sn-based solders are widely used in semiconductor and printed circuit board industry as interconnect between microprocessor and other components. Solders are electrodeposited from solutions of Sn(II) which is easily oxidized at the anode or due to contact with oxygen to Sn(IV) which purportedly has negative effect on the performance of electrodeposition and needs to be monitored. The task is extremely challenging due to high ratio of Sn(II) : Sn(IV) and presence of proprietary organic surfactants, complexing agents and alloying metals.

The presentation will examine the spectroscopic method for Sn(IV) based on the colorimetric reaction with bromopyrogallol red (BPR) [1]. Original method has very poor selectivity of Sn (IV): Sn (II). In order to determine Sn (IV) quantitatively, one need to convert Sn(II) to Sn(IV) by oxidation and then measure total Sn through BPR reaction. Sn (II) has to be measured separately by other methods, e.g. iodometric titration which is not affected by Sn(IV). The method is quite complicated and is based on finding the small difference between 2 large numbers: total Sn and Sn(II). We attempted an improved method for selective monitoring of Sn(IV) . Adjustment of experimental conditions and the analysis perspective allowed to significantly enhance selectivity towards Sn(IV). This avoids the need for complicated oxidation. Linear correlation was observed at a range of 0-5 g/L of Sn(IV) by addition of SnCl4 to the Sn(II)-MSA system and could tolerate a fluctuation of Sn(II) concentration up to 20 g/L.

[1] Huang X., Zhang W., Han S., Wang X., Talanta 44 (1997) 817-822

(146) **Non-invasive Monitoring of Powder Drying by Broadband Acoustic Emission Spectrometry in Comparison with Spectroscopic Techniques**

Alison Nordon[1], Denise Logue[1], Laura Wurker[1], David Littlejohn[1]; [1]University of Strathclyde

In the pharmaceutical industry, particles must be manufactured to ensure that critical quality attributes (particle size, crystal morphology etc.) fall within the required specifications. It is known that changes in particle properties can occur during a drying process, as a result of attrition, agglomeration and polymorphic transformation. Non-invasive measurement techniques can provide the opportunity to derive a drying curve, and determine the end point of the process, as well as detecting any changes in particle characteristics in real time. This work investigates the use of broadband acoustic emission spectrometry and near-infrared (NIR) spectroscopy, for the monitoring of powder drying processes. Acoustic emission (ultrasound) is generated through particles colliding with the inner walls of a process vessel and in this study signals were collected by a piezoelectric transducer attached to the outer wall of a drying vessel. Previous work has shown that acoustic emission can be used to derive the mixing profile during powder blending. It has also been shown that specific changes in acoustic emission spectra can be correlated with changes in particle size. The technique was assessed for the monitoring of drying in a small-scale powder blender, a bespoke vacuum agitated filter dryer and a continuous rotary vacuum filter dryer. Microcrystalline cellulose (Avicel) or aspirin were selected as test systems. The range 80 – 120 kHz was identified as the optimum frequency to study drying. Drying curves were produced by monitoring the change in peak area intensity in this frequency range over time. It was also shown that changes in the nature of the acoustic emission spectrum could be associated with changes in particle size. In some experiments, NIR spectroscopy was also used to monitor drying for comparison with acoustic emission measurements.

(147) **Ionic Liquids in GC for Water Analysis and for LC-MS of Trace Anions**

Daniel Armstrong[1]; [1]University of Texas at Arlington, Arlington, TX

The excellent stability of ionic liquids (ILs) to temperature, water and oxygen make them exceptional stationary phases for extreme conditions and/or direct analysis of "harsh-matrix" samples. By synthesizing ILs of specific architectures, good peak shapes and reasonable retentions for analytes like water can be obtained. Also it will be demonstrated that the amount of water in solids (including pharmaceutical products) can be easily accomplished using a specific IL – head space technique. Finally, recent results on the ultra- trace analysis of anionic pesticides and performance enhancing drugs by LC-MS, using specifically engineered IL cations, will be discussed.

(148) **Chemical Sensing Platforms Based on Ionic Liquid-Xerogel Hybrids**

Frank Bright; [1]UB, SUNY

Ionic liquids (ILs) have been used in a wide variety of areas ranging from batteries to biocatalysis. In our laboratories IL research has focused on: (i) biocatalyst structure and function in ILs, (iii) flexible biomolecule dynamics in ILs, and (iii) analyte responsive ILs. This presentation will summarize the analytical performance of fluorescent ionic liquids when they are incorporated within nanoporous xerogel glasses.

(149) **Ionic Liquid Facilitated Surface Modification of Natural Materials**

Paul Trulove[1], Luke Haverhals[1], E. Kate Brown[1], David Durkin[1], Aimee Brenner[1], Matthew Foley[1], Hugh De Long[2]; [1]U.S. Naval Academy, Annapolis MD; [2]Air Force Office of Scientific Research, Arlington VA

In this effort we are carrying out fundamental investigations of a process we call "Natural Fiber Welding" (NFW); this is an ionic liquid-based methodology that enables the generation of complex, functionalized composites from natural fibrous materials. A unique feature of fiber welding is the ability to selectively open and mobilize biopolymer structures while simultaneously preserving a portion of the biopolymer (micro and meso structures) in the native state. By precisely regulating process variables such as the purity, type, amount, and placement of ionic liquid solvent as well as the duration and temperature of treatment, controlled reorganization of natural material hydrogen bonding networks is achieved. NFW produces often dramatic enhancement and modification of physical and chemical properties without disruption to many of the desirable properties intrinsic to natural materials. In addition, NFW opens the fiber structure so that natural materials may be manipulated and/or modified to impart new functionalites. Our current work is focused on understanding the fundamental aspects of the polymer mobilization process and on procedures by which this process can be utilized to prepare novel materials. We have employed methods such as Con-Focal Fluorescence and Raman Microscopies to evaluate the movement and interaction of biopolymer substrates during the NFW process. In addition we have investigated novel methods for the specially controlled application of the NFW process, and we have studied the introduction of functional materials into natural polymer substrates using the NFW process.

(150) **Continuing Investigation of the Polyionic Ionic Liquid Stationary Phases for Capillary GC**

Leonard M. Sidisky, Greg Baney, Jamie Desorcie, Katherine Stenerson, Gustavo Serranoe, Daniel Shollenberger; [1]Supelco

Ionic liquids are a class of nonmolecular ionic solvents with low melting points. These liquids are unique combination of cations and anions and can provide a variety of different selectivities when used as stationary phases in capillary gas chromatography. The majority of the polyionic ionic liquid phases that we have been evaluating all provide polar and highly polar selectivities similar to polyethylene glycol based our biscyanopropylpolysiloxane phases. These phases will provide unique selectivity for the evaluation of a number of petrochemical samples. The purpose of our studies is to determine the effects changing the cation and spacer groups on the selectivity of the phases. Selectivity was determined and compared using various isothermal and temperature programmed test mixes. Particular cation and anion combinations appear to provide very unique selectivity for example shifting toluene to elute after tetradecane and possibly coeluting with pentadecane, which demonstrates some of the highest polarity phase selectivity we have evaluated.

(151) **Supramolecular Polysaccharide Composites: Synthesis and Analytical Application**

Chieu Tran[1]; [1]Marquette University

A novel, recyclable methods has been developed for the synthesis of nontoxic, biocompatible and biodegradable supramolecular composite materials from polysaccharides. Various spectroscopic and imaging methods including FT-IR and NIR spectroscopy and spectroscopic imaging, CP-MAS-NMR, X-ray diffraction, SEM, TGA, DSC were used to monitor the synthetic process, to characterize the materials and to determine their chemical and mechanical properties. Novel applications of the synthetic materials including antimicrobial activities, removal of pollutants (organic and heavy metal ions) and toxins will be described.

(152) **Time-dependent Studies of LIBS Plasmas: Correlation between Plasma Dynamics and LIBS Emission Signal**

Alessandro De Giacomo[1], Marcella Dell[2], Rosalba Gaudiuso[1], Olga De Pascale[2]; [1]University of Bari, Department of Chemistry; [2]CNR-IMIP

In this work the general features of Laser Induced Plasma (LIP) produced in gas, liquid and on modified target (shape and nanoparticles-enriched) are presented. The elementary mechanisms and the expansion dynamics are strongly correlated and determine the characteristics of the LIBS spectra for what concern, line intensity and broadening and whole plasma duration. Based on these considerations, the effect of ablation efficiency and of the background environment on the LIBS spectra is studied in order to increase the signal in specific applications. Particular emphasis will be given in nanoparticles enhanced LIBS and to its fundamental aspects and practical applications

(153) **Thomson Scattering from Aluminum Laser Plasmas in Air**

Matthieu Baudelet[1], Yuan Liu[1], Bruno Bousquet[2], Martin Richardson[1]; [1]Townes Laser Institute, CREOL – The College of Optics and Photonics, University of Central Florida; [2]Univ. Bordeaux, LOMA, UMR 5798

Electron density (N_e) and temperature (T_e) are two important and fundamental parameters describing laser plasmas, which have numerous applications in different fields. Thomson scattering, the scattering of electromagnetic waves by free charged particles, can be used as a powerful tool for ne and Te characterization without assumptions of specific equilibrium conditions. In this study, collective Thomson scattering signals were used to measure ne and Te of laser plasmas from solid aluminum targets in air, to which Thomson scattering method was rarely applied. Aluminum plasmas created by a focused Nd:YAG laser was probed by a frequency doubled Nd:YAG. The typical collective Thomson scattering spectrum is featured by satellite peaks around the 532 nm probe laser wavelength. Values of ne and Te were estimated through the fitting of the satellite peaks. By varying the delay time of the probe laser, time resolved measurements of can be obtained. The effective time window for Thomson scattering measurements coincidentally matches very well with typical detection windows for many experiments in Laser-Induced Breakdown Spectroscopy (LIBS). Such time resolved measurements brought insights into the verification of local thermodynamic equilibrium (LTE), which is an important assumption for LIBS plasmas. Although the McWhirter criterion was satisfied during the entire observation, the excitation temperature calculated from Boltzmann plots showed much lower temperature for both ionic and atomic species. Such temperature differences imply LTE condition was not satisfied. Thomson scattering can be used for electron temperature and density measurements of laser plasmas created off a solid target. Despite experimental complexity, this method of plasma characterization is powerful (simultaneous Te and Ne measurements, temporally- and potentially spatially-resolved) and precise (no requirements on special equilibrium conditions). Excitation temperature measured by Boltzmann plots may not well represent the electron temperature, when emission from the entire plasma was collected to generate spectra.

(154) **Sefl-Consistent Three-Dimensional Modeling of Laser Induced Pasma for LIBS Applications**

A. Hassanein[1], T. Sizyuk[1], S. Harilal[1]; [1]Purdue University

Understanding in details the effects of multi-physical processes occurring during laser target interactions is very important for various LIBS applications. These details include laser photon absorption, reflection, target erosion, atomic and plasma species evolution, plasma radiation and conversion efficiency of laser energy to specific photons energy range. Results of interdisciplinary study for several laser produced plasma (LPP) applications allowed extending our knowledge in plasma physics processes and their interpretation in computer models and packages. The HEIGHTS (High Energy Interaction with General Heterogeneous Target Systems) package has numerous integrated models that include 3D laser energy deposition and target thermal response, surface melt-layer formation and movement, 3D vapor and plasma magnetohydrodynamics evolution, extensive atomic physics package, and 3-D line and continuum photon radiation transport. We investigated laser parameters, target materials, and regimes appropriate for three major LPP applications: Laser-induced breakdown spectroscopy (LIBS) with usual laser intensities around 10^8-10^{10}</sup? W/cm2, extreme ultraviolet (EUV) Lithography with Tin as targets being most efficient material for the 13.5 nm photons production needed for next generation nanolithography with corresponding laser intensities 10^{10}-10^1 W/cm^2, and water-window (WW) microscopy with liquid nitrogen using laser intensities around 10^{12}-10^{13} W/cm2. Integrating advanced modeling with in-house experiments, we benchmarked our simulation results, analyzed the accuracy of physical processes involved and their effect in conjunction with target geometry or chamber environment. Based on these studies, we identified important laser-target interaction processes for each applications and the importance of including accurate details of target heating and erosion, plasma characteristics, photons radiation and their transport and the integrated self-consistent character of these processes.

(155) **Plasma Modeling for Calibration-Free LIBS: Expectations and Reality**

Igor Gornushkin[1,2], Ulrich Panne[1], S. V. Shabanov[3]; [1]BAM Federal Institute for Materials Research and Testing; [2]Humboldt-Universität zu Berlin, Department of Chemistry; [3]Department of Mathematics, University of Florida

Calibration-free analysis is a holy grail of any analytical method; so far only few methods may boast such the possibility. For a couple of decades LIBS struggles to be one of them; several approaches have been proposed based on plasma models of different degree of complexity.

A short comparative review of calibration-free LIBS models will be presented with emphasis on underlying plasma physics. Promises, shortcomings, and range of applicability of the models will be discussed.

(156) **Fraunhofer-type Absorption Line Splitting and Polarization in Confocal Double-Pulse Laser Induced Plasma**

Lev Nagli[1], Michael Gaft[1]; [1]Laser Distance Spectrometery

Strong line splitting and polarization are observed in Fraunhofer-Type Absorption (FTA) lines in Pb, Sn, Si, Cd, In, and Zn in confocal double-pulse laser induced plasma (DP-LIP). Plasma emission spectra measured in view direction perpendicular to π plane with analyzer direction E0 and E90 . Detailed of these experiments was described and discussed in our previous paper [1]. Polarization and splitting effects exist only during the second laser pulse (~7 ns)un. Absorption line polarization and splitting phenomena explained by a motional Stark effect in 2nd laser light magnetic field inside the laser plasma, created by the first laser pulse.

Based on axial and radial distributions of the continuum radiation and atoms absorbency, during 2nd laser pulse radiation model of FTA is proposed

[1]. L. Nagli, M. Gaft, and I. Gornushkin, Fraunhofer-type absorption lines in double-pulse laser-induced plasma, Applied Optics 51 (2012) B201-B212.]

(157) **Sub-diffraction Imaging and Single Particle Tracking in Cultured Cells**

Aleem Syed[1], Neha Arora[1], Michael Lesoine[1], Dipak Mainali[1], Emily Smith[1]; [1]Iowa State University

In cultured cells, sub-diffraction spatial arrangement of actin cyto-skeleton and the dynamics of trans-membrane integrin receptors are studied using stimulated emission depletion (STED) fluorescence microscopy and single particle tracking, respectively. High resolution spatial imaging of Alexa Fluor 594-phalloidin labeled F-actin protein is achieved by depleting the fluorescence from the periphery of conventional point spread function. Approximately 40 nm focal spot in lateral direction is generated by overlapping spatially aligned excitation beam (Gaussian profile) and depletion beam (doughnut profile) from a super continuum laser source. F-actin images with resolution below than that of the diffraction limit reveals branching and cross linking in polymerized protein projections (filopodia) and networks (lamellae), otherwise convoluted in diffraction limited confocal imaging mode. Single particle tracking experiment results have shown that the membrane cholesterol concentration plays a key role in governing the dynamics of integrin receptor protein in cultured cell membrane. Depletion of cholesterol from cell membrane leads to increase in integrin mobile percentage and the changes in dynamics are restored by restoration of the cholesterol. However, partial substitution of cholesterol with its stereo-isomer, epi-cholesterol failed to bring back the changes. Heterogeneous diffusion analysis via single receptor tracking has helped to understand the role of cholesterol on integrin diffusion in cell membrane. Further, interactions of cyto-skeletal actin network arrangement on integrin dynamics will be discussed.

(158) **Evaluation of Multilayer SERS Nanoprobes for Enhanced Intracellular Sensing**

Pietro Strobbia[1], Adam Mayer[1], Charles Klutse[1], Brian Cullum[1]; [1]University of Maryland Baltimore County

The development of photonic nanosensors (e.g. PEBBLES, quantum dots-based sensors, etc.) have had a great impact on intracellular studies over the last decade. Although their size has allowed for studying these previously inaccessible environments, they often suffer from biocompatibility issues, limited ability to monitor multiple species simultaneously, complicated and unique fabrication chemistries and other issues. Recently SERS immuno-nanoprobes have demonstrated the capability to overcome many of these limitations. However, functional intracellular SERS nanosensors require an optimized substrate geometry to achieve the sensitivity necessary to detect the trace analyte concentrations present. To address this, we have developed a novel SERS substrate architecture that consists of a multilayered metal nanostructure. Layers of metal and dielectric are alternatively deposited on a silica nanosphere generating multiple surface plasmons. This multilayer enhancement increases the sensitivity of the nanoprobes by two orders of magnitude while also improving their robustness. In this paper we investigate the sensitivity of SERS immuno-nanoprobes fabricated using this multilayered geometry and the additional SERS enhancements associated with both the multilayer design and the optical trapping of the nanoprobe during analysis. The nature of the dielectric dependence on the enhancement has been studied for several oxides (Ag_2O, TiO_2, Ta_2O_5). SAM dielectric spacer layers have also been used to model the dependence of the enhancement on the electron affinity of the dielectric spacer as well as on the number of layers of metal. In addition this talk will discuss a model of the mechanism for the multilayer enhancement and describe the sensitivity of the nanoprobes in a cellular matrix.

(159) **Variable Pathlength Spectroscopy in Biochemical Studies**

Darrell McCaslin[1], Daniel Wirz[1]; [1]University of Wisconsin

The relationship between the amount of light absorbed by a solution and the molecular properties and concentrations of its components and the thickness (pathlength) of solution through which light must pass is embodied in the well known Beer's law. This equation is routinely applied in the determination of concentration; however when the absorption is too high for reliable measurements, the sample must be further manipulated as for example by dilution to obtain accurate data and such dilutions contribute new sources of error and furthermore, may alter the properties of some the solution's constituents. Sample manipulation could be avoided by a simple change in pathlength, but the approach is rarely utilized due to the limited availability of cuvettes differing in pathlengths in most laboratories. The Solo VPE, an accessory for the Cary 50/60 line of spectrophotometers, was developed by C-Technologies Inc; exploiting fiber optics in a novel way, it permits the facile recording of complete spectra from 0.005 to 1.5 cm pathlengths using only a single sample. We have worked with an early version of the instrument to validate and explore its utility. Data will be presented demonstrating the use of the instrument for quantitation of protein solutions at high concentrations. Unlike the case of a single pathlength, small volume instrument, the Solo provides a direct check on the validity of Beer's law for the sample. The use of the instrument to record complete spectra of a heme containing protein without multiple dilutions illustrates the power of the variable pathlength approach for spectral studies over that of single pathlength measurement. The use of variable pathlength measurements in determining a complete extinction spectrum (200-350 nm) of a protein will be illustrated, where this measurement subsequently permits the exploitation of peptide absorbances for quantitative measurement. Other examples where variable pathlength measurements can simplify common biochemical operations will be discussed.

(160) **Melittin-Membrane Interactions through the Eyes of Deep Ultraviolet Resonance Raman Spectroscopy and Circular Dichroism**

Michael K. Eagleburger[1], Jason W. Cooley[1], Renee D. JiJi[1]; [1]University of Missouri

While it is estimated that 20-30% of the genome codes for membrane proteins, over 50% of drug targets are membrane proteins. Therefore, real-time methods are needed for the high-throughput analysis of membrane protein structure. Melittin, the main hemolytic component of honey-bee venom, is a 26-residue peptide that is both water and membrane soluble, making it an ideal model for development of techniques for membrane protein studies. Melittin is unfolded in an aqueous environment and folds into an α-helical conformation in a lipid environment. Membrane fluidity is known to affect the activity and structure of melittin and is dependent on lipid composition and temperature. By combining two structurally sensitive optical methods, circular dichroism (CD) and deep ultraviolet resonance Raman spectroscopy (dUVRR), we have identified subtle fluidity dependent structural fluctuations in melittin in DMPC liposomes. Temperature dependent CD and dUVRR spectra indicate that the helical structure of melittin is the most uniform around 22°C, the transition temperature of DMPC. Above and below 22°C, the intensity of the CD spectrum decreases concurrently with an increase in the intensity of the dUVRR amide III band at 1240 cm-1, a band associated with non-helical ψ dihedral angles. However, this increase in intensity is not coupled with an increase in the dUVRR amide S mode at 1386 cm-1 as would be expected with an actual loss of helical structure. An analog of cholesterol, 5α-cholestan-3ß-ol, was also used to modulate DMPC fluidity. At 10 molar percent a slight increase in both the amide III and amide S modes was seen with little change in the CD spectrum. This suggests that a small portion of the

peptide may be unfolded, but the majority of the helix remains intact with little distortion. At 25 molar percent 5α-cholestan-3ß-ol a large loss of CD intensity is observed, but with only small increases in the amide III and amide S dUVRR modes indicating the helix is less uniform but not unfolding. Complimentary oriented CD spectra also show that the tilt of the peptide increases with increasing molar percentages of 5α-cholestan-3ß-ol.

(161) **Detection of Pollen Allergens in the Air**

Jeremy Pronchik[1], M Thibaudon[2], M Hrabina[3], J Barberon[3], K Mercier[4], C Frydman[4]; [1]HORIBA Scientifc, USA; [2]RNSA, France; [3]Stallergenes, France; [4]Horiba Scientific, France

Surface Plasmon Resonance imaging (SPRi) is an ideal innovative optical technique to analyze molecular bio-affinity. It permits the label-free detection and the quantification of biomolecules in real-time and in array format. We will focus here on the detection of pollens. 10 to 20% of the population suffers from allergenic rhinitis, conjunctivitis, or asthma, caused by pollens. The increase of this kind of allergy, which would have doubled in 10 years, justifies the control of air quality. A biochip, especially designed to detect pollen allergens has been developed. In this study we are interested in birch, olive and timothy pollens, which are known to contain allergenic proteins and glycoproteins. Owing to SPRi technique, the interactions between pollen allergens and specific antibodies were monitored in real-time. The quantity of allergen in pollen grain was determined from a calibration curve. The affinity between antibodies and allergens was calculated from the kinetic curves. We demonstrate here, the interest of the SPRi technology, which is a multiplexed label-free technique for the simultaneous detection of allergens from pollen grains. The determination of the pollen quantity of each studied species in the air allows notifying quickly allergic patients to the presence of specific pollens in a particular area.
Until now no device has been able to estimate in real time and without labeling the molecules the amount of allergen collected in a particular environment.

(162) **Design and Analysis of NMR Relaxation Measurements for Understanding Complex Multiphase Mixtures**

Charles Eads[1], Carrie Furnish[1], Allison Talley[1]; [1]Procter & Gamble

Industrial materials are often multi-component, multi-phase mixtures containing surfactants, polymers, colloids, and small molecules. Finding and applying new and better ways to study and understand such materials is a challenge to experts in physical chemistry, soft matter sciences, and measurement sciences. NMR relaxation is powerful and promising in this regard because it reports on the structure and dynamics of all of the components and phases that make up the material samples. Unfortunately, the multicomponent nature of the samples leads to multi-exponential decay curves whose analysis is famously problematic. This talk will describe some new and existing tools to deal with these types of systems, including two-dimensional relaxometry, field cycling relaxometry, and new data parameterization methods. Together, these tools help us to extract the rich information present in the raw NMR data while living with the limitations inherent in multi-exponential datasets.

(163) **Applications of Target PLS in R&D**

Boiana Budevska[1]; [1]DuPont Crop Protection

Target PLS (1) is an extension of the PLS method which provides information about the presence of components with known spectra directly from the spectra of complex mixtures without prior calibration. We have applied target PLS to spectra collected during process monitoring experiments to calculate contribution profiles of compounds with known spectra. These contribution profiles are later used in the development of predictive PLS models for process monitoring purpose. As a result of this approach the calibration development phase is faster and more flexible compared to the traditional approach where a large number of grab samples need to be analyzed by a reference method. Our experience shows that this approach is very well suited to R&D environment where frequent changes in reaction conditions are expected. This presentation will demonstrate the applications of this approach to the development of an industrial process.

1. R. N. Feudale, S. D. Brown, "An inverse model for target detection", Chemometrics and Intelligent Laboratory Systems 77,75-84 (2005)

(164) **Applied Chemometrics and Near Infrared Spectroscopy in Grain and Vegetable Quality Assurance**

Bin Dai[1], Patrick Lann[1], Ping Feng[1]; [1]Monsanto Company

Near infrared spectroscopy (NIRS) is one of most broadly used nondestructive analytical techniques in agriculture. NIRS is routinely used for nondestructive compositional analysis of corn, soybean, cotton and vegetables for breeding selection or quality assurance purpose. Chemometric and statistical modeling techniques play a critical role in NIRS calibration and classification models development. In this talk, I will present two applications of NIRS. First application is related to rapid and nondestructive predictions of linolenic, protein and moisture contents in soybean. We will compare the analytical performances of two chemometric modeling techniques, partial least squares (PLS) and artificial neural network (ANN), respectively. Second application related to nondestructive prediction of Brix content of tomato fruit using NIRS.

(165) **Chemometrics in Polymer Research and Development at SABIC**

Nancy Jestel[1], Yusuf Sulub[1], Michael Hall[1], Cherie Pomeranz[1]; [1]SABIC

Chemometrics plays an important role in widely varying research and development (R&D) activities around engineering thermoplastics at SABIC. Traditional partial least squares (PLS) regression is a workhorse technique. Examples will be presented highlighting its valuable role in determining the composition of complicated polymer blends and monitoring process stream compositions and reactions. PLS requires the analyst to have quantitative reference values. This is not always possible for R&D programs, but usually some information is available about the system from other sources. In these cases, a calibration-free approach, such as multivariate curve resolution (MCR), is required and the supplemental data is used to guide and evaluate the proposed solution. This situation frequently arises when monitoring the progress of a new polymerization reaction with in-situ tools such as mid-infrared, near-infrared, or UV-VIS, evaluating the effect of heat treatments on a polymer with variable-temperature FTIR, or determining the chemical composition distribution of a sample via liquid chromatography – infrared spectroscopy (LCIR). Examples will be presented from these areas, along with a discussion of issues encountered.

(166) **Hyperspectral NIR Imaging to Determine Defects Localization for Epoxy Resins as an Insulator Material**

Nicolas Spegazzini[1], Yukihiro Ozaki[1]; [1]Kwansei Gakuin University

Epoxy resins have many applications in coatings, adhesives and composites. The chemistry of epoxides and the wide range of resin materials commercially available for use as pre-polymers allows for a variety of properties in the final product (i.e. co-polymer). The first commercial epoxy resin to be developed was bisphenol A diglycidyl ether (BADGE), and it remains one of the most widely used resins in the industry. Epoxy resins as an insulator material in circuits is one of the most important applications. Because the epoxy resins are excellent electrical insulators and protect electrical components from short circuiting, moisture and dust. In the electronics industry epoxy resins are the primary resin used in overmolding hybrid circuits, integrated circuits and transistors, and making printed circuit boards.

But the excellent electrical insulators of epoxy resins are diminished because depend of curing degree and shrinkage. Significant advances in studies of dynamics chemical systems are highly dependent on the meaningful extraction of chemical knowledge from large amounts of experimental data. Such experimental data for chemical systems can be obtained by using a variety of techniques. The vibrational spectroscopy (Raman, mid-infrared (IR), and near-infrared (NIR)) are specifically potential tools for this purpose. In our case near infrared (NIR) measurements have found widespread use in process analytical application due to its advantages for example, good sensitivity, high information content, and low noise. Moreover hyperspectral NIR image is excellent way for the polymer degradation, shrinkage or curing degree control, allowed the spatial identification, localization and distribution of these defects on circuits. The aim of this study is to explore the possibilities of hyperspectral near infrared (NIR) imaging to determine chemical-physical defects localization and distribution for epoxy resins as an insulator material on circuits. In combination with implicit calibration for obtain real-time information about kinetic parameters and chemical composition. Calibration-based methods are affected for the external perturbations and significant amount of effort is required to develop and maintain the calibration model. In this way we propose use direct implicit calibration (calibration-free approach) because is not affected for changes in the instrumental response or changes in the chemical formulation.

(167) **Programmed Assembly and Manipulation of Complex Particles by Electric Fields**

Orlin Velev[1]; [1]North Carolina State University

We will discuss how external AC fields could be used to directionally assemble and manipulate complex artificial or biological particles on any size scale. Examples of dielectrophoretic (DEP) manipulation of nanoparticles, microparticles of varying complexity and live cells will be presented. The structures that could be assembled on a chip include electrical connectors, switchable dielectric crystals, biocomposite wires, and sensor prototypes. We will discuss the interactions leading to the assembly of such structures, ways to simulate the dynamics of the process and the effect of particle size and properties on the type of structure obtained. Of specific interest is the use of on-chip dielectrophoresis to capture cells such as Baker's yeast, alga, or mouse fibroblasts and assemble them into chains and membranes. Experimental observations and electrostatic simulations of the DEP assembly dynamics show that when particles smaller in size than the cells are present, they get drawn and captured into the cell junctions by the electric field. These arrays can be bound into permanent biocomposites by using lectin-conjugated spheres as biocolloidal binders. Binding by particles with magnetic cores yielded live cell membranes and chains that could be manipulated by magnetic field. Such cell-particle assemblies may find applications in sensors, microassays, microsurgery, or in responsive biomaterials. Finally, we will discuss how an additional level of complexity can be engineered to turn miniature semiconductor diode "particles" into prototypes of electrically actuated microswimmers and micropumps. These motile particles suggest rudimentary solutions to problems facing self-propelling "microbots," including harvesting power from external sources, internally controlled movement, and potential for a range of additional sensing and response functions.

(168) **Dielectrophoretic Polarization of DNA Molecules**

Hui Zhao[1]; [1]University of Nevada Las Vegas

A continuum model is developed to predict the dielectrophoretic polarizability of DNA molecules under the action of an alternating current electric field. For a double stranded short DNA molecule, the model approximates it as a rigid rod. For a long coiled DNA molecule, the model approximates it as a charged porous spherical particle. The Poisson-Nernst-Planck equations accounting for ions' migration, diffusion, and convection are solved to compute the dipole moment which characterizes the polarization of DNA molecules. The model explains the discrepancies among scaling laws of polarizability of different-sized DNA molecules with contour length and such discrepancies are attributed to different hydrodynamic behavior. With no or one fitting parameter, theoretical predictions are in good agreements with various experimental data, even though in experiments there are some uncertainties in regards to certain parameters. Our model not only helps understand experimental observations and also goes beyond to guide the experimental design which has broad applications in microelectronics, biotechnology, and nanotechnology.

(169) **Particle Electrokinetics in Non-Newtonian Fluids**

Xiangchun Xuan[1]; [1]Clemson University

Electrokinetic flow is an efficient means to transport and manipulate fluids and samples in microfluidic devices for various lab-on-a-chip applications. To date, however, the majority of previous studies have been concerned on electrokinetic phenomena in aqueous buffer solutions that are Newtonian fluids. I will present in this talk some experimental results of electrokinetic particle transport in non-Newtonian fluid flows through a straight and a constriction microchannel, respectively. We investigate and compare the DC electrophoretic and dielectrophoretic motions of spherical polystyrene beads re-suspended in a phosphate buffer with (which is a non-Newtonian fluid) and without (which is a Newtonian fluid) the addition of polyethylene oxide (PEO) polymer. The effects of electric field, particle size, and PEO concentration on particle behaviors are examined. Some interesting results are found.

(170) **Using Gradient Insulator-based Dielectrophoresis to Capture Small Molecular Weight Proteins**

Ryan Yanashima[1], Mark Hayes[1]; [1]Arizona State University

Dielectrophoresis (DEP) has the potential to serve as a separation and concentration technique for small volume samples. Dielectrophoresis has typically been applied to particles or cells, but recently analytes with small molecular weights such as proteins, have been targeted. Protein dielectrophoresis has been demonstrated, with the first observations of protein DEP trapping about twenty years ago by Washizu et. al. (IEEE Trans. Ind. Appl., 1994, 30, 835-843). The smallest proteins to be captured thus far using techniques similar to ours are the proteins BSA at 66 kDa and streptavidin at 60 kDa. Proteins of smaller molecular weights have been studied, and even successfully manipulated using dielectrophoresis resulting in streaming (Electrophoresis, 2013, 34, 1085-1096), but discrete isolation in a pseudo steady state has not been shown. Here, we extend the range of capture down to 14.3 kDa by capturing lysozyme from chicken egg white, along with other small molecular weight proteins. Dielectrophoresis is carried out on a microfluidic device consisting of an insulating sawtooth-patterned microchannel such that an inhomogeneous electric field is induced in the channel when a DC potential is applied across the device. The gradient of dielectrophoretic forces in our device arises from the varying distances of each successive gate within the device: as the gates become narrower, the ratio of the dielectrophoretic force to the electrophoretic force increases. When the dielectrophoretic force is great enough to counteract all other forces a protein experiences within the channel, immobilization and concentration occurs.

One protein of great interest in the medical field is Aβ (1-40) amyloids. Aggregates of Aβ amyloid and other amyloids have been implicated in numerous human diseases, including Alzheimer's disease. While it is known that the fully-developed Aβ amyloid fibrils are related to this disease, recent research has suggested the smaller oligomers and protofibrils are more prevalent in disease pathogenesis and are more cytotoxic. The proteins for our research were chosen based on their small molecular weights such that their capture

conditions might be comparable to small oligomers of Aβ amyloid proteins. Future work includes studying the behavior of small Aβ amyloid oligomers in our device.

(171) **Development and Application of a Flexible Standoff Raman Imaging System**

Henric Östmark; [1]FOI Sweden

With stand off Raman imaging, spatial distribution of threat substances (explosives, drugs) can be obtained from a safe distance. Rather than averaging the spectra, originating from the whole excited sample area, this system maintains the spatial information by imaging the investigated scene on the detecting ICCD camera chip. Stepwise tuning of a filter results in a picture which contains an individual Raman spectrum in each pixel. Even small substance particles have their corresponding pixels which contain only spectral information of the substance. Therefore, the detection of much lower amounts is achieved, since no background signal is present in these pixels. Here, advances in the field of stand off Raman imaging are presented.

(172) **Noninvasive Identification of Concealed Hazards by Standoff Deep Raman Spectroscopy**

Emad Izake[1], Biju Cletus[1], Shankaran Sundarajoo, William Olds[1], Peter Fredericks[1], Esa Jaatinen[1]; [1]Queensland University of Technology

Time-resolved Raman Spectroscopy (TRRS), Spatially Offset Raman Spectroscopy (SORS) and Time-Resolved Spatially-Offset Raman spectroscopy (TR-SORS) have proven their capability for the non-invasive standoff detection of concealed hazards within diffusely scattering media. Our recent results confirm that the selectivity of a standoff Raman spectrometer towards the deep layers of a sample (e.g. a concealed explosive material in a highly fluorescing plastic container) can be enhanced by combining time and space resolve as in TR-SORS. The overall efficiency of TR-SORS in depth profiling, rejection of surface layer interference and fluorescence has been explained and proven to be due to the combined temporal and spatial resolution in TR-SORS.

(173) **Development of Trace Explosive Optical Standards for the Evaluation of Stand-off Raman Sensors**

Augustus Fountain[1], Raphael Moon[1], Ashish Tripahti[2], Jason Guicheteau[1], Steven Christesen[1]; [1]Research and Technology Directorate, Edgewood Chemical Biological Center, Aberdeen Proving Ground, MD; [2]Science Applications International Corporation, Aberdeen Proving Ground, MD

Edgewood Chemical Biological Center (ECBC) is leading an inter-agency working group to expand chemical inkjet printing techniques to fabricate witness cards in a controlled, uniform and quantifiable fashion for the evaluation of stand-off Raman systems. The U.S. Army has a critical need to remotely detect chemical, biological, and explosive materials on surfaces. Since the detection of trace contamination on surfaces is a difficult and potentially costly problem to solve; to mitigate these risks, the ECBC has been developing a predictive model for standoff detection of chemicals on surfaces. In this work, the Direct Jet 1309 printer (Direct Color Systems, Rocky Hill, CT) was use to generate the modeled distribution on relevant surfaces with actual chemicals. In addition to modeling agent stimulants, the printer has been used to deposit explosive materials on relevant surfaces for the calibration of standoff explosive systems. The model can be used to compare existing technologies as well as predict performances and identify system weaknesses. Currently, a generic Raman-based standoff detection system is being modeled and validated using laboratory measurements.

(174) **Standoff Detection and Imaging Based on Coherent Single-Beam Raman Spectroscopy**

Marcos Dantus[1,2], Marshall Bremer[2]; [1]Michigan State University, Department of Chemistry; [2]Michigan State University, Department of Physics and Astromnomy

Standoff detection of hazardous materials remains an important challenge which persists despite decades of research. A key facet of this broad goal is the ability to safely and non-destructively detect, at standoff, trace quantities of explosives as indicators of concealed dangers in public spaces. Due to the low vapor pressure of most explosives, an optical method capable of selectively detecting these compounds as micro crystals on different surfaces, including delicate garments, is highly desirable. This letter introduces a method based on the phenomenon of stimulated Raman scattering, simultaneously measuring stimulated Raman gain and loss within a single laser shot and capable of detecting and imaging nanogram quantities of explosives. We demonstrate the specificity and sensitivity by detecting and imaging sub-microgram analyte micro crystals on paper, fabric and plastic substrates at one to ten meter standoff distance using only 10mW of laser power from a single femtosecond laser.

(175) **Wide Field-of-View Standoff Raman Using a Small Spatial Heterodyne Raman Spectrometer**

Stanley Angel[1], Nirmal Lamsal[1]; [1]The University of South Carolina, Department of Chemistry & Biochemistry

In earlier work a spatial heterodyne Raman spectrometer (SHRS) was demonstrated at visible and deep-UV wavelengths. Using small 1-inch diameter, 150-gr/mm diffraction gratings the system was shown to have near-theoretical spectral resolution of about 5 cm-1 using 244-nm excitation, and a very large spectral range. The SHRS design offers advantages over dispersive Raman systems especially in the UV, including 10 to 100 times larger acceptance angle and subsequently a much larger field of view, 102 to 104 higher light throughput, very high resolution in a small package, and wide spectral range. In addition the design is amendable to miniaturization because the spectral resolution is not a strong function of device size. An important goal of ongoing work is to use the large acceptance angle of the interferometer for wide field-of-view standoff Raman measurements. Wide area measurements are useful to minimize laser-induced sample damage, especially important in the UV, and to minimize the time needed to characterize a large region of interest. We have demonstrated measurements of areas as large as 8 cm in diameter at just a few meters working distance with no loss of Raman signal or spectral resolution. We are also investigating ways to reduce the size of the SHRS. In this talk we will show the feasibility of UV SHRS spectrometers that are 5 mm or less in size, with 5 cm-1 spectral resolution and >4000 cm-1 spectral range. The SHRS design is amendable to such miniaturization because the spectral resolution is not a strong function of device size. The small size and spectroscopic performance of the miniature SHRS would immediately broaden the applicability of on-line, in-situ, in-vivo, and standoff Raman measurements. Applications of standoff SHRS measurements to planetary applications will be discusssed.

(176) **MS-based Strategies for the Elucidation of Nucleic Acid – Ligand Interactions**

Daniele Fabris[1]; [1]University at Albany

Ribozymes and riboswitches have keenly demonstrated that the function of nucleic acids is not always linked to the genetic information coded in their sequence, but can also depend on their 3D structure and ability to interact with a variety of species present in the cell. Owing to the versatility afforded by mass spectrometry (MS) in RNA analysis, this platform is rapidly assuming a prominent role in the investigation of structure-function relationships, which is realized by supporting the full characterization of natural and man-made

RNAs as well as the elucidation of specific interactions with cognate nucleic acids, proteins, metals, and small molecule ligands. The talk illustrates strategies for accessing functional information for nucleic acid complexes and discusses possible hurdles and experimental pitfalls. Examples are provided in which MS-based techniques are employed to characterize relevant interactions that could represent new therapeutic targets. Other examples illustrate approaches for elucidating the effects of metals and common nucleic acid ligands on such interactions. The experimental design necessary to assess the strength of binding/inhibition in either comparative or absolute fashion is also discussed. The potential afforded by ion mobility spectrometry (IMS) techniques is evaluated in the investigation of possible conformational effects associated with ligand binding. Owing to the extremely low sample consumption and high speed of analysis, these capabilities will be expected to greatly increase the utilization of MS-based approaches in drug discovery and therapeutics development based on specific nucleic acid interactions.

(177) **Characterization of the Breast Cancer Marker Candidate LAG3 in Human Plasma by Hyphenated SPRi-MALDI-MS Analysis**

Chiraz Frydman[1], F Remy-Martin[2], M El Osta[3], G Lucchi[3], R Zeggari[2], T Leblois[2], S Bellon[1], D Suckau[4], P Ducoroy[3], W Boireau[2,3]; [1]HORIBA Scientific, France; [2]Institut FEMTO-ST, Université de Franche Comté, CLIPP, France; [3]CLIPP, Université de Bourgogne, CHU Dijon, France; [4]Bruker Daltonik GmbH, Germany

Proteomics plays an important role in biomarker discovery for clinical applications. In this study, we coupled Surface Plasmon Resonance imaging (SPRi) with MALDI-TOF mass spectrometry to permit the multiplexed quantification of binding by SPRi and the molecular characterization of interacting partners by subsequent MS analysis. This adds a dimension of specificity as MS permits the differentiation of molecules that are difficult to tell apart by use of antibodies, such as truncation variants or protein isoforms. Proof of concept for the detection, the identification and the characterization of a potential breast cancer marker, the LAG3 protein at ~1µg/mL, spiked in human plasma was established. LAG3 was bound to α-LAG3 antibodies that were covalently attached to the chip surface via sulfo-NHS chemistry. SPRi binding kinetics were obtained in real time, followed by tryptic digestion, matrix deposition and MALDI peptide mass fingerprint and MS/MS spectra acquisition. LAG3 was identified through Mascot interrogation. The analytical performance of this new method was assessed. It is particularly noteworthy that the density of bound analyte on the surface (~7 fmol/mm²) was compatible with both, quantitative determination of binding parameters and the identification though bottom-up MS/MS analysis. MALDI image analysis of the chips confirmed the colocalization of LAG3 peptides with the array spots whereas serum albumin – used to block the reactive chip surface after α-LAG3 deposition – was detected between the array spots. Antibodies were only marginally digested by trypsin. The rapid, multiplexed and automated on-chip MALDI-MS analysis shows robustness at the femtomole level and opens numerous applications in the proteomic field such as ligand screening and lead optimization.

(178) **Quantifying Proteoforms Using High-Throughput Top-Down Proteomics**

John Savaryn[1], Adam Catherman[1], Archer Smith IV[1], Ryan Fellers[1], Bryan Early[1], Richard LeDuc[2], Paul Thomas[1], Neil Kelleher[1]; [1]Northwestern University; [2]Indiana University

Top-down proteomics using liquid chromatography and tandem mass spectrometry (LC-MS/MS) offers complete characterization of proteoforms within complex mixtures. For comparative studies, it is essential to be able to quantify proteoform abundances between samples. Here, we have developed a platform for label-free quantitative top-down comparative proteomics. Initially, we used a single fraction of size-based resolved S. cerevisiae lysates to acquire a randomized dataset of known intact protein relative abundances using high-resolution Fourier transform LC-MS/MS. Quantitation was performed by first 'Xtracting' mono-isotopic neutral masses of MS1 precursor ions and then integrating those neutral mass intensity values across the chromatogram using a 10ppm mass tolerance. The resulting data-frame was subjected to a linear hierarchical statistical model that parsed the signal variation for each proteoform mass into one of three groups: treatment, technical replicate, and residual. In parallel, we ran all the MS data (MS1 and MS/MS) through our conventional ProSightPC database search software for protein identification and characterization. We found greater than 100 proteoforms with statistically significant abundance differences near what we expected between the treatment groups. Using our ProSightPC search results, we were able to add proteoform identity to a large number of these statistically significant masses. Having validated our platform, we performed a quantitative top-down proteomics experiment on apoptotic yeast. Our results are pending. Collectively, we describe a new platform for label-free quantitative top-down proteomics that includes a linear hierarchical statistical model and is amenable to our well-developed and robust platform for high-throughput studies. We anticipate the application of this approach to proliferate throughout the top-down community soon.

(179) **Multiplex Quantification through Neutron-Encoded Mass Signatures (NeuCode)**

Nicholas M. Riley[1], Alexander S. Hebert[1], Joshua J. Coon[1]; [1]University of Wisconsin

The past decade has produced impressive advances in the ability of mass spectrometry to quantitatively characterize complex biological systems. Techniques that use stable isotopes, such as SILAC and isobaric tagging, have greatly enhanced quantitative abilities of mass spectrometers, enabling deep proteome characterization in addition to direct comparisons between biological systems of interest. A recent discovery demonstrated that small mass defects between isotopes caused by nuclear binding energies can be utilized to increase multiplexing with isobaric tags. We have further developed this idea, using the subtle mass differences (on the order of milliDaltons) in stable isotopes to provide multiplex capabilities for both metabolically and chemically labeled proteomes. Termed NeuCode, this approach addresses several issues in current quantification techniques by encoding the quantification in the MS1 scans while also offering the ability to easily conceal or reveal the quantitative data by varying the resolution. This eliminates precursor interference issues that challenge isobaric tagging while also increasing the dynamic range and multiplexing abilities that can otherwise limit traditional SILAC. Overall, NeuCode represents a new method to provide quantitative accuracy and precision with the ability to multiplex. Here we demonstrate the use of NeuCode multiplexing in a variety of biological systems.

(180) **Virtual 2D Gel Electrophoresis: Mass Spectrometric Imaging of Immobilized pH Gradient-Isoelectric Focusing Gels Reveals Intact Protein Heterogeneity in Proteomics**

Rachel Loo[1], Karen Lohnes[1], Joseph Loo[1]; [1]University of California-LosAngeles

Bottom-up proteomics strategies identify proteins in complex mixtures, but discard most information revealing protein isoforms, modifications, and unanticipated processing. Dominant top-down proteomic methods retain this information, providing both accurate intact mass and sequence data, relying on compatible protein separation technologies. Our goal is to develop a protein-based, proteome-scale mass spectrometry platform to identify and characterize intact protein isoforms and expression profiles, while linking to 2D-PAGE, the premier method to separate, visualize,

quantify, and assay intact proteins and their modified forms from complex biological samples.

The technology to mass-analyze intact proteins subsequent to gel electrophoresis is largely undeveloped. We seek to bridge this need by mass analyzing proteins embedded in dried isoelectric focusing (IEF) gels. Replacing the SDS-PAGE dimension of classical 2D-analysis by MALDI-MS links intact mass measurements to discrete 2D gel spots. Once linked to specific spots, the mass spectra have enduring utility, applying to every previous and subsequent 2D gel associated with that type of specimen, capitalizing on immobilized pH gradient-based 2D gels' interlaboratory reproducibility. By relating to the isoform-specific measurements accessible from 2D-PAGE (e.g., antibody blots, carbohydrate composition, synthesis/degradation rates, abundance) the mass measurements are placed in broader biological context.

Proteins from 4 to 100 kDa are measured directly from dried isoelectric focusing gels and related to other analyses performed by 2D-PAGE on Methanosarcina acetivorans, Methoanobrevibacter smithii, Syntrophus aciditrophicus, and on human salivary proteins. In-gel digestion and tandem mass spectrometry have also been explored from this imaging format, supporting the identification of multiple proteins. MALDI-TOF/TOF and MALDI-QqTOF "bottom-up" measurements all provide good sequence coverage, sufficient to identify proteins directly from IPG gels, while MALDI in-source dissociation (ISD) provides bonus "top-down" capability, such that even a short sequence tag from limited fragmentation can confirm a suspected identity. Moreover, interfacing to MALDI-FT-ICR-MS provides accurate mass measurement capability. Applications especially suited to this approach include visualization and mass analysis of small open reading frame products, glycosylated proteins, and membrane proteins.

(181) **Quantitative Analysis of Nanoparticle Interactions with Environmental and Biological Interfaces**

Howard Fairbrother[1], Julie Bitter[1], Gregg Duncan[2], Mike Bevan[2]; [1]Johns Hopkins University, Department of Chemistry; [2]Johns Hopkins University, Department of Chemical and Biomolecular Engineering

The detailed interactions of nanoparticles with environmental and biological surfaces in aqueous environments will determine their ultimate fate and effect by regulating sorption and transport properties as well as toxicity and bioaccumulation. Particle interactions with surfaces in aqueous environments occur on the kT-energy scale. Consequently, investigating these interactions takes extremely sensitive, non-intrusive measurements. To satisfy these stringent requirements we have used total internal reflection microscopy (TIRM) to track the interactions of silica and gold nanoparticles with silica surfaces, applying state-of-the-art evanescent wave scattering and video microscopy techniques. Quantitative analysis of TIRM data allows us to calculate important particle properties such as mean squared displacements and diffusion coefficients. Data on particle trajectories can also be used to determine the contribution from different forces (e.g. electrostatic, van der Waals and steric) that act between a nanoparticle and a surface, information that has been used to determine the effect that gel layers present on silica surfaces play in determining particle-surface interactions. By including an impermeable SiO_2 "gel layer" when fitting van der Waals, electrostatic, and steric potentials to measured net potentials, gel layers are estimated to be 10-20nm thick and display an ionic strength dependent but pH independent collapse. We have also used TIRM to measure the trajectories of gold rods interacting with silica surfaces as they diffuse through model two-dimensional porous media. Using dark field microscopy, gold nanoparticles (AuNP) functionalized with different surface coatings have been tracked as they interact with cancer cells. From particle trajectories, diffusivity and free energy landscapes of these AuNPs interacting with cells are constructed. The diffusion of the AuNP as a function of position in the cell allows us to differentiate between different modes of cell-surface diffusion and intracellular transport. Free energy landscapes of the cell surface help to identify specific regions on a cancer cell's surface with which AuNPs interact most favorably. From these landscapes, we can better understand how particle properties (e.g. surface chemistries) affect the transport and intracellular fate of nanoparticles interacting with biological interfaces.

(182) **Nanoparticle Toxicity Assessment in a Bacterial Model**

Christy Haynes[1], Ian Gunsolus[1], Benjamin Meyer[1], Catherine Murphy[3], Robert Hamers[2], Rebecca Klaper[4], Joel Pedersen[2]; [1]University of Minnesota; [2]University of Wisconsin, Madison; [3]University of Illinois, Champaign-Urbana; [4]University of Wisonsin, Milwaukee

Engineered nanoparticles are found in many everyday products and hold great potential as therapeutic agents. Accordingly, it is critical to consider how engineered nanoparticles interact with physiological and ecological systems. This work focuses on functional assessment of bacterial cell behavior following exposure to Au, nanodiamond, and semiconductor nanoparticles. Functional considerations include biofilm formation, cell delivery of chemical messengers, production of reactive oxygen species, and gene expression, among others. In this new collaborative study, obtained bacterial toxicity results can be compared to those obtained in other model systems (lipid bilayers and the multicellular water flea, Daphnia) to identify common modes of nanoparticle interactions and the resultant effects. The goal of this work is to discover critical nanoparticle features that determine cellular toxicity and then redesign nanoparticles to promote sustainable use.

(183) **Two high Aspect Ratio Nanoparticles Elicit Unique Molecular Responses that Explain Their Distinct Level of Cytotoxicity**

Galya Orr[1], Susan Tilton[4], Norman Karin[4], Ana Tolic[1], Yumei Xie[1], Xianyin Lai[2], Raymond Hamilton[3], Katrina Waters[4], Andrij Holian[3], Frank Witzmann[2]; [1]Environmental Molecular Sciences Laboratory, Pacific Northwest National Laboratory; [2]Department of Cellular and Integrative Physiology, Indiana University School of Medicine; [3]Department of Biomedical and Pharmaceutical Sciences, University of Montana; [4]Fundamental & Computational Sciences Directorate, Pacific Northwest National Laboratory

The growing use of engineered nanoparticles (NPs) in commercial and medical applications raises the urgent need for tools that can predict NP toxicity. We investigated mechanisms of cytotoxicity for two high aspect ratio NPs, multi-walled carbon nanotubes (MWCNT) and TiO2 nanobelts (TiO2-NB), presenting low and high cytotoxicity, respectively, using global proteomic and transcriptomic analyses. Using three cell types that represent the most common routes of human exposure to NPs, including macrophage like, small airway epithelial, and intestinal cells, we observed cell type-specific regulation of genes and proteins when exposed to the same NPs using identical reagents and protocols. We also observed patterns of response that were NP-independent at early time points, suggesting a generic early response to insult. In contrast, NP-specific responses were observed at later time points, describing mechanisms associated with differential toxicity. Both NP types are likely to elicit a stress response; however, MWCNT uniquely up-regulated cell proliferation, anti-apoptotic and DNA repair mechanisms associated with cell survival, while TiO2-NB differentially regulated inflammatory responses associated with cellular stress. In particular, our data shows that TiO2-NB uniquely activated molecular pathways associated with apoptosis, cell cycle arrest and DNA repair related to DNA replication stress and genomic instability. The data also point to oxidative stress responses associated with inflammatory cytokines

as possible mechanisms underlying TiO2-NB toxicity. In summary, this unbiased approach allowed us to decipher differences in responses of three different cell-types to the exact same particle properties and identify mechanisms likely to underlie high vs. low toxicity of high aspect ratio NPs.

(184) **Surface Functtionalization of Diamond Nanoparticles for Nanotoxicity Studies**

Robert Hamers[1], Marco Torelli[1], Joel Pedersen[1], Randy Goldsmith[1], Galya Orr[2], Franz Geiger[3]; [1]University of Wisconsin-Madison; [2]Pacific Northwest National Laboratory; [3]Northwestern University

Current efforts to understand fate and transport of nanomaterials in biological and environmental systems are hampered by the fact that most fluorescent nanoparticles can degrade over days to weeks in biological media. Nano-diamond has recently emerged as an alternative nanoparticle whose outstanding stability in aqueous media allows it to be used in a range of studies where more traditional nanoparticles cannot be easily used. Diamond particles as small as 4 nm diameter are available commercially. While pure diamond is a wide-bandgap semiconductor and is not fluorescent, diamond can be made fluorescent either through external chemical modification or by activating the NV center, a highly fluorescent defect that can be created in nitrogen-doped diamond. We have investigated several approaches to making the nanoparticles water-stable and fluorescent. These include heavy external oxidation, activation of the NV center by exposure to electron beams, and covalent grafting of fluorescent dyes to the nanoparticle exterior. In each case, single-particle fluorescence imaging experiments allow individual diamond nanoparticles to be detected and tracked in real time. In this presentation we will compare the advantage and disadvantages of these methods and discuss prospects for use of nanodiamond for biological and environmental tracking.

(185) **Spatial Distributions of Analyte Ions in an Inductively Coupled Plasma with Laser Ablation Sample Introduction**

Paul Farnsworth[1], Lance Moses[1]; [1]Brigham Young University

The spatial distribution of analyte ions in an inductively coupled plasma used as an ion source for mass spectrometry has a critical influence on the overall performance of ICP-MS instrumentation. The distribution of ions depends on a number of factors, among them the nature of analyte aerosol that is injected into the plasma. Solution nebulizers and laser ablation sample introduction systems produce dramatically different aerosols, so it follows that the spatial distributions of analyte ions produced by the two sample introduction techniques are also dramatically different. We have used planar laser induced fluorescence to image analyte ion distributions in an ICP using both solution and laser ablation sample introduction. In this lecture we will present the results of the fluorescence imaging measurements, and describe the effects of nebulizer gas flow rate, nebulizer gas composition, laser ablation fluence, and sample type on analyte distributions in the plasma.

(186) **Implications of Fundamental Processes on ICP-MS Measurements**

John Olesik[1], Fang Liu[1], Shi Jiao[1], Anthony Lutton[1]; [1]The Ohio State University

The fundamental processes of droplet desolvation, particle vaporization, ion formation, diffusion and space charge repulsion each affect practical ICP-MS measurements. Their affect on precision, accuracy and linear dynamic range of nano-particles and micro-particles will be discussed. Processes that produce matrix induced changes in ICP-MS sensitivity will also be considered, including space charge effects in the region where ions are focused.

(187) **Gas Flow Dynamics in ICPMS: Description, Explanation and Optimization**

Maryam Aghaei[1], Annemie Bogaerts[1]; [1]University of Antwerp

An inductively coupled plasma connected to a mass spectrometer interface is computationally investigated. The gas temperature, gas density, electron density and the velocity path lines of the gas flow inside the coil region as well as in the region close to the MS interface, are studied. A cooled metal interface lowers the plasma temperature and electron density on the axial channel very close to the sampling cone.

The effect of the operating conditions, i.e., injector gas flow rate, auxiliary gas flow rate, and applied power, is studied. There seems to be an optimum range of injector gas flow rate for each setup which guaranties the presence and also a proper length of the central channel in the torch. The general effect of increasing the applied power is a higher ionization in the coil region. However, the negative effect is reducing the length of the cool central channel. The effect of the operating conditions, i.e., sampler orifice diameter and distance of sampler cone above the load coil, is also studied. An increase in sampler orifice diameter leads to a higher central temperature and a much higher gas velocity at the place of the sampler, as well as a more efficient gas transfer through the sampler, by reducing the interaction of the plasma gas with the sampling cone. At increasing distance of the sampler from the load coil, the gas temperature at the place of sampler decreases slightly.

Also the formation of eddies, i.e., backward flow of the intermediate gas in the torch, is investigated. Eddies inside the torch can be avoided by increasing the injector gas flow rate at fixed auxiliary and plasma flow rates. For each auxiliary gas flow rate, there is a transition point for the injector gas flow rate beyond which eddies in the torch do not occur. At high enough plasma gas flow rates or high enough external power values, eddies do not exist. Moreover, for any specific purpose, either by changing the sampler orifice diameter or injector and auxiliary gas flow rates, it is possible to control whether only the central gas or also the auxiliary gas can exit through the sampler.

(188) **Spectrochemical Analysis and Diagnostics via Modeling**

Igor Gornushkin[1], Sergei Shabanov[2], Alexander Kazakov[3], Alexander Demidov[1], Ulrich Panne[1, 4]; [1]BAM Federal Institute for Materials Research and Testing, Berlin, Germany; [2]Department of Mathematics, University of Florida, Gainesville; [3]State University of Aerospace Instrumentation, St. Petersburg, Russia; [4]Humboldt-Universität zu Berlin, Department of Chemistry, Berlin, Germany

Laser induced plasma (LIP) is a core of laser induced breakdown spectroscopy (LIBS), a popular method for analysis of solid, liquid, and gaseous samples. Better understanding of LIP progressively leads to improved figures of merits in LIBS. Due to its remote capability, compactness, and no demand for sample preparation, the technique is suitable for using in field and harsh environments. Here, the additional capacity for rapid in-situ estimation of sample composition without using matrix-matched standards is highly desirable. The understanding of LIP through diagnostics and modeling opens up the gate to such the possibility. High precision Abel and Radon transform tomography is used to obtain the 3D emissivity distribution in single-pulse (SP) and double-pulse (DP) laser induced plasmas. The orthogonal DP plasma is especially apt for Radon tomography because of its intrinsic asymmetry. A radiative model of LIP is applied to match synthetic and experimental emissivity spectra and to reconstruct plasma temperature and species number densities. After the best fit is achieved, the spatially resolved temperature and number densities are read directly from the model. It is argued that the spectral fit method provides more accurate results than that obtained by the traditional Boltzmann plot approach. Time-resolved Radon reconstruction in white light is performed for the DP plasma to study effects of ablated aerosol and asymmetric compression shock on the

formation of LIP. The 2D collisional-dominated plasma model is developed based on the coupled Navier-Stokes, state, radiative transfer, and chemical kinetic equations. The output of the model is a dynamic plasma spectrum which can directly be compared to experimental spectrum. The model is used to predict absorption lines in early DP LIP, to map the dynamic distribution of atomic and molecular species in LIP, and to estimate concentrations of plasma constituents using solely experimental spectra and no matrix-matched standards. The possibility of semiquantitative spectrochemical analysis is demonstrated on the example of aluminum alloys and geological samples; the overall accuracy better than 50% is achieved for minor and major elements.

(189) **Assessment of the Liquid Sampling-Atmospheric Pressure Glow Discharge (LS-APGD) Rotational Temperature, Excitation Temperature, and Electron Number Density**

Benjamin T. Manard[1], Jhanis J. Gonzalez[2], Meirong Dong[2], Arnab Sarkar[2], Jose Chirinos[2], Xianglei Mao[2], Richard E. Russo[2], R. Kenneth Marcus[1]; [1]Clemson University; [2]Lawrence Berkeley National Laboratory

As the recent trends of miniaturization in analytical chemistry instrumentation has progressed, atmospheric pressure plasma sources have seen increased interest. Currently, there is a need to design spectrochemical instruments with lower power consumption, reduced sample sizes, compact footprint, and the ability to be operated under ambient conditions. Marcus and co-workers have developed a liquid sampling-atmospheric pressure glow discharge (LS-APGD), in which a glow discharge plasma is sustained between an electrolytic liquid, which flows out of a glass capillary tube, and the counter electrode placed ~2 mm away. Advantages of this excitation/ionization source hold true for not only the characteristics given above (ambient conditions, low power, small sampling size, and miniaturized footprint), but also, the APGD source has great versatility in sample analysis (solids, liquids, gases, laser-ablated (LA) particles). Recent collaborations with Russo at the Lawrence Berkeley National Laboratory (LBNL) have focused on utilizing the LS-APGD source as a secondary excitation source for LA-generated particles. This combination, LA-LS-APGD, has been shown to be qualitatively comparable to LA-ICP-MS and can excite particles produced from a nanosecond pulsed laser, which could be improved utilizing a femtosecond laser. When discussing plasma performance, fundamental properties (i.e. rotational, vibrational temperatures, etc.), must be evaluated to allow for design optimization and to give an understanding of excitation conditions, which vary with operation parameters. The research presented here, utilizes optical emission spectroscopy (OES) to evaluate the various glow discharge properties. Plasma emission was collected with an optical fiber connected to an Aurora six-channeled spectrometer (Applied Spectra, Inc), with CCD detection. Rotational, vibrational, and excitation temperatures were determined with a thorough parametric evaluation, studying electrode distance, applied current, and carrier/cooling gas (He). Molecular bands, OH (A2∑+→X2∏) and N2 second positive system (c3∏u→B3∏g), were utilized for rotational/vibrational temperatures while the emission of Mg atomic/ionic lines was utilized for the determination of excitation temperatures. Plasma characteristics were also evaluated when laser-ablated particles were introduced into the source. Studies revealed correlations of temperatures with changes in experimental parameters, demonstrating the ability to alter conditions to favor atomic or ionic emission, further improving the versatility of the LS-APGD source.

(190) **Model Diagnostics as Quality Control Tools for Near Infrared Calibration Models – Application to Raw Material Variability**

Benoit Igne, Carl Anderson[1], James Drennen[1]; [1]Duquesne University

The impact of raw material variability on the prediction ability of a near-infrared calibration model for theophylline was studied. Prediction models, developed from a quaternary mixture design comprised of theophylline anhydrous, lactose monohydrate, microcrystalline cellulose, and soluble starch were used to predict compacts whose raw material were intentionally varied. A full factorial design with two theophylline physical forms (anhydrous and monohydrate theophylline), three lactose particle sizes (50, 100, and 125 μm), and two starch manufacturers was created to test model robustness. To evaluate the effect of environmental conditions, powders and compacts were stored, in parallel, at room conditions and at a fixed relative humidity of 35%. Partial least squares regression (PLS) was used to develop the models. In addition, the possibility to select variables to mitigate the effect of raw material variability was studied. Dynamic backward PLS and genetic algorithms combined with PLS were used to develop parsimonious models. In addition to evaluating models based on their prediction statistics, residuals were analyzed by analyses of variance and model quality parameters such as Hotelling's T^2 and Q residuals. The full-spectrum PLS models were significantly affected by lactose particle size changes and trends existed when considering the differences in predictions with starch manufacturers. Models developed by selecting variables gave lower prediction errors than the full-spectrum PLS models and proved to be a good approach to limit the effect of changing raw material parameters. Multivariate diagnostic statistics (Hotelling's T^2 and Q residuals) provided valuable information that was not detectable when studying prediction trends.

(191) **Process Mass Spectrometers - Now a PAT Tool for Cell Culture**

Peter Traynor[1], Graham Lewis[1], Todd Colin[1]; [1]Thermo Fisher Scientific; [2]Thermo Fisher Scientific; [3]Thermo Fisher Scientific

Mass spectrometers have been used to provide online PAT for industrial fermentations for 30 years or more. They continue to provide valuable insight regarding the trajectory of batch and fed-batch processes. Their use has been somewhat limited in cell culture processes, however. The distinction between microbial fermentation and cell culture is important from a process control perspective since hardy bacteria need less protection from process variation than do mammalian cells which require tight control of temperature, pH and the sheer forces produced by agitation and aeration. Control of dissolved carbon dioxide is also important in cell culture control. Low and intermittent sparge rates provide challenges for mass spectrometers when 5-10 Liter bench-top bioreactors are used for process development. This paper discusses the challenges and introduces a new mass spectrometer specifically designed to accommodate low sample flows without compromising the high precision provided by magnetic sector technology.

(192) **Application of a TDLAS-based Water Vapor Mass Flow Rate Monitor for Lyophilization**

William Kessler[1], Michael Pikal[2], Puneet Sharma[2], Timothy Zwack[3]; [1]Physical Sciences Inc.; [2]University of Connecticut; [3]IMA Life, NA

An optically based Tunable Diode Laser Absorption Spectroscopy (TDLAS) water vapor mass flow sensor has been developed to enable real-time, non-intrusive mass flow measurements during lyophilization. The LyoFlux monitor continuously and non-intrusively measures the water vapor concentration (molecules cm-3) and gas flow velocity (m/s) in the duct connecting the lyophilizer chamber and condenser using Doppler-shifted near infrared absorption spectroscopy. The concentration and gas velocity

measurements are combined with the knowledge of the duct cross sectional area (m2) to determine the water vapor mass flow rate (grams/s). This presentation discusses important measurement considerations that led to data analysis methods that have enabled the development of an accurate mass flow monitor. The sensor relies upon line of sight absorption measurements through a developing gas flow profile to determine the flow rate. Fluid flow and water absorption lineshape modeling was performed to interpret the absorption measurements and provide accurate density and velocity determinations. The sensor has been applied in numerous academic and industrial settings to monitor pharmaceutical freeze drying processes. These uses have included the determination of primary and secondary drying endpoints, determination of product vial heat transfer coefficients (Kv) and the determination of dry product resistance and product temperature throughout the primary drying phase of lyophilization. The determination of Kv, resistance and product temperature are accomplished by combining the sensor measurements with a steady state heat and mass transfer model of vial freeze drying. Experiments were performed in both laboratory and pilot scale lyophilizers outfitted with a LyoFlux TDLAS mass flow monitor. During this presentation we will present the experimental results that show excellent agreement between the TDLAS-based, batch average temperature determinations and weighted average vial thermocouple based measurements. The TDLAS based non-intrusive temperature measurements demonstrate the potential to achieve enhanced process monitoring and control during both laboratory and production scale lyophilization. This is an important capability that will aid scale-up to manufacturing lyophilizers where thermocouple data are often inaccurate and unreliable.

(193) **The Extra Absorptions of Amino Acid Mixtures in THz Range**

Zhaohui Zhang[1], Haixia Su[1], Xiaoyan Zhao[1], Zhi Li[1], Han Zhang[1], Katherine Dunn[2], Micheal Johnston[2]; [1]University of Science and Technology Beijing; [2]University of Oxford

Generally, the THz quantitative measurement of a sample with multi-components is based on Beer-Lambert law, i.e., the superposition principle. But it's difficult to achieve a good accuracy because THz absorption is more susceptible to intra and inter molecules interactions than infrared. The heterogeneous granules of a mixture sample may lead to extra absorptions. In our special designed experiments, extra absorptions are observed in several mixture samples. Pure chemicals cystine (Gln),histidine (His),threonine (Thr) and glutamine (Cys) with 99.0% purities are grinded into μm scale, and then pressed into pellets under 8MPa at various configurations. Sample 1 is a uniform pellet with two components completely stirred, but sample 2 is a laminated pellet with two separated component layers. The additive PE is in form of 60μm granules for all samples. The absorption spectra are extracted by T. D. Dorney's algorithm. Peaks emerge at 1.719THz and 2.279THz from Gln spectrum, and 0.776THz and 2.098THz from His spectrum. Sample 1 with Gln and His gives rise to an extra peak at 1.892THz,while sample 2 doesn't give any extra peak beyond the expected 4 peaks. Similar phenomena occur in mixture samples of Thr and His, and of Thr and Cys. The results maybe come from co-crystals. The amino acid granules are in form of tiny crystals in which the molecules are ordered with hydrogen bonds between amine hydrogen atoms and carboxylate oxygen atoms. The corresponding THz spectrum relies on the vibration modes of these hydrogen bonds. When heterogeneous granules are pressed to be a mixture sample, co-crystals intend to be formed under high pressure. The newly produced hydrogen bonds in co-crystals lead to extra absorptions. Meanwhile, the laminated sample without extra absorption is a proof by contradiction due to very little probability of heterogeneous granules contacts.

(194) **Non-Aqueous Microchip Electrophoresis: A Promising Strategy for Biomarker Detection**

Larry Gibson[1], Paul Bohn[1]; [1]University of Notre Dame

Electrophoretic separation strategies coupled with universal detection comprise elucidative diagnostic systems capable of correlating the concentrations of target molecules suspended in patient biofluids with a wide range of disease states. This technology affords physicians the ability to monitor disease progression at the patient's bedside in real-time. Unfortunately, the products of lipid peroxidation, an important class of biomarkers linked to a number of neuroinflammatory and neurodegenerative diseases, are often excluded from this powerful strategy due to their low solubility in aqueous media. In order to overcome this limitation, non-aqueous microchip electrophoretic separations of lipid mixtures are executed using three-dimensional hybrid nanofluidic/microfluidic polymeric devices. This newly developed system supports rapid electroosmotic fluid flow for reproducible separations that achieve both high resolution and quality. Processed analytes are then detected using mass spectrometry via nanospray ionization. The proposed system offers a promising avenue for label-free detection of lipid biomarkers downstream of pre-processing strategies.

(195) **Using RNA-Seq and Mass Spectrometry to Expand the Detection of Protein Variations**

Gloria Sheynkman, Michael Shortreed[1], Brian Frey[1], Mark Scalf[1], Lloyd Smith[1]; [1]University of Wisconsin-Madison

Human proteomic databases required for mass spectrometry-based peptide identification are frequently updated and carefully curated, yet are still incomplete. Proteins exist in many different forms (proteoforms), which often are challenging to identify as they may not be present in generic databases. In particular, alternative splicing has been shown to be a major source of cell-specific proteomic variation. Many new alternative splice forms have been detected at the transcript level using next generation sequencing (NGS) methods, especially RNA-Seq, but it is not known how many of these transcripts are translated. Leveraging the unprecedented capabilities RNA-Seq, we created a bioinformatics pipeline that enables the discovery of novel splice-junction peptides. Novel splice-junction sequences were retrieved from the RNA data using Bowtie and Tophat software, and then RNA sequences were translated into the analogous polypeptide sequence in order to create a customized splice-junction database. This customized database was searched against high-resolution, shotgun mass spectrometric data and used to discover splice-junction peptides representing an array of different splicing events, including skipped exons, alternative donors and acceptors, non-canonical transcriptional start sites, and fully unannotated exon-exon connections. More recently, we have also used RNA-Seq data to detect peptides containing amino acid changes resulting from non-synonymous single nucleotide polymorphisms (SNPs) and insertions and deletions (indels). In this talk, we will present both the bioinformatics pipeline and analytical methods used for the discovery of novel protein variations.

(196) **Yb fiber Oscillator Developed for Laser-Induced Breakdown Spectroscopy**

Bai Nie, Greg Parker[1], Vadim Lozovoy[1], Marcos Dantus[1]; [1]Michigan State University

A Yb fiber oscillator, producing up to 450 nJ clusters of femtosecond pulses, is developed. This laser is tested for laser-induced breakdown spectroscopy (LIBS) on several samples, such as cu, brass, aluminum alloys, $PbNO_3$ films and a galena rock. Due to the high pulse energy of the pulse cluster and the fact that individual sub-pulses have pulse durations of ~100fs, this laser is capable of generating strong LIBS signals with low fluence threshold and insignificant continuum background. To the best of our knowledge, this is the first time that a Yb fiber oscillator or noise-like pulses are used for LIBS. Due to the

great performance and simple design, this laser can be an ideal candidate for the light source of portable LIBS systems.

(197) **Confocal Raman Spectroscopy: An Efficient Tool for the Fine Characterization of Single Electrospun Nanofibers**

Marie Richard-Lacroix, Christian Pellerin; [1]University of Montreal

Electrospinning is a widely used technique for producing continuous fibers with diameters ranging from a few microns to a few hundreds of nanometers. These fibers find application in domains such as catalysis, tissue engineering, filtration, biosensors, drug delivery, and electronic devices. However, their widespread application is limited by a lack of control and understanding of their properties because most techniques only provide bundle-averaged values for parameters such as crystallinity and molecular orientation. Here, we demonstrate that confocal Raman spectroscopy is a powerful tool for the fine characterization of molecular orientation and structural characteristics in single electrospun nanofibers with diameter down to 500 nm based on highly reproducible spectra with good signal-to-noise ratio, using poly(ethylene terephthalate) as a model system. Unlike other techniques, Raman spectroscopy offers the unique advantage of giving access to quantitative information on both the crystalline and the amorphous phases of these nanoscale materials. Our results reveal a broad distribution of orientation from fiber to fiber: some individual fibers are completely isotropic and amorphous while others present a orientation parameter as large as 0.75. The development of this large orientation happens through the formation of a highly oriented mesophase, a pre-crystalline phase that cannot be detected by any other technique at the nanofiber scale.

(198) **Analytical Performance of a Solution-Cathode Glow Discharge for Optical Emission Spectrometry with an Interference-Filter Wheel Spectral Sorter**

Andrew Schwartz[1], Steven Ray[1], Gary Hieftje[1]; [1]Indiana University

The solution-cathode glow discharge (SCGD) has enjoyed increasing interest over recent years due to the promise it shows as an alternative source for optical emission spectrometry (OES). In comparison to more conventional plasma sources (such as the inductively coupled plasma [ICP]), the SCGD is simple in design, inexpensive, requires no sample-solution nebulizer or compressed gasses, and operates at low DC powers (~70 W). Moreover, the SCGD offers performance competitive with more complex sources; detection limits are generally comparable to and in some instances better than those achievable with radially-viewed ICP-OES. Earlier work demonstrated that spectra produced by the SCGD are simple. Only the most intense atomic emission lines are observed, whereas ionic emission is weak or absent. Further, the continuum background produced by the source is weaker than that observed from some other plasmas, such as the ICP. As a result of this reduced background and a lowered likelihood for spectral interferences, the SCGD is an attractive source for use with lower-resolution, broader-bandpass methods of spectral sorting. Here, a simple, inexpensive wheel outfitted with several interference filters will be evaluated as a spectral-discrimination device for SCGD-OES. Analytical performance of the source with the wide bandpass (10 nm full-width half-maximum) filters will be critically compared to its performance with a traditional higher-resolution monochromator, with emphasis on limits of detection, linear range, and signal stability.

(199) **Emerging Trends in Infrared Spectroscopic Imaging: From Theory to Therapy**

Rohit Bhargava[1]; [1]Univ of Illinois at Urbana-Champaign

The use of label-free methods for imaging is rapidly emerging as an alternative to conventional labeling techniques. In particular, the use of spectroscopy to image molecular content is termed chemical imaging. We present here progress in a chemical imaging approach based on mid-infrared spectroscopic imaging that combines the spatial specificity of optical microscopy with the molecular selectivity of vibrational absorption spectroscopy. Instead of directly imaging probes, recorded data are related to the structural and functional state of the biological material using computation. This process, as has been realized over the past 3 years, is not straightforward and requires a deep understanding of the underlying optical physics. An overview of the recently developed theory is provided. Next, a computational strategy and statistical considerations underlying decision-making are described. It is now becoming clear that a combination of theory, re-designed instrumentation and signal processing forms an integrated approach to biochemical analyses. Our laboratory focuses, among other topics, on the analysis of biological materials for histopathology. Development of this technology will enable the rapid analysis of cells and tissue by fingerprinting the inherent biologic content, extraneous materials and metabolic state without the use of probes. In a variety of applications, we first describe attempts to diagnose and grade cancer in breast and prostate biopsies without human input. Results indicate that a rapid assessment of lesions is possible with high accuracy and their lethality may be predicted using a systems approach to pathology. Applied to engineered 3D tissue models for breast tumors, we show that the imaging technology is useful in rapidly assessing culture quality and that the model systems can act to inform researchers about the involvement of different cell types in cancer progression. Finally, we provide an overview of potential future directions and applications that will emerge from these studies.

(200) **Nano Scale - Mega Challenge? Raman Spectroscopy Approaching Molecular Dimensions**

Volker Deckert[1]; [1]Institute for Photonic Technology

Raman spectroscopy like many other analytical techniques constantly faced the challenge to probe smaller numbers of molecules. The challenge has two aspects: the number of analyte molecules can be restricted by a low concentration or by the sampling volume. With the advent of Raman microscopes, the sampling volume was shrinking dramatically, however, the small sampling volume was matched by the almost ideal collection efficiency of microscope objectives and also the high intensity at the sample spot due to very tight focussing of the laser beam. Hence, shifting towards smaller sample volumes provided even better signal-to-noise-ratio. Still the number of probed molecules in a microscope focus is rather high ~109 - 1012. Because of the diffraction limit smaller volumes could be only achieved by near-field optical methods. Instead of diffractive or refractive optics, light delivered via a sub-wavelength sized aperture can illuminate areas that are essentially limited by the size of that aperture. While this approach works, a serious limitation is the power that can be delivered through an aperture and the number of molecules that are irradiated. Hence, this approach worked only under well controlled conditions e.g. resonance Raman or surface enhanced Raman. The aperture based near-field optical approach towards Raman spectroscopy of minute amounts of sample demonstrated the need for additional amplification of the signal. This can be achieved by the combination of near-field optics and plasmon enhancement. Interestingly, both effects are intrinsically linked. A nanoscale gold or silver particle will show a plasmon resonance that enhances the electromagnetic field close to the sample and consequently also enhances the Raman signals of molecules in the vicinity. Furthermore, the plasmons are confined to the surface and specific areas of the particles, such further decreasing the sampled volume. Consequently sampling areas of less than 10 nm in diameter have been shown. This high spatial resolution allows to investigate even sub-sections of large molecules or the local behavior of specific molecules. While the signal intensity is usually not the main problem, signal fluctuations due to diffusion, orientation effects, influence of probe and surface, can make an interpretation quite challenging. The possibilities of such techniques for instance change the concept of

concentration or dilution in small dimensions. Considering all the possibilities and challenges nanoscale Raman spectroscopy is just scratching the surface of potential new applications.

(201) **Environmental Discourses in Borana Oromo: A Focus on Narratives**

Teshome Tafesse[1]; [1]Addis Ababa University

This study explored the discourses of environmental narratives as an organized, viable, and dynamic social force basic to the creation and dissemination of environmental messages in Borana Oromo of the southern Ethiopia. Under this major objective, the study discovered environmental beliefs and values, investigated environmental knowledge, power and ideology, and identified environmental positions the community has situated itself in. The study employed a qualitative approach in the analysis of data gathered through semi-structured interviews, focus group discussions, and extended participant and non-participant observations. The analysis was based on Fairclough's three-dimensional methodological approach of discourse analysis, which is helpful for elaborating empirically based theories.

The findings revealed dominant environmental beliefs and values, which are organized under discourses of environmental necessity and survival, scarcity and security, hopelessness, inclusion and exclusion, seniority, responsibility, and obedience and disobedience. The findings also unveiled that Borana narratives are embedded with environmental ideologies- interdependence and communalism, which are deep rooted in the social, cultural, religious and political context of the community. The findings, as part of the environmental discourses, also investigated aspects of the indigenous environmental knowledge of the Borana community. The findings also revealed that human-environment power relationships in the narratives are manifested in many ways including humans' possession of environmental knowledge and struggle to secure their lives (both materially and spiritually). The study also disclosed two dominant environmental positions-ecocentrism and restrained anthropocentrism that humans assume in their interactions with the natural environment in the community.

The significance of the study, thus, principally lies on what makes sense locally concerning modern environmental communication. The study contributes to the field of environmental discourse analysis both theoretically and practically, and offers implications for environmental workers, policy designers, educators, and curriculum developers.

(202) **Screening Method for Emerging Contaminants; For Ethenylestradiol and Chlormadinoneacetate, in Water by Derivative Spectrophotometry**

M. Ines Toral[1], Diego Pino[1], Gabriela Arriagada[1], Romina Otipka[1], Cesar Soto[2], David Contreras[2], Jorge Yanez[2]; [1]University of Chile; [2]University of Concepcion

At present, various unregulated contaminants denominated "emerging contaminants", have been found in water, some relevant examples of these compounds are: surfactants, pharmaceuticals, personal care products, gasoline additives, flame retardants, antiseptics, industrial additives, steroids, hormones and subproducts of water disinfection.In the present work, has been developed a screening method for the determination of ethenylestradiol (EE) and chlormadinoneacetate (ACM) in water samples by derivative spectrophotometry. In first instance, were obtained the spectra of the standard for both individual drugs dissolved in acetonitrile, the obtained spectra were overlapping, opting for using derivative spectrophotometry. Were selected second order, smoothing factor 8,000, scale factor 10,000 and λanal 291.8 and 296.6 nm for determining ACM and EE, respectively. With standards and differents relations of ACM / EE between 10/1 and 1/10 were obtained recovery percentages near to 100% with RSD < 2%. In these conditions were obtained limits of detection (LOD) and limits of quantification (LOQ) for ACM 3.43 x 10-7 M and 1.04 x 10-6 M, for EE 6.56 x 10-7 M and 1.99 x 10-6 M, respectively, obtained of the follow equation DU= 9.81 x 105 C + 1.43; DU = 2.94 x 105 C + 0.37 and blank deviation for ACM and EE, respectively. In order to increase the sensitivity, was performed a liquid-liquid extraction (15 min) from 50 mL of aqueous solution with 5 mL of chloroform, then it was removed with nitrogen and the remaining solids were redissolved in 5 mL of acetonitrile, which was evaluated in the conditions selected, under these conditions was achieved LOD and LOQ increased 10 times. This method was applied for the determination of ACM and EE in drinking water. To perform the determination of ACM and EE in drinking water, this was spiked with a mixture of both drugs and NaCl, in order to obtain lower concentrations and avoid mistakes in weighing. The recovery percentages were 84.3 ± 6.4% and 75.3 ± 2.7% for ACM and EE, respectively. In this context, the proposed method can be an excellent alternative as screening method from to chromatographic methods. The authors thank FONDECYT Project 1100103 and DIUC 2010021029-10.

(203) **Silica Nanoparticles Releases Fertilisers and Fungicides Slowly in Soil**

Erastus Gatebe, Harrison Wanyika[1], Paul Kioni[2], Zhiyong Tang[3]; [1]JKUAT; [2]DKUT; [3]National Center for Nanoscience and Nanotechnology

Nanotechnology-based agrochemical delivery systems would ensure efficient and economical utilization of these very important agricultural inputs. In this study, mesoporous silica nanoparticles with particle diameters of ~150 nm and pore sizes of ~2.5 nm were synthesized via liquid crystal templating mechanism. Urea , as a model agrochemical molecule, was entrapped in the mesopores of the siliceous material by simple immersion loading using aqueous urea solutions. About 15.5% (w/w) of urea was loaded inside the pores mainly by physisorption while the total adsorption capacity of mesoporous silica nanoparticles could reach up to 80% (w/w). Highly concentrated urea solution was found to be more effective due to high driving concentration gradient generated. Release process of the urea-loaded mesoporous silica nanoparticles in water and soil indicated a two stage sustained slow release-profile. The findings for soil release studies revealed at least

fivefold improvement in the release period. By the ability to entrap urea guest molecules into its mesopores and release them in a controlled manner, mesoporous silica nanoparticles demonstrated its great potential as a nanocarrier for agrochemicals.

(204) **Development of PVC Calibration Standards Having Elemental Mass Fraction Values Traceable to Values for Standard Reference Materials (SRM)**

John Molloy[1], Matthew Boyce[1], Caroline Bibb[1], John Sieber[1]; [1]National Institute of Standards and Technology

The Consumer Product Safety Improvement Act (CPSIA) was passed to restrict the levels of hazardous elements and compounds in children's products and consumer goods. Due to the broad range of substances incorporated into such products, new reference materials of appropriate matrices are needed for method validation and traceability to the International System of Units (SI). NIST is working to develop a SRM incorporating lead, cadmium, and other elements in a polyvinyl chloride (PVC) matrix. Most elemental analysis methods perform best when calibration standards and unknowns are of similar chemical and elemental compositions. Therefore it was necessary to develop a procedure to create PVC calibration standards in disk form. The ideal calibrants would be PVC containing homogeneous distributions of the elements of interest with the mass fractions of the elements traceable directly to other NIST SRMs. Disk form specimens are created from powdered,

virgin PVC resin mixed with aliquots of SRM 3100-series, dilute acid, single element solutions. These samples were analyzed using a variety of methods including Wavelength Dispersive X-ray Fluorescence (WDXRF), Laser Ablation Inductively Coupled Plasma Mass Spectrometry (LA-ICP-MS), and Inductively Coupled Plasma Optical Emission Spectroscopy (ICP-OES) for which these disks can be used as validation materials. This poster will explain the method for fabricating these disk-form calibration standards, and the associated measurement challenges that are present. It is anticipated that this process will be useful to any laboratory that performs quantitative elemental analyses of PVC.

(205) **Heavy Metals Levels in Urban Gardens and lawns**

Ibrahim Saeed[1], John Peters[1]; [1]University of Wisconsin-Madison

The US Environmental Protection Agency (EPA) estimates that about 80 millions US households dump nearly 90 millions pounds of agricultural chemicals on lawns in a year. It was well established that most of these chemicals contain heavy metals in trace amounts which may pose a hazard to human health and to the environment. A study was conducted to determine the levels of nine heavy metals in soil samples collected by owners from urban gardens and lawns in the city of Madison, WI and its surroundings. The dry soil samples were acid digested and then run through an Inductively-coupled plasma optical emission spectrometer (ICP-OES) calibrated for the simultaneous determination of the nine heavy metals. Results showed that lead was by far the element with the relatively highest concentration, while cadmium was the element with the lowest concentration. The average concentrations of the other heavy metals were found to be in the following order Zn>Cu>Cr>Ni>Li>Co>As. It was concluded that the relatively high levels of lead in these urban soils may be due to the peeling off of lead paint from old houses around which these gardens and lawns are located. It was recommended that urban gardeners whose gardens are close to old homes, screen their soil for the presence of lead and may be for other heavy metals as well.

(206) **The Qualitative Identification of Metals in Shisha Steam Stones Using ICPMS**

Amberlie Clutterbuck[1]; [1]University of Cincinnati

Over the last few decades, a substantial amount of evidence has been collected surrounding the constituents, addictive properties, and serious health effects of cigarette smoking, while little (but growing) parallel information has been performed and collected on hookah smoking. Heavy metals are one of the many tobacco smoke constituents that have been studied in cigarettes, as well as hookah tobacco. Due to the mounting evidence that cigarette smoking is detrimental to health, tobacco companies have been trying to develop and sell alternative tobacco substitutes, such as 'steam stones'. In terms of the potential health risks of inhaling vapor from using the steam stones, nothing is currently known. Two brands of steam stones, (Mya and Shiazo) flavor coating included, underwent a hot water extraction and were analyzed with an Agilent 8800 inductively coupled plasma triple quadruple mass spectrometer (ICP-QQQ). It appeared that both the Mya and Shiazo brand had Na, Mg, Ca, and K in the ppm range. The trace metals found in the Mya and Shiazo brand were V, As, Cd, and Pb in the ppb range. Finally, of all the trace elements (V, As, Cd, Pb), As seemed to be the most obvious difference between Mya and Shiazo. After determining the total metal analysis of the stones with the flavor coating, the metal content of the coating itself was determined to see what, if any, metals were present. The future work involves determining the total metal analysis as well as the toxic organic compounds given off by both the smoke that a hookah user could be exposed to during one smoking session as well as the charcoal heating source using SPME-GCMS.

(207) **Comparison of Trace Metals in Ricochet Bullets to Their Corresponding Cartridges and Ricochet Marks**

Victoria Robideau[1], Jason Hamilton[1], Guido Verbeck[1]; [1]University of North Texas

Bullet identification is an important part of crime scene reconstruction and has traditionally centered on striation matching using a comparison compound light microscope. Striations are molded by the rifling inside the barrel as the bullet exits the gun, creating a unique pattern specific to each firearm. However, in the case of a ricochet, it contorts; therefore distinguishing striation pattern can be challenging, if not impossible. The forensic community would benefit immensely from the implementation of a new method for the investigation of ricocheted projectiles. Using laser ablation inductively coupled mass spectroscopy (LA-ICP-MS) the surface of ricochet and non- ricochet copper bullet jackets were ablated to identify the trace metal compositions. The ablated bullets were then matched to the cartridges that also had comparable levels of trace metals. Key trace metals were identified on the exterior, notably aluminum, magnesium, tin, and zirconium. By measuring the quantities of these impurities, ricochet bullets can be matched to the corresponding cartridge. An additional method established is to match the residue from the mark on the ricochet surface to the bullet that produced it.

(208) **Infrared Multiple Photon Dissociation Action Spectroscopy of Proton-Bound Dimers of Cytosines: Effects of Modifications on Base-Pairing Conformations**

Bo Yang[1], Mary Rodgers[1]; [1]Wayne State University

The DNA *i*-motif conformation was discovered in (CCG)•(CGG) trinucleotide repeats, which are associated with fragile-X syndrome. The *i*-motif DNA secondary structure involves proton-bound dimers of cytosine. It has been found that methylation of cytosine results in silencing of the FMR1 gene and a deficiency of its protein product, fragile X mental retardation protein, leading to the fragile-X syndrome. The *i*-motif DNA secondary structure is a four-stranded structure consisting of parallel-stranded DNA duplexes zipped together in an anti-parallel orientation by intercalated proton-bound dimers of cytosine (C^+•C). Previous studies has shown that methylation at the N1 position of cytosine does not alter the structure of the proton-bound homo dimers. However, whether modifications at the C5-position of cytosine will cause formation of rare tautomers and alter the structure of the proton-bound dimer is presently unknown. Therefore, the gas-phase structures of proton-bound dimers of cytosine and modified cytosines and their d_6-analogues generated by electrospray ionization are probed via infrared multiple photon dissociation (IRMPD) action spectroscopy and theoretical electronic structure calculations. The modified cytosines examined include: the 5-methyl-, 5-fluoro- and 5-bromo-substituted species. IRMPD action spectra of seven proton-bound dimers exhibit both similar and distinctive spectral features over the range of ~2600–3700 cm^{-1}. The IRMPD spectra of all of these proton-bound dimers are relatively simple, but exhibit obvious shifts in the positions of several bands that correlate with the properties of the substituent. The measured IRMPD spectra are compared to linear IR spectra calculated for the stable low-energy tautomeric conformations, determined at the B3LYP/6-31G* level of theory, to identify the conformations accessed in the experiments. Comparison of the measured and calculated IR spectra indicates that only a single conformation, the ground-state structure, is accessed for all proton-bound homodimers, whereas the ground-state and a small population of the first-excited tautomeric conformations are accessed for all proton-bound heterodimers.

(209) **Imaging the Ion Beam in the Second Vacuum Stage of an ICP-MS Using Planar Laser-Induced Fluorescence**

Alisa J. Edmund[1], Scott D. Bergeson[2], Paul B. Farnsworth[1]; [1]Department of Chemistry and Biochemistry, Brigham Young University; [2]Department of Physics and Astronomy, Brigham Young University

Inductively coupled plasma mass spectrometry (ICP-MS) is an especially sensitive analytical technique because the plasma source creates an intense beam of analyte ions. One challenge associated with such an intense ion beam is that the coulombic repulsion by the ions makes consistent focusing of the beam difficult. In an ICP-MS the total ion flux varies with sample matrix, even when the concentration of a target analyte remains fixed. The resultant changes in charge density can affect ion beam focusing and ion transmission into the mass analyzer. These "space charge" effects are thought to be a source of matrix effects that are unique to analyses by ICP-MS.

In previous work we imaged a cross section of a Ca ion beam at the entrance to the mass analyzer in a commercial Varian 820 ICP-MS[1]. From this work it was determined that the beam from a solution containing only Ca analyte behaved as predicted by SIMION simulations. However, the addition matrices altered the beam trajectory, particularly with the addition of heavier matrices; while the matrix additions had only minor effect on beam shape. The most prominent effect was observed with the Pb matrix, which caused an order-of-magnitude drop in the Ca signal intensity of the mass spectrometer due to a shift in the direction and location of the Ca ion beam at the entrance into the mass analyzer. This work expands the previous work and will present images of a Ba ion beam. Images of a heavier analyte such as Ba will give greater insight into the shifting and distortion of the ion beam due to analyte concentration and matrix composition.

[1] A.J. Edmund, S.D. Bergeson, M. Lyon, N. Taylor, I. Kalinitchenko, P.B. Farnsworth. Evaluation of space charge effects in the second vacuum stage of a commercial inductively coupled plasma mass spectrometer by planar laser-induced fluorescence imaging, Spectrochim. Acta, Part B, 76 (2012) 109-118.

(210) **Absolute Number Densities of Helium Metastable Atoms in Helium-Based Discharges Used as Ambient Desorption/Ionization Sources**

Charlotte Reininger[1], Kellie Woodfield[1], Paul B. Farnsworth[1]; [1]Brigham Young University

Plasma sources have shown to be fast and effective ionization sources in the rapidly developing field of ambient ionization-mass spectrometry. Most proposed mechanisms for helium plasma-based ambient desorption/ionization (ADI) sources include energy transfer by collisions from helium metastable atoms, either directly to the analyte or to another intermediate species that then leads to analyte ion formation. Helium metastable atoms also play a crucial role in sustaining helium discharges. It follows, then, that the number density of helium metastable atoms in a discharge source should be a good indicator of source performance, and spatial distributions of the reactive atoms may provide valuable insights into ionization mechanisms. We have designed and built a laser based absorption spectrometer to determine absolute number densities of helium metastable atoms in helium plasmas. Line profiles also contain information on gas temperatures in the form of the Doppler contribution to the overall line width. In this presentation we will describe the development and use of our laser-based absorption spectrometer to measure absolute number densities of helium metastable atoms and plasma gas temperatures in helium-based discharges. We will present initial results from a high-frequency Dielectric Barrier Discharge (DBD) and from a Low-Temperature Plasma (LTP).

(211) **Infrared Multiple Photon Dissociation Action Spectroscopy of Protonated Nucleosides: Gas Phase Conformations and Energetics**

Mary Rodgers, Ranran Wu[1]; [1]Wayne State University

Nature uses protonation to alter the structures and reactivities of molecules to facilitate various biological functions and chemical transformations. For example, in nucleobase repair and salvage processes, protonation facilitates the nucleobase removal by lowering the activation barrier for glycosidic bond cleavage. Systematic studies of the structures of protonated 2'-deoxyribonucleosides and ribonucleosides may provide insight into the roles protonation plays in altering the nucleobase orientation relative to the glycosidic bond and sugar puckering. By comparing the structures of the protonated RNA nucleosides to their DNA analogues, the effect of the 2'-hydroxyl moiety may be elucidated. In this study, infrared multiple photon dissociation (IRMPD) action spectroscopy experiments in conjunction with electronic structure calculations are performed to probe the effects of protonation on the structures and stabilities of 2'-deoxyadenosine (dAdo), 2'-deoxycytidine (dCyd), 2'-deoxyguanosine (dGuo), thymidine (dThd), 2'-deoxyuridine (dUrd), adenosine (Ado), cytidine (Cyd), guanosine (Guo), Uridine (Urd) and 5-Methyluridine (Thd). Photodissociation as a function of IR wavelength was measured to generate the IRMPD action spectra. Geometry optimizations and frequency analyses are performed at the B3LYP/6-311+G(d,p) level of theory to characterize the stable low-energy structures and to generate their linear IR spectra. Single point energy calculations are performed at the B3LYP/6-311+G(2d,2p) and MP2(full)/6-311+G(2d,2p) levels of theory to provide relative energetics for the optimized conformations. The structures that are accessed in the experiments are then determined by comparing calculated linear IR spectra for the stable low-energy conformers to the measured IRMPD action spectra.

(212) **Hookah Smoking: Which is Worse – The Tobacco or the Charcoal?**

Ryan Saadawi[1], Matt Winfough[1], Traci Hanley[1], Julio Landero[1], Joseph Caruso[1]; [1]University of Cincinnati

Hookah smoking has been popular in the Middle East and surrounding regions for ages and its use is emerging rapidly in Western cultures making it imperative to study various aspects that may result in harm to the smoker, such as toxic trace metals, PAHs, etc. Many studies have been performed on cigarette, cigar, and pipe tobaccos while virtually no studies for these toxins have been performed on hookah tobacco. It is well documented the other tobaccos are known to contain toxic metals such as As, Cd, Cr, and Pb. However, little is known about the metal content in hookah tobacco formulations (e.g. tobacco, glycerin, honey and flavorings1. Charcoal, the heat/combustion source in hookah smoking is far different than burning cigarettes and cigars. Experiments show that some charcoal brands may have as high as 10 μg/g of arsenic, making an in depth study on charcoal imperative to assess not only total metals, but metal speciation (forms), particularly for toxic metals. Microwave assisted digestion in combination with ICP-MS was utilized to elucidate the toxic metal content in both charcoal samples and in an array of different brands/flavors of hookah tobacco smoke. Polycyclic aromatic hydrocarbons were extracted from hookah tobacco smoke using an organic solvent and analyzed by HPLC florescence detection. While the As totals are thought to be unacceptably high, clearly we must investigate which forms of As are present. Hence, a speciation study was undertaken to assess which inorganic or organoarsenicals are present in the charcoal neat and in the smoke.

1--Saadawi, R.; Landero Figueroa, J. A.; Hanley, T.; Caruso, J., The hookah series part 1: total metal analysis in hookah tobacco (narghile, shisha) - an initial study. Analytical Methods 2012, 4 (11), 3604-3611.

(213) **Optimization of MALDI-TOF ISD (In-Source Decay) for Protein Analysis**

John McDaniel[1], Amanda Bulman[1]; [1]Bruker Daltonics

Matrix Assisted Laser Desorption/Ionization (MALDI) mass spectrometry is a powerful tool in proteomic analysis. This technology can be used for intact protein sequencing (Top Down Sequencing, or TDS) through the use of In-Source Decay (ISD) techniques. By using specific matrices, it is possible to identify proteins with high levels of certainty and to perform *de novo* protein sequencing. However, minor changes in sample preparation or crystallization can lead to vast differences in the quality of the results, and the process of obtaining results is often difficult and time consuming. The optimization of MALDI-TOF ISD sample preparation and data collection will make the technology both more efficient in commercial use and more effective in a research setting. By experimenting with a number of variables, including the matrix, matrix solvent, concentration of the sample, pH of the sample, additives, application of the sample to the target plate, laser type/setting and collection parameters, it is possible not only to improve the data collection process, but also to improve the data quality and the completeness of TDS results. Bovine Serum Albumin (BSA) was used to test these variables and identify successful preparations. BSA was selected due to its wide availability and common use in analytical chemistry, as well as its tendency to decay only from the N-terminus, which simplified analysis and comparison. Initially, seven matrices were tested: DAN, SDHB, SA, CHCA, DHAP, MSA and DHB. After testing these matrices, it became clear that SDHB produced the best results, even in comparison with the popular ISD matrix DAN. While some of the matrices produced satisfactory results under very specific conditions, SDHB produced long ISD chains suitable for high-certainty protein identification under the majority of preparation conditions with the collection of data remaining straightforward (though some conditions did produce better results than others). These outcomes suggest that the refinement of SDHB as an ISD matrix will yield one or more preparation method that produce consistent results with a variety of protein targets.

(214) **Plasma Hydrodynamic Expansion and Relation to fs-LA-ICP-MS Signal Intensities and Elemental Fractionation**

Nicole LaHaye, Prasoon Diwakar[1], Sivanandan Harilal[1], Ahmed Hassanein[1]; [1]Purdue University

Laser ablation-inductively coupled plasma-mass spectrometry (LA-ICP-MS) is a commonly used solid sample mass analysis technique. Laser ablation (LA) is preferable to other sample introduction techniques because it allows for direct analysis of solid samples without preparation and requires a smaller sample size. LA, however, faces several challenges in accuracy and precision of results, one of which is elemental fractionation, defined as the change in elemental ratio as a function of time or the preferential ablation of particular elements in the sample. The use of femtosecond (fs) lasers for ablation is preferable to nanosecond (ns) lasers due to the lack of melting and thermal effects, which can increase elemental fractionation and cause collateral damage to the sample. Typically Ar and He gases are frequently used for transporting the aerosol from the LA to ICP transport and these gases affect the hydrodynamics expansion features of ablation plumes. The presence of ambient gas during laser ablation may lead to several interesting features which include plume splitting, instability formation, confinement, etc., and extensive studies have been carried out on this topic for ns LA plumes. However, the hydrodynamics of fs laser-produced plasmas are not well understood. This work investigated brass plasma hydrodynamic expansion features at high ambient pressure, typical of LA sample introduction to ICP-MS. Brass was chosen as a sample due to its well-documented fractionation effects, influenced by the differences in melting and vaporization temperatures of copper and zinc. Spectrally integrated, as well as spectrally filtered Cu (510 nm line) and Zn (481 nm line), ICCD images were taken to investigate plume expansion. In addition, spectroscopy was used to determine plasma density and temperature at various times. This work was correlated with ICP-MS results, Cu/Zn ratio, and signal RSD.

(215) **Provenance Study of Native Copper using fs-LA-ICP-MS**

Prasoon Diwakar[1], Harold Cooper[1], Sivanandan Harilal[1], Ahmed Hassanein[1]; [1]Center for Materials Under eXtreme Environment, School of Nuclear Engineering Purdue University, 500 Central Drive, West Lafayette, Indiana

Native copper, i.e., naturally occurring pure (>99% Cu) metal, was used for tools, adornment, and objects of spiritual significance by many different indigenous groups in North America prior to the arrival of Europeans. In addition to its widespread use over several millennia in eastern North America, it was also used by Native People in the Arctic, Subarctic, and Northwest Coast culture areas. The relationship, if any, between the origins of copper technology in these three culture areas is unknown. Identifying a method to distinguish geological sources of native copper within, and between these regions could help to identify the movement of this valuable raw material and its associated technology within and among communities across northwestern North America. This study presents the results of a pilot study using elemental and isotope analysis to distinguish between geological samples of native copper from sources in the Subarctic and Arctic regions. The fs LA-ICP-MS was used to identify major as well as trace elements and isotopes to track the source of the samples. For feasibility study, 17 samples in the form of nuggets were used from different sources. For the LA-ICP-MS study, 800 nm, 100 fs, 200 μJ pulses were used for ablation. Isotopes analyzed include 63Cu, 65Cu, 75As, 206Pb, 207Pb, 208Pb, 107Ag, 109Ag, 78Se, and 80Se. For analysis of the data, 2-D, 3-D correlation plots and statistical clustering analysis was performed using the ICP-MS data. The study showed that by using appropriate elements and isotopes and by applying appropriate statistical tools, fs-LA-ICP-MS could be used for provenance study of different kind of samples satisfactorily including geological samples and this could be further enhanced through optimization of such statistical tools.

(216) **Analysis and Discrimination of Inkjet Inks from Different Manufacturers using DART-MS**

Anna Raeva[1], Rhett Williamson[1], José Almirall[1]; [1]Florida International University

The analysis of printing inks is important in identification of counterfeit and fraudulent documents and for associating ink formulations from the same manufacturing source. In this study, 75 inkjet inks from different manufacturers were analyzed using an Ionsense direct analysis in real time (DART) as an ionization source and coupled to an Agilent 6530 Q-TOF mass spectrometer (MS). The polyethylene glycol (PEG) distributions provided MS information that could be used to distinguish between inkjet formulations for each ink analyzed. Simple visual comparisons of the spectra and linear discriminant analyses were used to differentiate between ink samples. It was found that, in most of the cases, inkjet inks from different manufacturers can be distinguished and inkjet inks from the same source produce similar DART-MS patterns. Mixtures (color samples) provide more analytical challenges. The spectra of inkjet inks exhibit PEG-like distributions (one or more series of ions 44 Da apart). It was also determined that DART-MS spectra of inkjet inks stored for over a month exhibited the same characteristic peaks as the original but relative intensities of peaks could change. DART-MS is demonstrated as a powerful analytical technique for the analysis and discrimination of inkjet printing inks.

(217) **Detection of Counterfeit Electronics through Ambient Mass Spectrometry and Chemometrics**

Kevin Pfeuffer[1], Jack Caldwell[2], Steven Ray[1], Gary Hieftje[1]; [1]Indiana University, Department of Chemistry; [2]Naval Surface Warfare Center, Crane, Indiana

Counterfeit electronic components have become an insidious problem for government as well as consumer applications. "Counterfeit electronics" refers to components, usually integrated-circuit chips, that have been mis- or re-labeled as having higher specifications or more recent manufacture date in order to be sold for a higher price. This problem has become troublesome as supply chains and manufacture have globalized, making it more difficult to monitor product origin and history. A common mechanism of counterfeiting is "blacktopping", in which a portion of the surface of a chip is removed and a new surface and lettering is substituted. Here, ambient mass spectrometry is coupled with chemometric approaches to distinguish between fake and authentic chips. Testing for counterfeit chips is typically done by a third party that relies on visual inspection/microscopy and solvent testing for residues, with results interpreted by a skilled operator. However, advanced techniques have been used, including x-ray fluorescence (XRF) spectrometry and X-ray imaging. Although effective, these techniques can be time-consuming, especially for large numbers (1000s-100K) of chips. Additionally, results can be subjective and rely on training and experience of the operator. In the present study we use an ambient desorption/ionization mass spectrometry source (the Flowing Atmospheric-Pressure Afterglow or FAPA) to examine the surface of chips and chemometric techniques for chip classification. Genuine chips, epoxy blanks and counterfeit chips were all examined with FAPA-MS to identify MS fingerprints for classification. Initially, unsupervised principal component analysis (PCA) was applied to normalized mass spectra for successful classification. However, the classification power of PCA is based primarily on visual grouping and does not offer a quantitative assessment of match probability. In contrast, the Bootstrapped, Error-Adjusted, Single-sample Technique (BEAST) provides a quantitative indication, in terms of standard deviations, of whether a new sample is part of the training set. In the present application, the BEAST indicates whether an unknown sample is part of the genuine or counterfeit sample sets.

(218) **Plasma Sheath Effects in the Sampler and Skimmer Cones of the ICP-MS**

Matthew Zachreson[1], Ross Spencer[1]; [1]Brigham Young University

In the ICP-MS, plasma neutrality and the associated issue of the plasma potential are governed by what happens in the plasma sheath. Plasma sheaths can generally be described by two model types: collisional, where the Debye length is long compared to the mean free path; and collisionless, where the mean free path is long compared to the Debye length. In the sampler cone, the Debye length is .3 micrometers, while the ion mean free path is 5 micrometers, nearly in the collisionless regime. In the skimmer cone, the Debye length is 2 micrometers, while the ion mean free path is 400 micrometers, well into the collisionless regime. Doing a full calculation with the Direct Simulation Monte Carlo algorithm, FENIX, would involve simulating electron physics, performing electrostatic field calculations, and resolving the small Debye length, all of which are computationally expensive. To approximate sheath formation in the sampler and skimmer, a forced ion flux model is made by first estimating the number of ions per second that should recombine at the wall using a simple, planar, collisionless sheath model, and then forcing the ions near the wall to have that flux by modifying their velocities each time step. The ion loss through the sheath results in a steep drop in the ion density at the nozzle wall which both diffuses and is sheared by the nozzle flow. Another plasma effect is that the sheath inhibits electron flow to the wall, greatly reducing thermal conduction to the wall. This means that the electron temperature of the plasma in the nozzle is hardly affected by the presence of the metal wall. In particular, setting the electron temperature equal to the wall temperature at the wall is inappropriate.

(219) **Desorption Electrospray Ionization Mass Spectrometry Imaging of an Endophytic Penicillium sp. Reveals the Spatial Distribution of Novel Polyhydroxyanthraquinone Constituents**

Alan Jarmusch[1], Mario Figueroa[2, 3], Huzefa Raja[2], Tamam El-Elimat[2], Jeffrey Kavanaugh[4], Alexander Horswill[4], Nadja Cech[2], Nicholas Oberlies[2], R. Graham Cooks[1]; [1]Purdue University; [2]University of North Carolina at Greensboro; [3]Universidad Nacional Autonoma de Mexico; [4]University of Iowa

New antibiotic strategies are currently needed in the treatment of drug resistant bacteria such as MRSA, VRSA, and drug-resistant *Klebsiella pneumoniae*. In the US alone, methicillin-resistant *S. aureus* (MRSA) causes more fatalities on an annual basis than all other bacterial pathogens or even HIV/AIDS. Anti-virulence therapies, one potential strategy, might utilize natural products which target non-essential pathways in bacteria related to pathogenesis. In the search for fungi derived anti-virulent compounds, an endophytic *Penicillium* sp. (G85) was isolated from the stem of a milk thistle plant [*Silybum marianum* (L.) Gaertn. (Asteraceae)] that produced distinct red guttates. A series of ten polyhydroxyanthraquinones were isolated, six of which were new to the literature, which all possessed quorum quenching activity in bioassays against *S. aureus* strains derived from community-associated MRSA. Reactive desorption electrospray ionization (DESI) played a role in confirming the structure of one novel polyhydroxyanthraquinone using phenylboronic acid derivatives, which selectively react with cis-diol functionalities. MS imaging using DESI was employed to investigate the spatial distribution of the endogenous constituents, including the polyhydroxyanthraquinones, revealing unique spatial distributions. Plotting of the data in two dimensions across the fungal surface and through the culture medium revealed correlations between compound localization and bioassay potency.

(220) ***In-situ* Monitoring of Form Change as a Function of Relative Humidity in the Solid State by Vapor Sorption Analysis-Raman Spectroscopy**

Candi Choi[1], Sruthi Janakiraman[1], Denette Murphy[1], Duohai Pan[1], Anisha Patel[1], Roxana Schlam[1], Shawn Yin[1]; [1]Bristol-Myers Squibb

Understanding changes that occur as a function of water activity has become an important aspect of physical characterization of the API in all stages of pharmaceutical product development due to the recent increase in number of compounds forming both stoichiometric and nonstoichiometric solvates and/or hydrates. Currently, moisture sorption isotherms are acquired to better understand the relationship between water activity and moisture content at a given temperature for an API form/material in the solid state. However, the additional complexity of API form/phase change that can occur during a sorption analysis can make the interpretation of the moisture sorption isotherm difficult. Integration of moisture sorption isotherm and Raman spectroscopy provides better understanding of these changes that may be occurring to the API as a function of equilibrated water content and/or %RH in the solid state. This poster illustrates, via three examples, applications of VTI/Raman in the pharmaceutical field.

(221) **Using Environment Sensitive Fluorescence Probes to Estimate Amorphous Solubility and Characterize Liquid-Liquid Phase Separation Behavior in Highly Supersaturated Solutions of Poorly Soluble Compounds**

Shweta A. Raina[1], David E. Alonzo[3], Yi Gao[2], Geoff G.Z. Zhang[2], Lynne S. Taylor[1]; [1]Purdue University, Department of Industrial and Physical Pharmacy, West Lafayette, IN; [2]NCE Formulation - LC, Research and Development, AbbVie Inc., North Chicago, IL; [3]Formulation & Process Development, Gilead Sciences, Inc., Foster City, CA

Objective**:** Enabling formulations containing polymers, surfactants, complexing agents and other additives often generate supersaturated solutions in-vivo. Colloidal species are frequently observed following dissolution of supersaturating dosage forms; however, the underlying mechanism of their formation is not well understood. Recent studies have demonstrated that colloid formation arises as a result of liquid-liquid phase separation (LLPS). In this project we present a novel fluorescence method involving environment sensitive fluoroprobes to accurately and reproducibly detect the onset of LLPS to characterize phase behavior of supersaturated solutions. Materials and Methods: Six compounds from the dihydropyridine class were chosen as model drugs. Equilibrium crystalline solubility of model compounds was determined in the absence and presence of polymers by incubating samples at 25C and 37C in 50 mM phosphate buffer at pH 6.8 for a 48 hour period. Samples were then ultracentrifuged, and solution concentration was determined using high performance liquid chromatography (HPLC) with ultraviolet (UV) detection. Amorphous solubility was calculated using Hoffman equation to obtain a first estimate and then corrected for moisture sorption. Fluorescence spectroscopy and environment sensitive probes were used to detect changes in solution polarity at 25C and 37C in the absence and presence of polymers. Phase diagrams were also generated using UV-visible spectroscopy. Results: All model compounds appear to undergo LLPS. Interestingly, some only undergo LLPS when polymeric crystallization inhibitors are present. A correlation was found between the onset of LLPS and the predicted amorphous solubility. Environment sensitive fluoroprobes showed spectroscopic changes when the colloidal phase was formed and thus could be used to detect the onset of LLPS at concentrations as low as 1 μg/mL. Good agreement was found between the LLPS concentrations determined by fluorescence (based on polarity environment of probe) and UV (based on extinction caused by light scattering of the new phase) spectroscopies. Conclusions: Environment sensitive fluorophores provide an alternate method to determine amorphous solubility and gain mechanistic insight into highly supersaturated solutions.

Acknowledgment: The authors thank Deliang Zhou of AbbVie Inc. for scientific discussions.

(222) **The Effect of Water on NIR Calibrations for Detecting API in Tablets**

Md.Nayeem Hossain[1], Benoît Igne, Carl Anderson, James Drennen[1]; [1]Duquesne University

Quantitative analysis by near infrared (NIR) spectroscopy involves establishment of a relationship between spectra, related to both physical and chemical information of a sample, and the corresponding parameter(s) of interest. To develop a robust model, unique sources of variability, not directly related to the components of interest, should be included in the calibration samples. One potential source of variability is moisture. Raw materials may have exhibit moisture differences as a function of manufacturing lot, the geographic location of a plant, storage conditions, or the seasonal variation. In a traditional calibration effort, tablets are often made at one unique time and in one unique location, reducing a model's robustness to moisture. The objective of this work was to study the effects of moisture on the performance of a near infrared tablet assay calibration and evaluate strategies for robustness to moisture variation. Tablets composed of acetaminophen, lactose, microcrystalline cellulose, HPMC and magnesium stearate were manufactured using laboratory scale equipment. A full-factorial design was used to vary acetaminophen (5 levels), and excipient ratios (3 levels) to generate tablets for calibration and test. Tablets were placed in humidity chambers over saturated salt solutions and equilibrated to 11.5%, 32%, 52% and 75% RH, respectively. Calibration and test tablets were scanned at each moisture level. Following spectral collection, the acetaminophen content was determined by HPLC. From each sample set representing tablets equilibrated at a single relative humidity, individual calibration models for acetaminophen were constructed. Test samples, stored at alternate relative humidity conditions, were predicted. When the moisture level was unique between calibration and test sets, the prediction error increased, indicating a degradation of the model performance when moisture variance was unaccounted for. A second calibration approach combining several moisture levels into a global PLS model was performed. These models gave significantly lower prediction errors for the test set than the individual models applied to all samples. These findings demonstrated the importance of accounting for expected sources of variance, such as moisture, by using a diverse calibration set to achieve robust calibrations. The effectiveness of feature selection and moisture related information removal were assessed for calibration enhancement.

(223) **Development and Implementation of Spectroscopy Methods for Quantitative and Qualitative Analysis of Pharmaceutical Reagents**

Bernard Agyei, John Wasylyk, Ming Huang, Robert Wethman; [1]Bristol-Myers Squibb

Off-line spectroscopy is a prevalent technique used for rapid evaluation of pharmaceutical raw materials and is suited for qualitative and well as quantitative purposes. Qualitative analysis is generally used for rapid material confirmation by comparing the Raman or NIR spectra to that of an established reference spectra. Quantitative methods are applied to both incoming reagents as well as prepared reagent solutions where a specified concentration is required by process requirements. The type of analysis and the level to which the method must be qualified in order to meet each goal depends on the level of sensitivity required. Specificity, linearity, precision and accuracy must be established regardless of the spectroscopic technique used for quantitation. Furthermore, robustness testing adds an additional level of reliability to the method when analyzing varying grades of reagents from multiple sources. Issues concerning cross-contamination from either the source of the material or from sampling techniques can impact the results and can often times be identified by the spectroscopy method. This study demonstrates the applicability of the off-line spectroscopy as a tool for identification and quantification, as well as challenges faced, when developing methods for rapid analysis of pharmaceutical raw materials and reagents.

(224) **Use of Electron Spin Resonance (ESR) for the Identification and Selection of Actives in Fragment based Drug Discovery of Small Molecule Inhibitors of Myeloperoxidase (MPO)**

Balagopalakrishna Chavali[1], Thierry Masquelin[1], Mark Nilges[2], David Timm[1], Stephanie Stout[1], Prabhakar Jadhav[1], William Matter[1], Gary Deng[1]; [1]Eli Lilly and Company; [2]University of Illinois, Urbana Champaign

Screening the molecule-libraries for lead candidates against target inhibition is crucial to streamline pharmaceutical discovery efforts. As an early visitor and as a critical player in the injured loci, neutrophil-derived MPO offers an attractive target to contain or modulate inflammation of the host tissue. We describe in detail how ESR as a biophysical technique was used to

• evaluate binding and on/off states
• rank order compounds
• test reversibility of binding
• derive the MOA (reversibility, active site binding)
• test whether bound complexes restrict the access of the heme to incoming H2O2, thereby preventing chlorination and peroxidase cycles.

(225) **Investigations into the Degradation of Polyquaternium-1**

Carina Gunder[1], Sharon Myers[1], Mary Lee Ciolkowski[1]; [1]Bausch & Lomb, Inc.

Polyquaternium-1 (PQ-1) has been used as a preservative in ophthalmic products for over twenty years. While biocidal efficacy is routinely monitored, it is highly desirable to have a supportive chemical assay method. PQ-1 may be assayed by various techniques; however, a correlation between assay and microbiological performance is not always demonstrated, particularly over product shelf life. Thus, it is not clear whether an apparent loss in PQ-1 chemical assay response (i.e. degradation) corresponds to a loss in preservative efficacy. The purpose of this study was to investigate chemical degradation of PQ-1. The study was undertaken in a simple matrix (water) at a higher concentration than present in ophthalmic products, in order to utilize a wider variety of analytical techniques to fully characterize the degradation process.

The study involved thermal stress of aqueous solutions containing PQ-1 at 40°C, 60°C, and 95°C over the course of 12 weeks. An ambient control was also tested at all timepoints. Data were collected using a variety of techniques: gel permeation chromatography (PQ-1 Mw and wt%), polyelectrolyte titration (PQ-1 wt%), acid/base titration (amine formation), pH, infrared and Raman spectroscopy, and NMR spectroscopy. The results provided evidence that elevated temperatures (≥ 60°C) resulted in random chain cleavage at the quaternary ammonium functionality, forming alkene and tertiary amine end groups.

Select test articles were screened for biocidal efficacy (1, 4, and 24-hour timepoints). No trend was observed for the bacteria tested, but the yeast (*C. Albicans*) and mold (*F. solani*) showed a loss of efficacy for the 60°C and 95°C samples at the 1 and 4-hour timepoints. The 60°C samples recovered efficacy by 24 hours, indicating that a trend would not be observed for preservative efficacy testing. The biocidal efficacy results for *C. Albicans* and *F. Solani* were consistent with the results from the chemical tests, which indicated significant PQ-1 degradation.

(226) **Application of Spectroscopy and Multivariate Analysis to Classify Source and Type of Commonly Used Pharmaceutical Excipients**

Ting Wang[1], Ahmed Ibrahim[1, 2], Alan Potts[3], Stephen Hoag[1]; [1]University of Maryland, Baltimore; [2]Misr International University; [3]United States Pharmacopeia

Purpose: To develop chemometric model to identify the excipient manufacturer and type based on NIR spectra. Manufacturer represents a combination of possible subtle differences in physiochemical properties of excipient. Therefore, first, we want to emphasize the discriminative power of high resolution NIR spectroscopy plus advanced chemometric method for the chosen problem; Secondly, to improve the procedure for qualifying excipients and hence better use of NIR in quality control of raw material. Methods: Microcrystalline cellulose (MCC) samples were collected from five manufactures with grades variations. Each lot was sampled three times and NIR spectra were measured from 400 to 2500 nm at a 0.5 nm resolution. The partial least square discriminate analysis was used to build predictive model and the model was tested using cross validation and external validation sets, as well as permutation test. Similarly, other two commonly used pharmaceutical excipient, lactose and povidone were examined in a same manner. Results: The model that correlates MCC NIR spectra to the manufacturer was significant. 85.32% of variations in Y-block (manufacturer category) were explained by 92.65% variations in the spectra using seven latent variables. The optimal preprocessing combination was identified. All the unknown samples in the independent validation sets were assigned correctly. The score and loading plots reveal that the amount of oxidized functional groups of cellulose, water content and state, and hydrogen bonds, degree of polymerization are responsible for the differentiation of manufacturers. Permutation test showed the prediction from the original model is significantly different from that of randomly generated models ($P<0.05$). The models for lactose and povidone are significant and the differences among manufacturers and types will be discussed case by case. The advantages and limitations of this modeling approach will be discussed. Conclusions: Our study clearly shows that high definition NIR spectra combined with appropriate chemometric methods can be used to discriminate between excipients samples of different sources, which may be related to differences in excipient performance. These predictions are based on the physiochemical properties that are specific to the manufacturing process or starting materials. NIR spectra demonstrate considerable potential use in excipient quality control and supply chain management.

(227) **Polarization Dependent Measurements by SHG Microscopy is Able to Detect Kinetically Trapped Meta-Stable Polymorphs of Organic Nano-Crystals**

Azhad Chowdhury[1]; [1]Purdue University

Polymorphism of an active pharmaceutical ingredients (APIs) can substantially affect shelf life, physical properties, dissolution rates and bioavailability. Chemical inkjet printing was investigated as a means for producing metastable polymorphs of the amino acids proline and serine upon rapid crystallization from racemic solutions. Racemic solutions can produce homochiral crystals or heterochiral crystals as conglomerates, racemates, or pseudoracemates. Previous studies show that crystallization from racemic aqueous solutions of both proline and serine produce centrosymmetric racemic co-crystals. Consequently, any noncentrosymmetric crystalline formation from such solutions would be metastable. However, conventional methods to study crystal polymorphism in the nano-scale is not trivial because of the lack of sensitivity and unable to identify small quantities of rare unfavored polymorphs selectively. Second harmonic generation (SHG) is highly selective for noncentrosymmetric crystals, and SHG microscopy is shown to enable detection of submicron sized chiral crystals with high resolution and sensitivity.1 SHG is the frequency doubling process of incident radiation arises from a second order nonlinear optical process. SHG is symmetry forbidden in cento symmetric media, and consequently amorphous solids, liquids, solvated molecules. By this symmetry argument only the chiral crystals can mitigate the criteria to be selectively detected under the SHG microscope. Polarization-resolved SHG microscopy can further enhance the information content of SHG measurements, given the sensitivity of polarized SHG to crystal form and orientation.

Principle component analysis (PCA) of polarization-dependent SHG images are able to detect different crystal domains in inkjet-printed amino acids. Synchrotron X-ray micro diffraction has been used to validate metastable polymorphs in inkjet-printed droplets from racemic solutions by rapid evaporation of solvent. The formation of metastable polymorphs also can be interpreted according to the Ostwald-Lussac's Rule of stages.2 Therefore, our findings may help guide future API formulations, especially those involving inkjet printing as a preparative method for APIs.

References

1.Wanapun, D., Kestur, U. S., Kissick, D. J., Simpson, G. J. & Taylor, L. S. Selective detection and quantitation of organic molecule

crystallization by second harmonic generation microscopy. Analytical chemistry 82, 5425–32 (2010).
2.Wilhelm, O. Studien ueberdie Bildung und Umwandlung fester Koerper. Zeitschrift fur physikalische Chemie 22, 289–330 (1897).

(228) **Application of Band Target Entropy Minimization Technique to Extract Eutectic Features from Raman Spectra**

Md Anik Alam[1,2], James Drennen[1, 2], Carl Anderson[1, 2]; [1]Graduate School of Pharmaceutical Sciences, Duquesne University, Pittsburgh, PA; [2]Duquesne University Center for Pharmaceutical Technology, Duquesne University, Pittsburgh, PA

A eutectic system is a mixture of components that melts at a lower temperature compared to its constituents. API and excipients can form eutectic system and alter physico-chemical behavior of drug products. Identification and characterization of eutectic systems can be critical for understanding drug performance. Spectroscopic characterization is a potential means of characterizing eutectic systems and is fast and non-destructive. However, substantial analysis of spectral data is necessary as a result of overlapping peaks in the data.

Salicylic acid and benzoic acid is a well-known binary eutectic system. Vibrational properties of these molecules were investigated individually as well as in eutectic system by Raman spectroscopy. A combination of backscattered and transmission Raman methods were employed in order to capture surface and bulk information about the samples. In the eutectic system, vibrational energy of molecular bonds can retain its original energy state as well as shift to a different energy state due to eutectic structure formation. The spectra resulting from eutectic sample can be comprised of pure-component spectral bands and novel or altered vibrational bands corresponding to the presence of eutectic structure. These novel or altered vibrational bands typically ovelap with pure component spectra and specific features can be difficult to extract. Band Target Entropy Minimization is a self-modeling curve resolution approach for reconstruction of pure-component spectra from mixture spectra. This technique was employed to extract information about novel or altered vibrational bands based on Shannon entropy minimization. The variance in the mixture spectra that was not explained by pure-component reconstruction was considered an effect of the eutectic structure.

(229) **Method Development and Validation for Analysis of Pharmaceutical Tablets by Transmission Raman Spectroscopy**

Yi Li[1], Benoît Igne[2], James K. Drennen, III[2], Carl A. Anderson[2]; [1]Graduate School of Pharmaceutical Science, Duquesne University; [2]Duquesne Center of Pharmaceutical Technology, Duquesne University

Raman transmission spectroscopy enables the in-depth analysis of pharmaceutical dosage forms. The technology is increasingly being used in the pharmaceutical industry for product content uniformity analysis and long-term stability test. This study aimed at demonstrating validation techniques for a transmission Raman spectroscopic (TRS) method using the ICH-Q2 Guidance as a template. The resulting method was demonstrated to be appropriate for routine content uniformity analysis of single dosage units. Specifically, Raman was used to develop a stability indicating method for niacinamide in tablet core. In the method development stage, a 3-level, 2-factor full factorial design was utilized to generate a partial least-squares model for API quantification. The major excipients were microcrystalline cellulose and dibasic calcium phosphate anhydrous. Other excipients were magnesium stearate and aerosol silicon dioxide. Model robustness to manufacturing and the effects of environmental variability on tablets was enhanced by compressing tablets at two forces and storing tablets in different humidity environments. An important aspect of a spectroscopic method validation is the development and testing of the multivariate model. Specifically, appropriate figures of merit for the calibration (multi-variate) are not specified in the current ICH guidance. Validation testing of the TRS model centered on figures of merit from 3 independent manufacture batches. The resultant model statistics were evaluated along with the linearity, accuracy, precision and robustness assessments. Method specificity was challenged by accurately determining niacinamide in the presence of niacin (an expected related substance). The method was demonstrated to be a suitable alternative method to HPLC with an added advantage of very short analysis times.

(230) **Determination of Degradation Pathways of Benzethonium Chloride in a Pharmaceutical Formulation by Accelerated Degradation Studies**

Janet de los Reyes[1], Channa A. Wijesinghe[1], Tristan Walters[1], Mugunthu Dhananjeyan[1], Samuel Molesworth[1]; [1]Hospira, Inc.

Accelerated degradation study is an important approach to understand the stability of pharmaceutical formulations. It provides insights of the possible degradation products that can be formed when a pharmaceutical formulation exposed to various stress conditions including light, thermal, oxidative, acidic, and basic conditions. Ultimately, it provides valuable information which can be implemented while in manufacturing, storing, and selecting packaging configurations to maintain drug product integrity. To ensure high quality pharmaceutical products are received by end users, all ingredients (active and non-active) should be evaluated with the same level of importance during the early stage of drug development; however, excipients have never been given the same level of scrutiny as API. Although excipients are not the main ingredients, they can also undergo degradation when stressing pharmaceutical formulations. Degradants of excipients can also affect the drug quality, have unintended side-effects and may be detrimental to the health of the end users. Therefore, it is also important to study excipient degradation pathways and their degradants. Benzethonium Chloride (BZT) is used as a preservative in pharmaceutical formulations as it has antimicrobial, antiseptic and disinfectant properties. Drug products with BZT usually contain no more than 0.01% BZT w/v. In this study, degradation pathways for BZT were investigated. A 0.01% BZT solution was separately stressed under thermal, light, oxidative, acidic, and basic conditions. The resulting exposed solutions were analyzed by an in-house developed UHPLC method. Degradants were separated by the UHPLC method and identified by UHPLC coupled with photodiode array detector and quadropole ion trap mass spectrometer. Other stability indicating attributes such as pH, color and clarity were also measured. Several degradants were observed under the stress conditions. It was also observed that the pH of the light-stressed BZT solution became more acidic than unstressed solution. It was found that the main degradation pathway resulted from the light-stressed condition and a degradation pathway was depicted. Within the experimental design of the study, this pathway has been probed to help gain understanding of the variables that can adversely affect the product integrity.

(231) **Long Wavelength 1064 nm Raman for Finished OTC Pharmaceutical Identification**

Mark Mabry[1], Claire Dentinger[2], Neville Broad[3]; [1]Rigaku Raman Technologies; [2]Rigaku Raman Technologoes; [3]NWB Spectroscopy

Identity testing is required as part of consumer, or over the counter (OTC), pharmaceutical product release for distribution. Identity testing usually involves product identification combined with a chemical assay for specified potency, carried out in a laboratory. This process could be accelerated by use of a handheld, long wavelength Raman spectrometer. Raman spectroscopy is an established research tool, but the miniaturization of optoelectronics during the past several years has led to implementation of Raman spectroscopy in production environments, most commonly for raw

material identification. The use of long wavelength, 1064 nm laser Raman excitation along with the shorter 785 nm excitation makes Raman analysis accessible to a greater variety of products. This is because for many materials, the use of 1064 nm excitation avoids fluorescence interference which precludes collection of meaningful Raman data with 785 nm excitation.

This presentation demonstrates potential applications of Raman in the pharmaceutical industry with an emphasis on finished product analysis. A dual band (785 / 1064) portable spectrometer was used to collect Raman data at both 785 and 1064 nm wavelengths of OTC pharmaceuticals. Using dual wavelength Raman measurements we demonstrate identifying the API and coating materials, distinguishing different polymorphs, confirming API potency.

(232) **A Complete Solution for Sample Prep Technique for New USP-**

David Gunn, Arshad Kokardekar; [1]Milestone Inc

Metals testing for API products has new general chapters USP <232> and <233> that will be effective May 1st 2014. From the general method <233> on Elemental Impurities, four procedures are described for sample preparation - Neat, Direct Aqueous Solution, Direct Organic Solution and Indirect Solution (Closed Vessel Digestion). The current challenge labs face is how to achieve complete digestions for their samples for backend analysis. Most labs have moved to closed-vessel digestions as the preferred process with microwave digestion the technology of choice. Before selecting a system for their needs labs have two critical aspects to consider for a complete solution:

• Temperature required for complete sample digestion
• Pressures generated at high temperatures during digestion

Given the challenging nature and range of sample types from pharmaceutical companies, closed-vessel digestion provides the best capability of obtaining complete digestions for sample sizes described in the method (0.50 g API). Microwave digestion also provides the most benefit for laboratories with time, flexibility and sample throughput as priorities for method selection, including a rich history with more than 30 years as the accepted instrumentation for sample digestion for oils, polymers, excipients and consumer products. The higher temperature and pressure capability provided by microwave digestion allow labs to successfully digest a wider range and more difficult sample types while providing digestates without particulate matter for analysis by ICP, ICP-OES and ICP-MS instrumentation. Because the system is closed, the loss of volatile components is minimized. Milestone offers a wide range of microwave sample prep tools depending on throughput needs, nature of the samples to be digested and the flexibility required with microwave instrumentation. This presentation will provide a guideline to sample preparation for the new USP methods to achieve good quality analytical data, the relationship of temperature and pressure while working in closed-vessel systems and an understanding of the key concepts in selecting instrument/vessels that will work for all sample types and needs. The presentation will also provide a detailed look at new technologies in microwave digestion instrumentation along with data analysis as a complete solution to sample prep for USP 232/233.

(233) **Computational Raman Activities for Raman Second Hyperpolarizability Determination and a Comparison with Experiments**

Wei Zhao[1], Anqi He[2], Yizhuang Xu[2]; [1]Department of Chemistry, University of Arkansas at Little Rock; [2]College of Chemistry and Molecular Engineering, Peking University

As an optical analogue to 2D NMR, doubly vibrationally enhanced (DOVE) four wave mixing spectroscopy involves two infrared transitions and a Raman transition. The magnitude of the DOVE second hyperpolarizability γ can be theoretically estimated if the values of the dipolar moments of the two infrared transitions and the γ of the Raman transition are known. The Raman γ can be measured by using four wave mixing interferometric method or conventional Raman spectroscopy in the presence of an internal standard. In this work, we examine if one can use the Raman activity computed from density functional theory calculation to determine the Raman γ of selected vibrational modes of several samples including deuterated benzene, acetonitrile, tetrahydrofuran, and sodium benzoate aqueous solution. The 992 cm^{-1} Raman band of benzene serves as an internal standard for organic solvents and the 880 cm^{-1} Raman band of hydrogen peroxide for the aqueous solution sample with known γ values. We have found that the predicted Raman γ values from the computational Raman activities match experimental data reasonably well, suggesting a facile approach to predict the Raman γ of interested systems.

(234) **Evaluation of Transfer Algorithms for Distribution of Spectral Libraries Across Different Instruments**

Jason Rodriguez[1], John Kauffman[1]; [1]Division of Pharmaceutical Analysis, Center for Drug Evaluation and Research, US Food and Drug Administration

Over the past few years, FDA's Division of Pharmaceutical Analysis (DPA) has built Raman and near infrared spectral libraries and developed library-based spectral correlation methods for the surveillance of pharmaceutical raw materials using portable spectrometers. Library-based spectral correlation methods are qualitative techniques that allow for rapid, nondestructive screening of pharmaceutical materials and can be easily used by investigators in the field with little or no expertise. Despite these advantages, library-based spectral correlation methods are hindered by the need to perform transfer algorithms prior to distribution of methods and libraries across different instruments. Moreover, given the wide range of instrument specifications in commercial portable/handheld spectrometers, an algorithm that works well for a particular set of spectrometers may not be optimum for a different set. We will present several different approaches we have used for Raman and near infrared library transfer and discuss the issues encountered when transferring spectral libraries across instruments from different vendors and platforms (e.g., laboratory, portable, and handheld).

(235) **Using deep-UV resonance Raman Spectroscopy to Monitor Protein-Lipid Interactions**

Jian Xiong[1], Rauta Yakubu[1], Michael Eagleburger[1], Jason Cooley[1], Renee JiJi[1]; [1]University of Missouri-Columbia

The interactions between proteins and biological membranes play an important role in many aspects of biochemistry including membrane protein folding and structure. Biological membranes comprise many types of lipids, but from a simplistic standpoint, a lipid's acyl-chain length, charge and saturation will vary. The effects of hydrophobic thickness, which is dictated by the lipids' length, on the secondary structure of hydrophobic leucine-alanine peptides and the amphiphilic β-amyloid peptide (Aβ) were investigated. Both deep-UV resonance Raman (dUVRR) and circular dichroism (CD) spectroscopies were used to monitor each peptide's structure and environment upon introduction of unilamellar vesicles with varying hydrophobic thicknesses. The intensity of the amide I mode in the dUVRR spectra of proteins is an intrinsic marker for lipid solvation and suggested that the peptides were indeed lipid solvated. The amide II, III and S modes were used to simultaneously monitor the secondary structure of each peptide. CD was also employed to characterize the secondary structure of the peptides. It was found that the shortest leucine-alanine peptide demonstrated the greatest structural plasticity, transitioning from a β-sheet structure in liposomes comprised of the longest (14:0) lipids used in this study to an increasingly more α-helical structure in liposomes comprised of shorter (12:0, 10:0) lipids. Hydrophobic thickness was also found to

be a determining factor in the conformation of the Aβ peptide. Residues 28-40/42 of Aβ are derived from the transmembrane region of the amyloid precursor protein (APP). In contrast to the shortest leucine-alanine peptide, Aβ was found to adopt α-helical structure in liposomes comprised of the longest (14:0) lipids and β-sheet structure in liposomes comprised of the shortest (10:0) lipids. These studies show that dUVRR spectroscopy is a powerful tool for studying the association and folding of lipid soluble proteins.

(236) **Orange Carotenoid Protein**

Elizabeth Kish Perrin[1], Diana Kirilovsky[1], Andrew Gall[1], Alberto Mezzetti[1], Riccardo Spezia[2], Bruno Robert[1]; [1]Commissariat à l; [2]Laboratoire analyse et modélisation pour le biologie et environnement

In photosynthetic organisms, high light intensities can result in cellular damage from the production of dangerous reactive oxygen species (ROS). In cyanobacteria, orange carotenoid protein (OCP) acts as a protective mechanism because in its active form it shuttles energy away from the light harvesting apparatuses, preventing the creation of ROS. For my PhD, I am biophysically characterizing OCP with resonance Raman spectroscopy (RRS) and other techniques. OCP is a photoactive protein that changes confirmation when exposed to intense blue light; it contains a carotenoid ligand (echinenone). This photoconversion phenomenon is interesting because the OCP has different colors in the nonactive and active form- it appears orange and red prospectively. Thus far, a crystal structure has only been elucidated for the orange (nonactive) form of the protein. My experiments consist of comparison between the orange and red structural forms of the protein, as well as mutants (demonstrating several key points- for example the existence of a salt bridge between residues 155 and 244 which breaks upon conversion to the active form) using RRS. Recently, we have some interesting results involving the possible appearance of an electron transfer state (ICT); it seems visible with red-shifted incident light during RRS. These results are especially compelling because the ICT state is the probable mechanism of action for OCP, and has not been recognized much with RRS, even though it likely exists for other carotenoid molecules. To develop this work I am collaborating with a theoretician that is using home built software to make spectral predictions based on the carotenoid confirmation, which we have extracted from the protein crystal structure. We are now doing predictions of the red form, running them with this program, and comparing the calculated and experimental results.

(237) **Time Resolved Raman Spectroscopy for Depth Analysis of Multi-Layered Mineral Samples[1]**

Jan-Hein Hooijschuur[1,2], Ingeborg E. Iping Petterson[1], Cees Gooijer[1], Gareth R. Davies[2], Freek Ariese[1]; [1]Department of Biomolecular Spectroscopy, LaserLaB, Vrije Universiteit Amsterdam, The Netherlands; [2]Department of Petrology, Vrije Universiteit Amsterdam, The Netherlands

Raman spectroscopy is one of the techniques that could potentially provide a first indication for life elsewhere in our Solar System. This study is designed to establish the range of Raman spectroscopic techniques pertinent for the detection of microbial life in extreme environments, for example on Mars and Jupiter's icy moons [2]. The challenge is to validate *in situ* methodologies for the detection of microorganism biomarkers that unambiguously prove evidence of (past) life. A combination of a picosecond laser and a gated ICCD detector provided depth resolution through different layers of minerals. Raman spectra from the second layer were detected through 10 mm of translucent calcite and up to 40 mm of transparent halite crystals. These results show a great potential for the use of Raman spectroscopy in future planetary exploration where Raman spectroscopy could be used as a non-invasive tool for profiling the (sub-)surface at cm-depth resolution. This research will elaborate on the combination of minerals and microorganisms from extreme environments on Earth. These environments mimic the conditions of the first billion years of Mars [3]. Microorganisms can use minerals both passively and actively as protection against dehydration and hazardous radiation (like UV-light). By applying different Raman spectroscopic methods such as: Time Resolved (TRRS), Resonance (RRS) and Spatially Offset (SORS) Raman Spectroscopy or a combination of these techniques, a higher selectivity and/or sensitivity for biomarker detection is obtained.

(1) J.H. Hooijschuur et al., accepted, J. Raman Spectrosc.
(2) C.P. McKay, Phil. Trans. R. Soc. A, 2011, vol. 369, pp. 594-606
(3) A.G. Fairén et al., Astrobiology, 2010, vol. 10, pp. 821-43

(238) **Wide Area Standoff Measurements Using a Spatial Heterodyne Raman Spectrometer**

Nirmal Lamsal[1], S. Michael Angel[1]; [1]University of South Carolina

A new type of Fourier transform (FT) Raman spectrometer, the spatial heterodyne Raman spectrometer (SHRS) is being developed for standoff chemical measurements. In earlier work, the SHRS was demonstrated at visible and deep-UV wavelengths. Using small 1-inch diameter, 150 gr/mm diffraction gratings the system was shown to have near-theoretical spectral resolution of about 5 cm-1 using 244-nm excitation, and a very large spectral range. The SHRS design offers several advantages over dispersive Raman systems especially in the UV, including 10 to 100 times larger acceptance angle and subsequently a much larger field of view, 100 to 10000 higher light throughput, very high resolution in a small package, and wide spectral range. An important goal of ongoing work is to use the large acceptance angle of the interferometer for wide field-of-view standoff Raman measurements. Wide area measurements are useful to minimize laser-induced sample damage, especially important in the UV, and to minimize characterization time for a large region of interest. We have demonstrated measurements of areas as large as 8 cm in diameter at just a few meters working distance with no loss of Raman signal or spectral resolution. We are also investigating ways to reduce the size of the SHRS. In this presentation, we will show the feasibility of UV SHRS spectrometers that are 5 mm or less in size, with 5 cm-1 spectral resolution and higher than 4000 cm-1 spectral range. The SHRS design is amendable to such miniaturization because the spectral resolution is not a strong function of device size. The small size and spectroscopic performance of the miniature SHRS would immediately broaden the applicability of on-line, in-situ, in-vivo, and standoff Raman measurements. Planetary applications of standoff SHRS will also be discussed.

(239) **Quantitative Analysis Using Raman by a Dummy**

Eunah Lee[1], Andrew Whitley[1]; [1]HORIBA Scientific

One of the most frequently asked questions about Raman analysis is whether and how it can be used for quantitative analysis. The answer is often "it depends", followed by long winded explanations, ambiguous comments and seemingly unrelated questions. While the 'ideal' way may be to study till understanding the technology and instrumentation enough to design experiments, to process data, and to interpret results, it is often the reality that there is little time to do so. This paper aims to demonstrate a common sense route to quantitative analysis using Raman data from the point of view of an analyst with a general understanding and experience. A simple and brief theoretical background is followed by experiment designs based on the empirical reasoning. Results are discussed with respect to the expectations, and the discrepancies, if any, are investigated.

(240) **Spectroscopic Investigation on the Effect of Naturally Occurring Polyphenolic Compounds on the Structure of the Amyloid-β Peptide**

Brittany Hagenhoff[1], Jian Xiong[1], Renee JiJi[1]; [1]University of Missouri - Columbia

Aggregation of the amyloid-β (Aβ) peptide is associated with the development of Alzheimer's disease. Aβ is a 39-43 residue cleavage product of the amyloid- β precursor protein (APP) and self-aggregates to produce plaques in the brain which are composed of cross β-sheet structured fibrils. Various polyphenolic compounds have been shown to interfere with Aβ aggregation. The interaction of Aβ with the naturally occurring polyphenolic compounds quercetin, epigallocatechin gallate, nordihydroguaiaretic acid, curcumin, rosmarinic acid, and baicalein was investigated via circular dichroism (CD), and deep-ultraviolet resonance Raman (dUVRR) spectroscopies. Thioflavin T fluorescence assays were used to categorize as the polyphenols as inhibitors or non-inhibitors of Aβ aggregation. It was found that quercetin, epigallocatechin gallate, and nordihydroguaiaretic acid inhibited aggregation, while rosmarinic acid and baicalein did not. Quercetin and baicalein have similar structures, as do rosmarinic and nordihydroguaiaretic acids. CD and dUVRR were employed to determine if interactions with aggregation inhibitors has a similar affect on Aβ's structure. It could not be determined via ThT assay whether curcumin inhibited aggregation. However, CD spectra of Aβ with curcumin showed significant β-sheet formation within only 45 minutes, indicating that curcumin did not inhibit aggregation. Multiple naturally occurring polyphenols were investigated for their ability to inhibit aggregation and alter Aβ's structure. The results from these studies will be presented.

(241) **Microfluidic Device for Single Experiment Limit of Detection Assessment**

Antonio Campos[1], Donghyuk Kim[1], Nathan Greeneltch[2], Christy Haynes[1], Richard Van Duyne[2]; [1]University of Minnesota; [2]Northwestern University

Recent attempts by an individual attempting to employ ricin as a bioterror agent against elected government officials highlight the need for sensitive, rapid, and label-free detection of analytes with the potential for use in bioterrorism attacks. By coupling the real-time detection of capabilities of microfluidic devices with the facile label-free detection method of intrinsic surface-enhanced Raman spectroscopy (SERS), analytes can be detected in a dynamic, stable environment requiring minimal quantities of sample. Additionally, detection platforms employing SERS require little sample purification, making the pairing of microfluidics and SERS ideal for analyte detection in complex matrices. To this end, a proof-of-concept microfluidic platform was developed with a gold film-over-nanospheres (AuFON) SERS substrate. The microfluidic platform generates a concentration gradient of introduced samples, facilitating both multiplex detection capability and simple limit of detection assessment in a single device. A calibration curve was created using 1,2-bis(4-pyridyl)ethylene (BPE) using this microfluidic SERS platform. SERS results were compared with fluorescence detection results for rhodamine 6G (R6G) to show that the microfluidic device is capable of real-time, quantitative analysis of BPE. In addition, this gradient microfluidic SERS platform has been utilized to quantify the b chain of the bioterror agent ricin in complex matrices using an aptamer-functionalized surface via SERS. This gradient microfluidic SERS platform shows promise for multiplexed, sensitive, real-time detection of bioterror agents.

(242) **Conformational stability, r0 structural parameters, vibrational assignment and ab initio calculations of ethyldichlorophosphine**

Charles Paquet[1], Ikhlas Darkhalil[1], Mohammad Waqas[1], Todor Gounev[1], James Durig[1]; [1]University of Missouri-kansas City

Variable temperature (-60 to -100°C) studies of ethyldichlorophosphine, $CH_3CH_2PCl_2$, of the infrared spectra (4000 to 400 cm^{-1}) dissolved in liquid xenon have been carried out. From these data, two conformers have been identified and their relative stabilities obtained. The enthalpy difference has been determined between the more stable gauche conformer and the less stable trans form to be 81 ± 4 cm^{-1} (0.9 ± 0.03 kJ/mol). The percentage of the gauche conformer is estimated at ambient temperature to be 57%. The conformational stabilities have been predicted from ab initio calculations utilizing several different basis sets up to aug-cc-pVTZ for both MP2(full) and density functional theory calculations by the B3LYP method. Vibrational assignments have been provided for both conformers which have been supported by MP2(full)/6-31G(d) ab initio calculations to predict harmonic force fields, wavenumbers of the fundamentals, infrared intensities, Raman activities and depolarization ratios for both conformers. Estimated r_0 structural parameters have been obtained from adjusted MP2(full)/6-311+G(d,p) calculations. The results are discussed and compared to the corresponding properties of some related molecules.

(243) **An Aberration Free Spectrograph for Improved Raman Spectroscopy & Imaging**

Brian C. Smith[1]; [1]Princeton Instruments

Traditional Czerny-Turner (CT) imaging spectrographs are commonly used to measure Raman spectra and images of samples. However, CT spectrographs suffer from optical aberrations including field astigmatism, spherical aberration, and coma. These aberrations cause poor spatial resolution resulting in poor image quality, and poor spectral resolution giving spectral peaks that are misshapen, broadened, and short. The net result is Raman spectra with a poor signal-to-noise ratio (SNR) and poor spectral resolution. These aberrations and the problems they cause grow worse towards the edges of the focal plane. We have developed a novel variant of the traditional CT spectrograph, called the Schmidt-Czerny-Turner (SCT) imaging spectrograph. The SCT spectrograph is astigmatism free at all wavelengths across the entire focal plane, and enjoys reduced levels of spherical aberration and coma. The resultant improved spatial resolution gives crisper, cleaner images. Reducing aberrations gives spectral peaks with the proper band shapes with improved spectral resolution and SNRs. Because the aberrations are low across the entire focal plane means researchers can be assured that the data that they obtain anywhere on a sensor will be of high quality. Examples of how the SCT spectrograph improves the quality of Raman images and spectra will be discussed.

(244) **Plasmon Enhancements using Coherent Anti-Stokes Raman Scattering**

Karen A. Antonio, Lawrence O. Itela[1], Zachary D. Schultz[1]; [1]University of Notre Dame

The combination of coherent anti-Stokes Raman scattering (CARS) and surface enhanced Raman scattering (SERS), surface enhanced CARS (SECARS), suggests a powerful label-free approach to understanding chemical interactions in cellular systems. We use a multiplex CARS microscope, synchronizing a picosecond pulsed beam for increased spectral resolution with a supercontinuum Stokes beam to obtain multiplex CARS spectra. The nonlinear properties of CARS and point-by-point scanning capabilities allow for three-dimensional imaging of the sample. To gain a better understanding of the surface enhancement mechanism of SECARS, we utilize gold (Au) nanorods of varying lengths to study the polarization dependence based on the localized surface plasmon resonance.

Further results from the Au nanorods in different solutions provide insight into the plasmonic dependence and nonresonant background arising from the metallic nanostructures. The ultimate goal is to utilize the Au nanostructures with the best enhancement as antennae to amplify signals in cells, providing three-dimensional imaging and chemical information at the molecular level.

(245) **Quantitative Monitoring of Biphasic Reactions Using Flow Systems by Raman Spectroscopy**

Gerald Cairns[1], David Angelone[2], Shaghayegh Abdolahzadeh[2], Johannes W. de Boer[3], Antoine Varagnat[1], Wesley R. Browne[2]; [1]Andor Technology plc, Belfast, United Kingdom; [2]Centre for Systems Chemistry, Stratingh Institute for Chemistry, University of Groningen, Nijenborgh, The Netherlands; [3]Catexel BV, BioPartner Center Leiden, Leiden, The Netherlands

Biphasic reactions offer tremendous opportunities in industrial chemical syntheses due to the ease at which the phases and hence reagents can be separated, thereby avoiding energy intensive separation processes such as distillations A contemporary challenge presented in the implementation of biphasic reaction conditions is to determine and control the chemistry occurring in each phase, in order to improve manufacturing processes. Inline HPLC techniques for monitoring biphasic reaction monitoring have already been developed and demonstrate the potential benefits of inline monitoring in controlling and optimizing reactions. In this contribution, our recent work in developing a fully automated system for monitoring changes in the composition of two immiscible phases by Raman spectroscopy using a flow sampling system is presented. This Raman/Flow system can acquire and distinguish Raman spectra of the phases present in an emulsified reaction mixture and offers a key advantage in the real-time information it can deliver. It takes advantage of the new generation of low dark current deep-depletion (LDC-DD) CCD technology to enable acquisition of the 'pure' species spectrum. This also demonstrates the extended spectral coverage (increase of ca. 1000 cm^{-1}) which is acquired with no loss in spectral resolution, due to the extended width of this new sensor type. The final goal is to obtain reliable real-time kinetic data on two phase reaction mixtures in which substrates in the organic phase undergo oxidation.

(246) **Raman Spectroscopy Reveals Evidence for Early Bone Changes in Osteoarthritis**

Jemma Kerns[1], Kevin Buckley[2], Panagiotis Gikas[1, 3], Helen Birch[1], Anthony Parker[2], Pavel Matousek[2], Allen Goodship[1]; [1]UCL Institute of Orthopaedics; [2]Central Laser Facility, STFC Rutherford Appleton Laboratory, Oxfordshire, U.K.Central; [3]Royal National Orthopaedic Hospital, Stanmore, U.K.

Osteoarthritis (OA) is a common, debilitating disease of joints involving degeneration of cartilage and bone. There are two competing theories for the initiation of osteoarthritis. Firstly, increased load on the joint leads to increased subchondral bone stiffness1. Secondly, composition of the subchondral bone changing towards homotrimeric collagen2. The aim of the study is to explore the hypothesis: chemical differences in the bone matrix of OA subchondral bone compared to matched individuals unaffected by OA are detectable by Raman spectroscopy. Samples were acquired (with ethical approval) from human tibial plateaus with established osteoarthritis (n=10), non-OA from amputees (n=5) and non-OA aged-matched cadaveric tissue (n=5). Subchondral bone samples were analysed with Raman spectroscopy (830nm excitation wavelength, Renishaw, UK)3,4, peripheral quantitative computed tomography (pQCT; for bone mineral density) and chemical analysis (collagen alpha chain ratios). Mineralisation ratios were calculated from spectra and multivariate analysis performed to assess variance across the spectral range (750–1800 cm-1)5. Results showed that bone from the affected (medial) compartment of the OA samples had a greater vBMD (p=0.05) and was thicker than the unaffected (lateral) compartment. The Raman results showed no spectral differences between medial and lateral areas of the plateau in OA. However, regardless of compartment, there were significant spectral differences between the OA and non-OA samples (p=0.02), and differences in type I collagen chemistry with medial OA samples exhibiting elevated levels of homotrimeric collagen.These results support the theory that there is a biochemical difference between OA and non-OA subchondral bone. Future efforts will assess Raman spectroscopy for characterising and detecting osteoarthritis during the subclinical phase.

The results suggest that Raman spectroscopy could be further developed as a screening tool for early detection of joint degeneration based on detecting molecular modifications in the subchondral bone.

1. Radin EL (2004).J.Rheum., 31,suppl 7.
2. Bailey AJ et al (2002). Int J.Biochem.Cell Biol., 34(2),176-82.
3. Buchwald T et at (2012). Biomed.Optics 17(1),017007.
4. Draper ER et al (2005).JBMR, 20(11),1968-72.
5. Martin F et al (2010).Nat.Prot.,5(11),1748-1760.

Acknowledgements We wish to thank the Royal National Orthopaedic Hospital and patients for supporting this study, and the EPSRC (EP/H002693/1) for funding it.

(247) **Nano -Edge Filters Offer Unparalleled Access to Low Wavenumber Raman Modes**

Catherine Aldous[1]; [1]Iridian Spectral Technologies

Raman bands in the 200 – 1800 cm-1 range can be used to identify and analyze materials, but lower wavenumber modes can also offer important information on other vibrations (shear modes, lattice modes, breathing modes, etc.). For example, these low wavenumber vibrations can reveal structural information of a crystal lattice that may not be extracted at higher wavenumbers. As Raman scattering is very weak, it is vital to block the excitation laser light from the detector. Dielectric thin film filters can offer optical density of 6 or better for isolation of the laser line, while transmitting the Raman scattered light. Most filters on the market, however, sacrifice low wavenumber Raman light in order to achieve this necessary blocking. The introduction of extremely steep edge pass (~94 dB/nm steepness) filters maintain this deep blocking of the laser line while passing low wavenumber Raman modes, offering access to otherwise hidden modes as low as 15-20 cm-1.

(248) **Novel 1064 nm Dispersive Raman Spectrometer and Raman Microscope for Non-destructive Pigment Analysis**

Lin Chander[1], Jack Qian[1], Owen Wu[1]; [1]BaySpec Inc.

High fluorescence backgrounds encountered in colorful samples have limited the use of Raman spectroscopy. FT-Raman has been the traditional solution for suppressing fluorescent interferences but is relatively cumbersome with constant moving parts and long acquisition times. This paper will introduce a new class of 1064 nm dispersive Raman spectrometers and microscopes, realized by highly efficient, patented VPG gratings, fast optics, and deep-cooled InGaAs detectors. The 1064 Raman spectrometers feature with high reliability, compactness, flexibility with modular accessories, making them great for field applications. The confocal Raman microscopes feature with multiple laser excitations (532, 785, and 1064 nm), fully automated operation and high spatial/spectral resolutions. This work will focus on the experimental results obtained from fluorescent samples crossing many fields, such as pigmented ambers, paints, inks, and other fluorescence materials. These data demonstrate that the 1064 Dispersive Raman is ultimately the solution for the analysis of the most complex fluorescence samples that traditional Raman systems are unattainable. It proves 1064 nm Raman a powerful tool in new fields such as forensics and counterfeit detection.

(249) **A Study of Varnish Degradation Processes in Art Conservation by Raman Spectroscopy**

Veronica M. Alvarez[1], Anahit M. Campbell[1], Lisa K. Kendhammer[1], Joseph H. Aldstadt[1]; [1]Dept. of Chemistry & Biochemistry, University of Wisconsin-Milwaukee

One of the major concerns in art conservation is the ageing of varnishes that have been applied to paintings and other artistic media. As varnishes age, they tend to yellow, crack, flake, and present other consequences that harm not only the appearance of the art work but also the stability of the materials used. To aid efforts to accurately restore these objects, a better understanding of the nature of the ageing process would be helpful, given that the composition of the original varnish as well as subsequent restoration(s) is seldom known. The goal of our work is to study the molecular mechanisms of degradation processes as a function of key environmental factors (e.g., heat, light, moisture, etc.). These factors cause the varnish layer to yellow, crack, and flake and present other consequences that harm not only the appearance of the work, but also the stability of the work itself. A quartz reaction chamber for precisely controlling these factors was designed, fabricated, and tested. The chamber fits inside the oven of a gas chromatograph, thereby facilitating precise control of temperature, and with minor modification, exposure to UV light and precise metering of specific atmospheres (through injection ports). We will describe our experiments in which common triglyceride (Linseed Oil and Tung Oil) and triterpenoid (Dammar and Mastic) varnishes were subjected to time-course experiments in which temperature, light, and atmosphere are varied. The aged varnish samples were characterized off-line by vibrational spectroscopy. We will describe our observations of changes in IR and Raman spectra that occur during the time-course studies and possible mechanisms that are characteristic of ageing processes.

(250) **Monitoring the Fate of Subcutaneously Injected Pharmaceuticals Using Raman Spectroscopy**

Oliver Stevens[1]; [1]Bristol University; [2]Bath University

Subcutaneous injection that overcomes the inconvenience of intravenous delivery and the challenges associated with oral delivery of protein pharmaceuticals, such as insulin and monoclonal antibodies, is the most commonly used route for administration of these therapeutic entities. However, little is known of the stability and the conformational changes that these molecules undergo post-injection into the subcutaneous space as they transition from the formulation environment into the physiological environment of the subcutaneous tissue. These changes may affect the extent of absorption of the molecules, and thus the therapeutic efficacy. Raman spectroscopy has potential to provide chemically specific in-situ monitoring of these formulations upon administration and highlighting any changes possibly taking place in the protein conformation after subcutaneous injection. We demonstrate a prototype system for in-situ monitoring of pharmaceutical preparations in subcutaneous tissue after injection using a Raman spectroscopy probe. The proposed system utilises an array of needles with fused fibres that will acquire Raman spectra over an area surrounding the injection site. The effectiveness of the probe has been demonstrated by discriminating between clinically relevant samples of proteins, and distinguishing between samples injected into pig subcutaneous tissue, simulating a human injection.

(251) **Microwave, Raman and Infrared Spectra, Conformational Stability, r0 Structural Parameters, and Vibrational Assignment of Cyclopentylamine**

Ikhlas D. Darkhalil[1], Nick Nagels[2], Wouter A. Herrebout[2], Benjamin J. van der Veken[2], Ranil M. Gurusinghe[3], Michael J. Tubergen[3], James R. Durig[1]; [1]Department of Chemistry, University of Missouri-Kansas City, Kansas City, MO; [2]Department of Chemistry, Universitair Centrum Antwerpen, , Antwerpen, Belgium; [3]Department of Chemistry, Kent State University, Kent, OH

FT-microwave spectrum of cyclopentylamine, c-$C_5H_9NH_2$, has been recorded, and the transitions have been assigned for the most stable conformer, and the rotational constants have been determined. The vibrational spectra have been investigated in detail with the recording of the Raman spectra (3800-50 cm^{-1}) of the liquid and the infrared spectra (3700-200cm^{-1}) of the gas. Additionally, the variable temperature (-60 to -10^0C) Raman spectra of the sample dissolved in liquefied xenon with complete spectra record at -60 and -100 °C. In the region where significant differences were observed in the relative band intensities the spectra were recorded at every ten degree intervals. From these data two conformers have been identified with one the trans-axial form and the other trans-equatorial conformer. The axial and equatorial orientations refer to the ring atoms whereas the trans and gauche orientations refer to the position of the NH_2 group. The four possible conformers have been identified and their relative stabilities obtained with enthalpy difference relative to the most stable conformer. The conformational stabilities have been predicted from ab initio calculations utilizing several different basis sets up to aug-cc-pVTZ from both MP2(full) and density functional theory calculations by the B3LYP method. Vibrational assignments have been provided for the observed bands for all four conformers which are predicted by MP2(full)/6-31G(d) ab initio calculations to predict harmonic force constants, wavenumbers, infrared intensities, Raman activities and depolarization ratios for all conformers.

(252) **Effects of Hypergravity on Crystallinity of Apatite, the Mineral Component of Bone**

Andrew Derry[1], Mary Tecklenburg[1]; [1]Central Michigan University

Bone density is affected by changes in gravity as experienced by astronauts in space. Under microgravity, pressure inside the human body decreases affecting the skeletal system. Hypergravity, a condition where g-forces exceed normality, and therefore, increases pressure opposite to microgravity, is of interest to space research. Astronauts not only experience elevated g-force upon takeoff and reentry, but hypergravity could be used as a means to slow or stop the effects of microgravity during long duration spaceflight. Apatite, the mineral found in bone, was studied under hypergravity to determine whether hypergravity increases or decreases the apatite crystallinity, the incorporation of carbonate ions in apatite, and whether it changes the kinetics of the amorphous to crystalline transition. Apatite-forming reactions were performed at room temperature of 24 °C and a pH of 7.4. Aqueous solutions of calcium chloride, sodium phosphate, and sodium phosphate/sodium carbonate were prepared in Tris buffered solution. Calcium chloride solutions were mixed with sodium phosphate solutions containing varying amounts of carbonate and were exposed to g-forces of 1G (control), 90G, and 185G. Variants of reaction times included 5 minutes, 50 minutes, 5 hours, and 10 hours. Hypergravity conditions were created using centrifugal force with a laboratory centrifuge. Collected samples were analyzed by ATR-IR and Raman spectroscopy. Bandwidths for phosphate and carbonate peaks decreased and peaks were resolved as g-force increased, indicating an increase in crystal domain length.

(253) **A Study of the Composition of Varnishes by Raman Spectroscopy and SPME Gas Chromatography**

Lisa K. Kendhammer[1], Sarah K. Patch[2], Joseph H. Aldstadt[1]; [1]Dept. of Chemistry & Biochemistry, University of Wisconsin-Milwaukee; [2]Dept. of Physics, University of Wisconsin-Milwaukee

The composition of common varnishes is often quite complex, further complicated by the lack of records of the types of varnish the artist applied or of restorations that may have occurred. Another major concern in art conservation is that the ageing process – generally, the yellowing, cracking, and flaking of varnishes over time – is poorly understood at the molecular level. To preserve the original intent of the artist, ideally the analytical chemist aims to determine the composition of the varnish that was originally applied. Thus methods for accurately characterizing aged varnishes are of great interest to art conservators. We studied common varnishes that are used in art conservation, such as Linseed Oil, China Wood Oil, Dammar, and Mastic. We will describe the creation of a Fourier Transform (FT)-Raman spectral database of representative carboxylic acids as a means to identify and quantify the composition of aged varnishes. The database contains spectra for 19 carboxylic acid standards as well as the four varnishes listed above. Through visual and chemometric analysis, results will be presented in which components in the FT-Raman spectral database were recognized as components of the aged varnish samples. Singular Value Decomposition (SVD) was applied to quantitatively study the utility of the database in identifying the varnish standards. We will also describe a method based upon Gas Chromatography (GC) that was developed to further characterize the short-chain carboxylic acids that are formed as a result of varnish degradation. In this method, a headspace solid-phase microextraction (SPME) approach was developed and optimized in which a 75 µm Carboxen-polydimethylsiloxane SPME fiber was used to determine six monocarboxylic acids.

(254) **Field Detection of Organic Mixtures in Air Using Glass Microfabricated Devices**

Alastair Lewis[1], Xiaobing Pang[1], Jacqueline Hamilton[1], Richard Lidster[1], Samuel Edwards[1], Stephen Andrews[1]; [1]Department of Chemistry, University of York, Heslington, York, UK

The measurement of trace volatile organic compounds in gaseous samples is needed for a diversity of applications, including indoor and outdoor air quality, product and materials testing, health diagnostics and security screening. The complexity of environmental organic mixtures, coupled to low concentrations, makes this a particularly challenging task. Fast *in situ* field measurements are particularly difficult to achieve, creating a requirement for analytical approaches that have very high specificity and sensitivity but low power, consumable and size characteristics. For some applications devices must have very low false positive rates to be useful. This presentation will highlight some developments in the production of microfabricated gas chromatography devices that can be used for selective field detection of volatile organic compounds. A simple borosilicate glass lab-on-a-chip comprehensive GC (GCxGC) device has been coupled to low power detectors such as photoionization and tested alongside standard laboratory instrumentation for air quality monitoring. The device is highly sensitive, capable of detection of individual species at the parts per trillion level, even when a high level organic background matrix is present. The range of organic compounds that can be quantified by field devices can further be expanded through the use of chemical derivitisation agents such as O-(2,3,4,5,6-pentafluorobenzyl) hydroxylamine (PFBHA). The development of a highly sensitive and selective micro-preparative stage for field GC will also be discussed, and some examples shown of its application for on-line detection of carbonyl compounds in air at the part per billion level. The use of a micro-preparative glass reaction chip designed for gas-liquid mixing and atmospheric derivitisation allows for the autonomous detection of difficult to measure compounds such as formaldehyde and glyoxal, without bench preparative stages and with very low consumable consumption.

(255) **Path Forward for Molecular Analysis Using Mass Spectrometry**

Zheng Ouyang[1], Linfan Li[1], Yue Ren[1], Morgan McLuckey[1], Jiangjiang Liu[1], Robert Cooks[1]; [1]Purdue University

Mass Spectrometry (MS) has demonstrated performance in analysis of complex mixtures. By providing information of molecular weight (through MS analysis) and molecular structures (through MS/MS analysis), high specificity is achieved for chemical analysis. The protocol for quantitative analysis has also been well established, typically with isotope labeled standards incorporated, and has been widely applied in drug development and clinical analysis. While MS technology continues to develop for proteomic research where comprehensive analytical performance is highly desirable, miniaturization of the MS system and streamlining the operation protocol for targeted analysis with clearly identified chemical or biomarkers could make the MS technology be used outside the labs and better serve the society. The examples of the potential applications include the clinical diagnostics, therapeutic drug monitoring for drug dosage adjustment, identification of smokers or users of drugs of abuse, and the control of the food quality. The goals along this path are to have miniature MS system developed that is of reasonable cost to own, to run and can be used by ordinary people who are not trained with chemical analysis. Strategy for technical approach set by the researchers at Purdue is to couple a small MS system retaining MS/MS capability with ambient ionization for direct sampling ionization. The current status of the development in fields of miniature mass spectrometer and ambient ionization will be reported. Methods to achieve qualitative analysis at high sensitivity and quantitative analysis at high accuracy will be discussed. The integrated systems for in-field and in-office operations will be presented with full performance characterizations.

(256) **Ultra-Sensitive Label-Free Detection In Fluids**

Zachary Schultz[1], Steven Asiala[1], Pierre Negri[1], Oluwatosin Dada[1], Kevin Jacobs[1]; [1]University of Notre Dame

Increased understanding of signal enhancements at metallic nanostructures has transformed Raman spectroscopy into an ultrasensitive method of detection. In solution, sensitivity is typically limited by the ability of molecules to diffuse away from a SERS substrate or the need to bind the analyte to a colloid. Recent work in our laboratory suggests that these challenges can be overcome by controlling molecular transport. Proof of concept experiments exhibit a 1000x increase in detection efficiency over other reports in the literature. Our approach is straightforward, avoids complex fabrication, and is readily incorporated into traditional Raman instrumentation. In this presentation we will discuss the extension of our Raman technology to the analysis of biological fluids.

(257) **Digital Microfluidics: A Versatile Platform for Sample Processing and Analysis**

Andrea Kirby[1], Aaron Wheeler[1]; [1]University of Toronto

Microfluidics is an attractive tool for miniaturized sample processing, as it offers fast reaction times, reduced reagent usage, the capacity for integrated, automated sample handling modules, and potential for high-throughput analysis. Digital microfluidics (DMF) is a microscale fluid handling technique that uses electric fields to manipulate individual liquid microdroplets on insulated electrode arrays. In contrast to the more common format of microfluidics that relies on microchannels and streams of fluid, sample handling in DMF is completely discretized, making DMF uniquely well-suited for carrying out sequential, multistep processes. We have developed DMF-based methods for many different applications, including

parallel-scale chemical synthesis, proteomic sample processing and analysis, integrated cell culture and cell-based assays, particle-based immunoassays, and rapid extraction and quantification of diagnostic biomarkers from tiny clinical samples. In this talk, I will discuss a number of these applications, highlighting the versatility of DMF as a sample preparation platform that can be interfaced with a variety of analytical tools for rapid and facile analysis. These examples and others suggest that DMF is an emerging new tool for sample processing and analysis, and will continue to develop as a useful platform for myriad applications in the laboratory and beyond.

(258) **Microscale Spectroscopic Probes**

Francis Esmonde-White[1], Cynthia Cipolla[1], Thitaphat Ngernsutivorakul[1], Michael Morris[1], Robert Kennedy[1]; [1]Dept. of Chemistry, University of Michigan

We will present a novel approach to fabricating miniature fiber optic probes for optical spectroscopy. Microscale spectroscopic probes are traditionally fabricated by aligning and bonding a sequence of microscale optical elements into a tube or onto a prepared planar substrate. We have adapted a soft-lithography method to create molds for casting polymer optical probes directly onto optical fibers. These monolithic polymer microprobes enable complex optical designs to be precisely fabricated into tiny probes, without rigorous optical micro-assembly steps. We will demonstrate the use of these probes as modular detection systems in several fluorescence and Raman applications, including for microfluidics and biomedical spectroscopy.

(259) **Searching for Rock Surface Alteration on Mars with the ChemCam Laser-Induced Breakdown Spectroscopy Instrument**

Nina Lanza, Samuel Clegg[1], Roger Wiens[1], Richard Léveillé[2], Noureddine Melikechi[3], Robert Tokar[4], Jennifer Blank, Nathan Bridges, Ben Clark, Matthew Deans; [1]Los Alamos National Laboratory; [2]Canadian Space Agency; [3]Delaware State University; [4]Planetary Science Institute

In its first 100 sols on the martian surface, the ChemCam laser-induced breakdown spectroscopy (LIBS) instrument onboard the Mars Science Laboratory (MSL) rover sampled ~25 rock targets. The LIBS technique uses a pulsed laser to ablate tens of micrograms of material from a target. By performing multiple laser pulses on one location, a compositional depth profile is obtained. In this way, ChemCam can detect rock surface alteration features such as coatings and weathering rinds. The composition and thickness of these surface features provide information about the style of chemical alteration and amount of water to which a rock has been exposed, potentially revealing details about both the climate and the presence and abundance of water in the surface environment. Previous martian rovers found evidence for alteration on the surfaces of martian rocks but did not have the appropriate instrument suite to analyze them. Here we present data from ChemCam's first 100 sols on Mars and compare these to laboratory LIBS experiments on well-characterized terrestrial rock samples with surface coatings and rinds. Initial results from Mars show that all rocks have the same composition in the first ~5 shots, beneath which the individual rock compositions become more distinct. The compositions of the first shots are similar to one another, suggesting a common source. Given the ubiquity of dust on the martian surface, the first few laser shots likely represent dust rather than alteration. However, it is important to be able to recognize the signatures of coatings and rinds in LIBS data in case they are encountered on Mars. To this end, we have performed a series of laboratory experiments on terrestrial rock samples to compare with martian data in order to better interpret the ChemCam data. Multiple depth profiles of 300-900 shots were obtained on both the interiors and exteriors of naturally weathered rocks. Preliminary results suggest that terrestrial coatings have trends in LIBS spectra that are very different from what is most likely martian dust; whereas dust is removed relatively quickly in ~5 shots, it appears that even thin coatings (~10-100 μm) can take up to 100 shots to penetrate.

(260) **Mars Mineralogy at Gale Crater as measured by the ChemCam LIBS**

M. Darby Dyar[1], Elly Breves[1], Hannah Blau[2], Tommy Boucher[2], Allan Treiman[2, 3], Ryan Anderson[4], Samuel Clegg[4], Nina Lanza[4], Horton Newsom[4], Roger Wiens[4]; [1]Mount Holyoke College; [2]University of Massachusetts; [3]Lunar and Planetary Institute; [4]Los Alamos National Laboratory

ChemCam, a remote sensing instrument package including a Laser-Induced Breakdown Spectrometer (LIBS) and remote micro-imager (RMI), is providing geochemical analyses and context imaging as part of the Mars Science Laboratory (MSL) Curiosity rover payload. ChemCam can to shoot multiple laser shots at a single location, providing information from successive LIBS spectra on chemical changes to depths (ca. 0.5 mm) into each rock. By averaging LIBS analyses of multiple locations (e.g., rasters) on a target, ChemCam obtains a bulk chemical analysis of the target, enabling geochemical classification and comparisons to chemical analyses from the Alpha-Particle X-ray Spectrometer (APXS) instrument also on MSL, which has a beam diameter of 1.7 cm. The small spot size (ca. 0.4 mm) of the ChemCam laser also allows the instrument to probe many rock samples with a beam size similar to the grain size of basaltic rocks that dominate global surface geology on Mars. Because the beam often samples pairs of phases and (infrequently) individual minerals, it is also possible to extract information about mineralogy. For this study, compositions at each location probed on Mars were determined using partial least-squares (PLS) multivariate analysis techniques. PLS results are reported using the geologic convention of wt.% oxides, so these analyses were converted to moles to enable use of elemental ratios to identify minerals by their stoichiometry. In many targets, multiple LIBS shots presented constant molar ratios such as Na/(Na+Ca), which are consistent with plagioclase feldspar minerals [$(Na,Ca)Al_{1-2}Si_{2-3}O_8$], the most common rock-forming minerals on Earth. The martian plagioclases have an average composition of $Na_{0.45}Ca_{0.55}Al_{1.5}Si_{2.5}O_8$, but individual spots span the entire range from Ca to Na end-members. A small K-feldspar component, generally <10 mole%, is present either in plagioclase or as a distinct alkali feldspar. These results are consistent with those calculated from CPIW norms using APXS data (from MSL and MER), and with typical plagioclase material in martian meteorites. Compositions of olivines, pyroxenes, and oxides are more difficult to discern from mixed-phase analyses, but initial work suggests that they are dominated by Fe>Mg phases, again consistent with APXS results.

(261) **Cluster Analysis for Provenance Determination of Gemstones: Emerald, a Case Study**

Catherine McManus[1], James Dowe[2], Nancy McMillan[3], Tristan Likes[1]; [1]Materialytics, LLC; [2]Analytical Data Services; [3]New Mexico State University

Provenance determination for precious gems has been pursued for centuries using a variety of techniques, including variations in color, mineral inclusions and other phases, the concentration of major and trace elements, and spectroscopic data. This presentation reviews the application of Laser Induced Breakdown Spectroscopy (LIBS) and multivariate analysis as a provenance determination method for the gemstone emerald, a variety of green beryl ($Be_3Al_2Si_6O_{18}$). The Laser-Induced Breakdown Spectroscopy (LIBS) data, presented in this study evaluate 450 emerald samples collected from 15 locations. Locations in this study include: the Khenj Mine, Afghanistan; Carnaiba Mine, Brazil; Winshan, China; Magara Mine, Tanzania; Crabtree Mine, United States of America; Mpumalanga, South Africa; Fwya Fwya, Zambia; Sandawana, Zimbabwe; and seven different mining areas in Colombia to include Chivor, Cosquez,

Gachala, La Pita, Muzo, Peñas Blancas and Ubala. Samples were analyzed using a Photon Machines Insight LIBS system with a Nd:YAG laser operating at 266 nm. Sixty spectra were acquired from each of the 450 samples in an argon environment. Using cluster analysis techniques of the LIBS data positive identification of country of origin for emeralds with success rate greater than 90% was achieved. In addition to country of origin being correctly established, greater than 90% positive identification of unique mining regions within a country was also seen.

Laser-Induced Breakdown Spectroscopy is an appropriate approach for the emerald provenance problem, as well as other complex geochemical problems. Previous techniques have only provided an indication of country of origin that requires a final decision to be made by a trained expert rather than a statically based determination using an algorithm.

(262) **Metabolomic Analysis of Cocaine Addiction using a Self-Organizing Map-Based Approach**

Cody Goodwin[1,2,3], Christina Marasco[3], Kevin Seale[3], Brian Bachmann[2, 3], John Wikswo, Nicole Schramm-Sapyta[4], John McLean[1, 2, 3]; [1]Vanderbilt University Department of Chemistry; [2]Vanderbilt Institute of Chemical Biology; [3]Vanderbilt Institute for Integrative Biological Research and Education; [4]Duke University Medical Center Department of Psychiatry

Conventional methods for determining prior cocaine abuse rely on the detection of cocaine metabolites, which are relatively transient *in vivo* (ca. detectable up to 2-5 days in urine). However, persistent physiological changes exist beyond cessation of cocaine administration. The presented research proposes the use of a self-organizing map-based method for metabolomic profiling of rat serum from cocaine addiction models as a means of depicting different metabolic phenotypes of abuse. We seek to define biomarkers specific to prior drug abuse not directly resulting from cocaine metabolism, and potentially identify metabolic differences in addicted models. Rats were trained to self-administer cocaine via an operant task, with rats given access to cocaine for up to 6 hours per day, with a limit of 50 infusions per day (0.8 mg/kg/infusion) [4]. After 10 days of such self-administration, this behavior was extinguished through the replacement of cocaine with saline. After extinction, rats were tested for reinstatement of cocaine seeking via drug-induced reinstatement (an intraperitoneal injection of cocaine was given to reinstate cocaine seeking in the operant chambers). Rats were then behaviorally classified as "addicted" or "non-addicted" based upon their reinstatement behavior. Rats that had never been exposed to cocaine were included as negative controls. Upon completion of the behavioral study, rats were sacrificed and their sera were analyzed using UPLC-ion mobility-mass spectrometry. Metabolomic analyses were performed using multivariate statistical analysis methods in parallel with a self-organizing map based approach to feature organization. Unique profiles were observed for cocaine experienced rats two weeks following the cessation of cocaine exposure. Significant metabolites were putatively identified that contributed to both cocaine exposure, and behavioral differences.The dynamic nature of the metabolome is an oft-neglected property in mass spectrometry-based measurements. Additionally, the underlying interconnectedness, an inherent biological property, is also underrepresented in conventional studies. In light of these shortcomings, we have applied a self-organizing map-based approach to the organization and prioritization of metabolic features according to dynamic similarities. This method uses a data-driven approach to iteratively organize features based upon trends in both sample abundance and dynamics.

(263) **Validation of UPLC/MS Methods for Trace Analysis of Dyes Extracted from Acrylic, Nylon and Polyester Fibers**

Molly R. Burnip[1], Kaylee R. McDonald[1], Scott J. Hoy[1], Stephen L. Morgan[1]; [1]University of South Carolina

Forensic fiber examinations involve comparison of trace evidence fibers to determine possible associations between victims, suspects, and crime scenes. While fast nondestructive methods are preferred, techniques such as microscopy, UV/visible microspectrophotometry, and infrared spectroscopy, do not identify dye mixtures. We are using microextraction, followed by ultra-performance liquid chromatography (UPLC) to distinguish similar fibers containing different, but similar, dyes by retention time matching, UV/visible spectra comparison, and structural analysis by mass spectrometry. Because dyes adhere to different polymer fibers with different mechanisms, extraction methods must be individually designed to disrupt those mechanisms and provide efficient extraction. For example, for nylon, an extraction solvent mixture of water, pyridine, and ammonia disrupts the electrostatic attraction of acid dyes to nylon. We have successfully extracted dyes from single fibers as small as 0.5 mm in length. A single gradient-based UPLC method has been developed for simultaneous separation of basic dyes on acrylic fibers, acidic dyes on nylon fibers, and disperse dyes on polyester fibers. Having a single chromatographic method for those three dye classes avoids using multiple columns/solvents and increases sample throughput. Method transfer has been accomplished to the forensic laboratory of the South Carolina Law Enforcement Division (SLED). To maintain American Society of Crime Laboratory Directors/Laboratory Accreditation Board (ASCLD/LAB) accreditation, we followed the Scientific Working Group for Toxicology (SWGTOX) validation guidelines. SWGTOX requires accuracy within 20%, limit of detection and limit of quantitation of 10 ng/mL or less, and a percent coefficient of variation less than 20% (within and between run). Our method for the three fiber types and their respective dyes for UPLC-DAD has resulted in a limit of detection of <570 ppb, a limit of quantitation of <1.89 ppm, and a coefficient of variation of <3.43% for all tested dyes. The profiling of dye formulations on trace fibers at ppm levels allows match conclusions to be made with higher reliability, and "results consistent with" will have increased probative significance.

(264) **Distance-of-Flight Mass Spectrometry with a Matrix-Assisted Laser Desorption Ionization Source: MALDI-DOFMS**

Steven Ray[1], Elise Dennis[1], Alex Graham[1], Christie Enke[1, 3], Charles Barinaga[2], Anthony Carado[2], David Koppenaal[2], Gary Hieftje[1]; [1]Indiana University, Department of Chemistry, Bloomington, IN; [2]Pacific Northwest National Laboratory, Richland, WA; [3]Department of Chemistry, University of New Mexico, Albuquerque, NM

A new type of mass analyser known as the distance-of-flight mass spectrometer (DOFMS) has been coupled to matrix-assisted laser desorption ionization (MALDI) source for the analysis of biomolecules. The DOFMS employs a velocity-based m/z-separation approach that is the complement of traditional time-of-flight mass spectrometry (TOFMS). Time-of-flight mass analyzers measure the m/z of an ion by imparting the same energy to all ions and then measuring the time required for each m/z to traverse a known distance and arrive at a single detector. In contrast, DOFMS measures the m/z of an ion by measuring the distance each ion travels during a set time period by employing a position-sensitive detector. Specifically, ions accelerated to a constant momentum separate in space according to their various m/z-dependent velocities, with ions of lower m/z traveling longer distances than ions of greater m/z. At a specific instant after acceleration, all m/z will achieve a sharp spatial focus and can then be directed onto the surface of a position-sensitive ion detector where their m/z is determined based upon location. The DOFMS strategy offers a number of significant benefits for

biological mass spectrometry. Like TOFMS, DOFMS is architecturally simple, rapid, and has an unlimited m/z range. However, DOFMS exploits an ion focusing strategy that is designed to reproduce the initial spatial distribution of ions upon the detector surface; thus, a surface ionization technique such as MALDI can be used to great advantage in DOFMS because the initial positions of ions created by the source are defined by the sample surface. As important, the DOFMS strategy permits new experiments to be performed not possible with typical TOFMS. Here, a commercial 1.5m MALDI-TOFMS has been modified for DOFMS. The theory of operation, experimental advantages, and the analytical performance of this new type of mass spectrometer will be described and compared with traditional MALDI-TOFMS.

(265) **Comparison of Soft-Landed Silver Nanoparticles and Traditional Matrices for Small Molecule MALDI-MS**

Barbara Walton[1], Guido Verbeck[1]; [1]University of North Texas

MALDI is one of the most widely used ionization techniques in mass spectrometry, however one of its biggest drawbacks is matrix interference, particularly in the low mass region. One possible method of overcoming this limitation is through the use of metallic nanoparticles as an alternative MALDI matrix. It has been demonstrated that energy absorption is independent of wavelength for nanoparticles, making them an interesting potential matrix because increased particle size would lead to increased energy absorption. Soft-landing ion mobility (SLIM) has been utilized for the creation and deposition of silver nanoparticles. SLIM is unique because it enables the deposition of gas phase ions on top of analyte molecules at kinetic energies low enough to avoid sputtering or fragmentation thereby preserving the nature of the underlying species. Silver particles were produced via pulsed laser irradiation of a solid silver target in the presence of He buffer gas. The ions travel down the mobility cell and are deposited onto a surface with kinetic energies in the thermal regime, < 1 eV. It is possible to optimize the particle size distribution and surface coverage for a specific application or system by varying the buffer gas pressure, laser power, and deposition time. Coupling SLIM to MALDI-MS has provided an alternative, easy way to administer effective matrix without compromising the quality of spectra. Specifically, our soft-landed silver particles have shown to enhance the low mass region of MALDI-MS, which is typically convoluted with matrix. Preliminary data also suggests that fragmentation of tryptamines like melatonin, is reduced with soft-landed silver compared to traditional matrix.

(266) **Touch Spray Ambient Ionization for Tissue Disease State Diagnosis by Spot Analysis**

Kevin Kerian[1], Alan Jarmusch[1], Liang Cheng[2], Timothy Masterson[3], Michael Koch[3], Ahmed Hamid[1], Livia Eberlin[1], R. Graham Cooks[1]; [1]Department of Chemistry and Center for Analytical Instrumentation Development, Purdue University; [2]Department of Pathology and Laboratory Medicine, Indiana University School of Medicine; [3]Department of Urology, Indiana University School of Medicine

A new spray based ambient ionization method has been developed for disease state diagnosis of tissue. Touch spray ionization utilizes a suitable probe, such as a teasing needle, to physically touch and remove a small amount of material from an area of interest from the tissue specimen. The probe is used to transfer material from its point of origin to the inlet of a mass spectrometer where high voltage and solvent are applied to the probe. Solvent travels over the material on the probe and creates a Taylor cone carrying extracted molecules into the mass spectrometer for chemical analysis. Negative ion mode mass spectra produced with touch spray ionization of mouse brain tissue sections show similar lipid patterns to what is commonly observed by desorption electrospray ionization (DESI), with dominant ions at *m/z* 788, 834, 885, and 888 in characteristic ratios for white or gray matter. Chemical mapping of coronal, sagittal, and transverse mouse brain sections have been performed to show reproducibility, specificity, and differentiation of the tissue when probing different regions of the brain. Recently, in collaboration with Indiana University's School of Medicine (IUSM), fresh cancerous specimens have been obtained from radical prostatectomy or partial nephrectomy surgeries and investigated with touch spray probes for rapid *in vitro* molecular analysis. It is envisioned that touch spray may be used during surgery to probe tissue of interest *in vivo* and *ex vivo*, producing molecular information indicative of disease state under a minute.

(267) **Top-Down Mass Spectrometry for Characterizing Large Protein Complexes**

Joseph Loo, Huilin Li, Jiang Zhang; [1]University of California, Los Angeles

The application of mass spectrometry (MS) for studying protein complexes has utility in biochemistry and biomedical research. Protein-protein interactions govern signals involved in cell growth, differentiation, and intercellular communication through dynamic associations between modular protein domains and their cognate binding partners. The role of protein assemblies in normal cellular processes and diseases warrants a practical and sensitive method for their study. Developments in protein MS and tandem MS (MS/MS) to define the structures of protein complexes will be discussed. "Top-down" MS of protein complexes can be used to assess protein assembly topology. Collisionally activated dissociation (CAD) of protein complexes usually results in the release of one or a few subunits that are located on the peripheral areas of the complex topology, but often CAD mass spectra are not consistent with the expected subcomplex composition. The electron-based dissociation methods, such as electron capture dissociation (ECD) and electron transfer dissociation (ETD), have been exploited to provide positional information for small ligand binding onto proteins. ECD-MS/MS has been used to address larger protein complexes also, as first demonstrated by the Gross lab (Washington Univ.-St. Louis). Using high resolution (15-Tesla) Fourier transform ion cyclotron resonance (FT-ICR) mass spectrometry and ECD, we have found that product ions result mainly from regions on the outer surface of the complexes (up to 500 kDa). For the smaller 64 kDa hemoglobin (Hb) complex, comparison of the ECD data for the Hb dimer and tetramer revealed enhanced fragmentation at the dimer/tetramer interface, and thus reveals the location of this interface. Also using top-down MS, the binding site of aptamers, short single-stranded RNA/DNAs that can bind a specific molecular target and exhibit high binding affinity, to their protein targets can be determined. This area of research is still in its infancy, and we believe that advancements in the methodologies can yield protein-protein contact information directly without resorting to cross-linking chemistries.

Acknowledgments: Support from the National Institute of Health (R01 GM103479) and the NIH/NCRR High-End Instrumentation Program (S10 RR023045, S10 RR028893) are acknowledged.

(268) **Enabling Large-Scale Discovery, Characterization and Quantitation of Neuropeptides via Tandem Mass Spectrometry**

Lingjun Li[1], Chenxi Jia[1], Christopher Lietz[1], Qing Yu[1], Robert Sturm[1]; [1]University of Wisconsin

Tandem mass spectrometry (MS/MS) of peptides and proteins has become an essential tool for proteomic and peptidomic studies. Comprehensive characterization of signaling peptides in a nervous system is often critical to deciphering the functionality of a neural circuit yet it presents a daunting challenge due to low level of these signaling molecules present in highly complex biological matrices. To address technical challenges of *de novo* sequencing of neuropeptides, we employed isotopic formaldehyde labeling to improve fragmentation patterns for unambiguous assignment of sequence-specific product ions. Furthermore, we incorporate this

labeling method followed by electron-transfer dissociation (ETD) fragmentation and ion mobility spectrometry (IMS) to study the underlying mechanism of resulting simplification of gas-phase tandem MS fragmentation. Our combined approach revealed a clear mechanism of blocking intermediate cyclic-b ion formation and elimination of sequence scrambling event that could lead to erroneous sequence assignment. In addition to large-scale *de novo* sequencing for discovery of novel neuropeptides, multiplex quantitation based on isobaric tagging reagents represent a new direction for high-throughput quantitative peptidomics/proteomics. Towards this end we developed novel tandem mass tagging reagents based on dimethylated amino acids and employed these new reagents to produce differential display of neuropeptidomes under different physiological conditions such as feeding. A potential limitation to the current isobaric tagging for quantitation is the underestimation of fold-changes due to precursor isolation interference. We propose and demonstrate novel use of ion mobility mass spectrometry to separate co-isolated precursor ions in the ion mobility drift cell followed by tandem MS fragmentation. This new strategy improves peptide identification and quantitation accuracy using isobaric tandem mass tags.

(269) **Cell Surface Chemoproteomics for Capturing States of Cardiac Differentiation from Pluripotent Stem Cells**

Rebekah Gundry[1]; [1]Medical College of Wisconsin

Human pluripotent stem cells (embryonic (ES) and induced (iPS)) provide a valuable tool for studying early stages of development. Recent improvements in our ability to reproducibly and robustly generate cardiomyocytes from ES/iPS cells has ushered in new opportunities to study early events in cardiac development and to generate cell types relevant for disease modeling, drug testing, and potentially therapy. However, major challenges include the inability to biochemically direct *in vitro* cardiac differentiation to specific, selected endpoints. While intracellular markers informative of major developmental stages have been identified (e.g. Mesp1,Isl1), these cannot be employed to isolate therapeutically relevant cells (i.e. require genetic modifications) and there are currently limited tools available for specifically tracking the primary heart field, which ultimately gives rise to the left ventricle. The overall goal of this study is to identify cell surface accessible proteins that will allow for the tracking and live cell isolation of ES/iPS-derived cardiac progenitor cells without genetic manipulations. Toward this end, the Cell Surface Capturing (CSC) Technology, an antibody-independent strategy that uses affinity enrichment of cell surface N-glycoproteins and high mass accuracy mass spectrometry to selectively identify cell surface proteins, was applied to human ES and iPS cells and ES-derived cardiomyocytes. In total, >800 cell surface proteins have been identified, including known markers as well as proteins never previously attributed to these cell types. We show for the first time a novel cell surface marker that shows temporal regulation similar to that of NKX2.5, a marker of mesoderm commitment. We also show temporal regulation at the transcript and protein level for five additional novel cell surface markers during cardiac differentiation.

(270) **Top-down Identification of Casein Isoforms Using a High Performance Benchtop Quadrupole Orbitrap Mass Spectrometer**

David Horn[1], Terry Zhang[1]; [1]Thermo Fisher Scientific

Whey proteins, most notably alpha-lactalbumin and B-lactoglobulin, are currently being investigated for their potential positive health benefits. Whey proteins are a substantial percentage of human milk (~60%) while such proteins are less abundant in cow milk (~20%). Currently, the nutritional requirements of infant formulas require comparison of their amino acid composition in comparison to human milk, but the calculation of the ratio of whey protein/casein protein currently is not required in most countries. However, in China, there is an emerging requirement that at least 60% of protein content in infant formula are from whey proteins but there currently is no standard method to calculate this ratio. The work described in this presentation describes the identification of the various proteoforms of caseins and whey proteins using top down tandem mass spectrometry on a benchtop Orbitrap mass spectrometer. A surprising number of casein protein forms were identified, including intact isoforms and many truncated products. This indicates that quantification based on single target casein protein masses will underestimate the amount of casein in a given sample.

(271) **Top-down Electron Capture Dissociation Mass Spectrometry for Deep Sequencing of Phosphoproteins**

Ying Ge[1]; [1]University of Wisconsin-Madison

Proteomics includes not only identification and quantification of proteins, but also characterization of protein modifications such as post-translational modifications (PTMs) and sequence variants. Top-down MS has emerged as a powerful tool for the analysis of protein modifications including PTMs (i.e. phosphorylation, proteolysis, acetylation) and sequence variants (i.e. mutants, alternatively spliced isoforms) simultaneously in one spectrum (a "bird's eye view"). Subsequently, each modified protein form can be isolated and fragmented in the mass spectrometer to locate the modification site. The incorporation of electron capture dissociation (ECD) greatly enhances the top-down MS capabilities. ECD is non-ergodic dissociation thus is especially useful for mapping labile post-translational modifications such as phosphorylation which are well-preserved during the ECD fragmentation process. We have shown that top-down MS with ECD has unique advantages in unraveling the molecular complexity, quantifying multiple modified protein forms, complete mapping of modification sites with full sequence coverage, discovering unexpected modifications, identifying/quantifying phosphorylated positional isomers and determining the order of multiple modifications. Specifically, I will present the application of top-down ECD MS for deep sequencing of important phosphoproteins in the heart such as cardiac troponin, tropomyosin, and cardiac myosin binding protein.

(272) **Electrophoretic Analysis of Individual Autophagosomes**

Edgar Arriaga[1], Chad Satori[1]; [1]University of Minnesota

Autophagy is a molecular pathway responsible for the degradation of intracellular cargo involving sequential formation of phagophores, autophagosomes or amphisomes, and autolysosomes. These are known as autophagy organelles. The dynamic nature of autophagy and the multiple autophagy organelles involved make bulk measurements, such as those done by Western blotting, inadequate to understand autophagy and its roles in aging and disease. Analytical techniques that monitor time-dependent changes in the properties and numbers of individual autophagy organelles are highly needed. Capillary electrophoresis coupled to laser induced fluorescence detection (CE-LIF) has been used previously to count and determine properties of individual organelles, but never used on autophagy organelles. Here we report on the labeling of autophagy organelles with GFP-LC3 and their individual analysis by CE-LIF. To determine time-dependent changes of the properties of individual organelles under basal and rapamycin-driven autophagy, we treated L6 cells expressing GFP-LC3 with vinblastine, which halts autophagy just before formation of autolysosomes. Comparison of organelle numbers and changes in GFP-LC3 fluorescence intensities or electrophoretic mobilities of individual organelles, that either accumulated or disappeared during vinblastine treatment, provided individual-organelle level detail of the autophagy process which is critical to investigate the complexity of autophagy flux and its critical role in response to drug treatments, aging, and disease.

(273) **Manipulation of Mitochondria by Insulator-based Dielectrophoresis**

Jinghui Luo[1], Gregory Wolken[2], Edgar Arriaga[2], Alexandra Ros[1]; [1]Department of Chemistry and Biochemistry, Arizona State University, Tempe, AZ; [2]Department of Chemistry, University of Minnesota, Minneapolis, MN

The study of mitochondria is important due to the organelle's significant contribution in many cellular functions such as energy production, metabolism, cellular signaling and apoptosis. Mitochondria have intrinsic heterogeneous size and morphologies, which suggests the existence of mitochondrial subpopulations. In particular, the atypically sized giant mitochondria have been observed in various pathological states and various models of aging and a proper subcellular separation method to distinguish normal and giant mitochondria is thus needed. Here, we study fundamentals of mitochondria dielectrophoresis (DEP) to elucidate fractionation and separation of cell organelles by this transport phenomenon. In DEP, polarization properties of a particle in a non-uniform electric field are probed. Microfluidic devices exhibiting insulating constrictions are capable of providing strong electric fields within small dimensions; this method is termed insulator-based DEP (iDEP). By integration of iDEP within a microfluidic device, mitochondrial migration by exploiting differences in a new dimension of analyte properties, i.e. their polarizability, becomes possible. Our preliminary work on iDEP of mitochondria includes the study of the trapping potential thresholds under a wide range of AC fields (10-50k Hz) with 0.9 μm polystyrene beads as model particles. Furthermore, we studied rat semimembranosus muscle mitochondria as well as the liver and hamstring muscle mitochondria of C57BL6 mouse. The applied AC potentials allowed to suppress electroosmotic flow (EOF) and moreover, to study iDEP of mitochondria in a conductivity range from 30 μS/cm to 2000 μS/cm to reveal distinctive trapping potentials. This preliminary study reveals specific trapping potentials, conductivity ranges and AC frequencies to further exploit iDEP for mitochondria, such as to distinguish normal and giant mitochondria via their dielectrophoretic properties.

(274) **Single Cell Capillary Electrophoresis Mass Spectrometry for Studying Neuron Heterogeneity**

Stanislav Rubakhin[1], Jordan Aerts[1], Jonathan Sweedler[1]; [1]University of Illinois at Urbana-Champaign

Assaying the chemical content of individual cells provides a wealth of information on organism and tissue organization, and a range of physiological and pathological processes. Both biological variability and functional heterogeneity are uncovered using single cell analytical measurements. The nervous system is one of most challenging targets for such studies with its highly dynamic nature and great cellular heterogeneity. Single cell capillary electrophoresis mass spectrometry (CE-MS) is capable of addressing many methodological challenges associated with single cell analysis including inherently small sample volume requirements and broad range of analytes. Using our CE-MS system, hundreds of endogenous metabolites are characterized with many quantified. Because of instrumental limitations, only a portion of the molecular cell content is characterized when single cell is investigated; here we demonstrate possibility of the increased analyte coverage by the sequential investigation of the same single cell sample using two different ionization approaches – electrospray ionization (ESI) and matrix assisted laser/desorption ionization (MALDI). MALDI-MS provides detail on the endogenous peptide content, and ESI-MS analyses generates lists of cellular metabolites. Typical biomedical studies require the assay of large numbers of samples. We increase the throughput of single cell cell CE-MS measurements via serial sample loading, leading to a three-fold increase in throughput. Moreover, this approach allows generation of calibration curves for analytes of interest during the same CE-MS run. These capabilities are demonstrated and validated using several well characterized identified neurons from the central nervous system of the classical neurobiological model, the sea slug *Aplysia californica*. CE-MS approach was also successfully applied to the less analytically studied individual mammalian neurons from rat dorsal root ganglia. Several hundred distinct peaks are detected, and more than twenty metabolites identified including classical neurotransmitters such as glutamate and gamma-aminobutyric acid. We also provide preliminary information on how selected metabolites change in specific neurons as a function of induced inflammatory pain.

(275) **Glutaraldehyde Enhanced Dielectrophoretic Cell Separation**

Zachary Gagnon[1]; [1]Johns Hopkins University

Dielectrophoretic cell separation takes advantage and exploits the unique differences in cellular dielectrophoresis (DEP) mobility that occurs between cell types. Such disparities in native DEP mobility are often subtle, however, and various cell chemical or physical modifications are often required to enhance these values in order to yield effective cell separation. High permittivity buffers, for example, have been used to facilitate separations, to increase the rate of DEP cellular velocity during separation, and to create ideal conditions for DEP mobility measurements. In addition, low conductivity solutions have also been exploited to, for example, effectively separate malaria-infected red blood cells from human blood. Others have chemically modified cell membrane electrical properties to amplify subtle differences among cell subpopulations. All of these techniques rely on the time consuming process of optimization, whereby the researcher must determine which chemical or physical difference to best exploit in order to achieve the desired separation scheme for a given cell population. This is common for all cell separation techniques, but proves particularly difficult when the separation phenomenon of interest is DEP. Here, we present an efficient method for determining and stabilizing the optimum electrolyte parameters for DEP-induced cell separations. DEP separation takes advantage of inherent or chemically modified differences in the electrical properties of the cell membrane, cytoplasm, and other organelles that become apparent when such cells are suspended in a specific electrolyte solution. Often, however, the buffer solution is nonideal and cellular constituents rapidly equalize with the surrounding buffer, either eliminating differences in DEP mobility or creating highly inconsistent time-dependent separation schemes. We utilize a cell membrane fixation agent glutaraldehyde to rapidly cross-link aminated membrane proteins of viable and nonviable yeast cells and to effectively prevent cell ion leakage in low conductivity buffer solutions. As such, cytoplasmic dependency on buffer conductivity is significantly reduced. Owing to these effects, we present simple buffer conductivity algorithm to determine optimal electrolyte conditions for DEP-based cell separations.

(276) **Investigation of Erythrocyte Age and Electrophoretic Mobility Correlations**

Christopher Harrison, Jack Fang[1]; [1]San Diego State Univeristy

The motivation for this work arises form our study of the ability to differentiate mixed populations of erythrocytes. Endurance athletes who desire to gain an advantage over the competition have on occasion resorted to prohibited autologous blood transfusions. The increased number of erythrocytes in circulation grants them a performance benefit. Additionally, by transfusing their own stored blood they can avoid the anti-doping detection methods designed to identify homologous blood transfusions; where the transfused blood comes from someone other than the athlete. We have developed a capillary electrophoretic (CE) method capable of identifying the presence of aged erythrocytes in a sample of fresh blood, in a simulated (*in vitro)* transfusion process, based on the electrophoretic mobility difference of the two cell populations. We will present our

current results for the effectiveness of this analysis for actual autologous blood transfusions performed with athletes. Investigating the window for detection of the transfusion as well as the influence of physical stress on the native population of erythrocytes in athletes. In addition we will examine the influence of the cellular membrane sialic acid residues on the overall charge and resultant electrophoretic mobility of the erythrocytes as they age. By selectively altering the sialic acid residues on the cells we can identify the influence their charges have on the erythrocytes.

(277) **Metabolic Profiling of Living Cells by Surface Enhanced Raman Spectroscopy**

Lawrence Ziegler; [1]Boston University

SERS studies of living cells for a variety of biomedical applications have been carried out. Results for investigations related to bacterial cell identification, whole human blood and red blood cell processes and cancer cell detection will be described. As demonstrated by these results, SERS based platforms have the potential to be highly successful, rapid diagnostic for a wide variety of human health concerns. This results from the SERS advantages of speed, sensitivity, multiplexing capabilities, specificity, ease of use, cost, portability and lack of need for extrinsic labeling, combined with efficient sample preparation procedures, appropriate instrumentation and novel multivariate data analysis techniques. In addition, SERS is found to be a sensitive and specific methodology for learning about the biological activity taking place at the outer layers and in the extracellular metabolome of single cells in real time. These capabilities are illustrated by progress in the development of SERS for bacteremia and urinary tract infection diagnostics, red blood cell aging and metabolic profiling of renal and breast cancer cells. This is the first demonstration of SERS use for whole cell metabolomics. Typically, NMR and mass spectrometry are the experimental techniques used for the identification of small metabolites. The biomedical use of SERS for spectroscopy is found to be a sensitive diagnostic indicating both species and strain specificity. The reproducible markers are due to purine metabolic degradation products from cells in their log phase. Red blood cells show the effects of these metabolic pathways as a function of time. In addition, these molecular markers also appear in the SERS spectra of cancer cells. These phenomelnological effects are demonstrated here and are clearly ubiquitous makers of the cellular activity of living organisms.

(278) **Multiplexed and Sensitive Molecular Diagnostics using SERRS**

Karen Faulds[1], Mhairi Harper[1], Kirsten Gracie[1], Duncan Graham[1]; [1]University of Strathclyde

Surface enhanced resonance Raman scattering (SERRS) is an analytical technique with several advantages over competitive techniques in terms of improved sensitivity and multiplexing. We have made great progress in the development of SERRS as a quantitative analytical method, in particular for the detection of DNA. However, the lack of quantitative data relating to real examples has prevented more widespread adoption of the technique. Detection of specific DNA sequences is central to modern molecular biology and also to molecular diagnostics where identification of a particular disease is based on nucleic acid identification. Many methods exist and fluorescence spectroscopy dominates the detection technologies employed with different assay formats. Another advantage of SERRS over existing detection techniques is that of the ability to multiplex which is limited when using techniques such as fluorescence. We have clearly demonstrated the ability to identify the presence of a mixture of 6 analytes in solution using data analysis techniques. Here we demonstrate the development of new molecular diagnostic assays based upon SERRS which have been used successfully for the detection of bacterial infections using modified SERRS active probes. The probes have been designed to give a specific SERRS response resulting in discernable differences in the SERRS which can be correlated to a specific DNA hybridisation event.

(279) **Raman Activated Cell Sorting using SERS Technique**

Wei Huang[1]; [1]University of Sheffield

Single cell Raman spectra (SCRS) provide label-free and intrinsic chemical 'fingerprint' of individual cells, containing rich information on nucleic acids, protein, carbohydrates and lipids. SCRS have been used to characterise cell types, physiological states and phenotypic changes. However, a key drawback of SCRS is the fact that spontaneous Raman signals are naturally weak, which hamper Raman application as a high throughput technique. We developed Ag/Au nanoparticles to achieve surface enhanced Raman scattering (SERS) at single cell level. Assisted with this single cell SERS technique, Raman activated cell sorting (RACS) and Raman activated cell ejection (RACE) has been demonstrated to achieve high throughput cell sorting based on Raman spectra. RACS and RACE have been applied to identify and sort uncultured bacteria for single cell genomics.

(280) **Inkjet-printed Fluidic Paper SERS Devices for Chemical and Biological Analytics**

Ian White[1], Wei Yu[1], Eric Hoppmann[1]; [1]University of Maryland

As a bio/chemical sensing technique, surface enhanced Raman spectroscopy (SERS) offers sensitivity comparable to that of fluorescence detection while providing highly specific information about the analyte. The high sensitivity of SERS detection results from the localized plasmons generated at the surface of noble metal nanostructures upon excitation by resonant electric fields at optical frequencies. Although single molecule identification with SERS was demonstrated over a decade ago, today a need exists to develop practical solutions for point-of-sample and point-of-care SERS systems. In recent years, optofluidic SERS has emerged, in which microfluidic functions are integrated to improve the performance of SERS. Advancements in optofluidic SERS are leading towards portable analytical systems, but the devices are currently too expensive and too cumbersome for limited resource settings. Recently, we demonstrated the fabrication of SERS substrates by inkjet printing silver and gold nanostructures onto paper. Using a low-cost commercial inkjet printer, we printed silver nanoparticles with micro-scale precision to form SERS-active biosensors. Using these devices, we have been able to achieve detection limits comparable to conventional nanofabricated substrates. Furthermore, we leverage the fluidic properties of paper to enhance the performance of the SERS devices while also enabling unprecedented ease of use. Paper dipsticks concentrate a relatively large sample volume into a small SERS-active detection region at the tip. Likewise, paper swabs collect samples from a large surface area and concentrate the collected molecules into a SERS sensor on the paper. In addition, the inherent chromatographic properties of paper enable sample cleanup and analyte separation to improve detection in complex real-world samples. In this presentation we will review the capabilities of SERS as a chemical and biological sensing technique. We will first introduce the fabrication of paper-based fluidic SERS device using inkjet printing. We will then present results of paper-based fluidic devices for SERS-based detection, and we will describe their use in a number of practical applications for point-of-sample chemical detection. Finally, we will discuss applications in highly sensitive point-of-care biological sensing for diagnostics that are currently under development, including nucleic acid sequence detection using lateral flow assays with multiplexed SERS detection.

(281) **SERS-based Biosensing and Assays**

Sebastian Wachsmann-Hogiu[1], Mehmet Kahraman[1], Zachary Smith[1], Cynthia Pagba[2]; [1]University of California Davis; [2]Georgia Tech

Highly sensitive detection of biomolecules has important significance in medicine, biology, environmental monitoring, and other settings. Optical spectroscopy has long played an important role in detection, tracking, and characterization of these molecules. However, the most successful optical techniques have relied on labeling of molecules of interest with fluorescent tags. There are many reasons why fluorescence tagging is disadvantageous, including potential inactivation of the target molecule, and photobleaching effects preventing accurate quantification of the molecule. Raman spectroscopy is a promising technique that provides chemically specific "fingerprints" of biomolecules without the need for exogenous labels. Of the many Raman-based techniques for molecular detection, Surface Enhanced Raman Spectroscopy (SERS) is the most sensitive, with the potential for single-molecule sensitivity. We present here SERS-based detection of biomolecules using aptamers as capturing agents or self aggregations of the molecules of interest. The development of novel SERS substrates aimed at high enhancement factors as well as improved reproducibility will also be presented. In addition, we use localization analysis of dynamic spectra for sub-wavenumber tracking of Raman and SERS peaks.

(282) **Chemometrics and Bruce; Some Fond Memories**

Svante Wold[1]; [1]Inst of Chemistry, Umea Univ., Sweden

The talk describes the conversion of a young physical organic chemist (SW, 1964), from a believer in 1.st principles models, to a middle aged chemometrician (SW, 1974) favoring empirical and semiempirical "data driven, soft, analogy" models for the design of experimental series and for the analysis of the resulting data. This conversion process was marked by a number of influential events, each tipping the balance towards the data driven, soft, analogy models until the point of no return in 1974. On June 10 that year, Bruce and I joined forces, and together with our research groups we formed the Chemometrics Society (later renamed to the International Chemometrics Society), and took off into the multidimensional world.This walk through my personal science history, inspired and encouraged by Bruce, is illustrated by examples of method development driven by necessity to solve given problems, and leading to data driven soft models, which, at least in my own eyes, were superior to the classical first principles approaches to the same problems.

These examples include:

(a) Using spline functions for kinetic data analysis, with a pharmacokinetic application.

(b) Disjoint principal components models for classification and discriminant analysis (the SIMCA method).

(c) PLS for multivariate regression when the variance-covariance matrix (X'X) is singular, with a data mining application.

(d) PLS extensions, e.g., PLS discriminant analysis, hierarchical PLS for distributed computing, and batch process modelling based on three way array unfolding, latent variable rotation, and PLS regression.

Then after 1990, Bruce and I gradually slided out of the academic world, and now Bruce has taken his final step.

(283) **Pattern Recognition Assisted Infrared Spectral Library Searching Applied to Forensic Analysis**

Barry Lavine[1], Ayuba Fasasi[1], Nikhil Mirjankar[1], Mark Sandercock[2]; [1]Department of Chemistry, Oklahoma State University; [2]Royal Canadian Mounted Police Forensic Laboratory

Pattern recognition techniques have been developed to search the infrared (IR) spectral libraries of the PDQ database to differentiate between similar but nonidentical IR clear coat paint spectra. The library search system consists of two separate but interrelated components: search prefilters to reduce the size of the library to a specific manufacturing automotive plant or plants corresponding to the unknown paint sample and a cross correlation searching algorithm to identify IR spectra most similar to the unknown in the set identified by the search prefilters. Using a genetic algorithm for pattern recognition to identify features in the IR spectra characteristic of the manufacturing plant from which the clear coat paint sample was obtained, search prefilters have been developed to facilitate searching of spectra in the PDQ data base. The search prefilters are robust as IR spectra collected on Thermo Nicolet instruments could be used to develop search prefilters that were able to identify the manufacturing plant from clear coat spectra collected on two older BioRad instruments. The library search algorithm cross correlates the unknown with each IR spectrum in the set identified by the search prefilters. Each cross correlated spectrum is simultaneously compared to the autocorrelated spectrum of the unknown using spectral windows that span different regions of the data from the midpoint. The top 5 hits identified in each search window are compiled and a histogram is computed that summarizes the frequency of occurrence for each selected library sample. The 5 library samples with the highest frequency of occurrence are selected as potential hits. Even in challenging trials where the clear coat paint samples evaluated were all the same make (General Motors) with a limited production year range (2000-2006), the make, model, and line of the automobile from which the unknown paint sample was obtained could be identified.

(284) **Data Analysis Strategies for Comprehensive Two-Dimensional Liquid Chromatography**

Sarah Rutan[1], Robert Allen[1], Hope Bailey[1]; [1]Virginia Commonwealth University

In recent years, there has been increasing interest in enhancing the performance of liquid phase separations, due to the desire to analyze samples of increasing complexity that contain non-volatile components. Proteomics and metabolomics are two examples of fields where enhanced peak capacities are critically needed. One means of doing this is by coupling two different liquid chromatographic systems and comprehensively sampling the eluent from the first system for analysis on the second system. Recent improvements in instrumentation have led to the ability to carry out a complete analysis in 30 minutes or less. However, important challenges remain in bringing this technology into widespread use for quantitative purposes. In this presentation, I will discuss some of these challenges and describe some new strategies for extracting the maximum amount of quantitative information from comprehensive two-dimensional liquid chromatographic data.

(285) **Applying Improved Instrument Design with Chemometrics to Difficult Spectroscopy Applications**

Jerome Workman[1]; [1]Unity Scientific

What are the instrumentation design and performance requirements for high quality multivariate calibrations? Are chemometric approaches, rather than improved signal quality by improved instrumentation, the primary answer to most analytical applications? Is the "Math is Cheaper than Physics?" refrain true or is there more to the reality behind this question? A dual approach including hardware modifications combined with chemometric approaches involves altering instrument design characteristics specific to analytical application requirements. One must ask if the use of first principles is a primary solution to reliably applying multivariate models? This paper discusses the potential of using primary reference standards for the maintenance and monitoring of spectrometers in real time.

(286) **Raman Spectroscopy of Biological Cells: Potentials and Problems**

Juergen Popp[1,2]; [1]Institut für Photonische Technologien, Jena, Germany; [2]Institut für Physikalische Chemie and Abbe Center of Photonics, Friedrich-Schiller-Universität Jena, Jena, Germany

Raman spectroscopy has been recognized to be a powerful tool to study biological cells. In this contribution, we review our results to characterize prokaryotic and eukaryotic cells. In the first part, we will show that Raman microspectroscopy in combination with innovative chemometrics offers a great potential for the identification of single bacterial cells without the need of any cultivation step. Such a fast detection of e.g. disease causing microorganisms is important for many invasive infections. In cases of sepsis a rapid detection and identification of the inducing pathogens is crucial for choosing a proper initial antibiotic therapy. It will be shown that Raman microspectroscopy allows for a direct identification of different sepsis-relevant genera out of urine samples of real patients without any precultivation steps. Furthermore, we were able to detect and identify anthrax endospores within less than two hours even in the presence of other non-pathogenic Bacillus species. Finally, the application of this Raman microbial analysis approach for food analysis that is for the detection of pathogens in milk and meat is highlighted. The main focus within the second part of this presentation is concerned with Raman studies on eukaryotic cells for biomedical applications. Overall, we will report about the great potential of Raman spectroscopy for a label-free discrimination between normal and tumor cells based on their biochemical composition or towards establishing a Raman spectroscopic hemogram i.e. characterizing leukozytes. Thereby cellular Raman spectra were recorded after drying, in laser tweezers or trapped in a microfluidic environment. In particular we will report about recent progress we made towards Raman activated cell sorting (RACS) by coupling Raman spectroscopy with microfluidics and micromanipulation approaches. In a first step, a microfluidic chip made of quartz was introduced which integrates injection of cells, trapping by fiber lasers and sorting of cells. Second, an all-fiber Raman-on-chip setup was introduced which accommodates laser excitation fibers and multi-core single-mode collection fibers. Without microscope, this Raman-on-chip setup offers low detection limits for solutions and enables to collect Raman spectra of trapped cells. Fiber Bragg gratings were inscribed into the collection fibers to suppress elastic scattered light.

(287) **Nanoparticle Based Imaging of Cells and Tissue**

Duncan Graham[1], Sarah McAughtrie[1], Derek Craig[1], Karen Faulds[1]; [1]University of Strathclyde

Metallic nanoparticles offer many opportunities in terms of detection including light scattering, surface plasmon resonance and surface enhanced resonance scattering (SERS). We are interested in the optical properties of metal nanoparticles and their potential application in a range of different biological studies. We can make use of the optical properties of nanoparticles in two ways.

1. The nanoparticle can act as an extrinsic label for a specific biomolecular target in the same way as a fluorescent label is used. The advantage of using the nanoparticle is its optical brightness (typically several orders of magnitude more than fluorophores) and the lack of background vibrational signals. Functionalisation of the nanoparticle with a specific targeting species such as an antibody or peptide aptamer allows this approach to be used in a wide range of studies including cell, tissue and *in vivo* analysis.

2. Nanoparticles can be designed to contain a specific recognition probe designed to cause a change in the aggregation status of the nanoparticles resulting in a discernible optical change when it interacts with its biomolecular target. This allows separation free analysis of specific biomolecular interactions and can be applied to a range of different probe/target interactions such as DNA-DNA, peptide-protein and sugar-protein. We have been making use of nanoparticles in both of these approaches in conjunction with SERS which is an advanced vibrational spectroscopy. To demonstrate the applicability of the two different approaches examples will be given on the use of nanoparticles for cell imaging in two and three-dimensions, imaging of nanoparticles at centimetre depths through tissue and also their ability to report on biological molecules *in vitro* and *in vivo*.

(288) **Advances in Ultrahigh Vacuum Tip-Enhanced Raman Spectroscopy**

Richard Van Duyne[1]; [1]Northwestern University

Tip-enhanced Raman spectroscopy (TERS) has emerged as a promising technique for *in situ* chemical analysis on the nanoscale. The isotopologue proof of single molecule sensitivity in ambient TERS will be demonstrated. A low temperature, ultrahigh vacuum tip-enhanced Raman spectroscopy (LT-UHV-TERS) instrument has been constructed. Atomic resolution imaging of the surface and sub-molecular resolution imaging of the adsorbate with laser illuminated plasmonic (Ag, Au) tips has be demonstrated. The UHV-TERS capabilities of this machine are shown with the copper phthalocyanine (CuPc)/Ag(111) and Rhodamine 6G (R6G) /Ag(111) systems. We estimate that the high S/N spectra for the R6G/Ag(111) system are contributed by less than ~100 molecules. We will also present TERS of rhodamine 6G (R6G) on Ag(111) at 19 K in which multiple peaks are observed to narrow to below 10 cm-1 at full width at half maximum. These are the first TERS spectra recorded at near LHe temperatures. LT-UHV-TERS allows the interactions between molecular adsorbates and binding sites on solid surfaces to be probed with unprecedented spatial and spectroscopic resolution.

(289) **Spatio-spectral Vibrational Nano-imaging of Intermolecular Coupling and Dynamics**

Markus Raschke[1]; [1]University of Colorado

Molecular self-assembly, the function of biomembranes, and the performance of organic solar cells all rely on interactions on the molecular scale. The understanding and design of such intrinsic or engineered heterogeneous functional soft matter has long been impeded by a lack of spectroscopic tools that have the necessary nanometer spatial resolution, attomolar sensitivity, and intermolecular spectroscopic specificity. We implement vibrational scattering-scanning near-field optical microscopy in a new multi-spectral modality with unprecedented spectral precision to investigate the structure-function relationship in self-phase separated nanocomposites. We resolve, with few nanometer spatial and 0.2 cm−1 spectral resolution, spectral Stark shifts and line broadening correlated with molecular-scale morphologies using a vibrational resonance which serves as a sensitive reporter of local structure, coupling, and dynamics. By creating mesoscopic images of vibrational solvatochromism, we derive local variations in electric fields with semiquantitative agreement with dielectric continuum models. This new nano-chemometric ability to directly probe both nanoscale morphology and associated intermolecular interactions can form a basis for the systematic control of functionality in multicomponent soft matter systems.

(290) **Absolute Temperature Determination with Stokes/Anti-Stokes Raman Spectroscopy**

Hiro-o Hamaguchi[1]; [1]National ChiaoTung University

We calibrate the sensitivity of a Raman spectrometer highly accurately using the pure rotational Raman spectra of diatomic molecules as intensity standards. The Stokes/anti-Stokes rotational transitions starting from the same rotational quantum number J are used so that the effect of temperature is eliminated. The effect of rotation-vibration interaction on the pure rotational Raman intensities is taken into account. The Stokes/anti-Stokes Raman intensity ratios

measured with thus calibrated spectrometer provides absolute temperatures of molecules with high accuracies. This method is applicable to whatever the system we are interested in including gas, liquid, solid, film and so on.

(291) **Enhanced Molecular Level Understanding of Nano–TiO2 Toxicity through Phosphorylated Protein Identification**

Keaton Nahan[1], Joseph Caruso[1]; [1]University of Cincinnati

Titanium dioxide, TiO2, is known as the most widely used nanoscale metal oxide. TiO2 nanoparticles are used in a variety of sunscreens and cosmetics (Botta et. al., 2011). Though nano-TiO2 has previously been found to have negligible toxic effects, studies have shown that nano-TiO2 generates reactive oxygen species (ROS) (Hartmann et. al., 2010).

Previous studies have focused on the nano-TiO2 toxicity in the European Committee for Standardization (CEN) ISO 8692:2012 test organism, Pseudokirchneriella subcapitata (Hartmann et. al., 2010). The goal of the current research includes examining changes in cell signaling through analysis of signaling changes via differential protein phosphorylation, to uncover molecular level changes occurring in Pseudokirchneriella subcapitata. The proteins were extracted and analyzed via Size Exclusion using an Agilent 1100 High Performance Liquid Chromatographic System coupled to an Agilent 8800 Inductively Coupled Plasma Triple Quadrupole Mass Spectrometer. The Agilent 8800 provides greater sensitivity and lower detection limits for phosphorous by using reaction cell technology. Fractions of interest were collected and freeze dried. Future studies include subjecting fractions to enzymatic digestions and analyzing the digests using Electrospray Ionization/Iontrap Mass Spectrometry to obtain MS/MS data to identify and quantify potential proteins.

(292) **Coupling Micellar Elektrokinetic Chromatography to ICP-MS: New Possibilities for Separation and Characterization of Nanoparticles**

Bastian Franze[1], Carsten Engelhard[2]; [1]University of Muenster; [2]University of Siegen

Engineered nanomaterials are used increasingly around the world in consumer and industrial products. In recent years, environmental concerns are being raised that call for risk assessment, toxicity studies, nanomaterial safety policies, and regulations. Therefore, it is important to provide analytical tools that are able to characterize and quantify various types of nanomaterials.

In this study, a method for size characterization of gold nanoparticles was developed through the use of micellar electrokinetic chromatography (MEKC) coupled to inductively-coupled plasma mass spectrometry (ICP-MS). In MEKC, surfactant molecules in the buffer solution attach to the surface of a nanoparticle and act as the main charge carrier. The resulting charge of the surfactant-bound particle is size dependent [1]. Separation in an electric field is possible with the particle migration time increasing proportionally to size. After coupling MEKC to ICP-MS, low detection limits for selected nanoparticles were achieved. For example, an injected mass of less than 1 pg (absolute) AuNP was successfully detected. The presentation points out key features (e.g. achievable resolution) and new possibilities. For example, this method was used for speciation analysis of metal ions and nanoparticles in the same run demonstrated by the analysis of a dietary supplement containing gold nanoparticles.

References:

[1] F.-K. Liu, G.-T. Wei, Analytica Chimica Acta 510 (2004) 77–83

(293) **Elemental Mapping of Al-substituted Li7La3Zr2O12 using fs-Laser Induced Breakdown Spectroscopy**

Huaming Hou[1,2], Lei Cheng[1], Joong Sun Park[1], Guoying Chen[1], Thomas Richardson[1], Jordi Cabana[1], Marca Doeff[1], Ronger Zheng[2], Vassilia Zorba[1], Richard E. Russo[1]; [1]Lawrence Berkeley National Laboratory; [2]Optics and Optoelectronics Laboratory, Ocean University of China

Laser Induced Breakdown Spectroscopy (LIBS) is a powerful analytical tool for direct chemical analysis. Compared to nanosecond laser ablation, femtosecond (fs) laser ablation is more suitable for spatially resolved chemical analysis because of the confined nature of the fs laser-material interaction. In this work we use fs-LIBS to chemically image all-solid-state lithium-ion battery LLZO ($Li_7La_3Zr_2O_{12}$) electrolytes. The atomic ratios of Li, Zr and minor element Al to La were mapped in LLZO in 3D with a depth resolution of 700 nm. Differences in the elemental distribution and atomic ratios of Li/La, Al/La were observed as a function of depth from the surface for LLZO samples prepared under different conditions. This work demonstrates the ability of fs-LIBS for direct 3D elemental imaging of Li-ion battery solid state electrolytes.

(294) **Development and Fundamental Investigation of Desorption/Ionization Source using High-Power Pulsed Microplasma Jet**

Takahiro Iwai[1], Kensuke Okumura[1], Ken Kakegawa[1], Yoshitaka Utsunomiya[1], Hidekazu Miyahara[1], Akitoshi Okino[1]; [1]Department of Energy Sciences, Tokyo Institute of Technology

In the field of ambient mass spectrometry, plasma ionization sources such as Direct Analysis in Real Time (DART) and Low Temperature Plasma (LTP) probe have been developed for direct mass analysis of materials on the surface. These devices are suitable for in-situ analysis because they do not require any sample preparation. However, DART is operated at a high gas temperature (>250 °C) so it is difficult to apply to heat sensitive materials such as human skin. LTP has moderate gas temperature (30 °C) but the analytical sensitivity is typically not so high because it operates with low-density dielectric barrier discharge plasma. In this study, a high-power pulsed microplasma jet was developed and applied to ambient mass spectrometry to realize high sensitive analysis. In this plasma source, micro-hollow cathode discharge is generated in a small hole (500 μm in diameter) using laboratory-built pulsed power supply. Short-duration high voltage pulse (less than 100 ns, ~2.5 kV) is applied for plasma ignition followed by longer duration pulse (~20 μs, ~0.5 kV) for forming the main discharge. This system can realize 3,000 times higher power density compared with common inductively coupled plasma (ICP) and so it should makes the plasma high density. The downstream region of the discharge has relatively low gas temperature (30~60 °C) because it is not continuous but pulsed discharge. Therefore the plasma gives no thermal or discharge damage to the target. So, we can directly apply it to human skin. To demonstrate the analytical capacity, the plasma was applied for direct solid sample analysis of various compounds. Sample compounds were deposited on the glass plate and directly probed with the He plasma. Ionized species were directly introduced into a time-of-flight mass spectrometer (micrOTOF Ⅱ, Bruker Daltonics, Germany). As a result, mass signals from various compounds successfully measured with little fragmentations. The limits of detection (LOD) of caffeine, propyohenazone and ethenzamide were 15, 1.4 and 3.8 fmol, respectively. These values are almost same level as that of DART. The optimal plasma source configuration and effect of gas-purge cell were also investigated. These results will be presented as well.

(295) **Metalloproteome of Histoplasma Capsulatum: The Role of Metals in Microbial Growth**

Anna Daigle[1], Julio Landero[1], Kavitha Subramanian[2], George Deepe[2], Joseph Caruso[1]; [1]University of Cincinnati Department of Chemistry; [2]University of Cincinnati College of Medicine

Investigations into the area of proteomics have grown tremendously in the past few decades and have expanded to include metal-containing proteins, known as metalloproteins. Exploring the set of metalloproteins expressed by an organism, known as the metalloproteome, of pathogenic organisms provides valuable information regarding the relationship between pathogen and host as well as an overall greater understanding of the pathogenic organism. Utilizing metal-based purification and identification to study the metalloproteome of a pathogenic organism is currently being applied to *Histoplasma capsulatum* in Dr. Caruso's Metallomics Laboratory. *Histoplasma capsulatum* is a dimorphic fungus which grows into a yeast at 37°C when inhaled, and causes a respiratory infection known as Histoplasmosis. Examination of metal acquisition and identification metalloproteins within *Histoplasma capsulatum* would allow for better understanding of the microbial growth and toxicity mechanisms that may partially function through metal up or down regulation. This information could potentially lead to treatments that would reduce and possibly eliminate symptoms for individuals infected with the disease. Several analytical instruments including the Inductively Coupled Plasma Mass Spectrometry, High Performance Liquid Chromatography and Electrospray Ionization/Iontrap Mass Spectrometry allow for a robust metal-based approach for the study of metal acquisition and identification of metalloproteins within *Histoplasma capsulatum*. *Histoplasma capsulatum* culturing conditions were modified in order to understand the effects of copper, iron, and zinc on fungal growth.

(296) **Has the Flow Changed? From Micro Reactors to Continuous Production**

Paul Watts; [1]NMMU

When micro reactor technology was first introduced it was seen as being a research and development tool suitable for small scale production. However the most topical examples discussed in the literature include the Ritter reaction performed on an industrial scale by DSM (Austria) which has to date generated over 4000 tonnes of product and the synthesis of nitroglycerine in China. The key driver in these examples being safety, where the excellent mixing and heat transfer characteristics of micro structured reactors enables these highly exothermic reactions to be safely performed. Nevertheless there is now a plethora of commercial reactors on the market, which means that most companies are investigating this technology to rapidly screen reactions utilising continuous flow, leading to the identification of reaction conditions that are suitable for use at a production level. Furthermore the inherent safety associated with the use of small reactor volumes enables users to employ reaction conditions previously thought to be too hazardous for use within a production environment; such as extreme reaction conditions or the use of hazardous compounds. Consequently, the types of reactions available to the R&D chemist increases through the use of this technology. It is this system flexibility that has the potential to reduce both the time taken and risk associated with transferring reaction methodology from research to production. A review of the technology will be outlined.

(297) **Streamlining Pharmaceutical Processes into Continuous Operations**

Frank Gupton[1]; [1]Virginia Commonwealth University

Technology advancements in chemical processing have more recently been driven by the development of novel equipment and methodologies that have the potential to transform our concept of chemical manufacturing. These efforts have been motivated by the growing need to develop safer, more environmentally friendly and more sustainable chemical processes which share a common focus on process intensification. The concept of process intensification consists of technological innovations (equipment and/or methods) which produce dramatic improvements in the form of energy consumption, throughput, waste reduction or capital investments resulting in a strategic cost advantage. These advancements are typically driven by expanding the window of process operability through immense increases in heat transfer and operational pressure. Recent advancements in continuous chemical processing technology have led to the development of new mesofluidic reactor systems. These continuous chemical processing systems provide the potential to streamline existing pharmaceutical processes and improve process operability. Specific applications for the continuous synthesis of active pharmaceutical ingredients will be provided to demonstrate the advantages of this alternative approach to drug synthesis

(298) **Development of a Process Analytical Sampling System for Real-Time Monitoring of Continuous Flow Reactors**

Michael F Roberto[2], Thomas I Dearing[1], Brian J Marquardt[1]; [1]University of Washington, Applied Physics Laboratory; [2]University of Washington, Department of Chemistry

Continuous flow reactors (CFRs) are flow cells that are optimized for the continuous production of a target compound. Currently, production of pharmaceuticals relies on large-scale batch processes that are intensified from the laboratory scale. This scaling up to a production scheme has many inherent inefficiencies, including long reaction times, poor mixing, large temperature gradients, and significant cost of development. Compared to batch reactors, CFRs have greater energy efficiency due to their superior mixing schemes and heat transfer properties. Due to this efficient heat transfer, reactions that require cryogenic temperatures in batch, such as the Swern oxidation, can frequently be performed at much milder temperatures in CFRs, significantly reducing temperature control costs. In addition, reactions carried out in CFRs are typically much faster than in batch and require smaller quantities of solvent, significantly reducing the amount of waste generated. Small volume CFRs can also mitigate the inefficiencies of batch chemistry scale-up through modular scale-out of reactors. Though these features make CFRs attractive to process-intensive industries, they are currently limited by a lack of on-line analytical technologies suitable for small-volume, high-throughput measurements. Recently, a program was initiated to evaluate the use of Process Analytical Technology (PAT) and NeSSI sampling systems for the validation of CFRs performing a Swern oxidation. A four reagent sampling system is interfaced to a continuous low-flow reactor enabling reaction monitoring using a four channel process Raman spectrometer and a process ATR infrared probe. Real-time process control will be achieved by monitoring a series process control parameters that include flow rate, stoichiometry, and reactor temperature and pressure. Establishing control of the process will allow for optimization, minimizing the production of waste and removing the need for off-line quality control analytics. Real-time chemical modeling will be performed to determine product quality using multivariate statistical methods. Results from initial experiments show that the oxidation, which requires cryogenic temperatures in batch, can be performed at much milder temperatures in continuous flow.

(299) **PAT to Enable Continuous Manufacturing at GSK**

Peter Hamilton[1]; [1]GSK

For some time now, the pharmaceutical industry has been under pressure to develop more robust, greener processes whilst establishing a deeper understanding of the process parameters deemed critical to the quality of material. This initiative spans the input starting materials, all processes throughout the entire manufacturing chain and ends with the final drug product dosage

form given to the patient. Through time, concepts such as Quality by Design (QbD), six sigma and lean manufacturing have emerged, and the industry has responded by investing in new and innovative ways of manufacturing their products with reduced variability while implementing process control in-situ. Traditionally, the industry has operated predominantly with batch processes with product quality testing at the end of each manufacturing stage; however, recently there has been a renewed drive to transition to continuous processing ranging from drug substance to oral solid dose manufacturing. Process Analytical Technology (PAT) has become a well established term within the sector, especially since the FDA's 2004 PAT initiative was established. Since then, PAT has already made great strides in improving process understanding and there are many examples of cases where a PAT application has replaced end product testing for a material attribute leading to real-time release. However, as the industry continues to evolve, the need for accurate and representative PAT instrumentation is greater than ever. In this presentation, the application of PAT to enable continuous manufacturing of crude active pharmaceutical ingredient will be described. Particular attention is given to using all of the available data in real-time to rapidly detect process shifts and deviations from steady state that ultimately help to ensure quality of the product. Lastly, some ways being considered to improve the on-/ in-line monitoring capability for continuous processes will be discussed.

(300) **Nanoscale Surface Characterization of Chemically Modified Graphene**

Mark Hersam[1]; [1]Northwestern University

The outstanding electronic transport properties of graphene have been established on pristine samples in idealized conditions. However, for nanoelectronic applications, graphene needs to be interfaced with other materials in a manner that either preserves its intrinsic properties or modifies its properties in a manner that enhances functionality [1]. For example, several noncovalent chemistries have been demonstrated and characterized at the molecular scale with ultra-high vacuum scanning tunneling microscopy including 3,4,9,10-perylenetetracarboxylic dianhydride (PTCDA) [2-4] and 10,12 pentacosadiynoic acid (PCDA) [5]. PTCDA is shown to be an effective atomic layer deposition (ALD) seeding layer for high-k dielectrics such that the PTCDA monolayer remains intact as a well-defined passivating layer at the graphene-dielectric interface following ALD [6-8]. On the other hand, PCDA forms one-dimensionally ordered self-assembled monolayers on graphene that are promising templates for one-dimensional ALD-grown oxide nanostructures [9]. Beyond noncovalent self-assembled monolayers, this talk will also explore covalent modification schemes for graphene based on free radical chemistries [10]. In particular, atomic oxygen enables homogeneous functionalization of graphene with epoxide groups [11]. In addition to chemically doping graphene, epoxidation yields local modification of the graphene bandstructure and provides pathways for further chemical functionalization [12].

[1] Q. H. Wang and M. C. Hersam, MRS Bulletin, 36, 532 (2011).
[2] Q. H. Wang and M. C. Hersam, Nature Chemistry, 1, 206 (2009).
[3] Q. H. Wang and M. C. Hersam, Nano Letters, 11, 589 (2011).
[4] J. D. Emery, et al., Surface Science, 605, 1685 (2011).
[5] A. Deshpande, et al., Journal of the American Chemical Society, 134, 16759 (2012).
[6] J. M. P. Alaboson, et al., ACS Nano, 5, 5223 (2011).
[7] J. E. Johns, et al., Journal of Physical Chemistry Letters, 3, 1974 (2012).
[8] V. K. Sangwan, et al., Nano Letters, 13, 1162 (2013).
[9] J. M. P. Alaboson, et al., Nano Letters, in press, DOI: 10.1021/nl4000932 (2013).
[10] Md. Z. Hossain, et al., Journal of the American Chemical Society, 132, 15399 (2010).
[11] Md. Z. Hossain, et al., Nature Chemistry, 4, 305 (2012).
[12] J. E. Johns and M. C. Hersam, Accounts of Chemical Research, 46, 77 (2013).

(301) **Femtosecond Transient Absorption Microscopy of Carrier Dynamics in Single Nanostructures**

Libai Huang[1,2]; [1]University of Notre Dame; [2]Notre Dame Radiation Laboratory

I will present our recent work on transient absorption microscopy (TAM) as a novel tool to image carrier and phonon dynamics in single nanostructures with simultaneously high spatial (~ 200 nm) and temporal resolution (~ 200 fs). Until now, the majority of dynamical measurements on single nanostructures are based on photoluminescence (PL). Transient absorption imaging approach offers two key advantages over PL based methods: 1) A time resolution of ~ 200 fs. This fast time resolution is important because many critical events such as electron-phonon coupling occur on such sub-picosecond time scales. 2) The measured signal is based on absorption, which means we can also study samples with low or even zero fluorescence quantum yield. I will discuss two examples of such transient absorption microscopic studies. Femtosecond transient absorption microscopy was employed to study the excited-state dynamics of individual semiconducting single wall carbon nanotubes (SWNTs). This unique experimental approach removes sample heterogeneity in ultrafast measurements of these complex materials. Transient absorption spectra of the individual SWNTs were obtained by recording transient absorption images at different probe wavelengths. These measurements provide new information about the origin of the photoinduced absorption features of SWNTs. Transient absorption dynamics traces were also collected for individual SWNTs. The dynamics show a fast ~ 1 ps decay for all the semiconducting nanotubes studied. We attributed this fast relaxation to coupling between the excitons created by the pump laser pulse and the substrate. Recent success in fabricating graphene has inspired researchers to search for semiconducting analogues of graphene in hopes to retain 2D crystallinity while providing a bandgap. In particular, monolayer MoS2 has recently emerged as a promising candidate. The second study I will present is the investigation of exciton dynamics in atomically thin and semiconducting MoS2 crystals. By controlling the dielectric environment around monolayers of MoS2 crystals, our measurements provide a comprehensive understanding on intrinsic exciton dynamics, quantum confinement effect, exciton-phonon coupling, as well as how the dielectric environment alters optical properties and energy relaxation processes in these novel 2D crystals.

(302) **Optical Spectroscopy of Novel Two-Dimensional Semiconductors**

Jie Shan[1]; [1]Case Western Reserve University

Many solids such as graphite are built up of van der Waals bonded layers, which can be separated into stable units of atomic thickness. These two-dimensional (2D) materials, as demonstrated in graphene, have exhibited many remarkable physical properties, which are absent in their bulk counterparts. Optical spectroscopy (absorption, photoluminescence and Raman) has emerged as a primary characterization tool of the electronic and phonon structures of these novel materials. In this talk, I will present recent optical studies on atomically thin MoS2, a prototype 2D semiconductor. Through characterization of the optical properties of the material as a function of thickness, we show that quantum confinement effects lead to a crossover in MoS2 from a bulk indirect gap semiconductor to a direct gap semiconductor at monolayer thickness. We also show that the electronic band structure can be continuously tuned via strain engineering. Furthermore, as is common for lower-dimensional materials, many-body interactions are found to be significant in MoS2 monolayers, as demonstrated by our recent observation of

negative trions, quasi-particles of two electrons and a hole, in n-doped MoS2 monolayers.

(303) **Using Coherent Multidimensional Spectroscopy to Observe Excited State Dynamics of Quantum Confined Structures**

Daniel Kohler[1], Schuyler Kain[1], Andrei Pakoulev[1], John Wright[1]; [1]University of Wisconsin-Madison

Quantum-confined nanostructures remain promising candidates for energy transfer applications due to their unique and tunable properties. Following the excited state evolution of such structures, however, is difficult because of sample inhomogeneity, overlapped spectral features, ultrafast dynamics, and sensitivity towards the number of excitons created. Our group has applied Coherent Multidimensional Spectroscopy (CMDS) in the mixed-time-frequency domain in an effort to deconvolve such effects. In this talk we present insights gained from applying CMDS to lead selenide quantum dots, including the identification of resolvable features in the multidimensional space that seem confounding or nuanced in a more constrained experiment.

(304) **Ambient Imaging Mass Spectrometry with Separations**

Kermit Murray, Sung Gun Park[1], Yonathan Merid[1]; [1]Louisiana State University

Ambient imaging mass spectrometry involves the creation of ions from a sample at atmospheric pressure followed directly by mass spectrometry. In order to observe less abundant species in complex samples, a separation step can be added between material removal and mass spectrometry. We are developing methods for ambient mass spectrometry that incorporate separations after mid-infrared laser ablation material removal and prior to mass spectrometry analysis. The sample material is ablated, captured in a solvent stream, and separated by liquid chromatography or capillary electrophoresis before ion formation by electrospray. The samples are deposited on a microscope slide and ablated in transmission (back side irradiation) mode using a wavelength tunable pulsed infrared optical parametric oscillator. The ablated material is captured in an exposed flowing solvent stream either on an exposed section of a microfluidic chip or the exposed section of a capillary tube. Another aspect of this research is the development of a system for nanometer scale laser ablation sampling of single cells coupled with electrospray ionization mass spectrometry. This system uses apertureless near-field laser ablation to transfer peptides, proteins and other biomolecules to a microdroplet that is used for ultra high sensitivity electrospray ionization.

(305) **Digital Microfluidic Sample Preparation for Mass Spectrometry: -Omics and Beyond**

Andrea Kirby[1], Aaron Wheeler[1]; [1]University of Toronto

Since the coupling of electrospray ionization (ESI) with mass spectrometry (MS) and the development of matrix assisted laser desorption/ionization (MALDI), MS has become a one of the most important and powerful tools in laboratory science. Despite the widespread use of MS, it is not ideal for all analyses; sample preparation before introduction into a mass spectrometer can be laborious and time-consuming, and many applications are limited by the inconvenience of off-line MS detection. Microfluidics presents a potential solution to these problems, as it offers the benefits of reduced reagent consumption and processing times, the capacity to integrate multiple functions on a single device, and potential for automated and high-throughput analysis. An emerging paradigm in microfluidics, digital microfluidics (DMF), is particularly well equipped for sample processing. DMF is a microscale liquid handling technique characterized by the manipulation of discrete droplets on an open array of electrodes. Application of potential to these electrodes permits droplet manipulations such as dispensing from reservoirs, merging, mixing, and splitting. Using DMF, samples are individually addressable, allowing for total process control. We have recently developed several methods employing DMF as a sample processing platform for MS analysis. In this talk, I will discuss a number of these new tools, including DMF-based techniques for proteomic sample processing and analysis, extraction and quantification of hormones from clinical samples, analysis of markers of metabolic disorders from dried blood spots, and microscale chemical synthesis.

(306) **Alignment of Cells under Unidirectional Electric Pulses**

Despina Loufakis[1], Chang Lu[1], Zhenning Cao[1], Sai Ma[1], David Mittelman[1]; [1]Virginia Tech

The movement of cells under an electric field is widely practiced in microfluidics. The specific characteristics of the cell trajectory are strongly affected by the properties of the electric field (EF) and the cell surface. Cell surface is covered by glycoconjugates that may be potentially charged depending on the pH. Cells that are exposed to an unidirectional EF typically move in one direction due to electrophoresis and electroosmotic flow. In the report, we demonstrate a microfluidic device, in which unidirectional, homogeneous dc pulses drive eukaryotic cells to align at the center of a sealed chamber. Cells were scattered in a microfluidic chamber which had two microfabricated gold electrodes positioned at the two ends of the chamber. The chamber was sealed up during the period when multiple dc pulses of the same direction were applied. We observed interesting movement of cells at various parts inside the chamber toward the center. We postulate that electrochemical effects dominate the tiny space and the generated pH gradient determines the cell surface charge at a local spot and produces the surprising concentration effect. This novel manipulation of a low number of cells in a mcirofluidic environment may have important applications to a number of cellular studies.

(307) **Correlating Neuronal Activity and Neurochemistry: Cytoplasmic Sampling of Selected Cells using Patch Clamp Approach Combined with Capillary Electrophoresis Electrospray Ionization Time of Flight Mass Spectrometry**

Jordan T. Aerts[1], Kathleen R. Louis[1], Shane R. Crandall[1], Gubbi Govindaiah[1], Stanislav S. Rubakhin[1], Charles L. Cox[1], Jonathan V. Sweedler[1]; [1]University of Illinois

Plant and animal tissues are composed of different types of cells that undergo a variety of dynamic changes. Even the same type of cell exhibits broad biological variability and functional heterogeneity. The nervous system presents an extreme case of such cellular heterogeneity. Investigation of the chemical nature of cellular heterogeneity requires sensitive analytical approaches capable of characterizing the complex neurochemical complement of miniscule sample volumes. Capillary electrophoresis with electrospray ionization time-of-flight mass spectrometry (CE-ESI-TOF-MS) is well suited for analysis of single cell and subcellular samples. The approach is especially powerful for quantitative and qualitative investigation of metabolomes of single cells as hundreds of analytes are detected. However, quality of obtained information in such experiments is compromised by an inability to obtain pure cell samples, functionally characterize particular cell of interest, and collect the cell at specific time point in its activity. To overcome these challenges, we demonstrate a subcellular sampling approach allowing the collection of only intracellular content, therefore, excluding such extracellular structures as synaptic boutons of different cells which may stick with the cellular membrane of analyzed cells during sample preparation. The approach uses glass micropipette pressure-assisted sampling of intracellular content from live or stabilized invertebrate and vertebrate cells. The glass micropipettes are also used for monitoring of electrical activity of live cells in mammalian brain slices which allows us to distinguish neurons from glia and identify functional types of neurons for the

same samples that are chemically assayed. This sampling approach fits well with CE-ESI-MS's nanoliter sample injection volumes and attomole limits of detection. After describing the approach and figures of merit, we present information on the subcellular metabolite content of individual functionally characterized cells as small as ~7 µm in diameter and correlate chemical signatures with electrical activity. The ability to tie together physiological properties and neurochemical data appears well suited to understanding aspects of cellular heterogeneity.

(308) **Capillary Electrophoresis with Post Separation Droplet Formation and Collection**

Christopher Harrison[1], Shay Lin[1]; [1]San Diego State University

Capillary electrophoretic (CE) separations inherently involve very small sample volumes, with the typical injection volume being on the order of nanoliters. Consequently, the ability to recover sample from a separation is not viable without massive dilution of the sample in much larger (hundreds of microliters) buffer vials. This limits the ability of CE separations, which can be incredibly effective, to be further exploited by post-column analysis or manipulation techniques. We will present our development of a device capable of continuously generating droplets of aqueous effluent from the separation capillary within a stream of perfluorocarbon liquid. Crucially, this has been accomplished with routine chromatographic fluidic components, allowing any lab to couple a post capillary droplet system with existing homebuilt CE instruments. Though diluted, samples collected in droplets remain in the nanoliter volume range, allowing for further manipulation and analysis. We will present our capabilities of performing separations of simple biomolecules and the ability to perform both on and off capillary detection of these analytes.

(309) **ChemCam Quantitative Geochemical Analysis on the Mars Curiosity Rover**

Samuel Clegg[1], Olivier Forni[2], Jeremie Jasue[2], Ryan Anderson[3], M. Darby Dyar[4], Steven Bender[1], Robert Tokar[1], Sylvestre Maurice[2], Roger Wiens[1], ChemCam Science Team; [1]Los Alamos National Laboratory; [2]Institut de Recherche en Astrophysique et Planétologie; [3]United States Geological Survey; [4]Mt. Holyoke College

The ChemCam instrument on the Mars Curiosity rover consists of a remote Laser-Induced Breakdown Spectrometer (LIBS) and a Remote Micro-Imager (RMI). The ChemCam LIBS instrument probes soils and rocks from 1.5 to 7 m from the rover mast by focusing up to 14 mJ/pulse on a 350 – 500 µm diameter spot, with spot size depending on distance. The telescope on the rover mast serves to focus the laser as well as collect the LIBS emission and direct some of the signal to the spectrometers in the rover body through an optical fiber. The RMI is also integrated into the telescope, and records high resolution (90 µrad) context images of the geologic samples probed. This paper will focus on the multivariate analysis techniques developed to analyze the ChemCam data. Quantitative elemental compositions are extracted from the ChemCam LIBS spectra using Partial Least Squares (PLS) models generated with calibration spectra collected from geochemical standards before the instrument was integrated into the rover. Ten calibration targets are onboard the rover to help track the instrument performance and refine instrument calibration. Principal Components Analysis (PCA) and Independent Components Analysis (ICA) are used to constrain the sample's geochemical identification. Analysis of the LIBS spectra involves several preprocessing steps that include subtraction of the dark spectrum, removing noise and the continuum, and spectral calibration and resampling. Finally, an instrument response function is applied to correct for the spectral response and facilitate comparisons with laboratory experiments. This paper will describe these analysis procedures and highlight some of the ChemCam LIBS and RMI observations from the Gale Crater region on Mars.

(310) **Quantitative LIBS Measurements of Silica in Coal Dust Collected on Filters**

Christopher Stipe[1], Arthur Miller[2], Jonathan Brown[1], Susan Bredberg[1], Megan Conville[1]; [1]Seattle University, Seattle, WA; [2]National Institute of Occupational Safety and Health

Free silica in coal dust was quantified using Laser-induced breakdown spectroscopy (LIBS), with an eye toward developing a new technique for monitoring airborne silica dust in near real-time. Inhalation of silica is a respiratory hazard that can lead to silicosis, a potentially fatal lung disease. Pure silica (Minusil-5), Georgia kaolin, and Pittsburgh-4 and Illinois-6 coal dusts were deposited on 37-mm PVC filters at multiple mass loadings. LIBS-generated silicon emission was monitored at 288.16 nm, and non-silica contributions to that signal from kaolinite were removed by simultaneously detecting aluminum. Measurements of Minusil-5 and Georgia kaolin were used to calculate limits of detection (LOD) for silicon and aluminum of approximately 0.08 µg/cm2 and 0.05 µg/cm2, respectively (corresponding to 0.16 µg/cm2 and 0.20 µg/cm2 for silica and kaolinite, respectively). Results demonstrate that LIBS can dependably quantify silica on filter samples of coal dust and confirm that accurate quantification can be achieved for very lightly loaded samples, which supports the potential application of LIBS to near real-time monitoring. The development of a filter-tape LIBS apparatus will be highlighted.

(311) **Laser Induced Breakdown Spectroscopy: Application to Slurry Samples**

Jagdish P. Singh[1], Krishna K. Ayyalasomayajula[1], Fang Yu Yueh[1]; [1]Mississippi State University

This paper examines the experimental conditions associated with the laser induced breakdown spectroscopy (LIBS) analysis of slurries in order to achieve better measurement precision. Various experimental configurations and sampling methods were tested. We found that using a pick up lens to direct couple the signal to the optical fiber aligned 45° with laser beam can improve LIBS signal about 5-10 times as compared to the standard backward detection method. Sample preparation procedures that can produce same thickness of samples for analysis have been developed based on a spin coating method. For this method, a drop of slurry was placed on the glass substrate. The slurry is then coated on the substrate via a spin coater machine. The thickness of the sample layered on the substrates is dependent upon the weight, original water content in the sample and the type of substrates. Different substrates for the sample preparation method have been evaluated. It was determined the double sided tape attached to a glass slide gave reproducible thickness for the samples and LIBS results without contribution/ interference from the glass substrate. Four calibration samples and an unknown were prepared by adjusting the base simulant composition for SRS Tank 8F sludge simulant. LIBS data of the calibration sample were taken to develop a calibration curve for specific slurry constituents such as Fe, Al, Ni, Ca, and Si. Various data processing techniques have been evaluated to develop these calibration curves. The concentration of the various elements from the unknown are measured and compared with inductively coupled plasma (ICP) data to evaluate the quantitative measurement capability of the LIBS techniques.

(312) **Laser-Induced Breakdown Spectroscopy for Simultaneous Determination of Size and Concentration of Colloidal Solutions of Noble Metal Nanoparticles**

Alessandro De Giacomo[1,2], Marcella Dell[2], Olga De Pascale[2], Remah Elrashedy[1], Rosalba Gaudiuso[1], Can Koral[1]; [1]University of Bari; [2]CNR-IMIP

Chemical applications of noble metal nanoparticles (NPs) are receiving growing interest in the scientific community and in the industrial world, as their use is involved in many fields of modern technology, spacing from energy to biomedical. The opportunity of having a fast technique for estimating the NPs average size and the concentration of the NP solutions themselves is extremely attracting. In this context Laser-Induced Breakdown Spectroscopy (LIBS) may play an important role as it provides fast response and requires minimum sample preparation. With this aim, LIBS has been applied in this work to the analysis of noble metal colloidal solutions with the standard calibration curve method. Sample have been prepared depositing 0.7 µl drops of the colloidal solution on a silicon substrate and then irradiating with one single focused shot in the center of the drop. As a result of the laser irradiation, the solvent is dried and the NPs are distributed around the laser-induced crater in an area of few millimeters of diameter. The sample so prepared is then used for the LIBS analysis using an unfocused beam and covering all the area where the NPs have been spread out during the sample preparation. The calibration curve, for different NPs size ranging from 6 to 40 nm diameter, has been obtained by diluting standard NPs solutions and other solutions prepared by laser ablation in liquid. The obtained calibration lines display high reproducibility and correlation factor close to unity. It is extremely interesting that the slope as well as the intercept of the obtained lines strictly depends on the size of the NPs in the solution. This allows estimating their size and then determining the concentration of the solution with a LOD of a few ppb. Moreover, results of LIBS analysis on Ag-NPs solutions have shown good agreement with those of other techniques, i.e., NPs plasmonic absorption, dynamic light scattering and TEM. A discussion on the physical reasons of the calibration curve dependence on NPs size is also presented, by investigation of plasma parameters during the LIBS measurements.

(313) **Forensic Analysis in an Expeditionary Military Environment**

Roman Aranda[1]; [1]Defense Forensic Science Center; [2]Forensic Exploitation Directorate

The Defense Forensic Science Center (DFSC) is the designated laboratory whose mission is to provide full-service forensic support for the Department of Defense (DoD). DFSC operates in the traditional forensic arena for military criminal investigations and to provide forensic support during military operations. The traditional military criminal investigations remain under the United States Army Criminal Investigation Laboratory (USACIL) and the expeditionary forensic support division is under the relatively-new Forensic Exploitation Directorate (FXD). This presentation will focus on the expeditionary component of DFSC, a brief overview of current research projects at FXD, and discuss current needs, gaps, and challenges that currently exist in the deployable forensic laboratories. Within the DFSC, the FXD's central mission is to aid military operations through forensic laboratory services. FXD also has the ability to provide forensic services to law enforcement in partner nations and during humanitarian operations. FXD maintains and has provided full-service deployable expeditionary forensic laboratories (EFLs), providing comprehensive, state-of-the-art forensic examinations in the following disciplines: latent prints, DNA, forensic chemistry (drug and explosive), and firearms and toolmarks. Forensic material that cannot be assessed at a deployable FXD laboratory may be submitted to DFSC for reach-back analysis. The deployable nature of the EFLs presents many challenges, including, but not limited to, power sources, water and solvent usage, footprint of instrumentation, lab cleanliness, etc. These challenges directly limit the range of instrumentation that may be utilized for forensic analyses. Due to these constraints, existing needs and gaps are present in the EFLs. To combat these challenges, DFSC seeks and evaluates new prototypes, methodologies, and research that are applicable in an EFL setting. Current FXD research and development areas include novel analytical chemistry methods which enhance sensitivity and selectivity over currently existing capabilities; innovative approaches for source attribution of samples (e.g. explosives, drugs); evaluation and development of new methods for extracting information from mixed DNA samples; and development of new analytical protocols for patterned latent print forensic analyses. The FXD is continually seeking innovative research and prototypes to analyze samples more quickly, and with greater precision and accuracy while aiding military operations.

(314) **Forensic Analysis in Military Criminal Investigations**

Candice Bridge[1]; [1]Defense Forensic Science Center

The Defense Forensic Science Center (DFSC) is a unique forensic center whose mission is to provide full-service forensic support (traditional, expeditionary and Reach-Back) to the Department of Defense (DoD) and facilitate research that benefits the forensic science community. Therefore, it is necessary that the Center is aware of novel techniques that can enhance our current capabilities such that we can provide a better service to our customers. This presentation will focus on showing how forensic analysis is utilized in the military, providing an overview of current research projects and presenting current needs and gaps. A subcomponent of the DFSC is the United States Army Criminal Investigation Laboratory (USACIL) whose central mission is to provide forensic laboratory services to the DoD's military criminal investigation organizations (Air Force Office of Special Investigations, Naval Criminal Investigation Service, and the Army Criminal Investigation Command) and other DoD customers. It is a full service forensic laboratory, which provides comprehensive, state-of-the-art forensic examinations in the following disciplines: digital evidence, drug chemistry, firearms and toolmarks, forensic documents, latent prints, serology/DNA, and trace evidence. To continue fulfilling this mission, we need to stay connected to the needs of our customers as well as the current research that can increase our ability to service our customers. Therefore, we are constantly searching for and evaluating new prototypes, methodologies and research areas that could be applied to forensic analysis. Current research and development areas include novel analytical chemistry tools and techniques which enhance sensitivity and selectivity over current capabilities; innovative approaches for source attribution of samples (e.g. explosives, drugs); new methods for extracting information from mixed DNA samples; and development of new protocols for patterned forensic that utilize a quantitative rather than qualitative approach. The USACIL is continually seeking innovative approaches that can make analysis more accurate and faster, while simultaneously providing more valuable information than current techniques so we can provide our customers with the best answers available in the scientific disciplines we offer.

The opinions or assertions contained herein are the private views of the author and are not to be construed as official or as reflecting the views of the Department of the Army or the DoD.

(315) **A Nanomanipulation, Probing Station Coupled to Mass Spectrometry for Applications in Expeditionary Laboratories**

Guido Verbeck[1]; [1]University of North Texas

The multistage workstation developed in our group has wide-ranging applications in the biological, chemical, and forensic sciences. The workstation consists of a platform with four nano-positioners that hold end-effectors and capillaries used to manipulate, probe, and

characterize objects of interest. The multistage workstation has been coupled to nanospray mass spectrometry allowing for precise and accurate analysis of trace chemical analytes. We have demonstrated this technique by probing chemical residue (drugs and biological) from individual fibers, electrostatic lifts, fingerprints, and direct samples of interest and analyzing them using nanospray mass spectrometry. Using a single instrument to manipulate, probe, and characterize an analyte minimizes the need of having multiple devices and instruments; this saves time moving devices and instruments on and off the microscope stage through different parts of an experiment. Extraction of residue in combination with the biometric data can lead investigators to thwarting potential events. If explosives are identified within the fingerprint transfer, this can lead investigators to potential suspects in terrorist activity, and have a biometric record.

(316) **STARR: Shortwave-infrared Targeted Agile Raman Robot for the Identification and Confirmation of Emplaced Explosives**

Nathaniel Gomer[1], Oksana Klueva[1], Charles Gardner[1]; [1]ChemImage Corporation

In order to combat the threat of emplaced explosives (land mines, etc.), ChemImage has developed a fusion based, robot mounted sensor capable of identification and confirmation of potential threats. The system, known as STARR (Shortwave-infrared Targeted Agile Raman Robot) , utilizes shortwave infrared spectroscopy for the identification of potential threats, combined with a visible short-range standoff Raman hyperspectral imaging (HSI) system for material confirmation. The entire system is mounted onto a Talon UGV (Unmanned Ground Vehicle), giving the sensor an increased area search rate and reducing the risk of injury to the operator. The Raman HSI system utilizes a fiber array spectral translator (FAST) for the acquisition of high quality Raman chemical images, allowing for increased sensitivity and improved specificity. An overview of the design and operation of the system will be presented, along with initial detection results of the fusion sensor.

(317) **Low Frequency/THz-Raman spectroscopy: Using Structural Information for Material Identification**

James Carriere[1], Frank Havermeyer[1], Randy Heyler[1]; [1]Ondax, Inc.

Raman and Terahertz spectroscopy are both widely used for their ability to safely and remotely identify unknown materials. Each approach has its advantages and disadvantages. Traditional Raman spectroscopy typically measures molecular energy transitions in the 200-5000 cm^{-1} region corresponding to sub-molecular stretching or bending transitions, while Terahertz spectroscopy measures molecular energy transitions in the 1-200 cm^{-1} region (30GHz-6THz) that correspond to low energy rotational modes or vibrational modes of the entire molecule as well as lattice modes. However, THz signal generation is often expensive, many THz spectroscopy systems are limited to just a few THz range, and strong water absorption bands in this region can act to mask certain transitions if great care isn't taken during sample preparation. Alternatively, low-frequency or "THz-Raman" spectroscopy, which covers the ~5cm^{-1} to 200 cm^{-1} (150GHz-6 THz) regions and beyond, offers a powerful, compact and economical alternative to probe these low energy transitions. Combining the information from both the low frequency and "fingerprint" regions of the spectrum can be quite powerful in identifying materials that have very similar chemical structure but different physical structure. Polymorph discrimination can be achieved via changes in the low frequency signals. This is critically important in the manufacturing process of many active pharmaceutical ingredients (APIs) for example where bioavailability will be affected by the form of the material. Process contaminants and co-solvents have also been shown to affect the low frequency structure in these materials. Finally, many difficult to detect explosives and other hazardous chemicals are known to have multiple relatively strong transitions in this low frequency regime, suggesting this method as a powerful complementary approach for identification. We present results from a new approach for extending the range of Raman spectroscopy into the Terahertz regime using an ultra-narrow-band volume holographic grating (VHG) based notch filter system. An integrated, compact Raman system is demonstrated utilizing a single stage spectrometer to show both Stokes and anti-Stokes measurements down to <10cm^{-1} on polymorphic compounds and traditionally difficult to detect explosives, as well as other chemical and biological samples.

(318) **Analysis and Synthesis with Ions: Societal Applications of Mass Spectrometry**

Joshua Wiley[1], R. Graham Cooks[1], Thomas Mueller[1], Xin Yan[1], Xin Li[1], Kevin Kerian[1], Alan Jarmusch[1], Michael Wleklinski[1], Paul Hendricks[1], Zheng Ouyang[1]; [1]Purdue University

Charged micro-droplets are used in three types of experiments in this presentation: (i) for intrasurgical tissue analysis to characterize the disease state of the tissue from the lipid profile recorded in the open air; (ii) for on-line monitoring of the course of chemical reactions, especially high concentration bulk preparations representative of industrial processes, and (iii) to perform microscale synthesis rapidly based on the rate acceleration that occurs in confined volume systems. Intrasurgical ambient ionization has been used to record lipid profiles which are compared with library examples. A modified version of nano ESI in which the voltage is applied inductively is used to continuously monitor high salt concentration organic reactions, including cases which involving water- and air-sensitive reagents. A number of examples of microscale chemical synthesis by MS are discussed, including carbon-carbon bond formation using Claisen-Schmidt and thiamine catalyzed benzoin condensations. Milligram amounts of organic compounds are synthesized by electrospraying the reaction mixtures for a minute or two onto a high area inert surface where the product collects.

(319) **Intercepting Transient High-Valent Iron-Oxo Catalytic Intermediates Using Desorption Electrospray Ionization Mass Spectrometry**

Richard H. Perry[1], Kevin C. Peters[1], Kevin Parker[1]; [1]University of Illinois Urbana-Champaign

Intercepting transient reaction intermediates in solution is important in both science and industry for developing more efficient catalysts. Recently, Zare and coworkers demonstrated that reactive desorption electrospray ionization mass spectrometry (DESI-MS) can intercept transient intermediates of organometallic catalytic systems on millisecond time scales. In this experiment, a stream of fast-moving microdroplets containing reagents impact a surface on which the organometallic catalyst precursor was deposited. The reaction is initiated upon impact and proceeds in desorbed secondary microdroplets travelling to the mass spectrometer. The short lifetime of the microdroplets results in reaction times of a few milliseconds, allowing detection of transient species. Non-heme high-valent iron-oxo porphyrin complexes are powerful oxidation catalysts. Using a conventional reactive DESI setup, unwanted reactions occur between the reagents in the DESI spray. Using a dual-spray reactive DESI source, we were able to identify unique transient high-valent iron intermediates in both catalytic and degradation pathways, providing valuable information about the catalytic mechanism.

(320) **Nanospray Desorption Electrospray Ionization Mass Spectrometry: a New Technique for Imaging Lipids, Metabolites and Drugs in Biological Systems**

Ingela Lanekoff[1], Mathew Thomas[2], James Carson[2], Kristin Burnum[2], Allan Konopka[2], Julia Laskin[1]; [1]Physical Sciences Division, PNNL, Richland, WA; [2]Biological Sciences Division, PNNL, Richland, WA

Mass spectrometry imaging (MSI) enables simultaneous spatially-resolved analysis of numerous ionizable molecules on a sample surface. Ambient ionization techniques are attractive because they enable imaging without sample pretreatment. Nanospray desorption electrospray ionization, nano-DESI, is a novel ambient technique developed at PNNL that enables sensitive imaging and analysis of molecules on surfaces. Nano-DESI utilizes localized desorption of analyte molecules from surfaces into a liquid bridge formed between two fused silica capillaries, the nano-DESI probe. The liquid bridge is formed by continuously supplying a solvent through the primary capillary to the surface and removing it with a self-aspirating secondary capillary. Analyte molecules from the surface are desorbed into the solvent, transferred to a mass spectrometer inlet in a controlled fasion, ionized via electrospray, and detected by a mass spectrometer. Ion images of molecules on the surface are created by continuously moving the sample under the nano-DESI probe and collecting mass spectra. Data visualization is achieved via in house developed software, MSI Quickview. We present the spatial distribution of lipids, metabolites and drugs in cryo-sectioned tissue sections and show that ion suppression effects can be eliminated by use of internal standards in the nano-DESI solvent. For example, by doping the nano-DESI solvent with deuterated nicotine ion suppression effects from endogenous substances in the rat brain could be eliminated, allowing for quantification of nicotine in the tissue section at sub-femtomole levels. Additionally, we present the use of nano-DESI to detect and profile lipids and metabolites directly from living bacterial colonies on agar. Specifically, we examined chemical gradients produced by colonies of cyanobacteria on agar containing high amounts of salt without affecting the viability of the colony and demonstrated that the age of the colony has a significant effect on the chemical gradient.

(321) **Deconstructing Desorption Electrospray Ionization to Address Protein Analysis**

Kevin Douglass[1], Andre Venter[1]; [1]Western Michigan University

Mass spectrometry is a powerful tool for protein analysis. In particular, ambient mass spectrometry is gaining momentum since these methods require little sample preparation and can be successfully applied to the imaging of biologically significant macromolecules such as proteins. However, DESI-MS and other ambient methods that use a spray desorption sampling process for ionization appear limited to proteins with molecular masses of 25 kDa or less. In addition, a decreasing instrumental response with increasing protein size has been observed. It has been suggested that this limit results from the inability of some proteins to easily desorb from the surface during sampling. Using spray desorption collection (SDC) and reflective electrospray ionization (RESI), we have investigated the apparent mass dependency of the instrumental response observed during the DESI-MS analysis of proteins. Proteins as large as 66 kDa are shown to be quantitatively removed from surfaces using SDC, confirming that desorption is not the limiting factor. Instead, incomplete dissolution and the formation of protein-protein and protein-contaminant clusters appear to be responsible for the mass dependent loss in sensitivity for protein analysis. Alternative ambient mass spectrometry approaches that address some of the problems encountered by spray desorption techniques for protein analysis are discussed along with ideas for the development of DESI-MS and related techniques towards improving protein analysis.

(322) **Integration of Online Digestion and Electrolytic Reduction with Mass Spectrometry for Rapid Disulfide-Containing Protein Structure Analysis**

Hao Chen[1], Qiuling Zheng[1], Hao Zhang[2]; [1]Ohio Univeristy; [2]Washington University in St Louis

Bottom-up structural analysis of disulfide-bond containing proteins usually involves time-consuming offline enzymatic digestion, chemical reduction and thiol protection prior to mass spectrometric detection, which takes many hours. This paper presents an expedited approach for this purpose, employing desorption electrospray ionization-mass spectrometry (DESI-MS) coupled with online pepsin digestion and online electrochemical reduction of disulfide bonds. Peptides are generated in high digestion yield as its precursor protein in acidic aqueous solution flows through a pepsin column, which can undergo direct electrolysis. The electrolytic behaviors of peptides, as online monitored by DESI-MS, not only tells the presence/absence of disulfide bonds in the peptides, but also provides information to relate disulfide bond-containing peptide precursors to their corresponding reduced products. Furthermore, selective electrolysis simply using different reduction potentials can be adopted to generate either partially or fully reduced peptides to assist disulfide bond mapping. In addition, it turns out that DESI is suitable for ionizing peptides in water without organic solvent additives that would not be compatible with the use of pepsin column. The feasibility of this method was demonstrated using insulin, a protein carrying three pairs of disulfide-bonds as an example, in which all disulfide bond linkages and most of the protein sequence were successfully determined. Strikingly, this method shortens the sample digestion, reduction and MS detection from hours to 7 min, which could be of high value in high-throughput proteomics research.

(323) **Disinfection By-Product Formation and Mitigation Strategies in Point-of-Use Chlorination of Turbid and Non-Turbid Waters in Western Kenya**

B.C. Blount[1], D. S. Lantagne[2], F. Cardinali[1], R. Quick[2]; [1]Division of Laboratory Sciences, National Center for Environmental Health, U.S. Centers for Disease Control and Prevention; [2]Foodborne and Diarrheal Diseases Branch, U.S. Centers for Disease Control and Prevention

Over 1.1 billion people in the world lack access to improved drinking water, and diarrheal diseases cause an estimated 2.2 million deaths per year. The Safe Water System (SWS) is a proven household water treatment intervention that reduces diarrheal disease incidence in users in developing countries. Because the SWS recommends adding sodium hypochlorite to unfiltered water sources, concerns have been raised about the potential long-term health effects of exposure to disinfection by-products resulting from SWS use. This study investigated the production of trihalomethanes (THMs) in water treated with sodium hypochlorite from six sources used for drinking water in Western Kenya. The turbidity values of these sources ranged from 4.23 NTU to 305 NTU. THM concentrations were analyzed at 1, 8, and 24 hours after sodium hypochlorite was added to the source water. No treated sample exceeded the World Health Organization (WHO) guideline values for any of the four THMs: chloroform, bromodichloromethane, dibromochloromethane, or bromoform. In addition, no sample exceeded the WHO additive total THM guideline value. These results clearly show that point-of-use chlorination of a variety of realistic source waters did not lead to THM concentrations that pose a health risk to SWS users.

(324) **World Health Organization, Tobacco Laboratory Network (WHO TobLabNet)**

Ben Blount[1], Rayman Stanelle[1], Maria Damian[1], Megan McGuigan[1], Cliff Watson[1]; [1]U.S. Centers for Disease Control and Prevention

Over 8,400 compounds have been identified in tobacco smoke and many of those are harmful such as volatile organic compounds

(VOCs), tobacco specific nitrosamines (TSNAs), and polycyclic aromatic hydrocarbons (PAHs)1. Tobacco use increases risk of cardiac disease, cancer, and many other pathophysiological conditions2. Approximately 20% of all cancer deaths worldwide can be attributed to tobacco use3. Despite over 50 years of efforts to address this epidemic, tobacco use remains the leading cause of preventable disease in the United States, and an increasing source of disease burden in developing countries. To improve global efforts to characterize harmful and addictive constituents of tobacco products, the World Health Organization (WHO) Tobacco Free Initiative (TFI) established the WHO Tobacco Laboratory Network (TobLabNet) as specified by the WHO Framework Convention on Tobacco Control (FCTC). TobLabNet is a global network of government, academic, and independent laboratories working together to strengthen national and regional capacity for the testing and research of the contents and emissions of tobacco products pursuant to Article 9 of the WHO FCTC. The goal of the Network is to establish global tobacco testing and research capacity to test tobacco products for regulatory compliance, to research and develop harmonized standards for contents and emissions testing, to share tobacco research and testing standards and results, to inform risk assessment activities related to use of tobacco products, and to develop harmonized reporting of such results so that data can be transformed into meaningful trend information that can be compared across countries and over time. Once capacity is established, TobLabNet will be positioned as a primary source of laboratory support, methods development, and scientific information in the areas of tobacco testing and research for national governments to fulfill their requirements and needs related to the Framework Convention on Tobacco Control (FCTC). A global tobacco testing laboratory network is crucial for improving public health by advancing tobacco control. Combining testing and research at the global level is a new approach to match the tobacco industry's expert product testing capabilities.

TobLabNet requires expert advice for overall scientific and technical guidance on issues of tobacco product testing relevant for public health. Such advice and support is provided the Centers for Disease Control and Prevention which is a member of the Executive and Steering Committee of TobLabNet.

1) Alan Rodgman A, Perfetti TA. The chemical components of tobacco and tobacco smoke. Boca Raton: CRC Press, 2009:1784.
2) Novotny T, Giovino G. Tobacco use. In: Brownson RC, Remington PL, Davis JR, Chronic disease epidemiology and control. Washington, DC: American Public Health Association, 1998:117.
3) Mackay J, Eriksen M, Shafey O. In: The Tobacco Atlas, American Cancer Society, 2006: 58.

(325) **Analytical Chemistry towards Enhancing Risk Reduction from Chemicals Exposure and Environmental Protection in Africa and Globally**

Oladele Osibanjo[1,2]; [1]Department of Chemistry, University of Ibadan; [2]Basel Convention Coordinating Centre for Training and Technology Transfer for the African Region in Hazardous Waste Management, University of Ibadan

Chemicals play an important role in human life and economic development and prosperity, yet they can also have adverse impacts on the environment and human health. The diversity and potential consequences of such impacts, combined with the limited capacity in developing countries and countries with economies in transition to manage these impacts, make sound chemicals and wastes management a crucial issue for sustainable development[1]. Hence the internationally agreed goal to achieve by 2020 sound management of chemicals throughout their life cycle and of hazardous waste in ways that lead to minimization of significant adverse effects on human health and the environment, more so as UNEP has declared that exposure to hazardous substances worsen poverty. Toxic chemicals have been implicated of contamination of soil, water, air and food both for domestic consumption and export[2]. The vulnerable group from chemicals exposure in developing countries is old women and children working informally in agricultural and industry sectors without environmental safeguards as well as waste scavengers. The barriers to effective sound chemicals management and minimization of risks in developing and emerging economy countries include lack of scientific data for informed decisión making, knowledge of chemicals life cycle , lack of comprehensive regulations and weak enforcement of existing legislation, weak technical and organizational capacities including analytical laboratories, poor public awareness and cooperation and lack of funds.[3] It is imperative that chemicals level data in environmental media and human exposure be generated to guide decision-making on sound internatiional, regional, and national management especially as there has been increasing shift of chemicals production from developed countries to emerging economy countries BRICS(Brazil, Russia, .India, China and South Africa) many of which have not been adequately tested for their environmental and human health safety.Yet there is inadequate analytical chemistry capacity and capability in most developing countries to generate quality scientific data on chemical pollutants environmental levels, toxicological and ecotoxicological characteristics.[3] This calls for extant environmental data gaps to be filled as a matter of priority as meaningful policy interventions to protect humans and the environment from risk of exposure to hazardous substances cannot be achieved in a data vacuum.

(326) **Let's Talk Trash! How Measurement Science Can Enable the Transformation of Waste to Worth**

Jill Boughton[1]; [1]W2Worth Innovations, LLC

Every year we burn, pile and bury nearly 2 BILLION tons of waste globally. With increasing populations and consumption, this number is expected to triple by the year 2050. In addition to the obvious environmental toll caused by unmitigated waste, improper waste solid waste management is a known drain on public health, contributing to an estimated 4.6 million deaths per year. But does it have to be this way?

W2Worth Innovations (W2WI) is an organization that emerged out of project from Procter & Gamble to deliver upon their long term vision to eliminate consumer and manufacturing waste going to landfill. W2WI seeks to shift the paradigm about waste and enable its use as a valuable economic resource as a means for stimulating long term solutions for this growing crisis. The goal is to move beyond the limited reality of simply eliminating waste to a reality in which value can be extracted from ALL waste. W2WI is innovating to create this reality – unleashing the power of digital tools and data to provide stakeholders with information that enables the maximum extraction of value from waste. Measurement science is becoming increasingly important to provide stakeholders with sound and robust data to inform these "waste to worth" constructs and ensure responsible implementation. Please join the second SciX Conference "Analytical Chemists Easing World Poverty" session to learn how measurement science can help turn trash to cash!

(327) **How Are Analytical Chemists Easing World Poverty?**

Diane Parry[1]; [1]The Procter & Gamble Co.

In 2010, a future-focused discussion at a meeting of the Society for Applied Spectroscopy led to an invitation to create a SciX Special Session on "Analytical Chemists Easing World Poverty." Through three years and four SciX/PittCon "Analytical Chemists Easing World Poverty" sessions, we have explored a number of the major social interventions that depend on measurement scientists working around the world right now. Analytical chemists and organizations like the Royal Society of Chemistry, the Gates Foundation, and IDRI, recognize unmet measurement needs, and are trying to find new ways to provide essential help in under-served regions. For example, work

by the RSC is directly helping address the WHO-requirement for Mass Spectrometry data to check drug safety, in African regions with only part-time generator power. Comprehensive field checks of water, air, and soil quality, better garbage management, worker safety, and food quality all require measurement scientists to develop rugged, portable test protocols and instrumentation. Training of global measurement scientists, including instrument repair personnel, and reliable supply chain development are all critical contributions that are needed to provide sustainable global help. There are plenty of opportunities to make a difference, so come and hear this talk to get proud of the international impact of your chosen field, get excited about the contributions your colleagues are making, and get involved yourself.

(328) **NMR vs. NIR: Instruments, Applications, and Methods**

Fred LaPlant[1]; [1]3M Inc

Low-field NMR and Near-IR instrumentation are widely distributed in industrial and quality control labs because of their relatively low cost, ease of use, and application to a wide variety of measurements. These techniques overlap strongly in some applications, provide complimentary information in others, and in some offer unique information about a material. This talk will directly compare the advantages of each technology, with special focus on areas of overlap where cost of ownership, ease of method development, sample presentation, and quantitation accuracy may be important in selecting the appropriate technique.

(329) **Recent Developments in the Use of Online NMR Reaction Monitoring in the Pharmaceutical Industry.**

Mark Zell[1], David Foley[1], Brian Marquez[1]; [1]Pfizer Global Research and Development

Monitoring chemical reactions utilizing NMR spectroscopy to analyze a flowing reactant stream has become increasingly popular, as it utilizes the power of NMR spectroscopy to understand the complex interplay between molecules during a chemical reaction while providing an accurate picture of what is actually occurring in the reaction vessel. This makes NMR particularly well suited for interrogating the presence of transient intermediates, providing detailed kinetic information via multiple nuclei (1H, 13C, 19F, 31P), as well as providing quantitative information for monitoring mass balance throughout the reaction. Much of our work has been conducted at high field (400 MHz) using a traditional superconducting NMR spectrometer and custom-built flow system to mate the reactor with the NMR spectrometer.

We have recently undertaken the utilization of smaller, more flexible NMR systems for reaction monitoring for the multiple benefits they provide, including both price and portability. These lower field NMR systems are “cryogen free” in that they use either a permanent magnet (60 MHz) or new generation HTS superconducting magnet (200 MHz), are in many cases less expensive to purchase than a traditional high-field superconducting NMR system, eliminate the need for costly cryogens as well as an engineer to service the magnet, and can allow the NMR to be taken to the chemistry rather than requiring the chemistry be brought to the NMR lab. An overview of our work utilizing NMR for reaction monitoring will be outlined, and the application of 60 MHz permanent magnet, 200 MHz HTS magnet, and 400 MHz traditional magnet-based NMR systems to reaction monitoring and process development will be discussed.

(330) **Application of Low-Field NMR to Quantification of Polymer Composition**

John Battiste; [1]3M

Low-Field Benchtop NMR instruments have been more popularly applied to relaxometry applications in industrial settings. As designed, standard low-field instruments have poor homogeneity and are ill-suited for spectroscopy applications involving resolution of chemical structure. However, several new entries into the low-field NMR market have improved the magnet homogeneity and resolution capabilities of these benchtop instruments. We have used a PicoSpin-45MHz NMR system to investigate the suitability of a low field NMR instrument for Quality Control applications involving quantification of polymer raw materials. Examples will be shown for determination of the monomer ratios in a polyester and quantification of the amount of polycarbonate in a polycarbonate/polyester blend. Determination of the amounts of the major components of the polymers were determined with %RSD values as low as 1%. The suitability of a low-field benchtop instrument for QC of a particular polymer is still dependent upon the complexity of the polymer and the available resolution of the instrument. Therefore, the use of benchtop NMRs for QC may not generally applicable for quanitative analysis, but could be used on a case by case basis.

(331) **Going Further Beyond Conventional NMR: Fast Field Cycling Relaxometry Tools, Method and Applications**

Richard J. Stevens[1], Salvatore Bubici[2], Gianni Ferrante[2], Rebecca Steele[2]; [1]Molecular Specialties, Inc.; [2]Stelar, s.r.l.

Fast Field Cycling relaxometry is a non destructive, low-field magnetic resonance technique, which is used to determine the nuclear spin-lattice relaxation rate constant (1/T1) as a function of the applied magnetic field strength, without varying the frequency of the spectrometer. This provides a unique characterization of the local molecular dynamics of molecules over a wide frequency range (Bo-fields spanning about six decades, from about 10`6 Tesla up to ~1 Tesla or 3 Tesla). The magnetic field dependence 1/T1 of any given substance or material is shown in the graphical form as Nuclear Resonance Dispersion (NMRD) profile. The main information that can be extracted from the NMRD profiles is that concerning molecular motions characterized by the temperature-activated frequencies and described by means of the spectral density. Data obtained from this technique may be correlated directly to the physical/chemical properties of complex materials . The use of radio frequency (RF) allows the easy penetration of most materials, permitting, the exploration of the slow dynamics, which are often difficult to study in heterogeneous materials - liquids, solids and gels - by other spectroscopic methods. Furthermore, the benefit of exploring the range of low Larmor frequencies is to detect typical relaxation features associated with molecular processes, characterized by very long correlation times, such as the molecular surface dynamics and collective effects. FFC NMR relaxometry shows greatest potential where the characteristics of a sample depend intimately on the molecular dynamics and/or the state of aggregation. Herein we describe the technique of FFC NMR relaxometry and demonstrate how NMRD profiles have been used in research in understanding fundamental molecular dynamics information or provide simple qualitative characterization. The technique has been applied in numerous fields, ranging from polymers to contrast agents, electrolytes to proteins, rock cores to foodstuffs, to name a few examples. Recent developments are noteworthy as they show how FFC NMR relaxometry is evolving towards solving more practical problems, and their potential applications in quality assessment and off-line process monitoring.

(332) **Multivariate Curve Resolution 1990-2012: A Different Way to Examine Chemical Data**

Roma Tauler[1]; [1]IDAEA-CSIC

During the last 20 years, Multivariate Curve Resolution (MCR) has emerged as a powerful approach to investigate (bio) chemical data sets. The only requirement for the application of MCR methods is to have a set of multivariate responses ordered in a data table or data matrix which can be approximated by a low rank bilinear model. MCR methods decompose this data matrix into a reduced set of contributions, whose profiles in the two measurement modes have

chemical meaning. Although this bilinear decomposition is ambiguous (not unique), it can be constrained appropriately giving a reduced set of feasible solutions. Possible constraints in MCR methods include natural constraints like non-negativity, unimodality or closure (mass-balance), but also structural constraints like those derived from local rank information, from multinear modeling, from physicochemical modelling (like rate law in kinetics, or mass action law in equilibria systems), or from any other analytical source (quantitative calibration information, known spectra profiles, source composition). This MCR bilinear modeling approach can be implemented by means of an Alternating Least Squares algorithm (MCR-ALS), which allows for an easy and individual implementation of constraints (by component profile and by data set) and a very flexible approximation to different complex situations. In the recent years, MCR-ALS has been proposed for the analysis of new challenging problems such as environmental source apportionment, hyperspectral image analysis or –omic sciences megavariate data analysis. And new advances have been proposed for the evaluation of the extent of rotation ambiguities, for the study of the conditions of unique solutions, for the investigation of the reduction of the effect of noise and its propagation. MCR-ALS has been recently adapted to more complex data structures with missing or incomplete data and to quadrilinear and mixed linear interaction models.

(333) **Using Data Fusion to Improve Prediction of Protein Secondary Structure**

Renee JiJi[1], Olayinka Oshokoya[1]; [1]University of Missouri-Columbia

There is an increasing need to develop analytical methods to assess protein structure and conformational changes in real or near-real time. Protein conformational changes are associated with a number of diseases and protein interactions with small molecular compounds can also lead to subtle but important structural changes. Structurally sensitive, optical methods derived from UV absorption, infrared and Raman spectrosopies are ideal candidates for addressing this need. However, each technique has its own strengths and weaknesses. Circular dichroism (CD), the gold standard in protein secondary structure analysis provides little more than a rough estimate of secondary structure content, with β-sheet and disordered conformations being poorly approximated. While changes in secondary structure can be easily identified by CD, assignment of those changes is much more ambiguous. Deep-UV resonance Raman (dUVRR) spectroscopy is an emerging technique in the field of protein secondary structure analysis. Though conformational changes are more easily assigned by dUVRR, prediction of secondary structure content by dUVRR suffers the same limitations as CD with α-helical and disordered structure being poorly approximated. In order to take advantage of the unique selectivity's of each technique, chemometric methods are needed to combine information derived from multiple spectroscopic techniques. While combining two types of spectral data is the most straight-forward data fusion strategy, unequal spectral intensities, noise levels and spectral overlap can result in poorer prediction. Two alternate data fusion strategies to improve prediction of secondary structure content will be compared. The first involves fusion of the output scores after an initial multivariate analysis step, followed by regression on the fused scores. The second strategy involves the iterative optimization of the output scores with the constraint that the scores must be the same for both spectral techniques.

(334) **Modeling the Impacts of Environmental Chemical Conditions on Microalgal Biomass**

Frank Vogt[1], Lauren White[1], Kendhl Witt[1], David Martin[1]; [1]University of Tennessee - Department of Chemistry

With an increase of industrialization, the production of anthropogenic CO2 is rising and the fate of this high-impact greenhouse gas has become a serious concern. On the other hand, it has been estimated that about half of the global primary carbon production is based on CO2 sequestering by algal photosynthesis. Hence, phytoplankton counterbalances the CO2 production and thus is ecologically important. The amount and chemical composition of the produced microalgal biomass has been linked to the availability of inorganic microalgae nutrients such as C, N, and P. Furthermore, it has been observed that microalgae cultures develop biomass of different chemical composition when grown among other algae species possibly due to nutrient competition processes. Based on these latter findings, it has been hypothesized here that the amount and chemical composition of produced phytoplankton biomass as well as the production kinetics are driven by nutrient availability and competition. For an accurate assessment and prediction of microalgae-based transformation of CO2 and other inorganic compounds into biomass, a more detailed understanding of these processes is essential. This project investigates the relevance of nutrient competitions for the extent and kinetics of phytoplankton biomass production and thus for phytoplankton's role as sink of atmospheric CO2. The present study has two goals: (i) Determine whether a species growth rate, i.e. the kinetics of biomass production, is impacted by the presence of nutrient competitors. (ii) Determine whether the amount of produced biomass is impacted by the presence of nutrient competitors. Because the total amount of biomass is the product of number of cells times their size, topic (ii) is split into two aspects i.e.: (ii-a) number of cells per species and (ii-b) size distributions of each species. For investigating these topics, two microalgae species have been selected and cultured under series of different nutrient conditions separately and in mixture. While keeping all ambient parameters for the single-species and the mix-species culture the same, significant differences in growth rates, number of produced cells, and their size distributions are strong indicators for competition effects. A comprehensive understanding of phytoplankton-driven processes transforming inorganic nutrients into biomass is expected.

(335) **Living Bruce's Vision for Industrial Chemometrics at The Dow Chemical Company**

Mary Beth Seasholtz, Randy Pell; [1]The Dow Chemical Company

Bruce Kowalski had a vision for the many ways that chemometrics could benefit the chemical industry. After studying with Bruce Kowalski at the Center for Process Analytical Chemistry (CPAC), the authors have been able to live out this vision at The Dow Chemical Company, 1990 – present. This talk will review several areas of research as well as applications. The applications span process analytical, laboratory analytical and process chemometrics. Finally, some thoughts about the future will be given.

(336) **Immobilization of Gold Nanorods onto Electrospun Polymer Nanofibers via Polyelectrolyte Decoration—A Generalized SERS Substrate**

John Rabolt[1], Wenqiong Tang[1], Bruce Chase[1]; [1]University of Delaware

The fabrication of a homogeneous and highly dense gold nanorod (AuNR) assembly on electrospun polycaprolactone (PCL) fibers using electrostatic interaction as the driving force will be described. Specifically, decoration of a poly(sodium 4-styrenesulfonate) (PSS) layer onto the AuNRs created negative charges on the nanorod surface and the interactions between PSS and the AuNRs were investigated using Attenuated Total Reflection Fourier transform infrared spectroscopy (ATR-FTIR). Positive charge on the PCL fibrous substrate was produced via polyelectrolyte layer-by-layer (LBL) deposition, which was investigated using multiple characterization techniques. Driven by the attractive electrostatic interaction, immobilization of AuNRs on the PCL fibers was initiated upon substrate immersion and the kinetics of the immobilization

process were studied using UV-Vis spectroscopy. Electron microscopy characterization of the AuNR/PCL nanocomposite fibers reveals a uniform AuNR coating on the fiber surface with the immobilized AuNR density being high enough to provide full surface coverage. By using both 4-mercaptopyridine (4-MPy) and Rhodamine 6G (Rh6G) as the probe molecules, the performance of the AuNR/PCL fibers as a generalized surface enhanced Raman scattering (SERS) substrate was investigated. The nanocomposite fibers allowed detection at concentrations as low as 10-7M of the probe molecule in solution and exhibited excellent reproducibility in the SERS measurements.

(337) **Infrared Spectroscopy with 100-nm Spatial Resolution: Applications in Polymers and Life Sciences**

Curtis Marcott[1], Michael Lo[2], Qichi Hu[2], Kevin Kjoller[2], Craig Prater[2]; [1]Light Light Solutions; [2]Anasys Instruments

Atomic Force Microscopy (AFM) and infrared (IR) spectroscopy have been combined in a single instrument capable of producing 100-nm spatial resolution IR spectra and images. This new capability enables the spectroscopic characterization of domains in polymeric samples at levels not previously possible. A tunable IR laser source generating pulses on the order of 10 ns was used for excitation of cast sample films or thin cross sections deposited on IR transparent ZnSe prisms. Short duration thermal waves, due to infrared absorption, were studied by monitoring the resulting excitation of the contact resonance modes of the AFM cantilever. Differences in the IR spectra as a function of spatial position provide insight into polymer blend miscibility, microdomain formation, and can lead to increased understanding of how fibers and other nanomaterial additives affect the molecular structure and properties of polymer materials. Additional applications of AFM-IR spectroscopy to samples of biological interest will also be presented.

(338) **FTIR Spectroscopic Imaging without Optical Aberrations**

Sergei Kazarian[1], Andrew Chan[1]; [1]Imperial College London

While the micro ATR imaging approach provides the highest spatial resolution achieved with FTIR spectroscopic imaging [1], transmission mode still remains as the most common sampling method for imaging of biomedical samples, such as tissues and cells. However, when samples are sandwiched between infrared windows or placed underneath a layer of liquid for imaging in transmission, dispersion and refraction of infrared light occurs which result in different focal lengths for the different wavenumbers of the infrared light (chromatic aberration). We present a relatively simple method of eliminating the effects of refraction and dispersion which are encountered in FTIR spectroscopic imaging in transmission. This has been demonstrated by introducing a lens on top of the window of a standard transmission infrared liquid cell, a pseudo hemisphere lens is formed on the sample and the dispersion and refraction effects are removed. Through this lens refraction of light is removed and the light across the spectral range has the same focal depth. We show that this approach can be applied to image cross section of human hair, breast tissue and live cells in transmission mode without chromatic aberration and with an improvement in spatial resolution; scattering effect across the edge of cross section of tissue was also minimised with the presence of the lens. In a further development, a second set of lens to create pseudo sphere (rather than hemisphere) was introduced to obtain focused images of aqueous systems for imaging of live cells in microfabricated devices. This approach is significant as spectroscopic imaging of live cells was achieved without the recourse to a synchrotron source of infrared radiation and that FTIR images of live cells have been measured in microfluidics in aqueous solutions and in droplets. This powerful approach may be beneficial for FTIR spectroscopic imaging in transmission for the study of liquid samples.

References

[1] S. G. Kazarian, K. L. A. Chan Applied Spectroscopy 64 (2010) 135A-152A.
[2] S. G. Kazarian S. G, K. L. A. Chan K. L.A. Analyst (2013) 138, 1940-1951.
[3] K. L. A. Chan, S. G. Kazarian Analytical Chemistry 85 (2013)1029-1036.
[4] K. L. A. Chan, S. G. Kazarian Analyst (2013) in press.

(339) **Multivariate Analyses of NIR Reflectance Hyperspectral Images using a Tunable Laser**

David Haaland[1], Howland Jones[2], Lam Nguyen[2], Gregory Israelson[3], Eli Margalith[2]; [1]Spectral Resolutions; [2]Opotek Inc.; [3]Nestle Purina PetCare

OPOTEK Inc. has developed a hyperspectral imaging system (HySPEC™) that relies on an optical parametric oscillator tunable laser rather than a traditional broadband light source and spectrometer to collect spectral images. The advantage this system has over traditional imaging systems is its ability to collect high spectral resolution and high signal-to-noise image data with no sample heating and without spectral artifacts associated with a spectrometer (e.g., smile and keystone distortion artifacts). This imaging system is capable of a spectral resolution of 1 nm with fields of view ranging from a few mm to greater than 20 cm which makes this system ideal for many imaging applications (e.g., food and pharmaceutical, product tampering and adulteration, detecting counterfeits, forensic investigations). Although this presentation will be focused on near-infrared imaging using an InGaAs FPA camera, the tunable laser is capable of illuminating samples with wavelengths ranging from 1000-2400 nm. Depending on the spectral region of interest and desired application, different FPA cameras (InSb or MCT) can be employed. To analyze the hyperspectral image data generated from this unique imaging system, we use fast and efficient Multivariate Curve Resolution (MCR) algorithms to extract the pure-component spectral components and the corresponding quantitative relative concentrations for each pixel within the image. MCR is a powerful technique when combined with hyperspectral imaging because it can analyze the image data without the need for standards, and it can discover all independently varying spectral species present in the image data that are above the noise. Once the spectral components have been identified by MCR, these spectral components can be used for subsequent analyses by either initiating the MCR analyses with these known spectral components or by using Classical Least Squares analyses to estimate the pixel concentrations using these discovered spectral components. In this presentation, we will discuss the steps that are necessary to implement MCR for the analyses of the hyperspectral image data acquired from this HySPEC™ imaging system, including data preprocessing steps. Finally, we will demonstrate the power of this imaging system when combined with multivariate analysis techniques by showing imaging results from multiple real-life applications.

(340) **Structure and Morphology in Triaxial Electrospun Fibers**

Bruce Chase[1], John Rabolt[1], Wenwen Liu[1]; [1]University of Delaware

Electrospinning is a fiber forming technique that has recently experienced a dramatic increase in interest and activity. The production of fibers though this approach allows the control of polymer structure and morphology with fiber diameters as small as 50 nanometers. The chemical and mechanical properties of these nanofibers are often critical to the macroscopic performance of the fiber mat in applications as diverse as filtration and cell growth. There is a limited range over which mechanical properties can be varied for a given polymer fiber. However if a heterogeneous fiber structure can be created, then the possibilities for changing both chemical and mechanical properties becomes much broader. One approach to this involves creating a radially heterogeneous fiber structure through co-axial and triaxial electrospinning. Such an

approach has been developed using concentric needles in a conventional electrospinning arrangement. Results for both co-axial and triaxial fibers will be discussed.

(341) **Imaging of Pharmaceutical Systems using Nanoscale Infrared Spectroscopy**

Lynne Taylor, Aaron Harriosn[1], Rajesh Dave[2], Ramani Susarla[2], Steven Beaudoin[1]; [1]Purdue University; [2]New Jersey Institute of Technology

As pharmaceutical dosage forms become increasingly complex, it is imperative to implement analytical tools that can interrogate chemical and structural features at high spatial resolution. Nanoscale infrared spectroscopy is an emerging technique which couples atomic force microscopy with mid infrared spectroscopy, enabling chemical information to be accessed from submicron domains. Recently, we have successfully implemented this technique to characterize partially miscible drug-polymer and polymer-polymer blends of pharmaceutical relevance. Even more recently, we have commenced the evaluation of organic crystalline nanoparticles dispersed in a polymer matrix. Preliminary results suggest that sub 100nm particles can be successfully imaged. Thus this technique holds great promise for the characterization of the nanoscale structure of drug delivery systems.

(342) **Pharmaceutical Blend Characterization Using *in situ* Near-Infrared Imaging**

Gabor Kemeny[1]; [1]Middleton Research

Pharmaceutical powder blending is a complex process widely studied in recent years. The characterization of the homogeneity of blends as a whole, using the dosage size as the scale of scrutiny (macro-mixing characterization), has been the main focus of past studies.

The present talk introduces a new *in situ* near-infrared chemical imaging (NIR-CI) technique (imMix™) designed to characterize micro-mixing in pharmaceutical powder blends. This technique uses in-line, non-contact monitoring of the blending process, eliminating the bias introduced by commonly used powder sampling techniques. A Science-Based Calibration (SBC) chemometric method, which uses pure component spectral data to create a calibration model, is used to create concentration maps of blends. The advantage of SBC over the alternative Partial Least Squares (PLS) or Principal Component Analysis (PCA) calibration methods is that it does not require a large number of samples to create a calibration. The imMix system is useful in monitoring the distribution and aggregate sizes of drugs and excipients, either in the laboratory or on-line. In the laboratory, one can detect changes in the constituents and other experimental parameters in a small blender (e.g. 1-liter) as a function of blending time. Similar on-line measurements can be made with a camera positioned under a chute of moving powder. The use of these techniques can help in the development of pharmaceutical powder blend formulations and in on-line monitoring.

(343) **Determination of Spatially Resolved Tablet Density and Hardness using Near-Infrared based Chemical Imaging (NIR-CI) and Micro-Indentation**

Sameer Talwar, Rahul Roopwani[1], Ira Buckner[1], James Drennen, III[1], Carl Anderson[1]; [1]Duquesne University

NIR spectroscopy has significantly developed over recent years for analysis and control of pharmaceutical manufacturing processes. NIR-based chemical imaging (NIR-CI) combines spectroscopy with digital imaging. This allows spatially resolved chemical and physical analysis and thus local characterization of pharmaceutical samples. Hardness is the basis of many performance characteristics, and thus a key physical property of tablets. Its local characterization in tablets is a potentially important approach to detect deficiencies in formulation or manufacturing process. This study was aimed at developing a NIR-CI based analytical method to predict spatially resolved hardness in tablets utilizing predicted spatially resolved density. The density distribution in a tablet itself is also important for predicting tablet failures such as capping and sticking. This study followed a two-step procedure, where NIR-CI was used to develop density prediction followed by micro-indentation to create a hardness prediction model. Gabapentin was used as a model material for this study. Pure Gabapentin tablets (13 mm, flat-faced) were made at a speed of 1 mm-min to solid fractions between 0.60 and 0.90. NIR chemical images were collected for both top & bottom tablet faces, with each pixel spectrum representing a spatial location. A PLS density model was created by regressing the spectra of most representative pixels of each tablet against its volumetric density as the reference. Pixel selection was carried out on the basis of spectral Euclidean Distance from the median spectrum of each tablet, where pixels within a certain threshold distance were selected. Later, micro-indentation was used to obtain spatial hardness values for tablets. A univariate model was developed by regressing local hardness as a function of predicted density from NIR-CI based model. Subsequently, the models were used to predict density and hardness for each pixel in the tablet. This produced spatially resolved distribution of these physical properties of tablets.

(344) **Physical Characterization of Drug Product Intermediates using Confocal Raman Imaging and Spectroscopy**

Duohai Pan[1], Shih-Ying Chang[1], Joshua Engstron[1], Daniel Hsieh[1], Chiajen Lai[1], San Kiang[1], Shawn Yin[1]; [1]Bristol-Myers Squibb

A drug product intermediate (DPI) is not an API. It is an intermediate material during processing of the API to the final Drug Product (DP). DPI's is therefore composed of the API and one or more excipients. Understanding the material properties of drug product intermediates can help pharmaceutical scientists and engineers to enhance the processability and quality of the formulation process itself and may also improve the stability of the drug product. In this presentation, the confocal Raman imaging technique combined with vibrational spectroscopy is used for the physical characterization of drug product intermediates. Our investigation focused on the following critical material attributes: API form identification, API crystallinity, API particle size, AP/excipient distribution, API-excipient interactions, and polymer coating uniformity and thickness. The investigation of three DPI's prepared by either a co-precipitation or adsorption techniques will be presented. The information obtained from the Raman imaging demonstrates that confocal Raman imaging, a non-destructive chemical imaging tool, can play a key role in providing critical material attributes of drug product intermediates. This mechanistic understanding can lead to the development of more robust formulation processes.

(345) **Terahertz Imaging and Spectroscopy of Small Samples: A Study in Pharmaceutical Beads**

Xiao Hua Zhou[1], Richard McKay[1], Edward King[1], Eiji Kato[2], Mark Sullivan[1], David Heaps[1], Akiyoshi Irisawa[2], Motoki Imamura[2]; [1]Advantest America, Inc.; [2]Advantest Corporation

Terahertz imaging and spectroscopy of pharmaceutical tablet preparations can yield a wealth of valuable information. This includes information on the strength and integrity of the tablet coating, layer thickness in multi-layer tablets, crystalline content, moisture content and chemical identity of polymorphs. Commercial terahertz systems are adept at handling tablets of many different shapes and sizes. However, many pharmaceutical products are administered in multi-particulate drug delivery systems for their benefits in bioavailability and safety over monolithic tablets. As these beads are typically under a millimeter in diameter yet contain multiple drug and coating layers, they present a number of sample handling and data acquisition challenges. As variations in bead diameter and layer thickness can have a dramatic effect on the release profile of the active pharmaceutical ingredient, the manufacturing

process must be monitored and controlled to assure the desired therapeutic effect. We discuss here solutions to a number of the challenges posed by such samples and present a viable solution for the rapid and convenient imaging and spectroscopic analysis of such samples. We include data demonstrating two different methods for accurate and non-destructive measurement of multiple functional layers for beads in a multi-particulate drug delivery system. One method utilizes time-of-flight terahertz reflection measurements to identify the layer interfaces and accurately calculate layer thicknesses in individual beads. Another makes use of scattering information from terahertz spectroscopy on a collection of beads. The terahertz data are compared to more traditional, but destructive and time-consuming, methods of bead layer thickness analysis.

(346) **Catalytic Flow Chemistry and Real-time Monitoring Challanges**

D. Tyler McQuade[1,2]; [1]Florida State University, Department of Chemistry and Biochemistry; [2]Max Planck Institute of Colloids and Interfaces, Department of Biomolecular Systems

The increased demand for complex molecules combined with rising energy and raw material costs portend a future where chemical synthesis must become far more efficient in order to effectively meet world needs. We focus on the development of new microreactor-based continuous processes and novel catalytic reactions in an effort to create more efficient syntheses. The seminar will include results from McQuade and McQuade/Seeberger efforts with particular emphasis on catalysis in flow and how continuous monitoring if implemented could accelerate the pace of discovery.

(347) **Reaction Characterization and PAT for the Development of Continuous Processes**

Adam McFarland[1]; [1]Eli Lilly and Company

Development of continuous flow processes for the manufacture of active pharmaceutical ingredients or intermediates presents several opportunities and unique challenges for the application of novel analytical approaches. In all cases, a fundamental understanding of reaction mechanisms and kinetics are required to design efficient, robust processes. Often, process monitoring or feed-back/feed-forward control can be implemented to further ensure that process steady-state operation and product quality are maintained. This presentation describes examples of an analytical strategy that has been implemented to elucidate reaction mechanisms, obtain relevant kinetic parameters, and facilitate the development of process analytical technology (PAT) to support continuous flow process optimization. Central to this strategy is the application of in-line nuclear magnetic resonance (NMR) spectroscopy to thoroughly characterize small-scale (i.e., ≤100-mL) batch reactions. NMR has proven to be an invaluable tool for studying reactions involving multiple reactive intermediates or those in which any of the species present are incompatible with the conditions used for chromatographic separation. Furthermore, the exceptional specificity and inherently quantitative nature of NMR enables facile calibration of complementary analytical methodologies (e.g., infrared spectroscopy) that are simultaneously applied for in-line reaction monitoring, but would otherwise require empirical determination of specificity and molar responsiveness. This approach has been utilized to identify and quantify relevant species in the formation of Grignard reagent and to subsequently develop PAT for process control of a continuous flow Grignard reaction. Ultimately, significant time and resources savings are realized through the generalized implementation of this strategy, in addition to the enhanced reaction understanding provided by the detailed mechanistic characterization.

(348) **Recent Advances in Continuous Flow Chemistry using Real-Time *in situ* FTIR (Fourier Transform Infrared Spectroscopy)**

Dominique Hebrault[1]; [1]METTLER TOLEDO

Modern continuous flow reactor technologies have proved to significantly expand the range and scope of possible chemistries available to today's synthetic chemist, and allow for rapid testing, optimization, and scaling of chemical sequences. This is reflected in the dramatic increase in the variety and depth of published chemistry over the last few years. However, a limiting factor with these methods relates to inline monitoring as it facilitates and enhances optimization and synchronized control of single and multi-step reactions. Real-time *in situ* FTIR analysis has already become a standard tool, increasingly utilized to investigate chemistries challenging to analyze using standard offline techniques. This paper will review recent research projects in continuous flow organic synthesis where this powerful non-destructive method technique allowed the formation of products and reactive intermediates to be monitored in real time. Several ongoing investigations in flow will be detailed, including:

- The Development of a Heterogeneous Catalyst for Highly Stereoselective Mannich Reaction
- Safer Control of Vilsmeier−Haack Formylation Transformations
- More Efficient Preparation of Aryl Magnesium Reagents
- Integrated Preparation and Purification of Aryl Azide Derivatives
- Faster Screening and OptiMax of a Modified Knoevenagel Reaction

(349) **Seamless Scale- Up with Corning® Advanced-Flow™ Reactors**

Jeremy Jorda[1], Alessandra Vizza[1], Marc Winter[1]; [1]Corning S.A.S.

Conventional "batch" synthesis with mixing and reactions done in bulky vessels often generates by-products. It may even represent a safety issue when dangerous processes or highly toxic reagents are involved. Corning developed continuous reactors with hydraulic diameter in the range of millimeters that are easily scalable and can be customized to particular needs. A process performed in Corning® Advanced-flow™ reactors allows having more efficient and safe process while keeping a constant quality of the final product. Implementing continuous technology requires a different approach compared to traditional batch processes. Corning fills this know-how gap in the transition from traditional to continuous technologies, offering a full range of reactor products suited to meet the needs of a particular reaction or a wide portfolio of reactions. This technology provides a seamless scale-up and allows a reduction of capital investment and operation expenses.

(350) **Characterization of NMPPAS for Brain Tumor Margining and Related Biosignature**

Sudhir Dahal, Brian Cullum; [1]University of Maryland Baltimore County

Non-resonant multiphoton photoacoustic spectroscopy (NMPPAS) been shown to be capable of differentiating between excised flash-frozen brain tumor (grade III astrocytoma) and healthy tissue has with over 99% accuracy. This powerful technique bears a great potential for use as a real-time surgical guidance tool during brain tumor surgery. This work describes the characterization of NMPPAS in terms of the depth at which excitation of the sample can occur via two-photons, the spatial resolution of the analysis, and the individual endogenous species producing the resulting NMPPAS spectra. Tissue phantoms, that mimic the light scattering properties of real brain tissues, were employed for controlled characterizations studies. Depth characterization measurements demonstrate that NMPPAS signals can be generated and detected from depths of greater than 1.3 cm, which is sufficient for most brain tumor margining applications. Similar studies have also revealed the lateral spatial resolution for such NMPPAS measurement can be approximately 50 μm. In

addition to this measurement characterization work, endogenous species such as NAD^+/NADH, flavins and hemoglobin were analyzed to understand their contribution to the NMPPAS spectra in the optical diagnostic window (700nm-1100nm), helping to understand how the key endogenous species affect NMPPAS signal, and hopefully ultimately leading to the deconvulation of NMPPAS spectra of brain tumor tissues and healthy brain tissues.

(351) **Infrared Spectroscopic Studies of Cells and Tissues: Triple Helix Proteins as a Potential Biomarker for Tumors**

Allison Stelling[1], Deidre Toher[2], Ortrud Uckermann[3], Jelena Tavkin[1], Elke Leipnitz, Julia Schweizer[1], Holger Cramm[1], Gerald Steiner[1], Kathrin D. Geiger[4], Matthias Kirsch[3]; [1]Clinical Sensing and Monitoring, Faculty of Medicine, Dresden University of Technology, Dresden, Germany; [2]Department of Engineering Design and Mathematics, Faculty of Environment and Technology, University of the West of England, Bristol, England; [3]Department of Neurosurgery, Faculty of Medicine and University Hospital, Dresden University of Technology, Dresden, Germany; [4]Department of Neuropathology, Institute of Pathology, Faculty of Medicine and University Hospital, Dresden University of Technology, Dresden, Germany

In this work, the infrared (IR) spectra of living neural cells in suspension, native brain tissue, and native brain tumor tissue were investigated. Methods were developed to overcome the strong IR signal of liquid water so that the signal from the cellular biochemicals could be seen. Measurements could be performed during surgeries, within minutes after resection.

Comparison between normal tissue, different cell lineages in suspension, and tumors allowed preliminary assignments of IR bands to be made. The most dramatic difference between tissues and cells was found to be in weaker IR absorbances usually assigned to the triple helix of collagens. Triple helix domains are common in larger structural proteins, and are typically found in the extracellular matrix (ECM) of tissues. An algorithm to correct offsets and calculate the band heights and positions of these bands was developed, so the variance between identical measurements could be assessed. The initial results indicate the triple helix signal is surprisingly consistent between different individuals, and is altered in tumor tissues. Taken together, these preliminary investigations indicate this triple helix signal may be a reliable biomarker for a tumor-like microenvironment. Thus, this signal has potential to aid in the intra-operational delineation of brain tumor borders. Link to PMC of article: http://www.ncbi.nlm.nih.gov/pmc/articles/PMC3604012/

(352) **Precision Performance of Raman Spectroscopy in the Assessment of Bone Quality**

Gurjit S. Mandair[1], Jaclynn M. Kreider[2], Steven A. Goldstein[2], Robert R. Recker[3], Michael D. Morris[1]; [1]Department of Chemistry, University of Michigan, Ann Arbor, MI; [2]Orthopaedic Research Labs, University of Michigan, Ann Arbor, MI; [3]Osteoporosis Research Center, Creighton University, Omaha, NE

An important performance criterion for the assessment of osteoporosis is the long-term precision of bone mineral density (BMD) measurements. Similar performance criteria could also be equally applied to Raman spectroscopy, an emerging clinical diagnostic for the assessment of bone quality. In this study, the precision performances of key Raman measures of bone composition are examined before and after a series of instrument upgrades. Intrinsic variability in bone composition is also examined after re-sampling a small subset of resectioned bone biopsies that were obtained from postmenopausal women. During the instrument upgrades, the microscope frame was replaced, optics realigned, wavelength recalibrated, and processing scripts rewritten. Micro-computed tomography (microCT) was used to estimate the thickness of the biopsies after resectioning. Select cortical and cancellous bone sites were mapped using a Raman microscope equipped with a 785 nm laser. On a pixel-by-pixel basis, the following composition maps were created: phosphate/proline, carbonate/phosphate, and phosphate/amide I. The means were calculated for each Raman map. The mineral crystallinity parameter was estimated using the full-width at half maximum (FWHM in cm^{-1}) of the phosphate symmetrical stretch at 960 cm^{-1}. Precision of Raman measurements after a series of instrument upgrades was expressed as their percent coefficient of variation (% CV). Similarly, % CV was used estimate the intrinsic variability in bone compositional parameters after resectioning the biopsies. According to microCT analyses, the mean difference between the original and resection biopsy thickness was 0.75 ± 0.1 mm. Preliminary results show that the precision of cortical and cancellous bone Raman measurements after instrument upgrades ranged from 0.3-1.3 % and 0.1-2.0 %, respectively. The intrinsic variability in bone composition was ≤ 5.1 % for the majority of the Raman parameters, except when using the phosphate/amide I parameter, which achieved a precision of 13.0-17.5 %. Because the studies are ongoing and that the blind has not been removed, it remains to be seen which of the Raman parameters and if the magnitude of the variations will be important criteria for the assessment of bone quality.

(353) **Transcutaneous Measurement of Bone Mineral-to-Collagen Ratio *in vivo* using Spatially Offset Raman Spectroscopy and Various Multivariate Techniques**

Kevin Buckley[1,2], Jemma G. Kerns[2], Anthony W. Parker[1], Allen E. Goodship[2], Pavel Matousek[1]; [1]Science & Technology Facilities Council; [2]University College London

Spatially Offset Raman Spectroscopic (SORS) [1, 2] examination of complex multilayer systems, such as biological tissues, requires the use of advanced methods to decompose the constituent spectra. Often, this data processing is the step which limits the accuracy of the experiment and more effective reconstruction methods could yield more accurate spectra with the same data set. In this study we combine SORS with three different multivariate techniques (Band-target entropy minimization (BTEM), Multivariate Curve Resolution (MCR) and Parallel factor analysis (PARAFAC)) and characterise their performance on a spectrally challenging plastic model-system and an even more challenging problem, the analysis of human bone transcutaneously *in vivo*. For the *in vivo* measurements PARAFAC's requirement of multidimensional orthogonal data is addressed by recording SORS spectra both at different spatial offsets and at different anatomical points, the latter providing added dimensionality through the natural variation of skin/soft tissue thickness. The BTEM and PARAFAC methods were the most effective for the plastic-system with the BTEM more faithfully reconstructing the major Raman bands, PARAFAC was more effective for the smaller heavily overlapped features. All three multivariate techniques succeeded in reconstructing a pure bone spectrum from transcutaneous data and gave accurate figures for the phosphate-to-carbonate ratio; the PARAFAC gave the most accurate figure for the mineral-to-collagen ratio. Previous studies of excised bones have shown that certain bone diseases (such as osteoarthritis, osteoporosis and osteogenesis imperfecta) are accompanied by compositional abnormalities that can be detected with Raman spectroscopy. The PARAFAC approach presented here enables the retrieval of more accurate Raman spectra from bone *in vivo* and may aid the detection of bone disease noninvasively using SORS. The results also have relevance to the use of SORS in general.

[1] Matousek P. et al., Applied Spectroscopy, 59(4):393-400,(2005)
[2] Schulmerich M.V. et al., Journal of Biomedical Optics, 11(6):060502,(2006)

(354) **Characterizing Enzymatic Activity Using NIR Dyes**

Gabor Patonay[1], Maged Henary[1], Garfield Beckford[1], Holly Ellis[2]; [1]Department of Chemistry, Georgia State University, Atlanta, GA; [2]Department of Chemistry and Biochemistry, Auburn University, Auburm, AL

Near-Infrared (NIR) absorbing carbocyanine dyes have been increasingly used in analytical, biological and medical field. These dyes can be useful for studying and characterizing biomolecular interactions or developing bioanalytical methods. NIR dye characteristics such as spectral dependence on microhydrophobicity are frequently utilized for this purpose. NIR dyes are known to bind biomolecules which often results in significant spectral changes. The approach discussed in this presentation, the use of NIR dyes to report on enzymatic activities has not been utilized in the past. Carbocyanines containing alkylsulfonate moieties do not exhibit significant fluorescence change upon binding to biomolecules or changes in the hydrophobicity of the microenvironment however otherwise identical dyes that contain alkylaldehyde moiety at the same position do. This phenomenon can be used for the detection of alkenesulfonate monooxygenase activity. These studies are designed to detect and monitor the enzymatic activity of alkanesulfonate monooxygenase using near infrared dyes as substrates. In this spectroscopic bioanalytical assay a group of Fischer based n-butyl sulfonate substituted dyes that exhibit distinct variation in absorbance, fluorescence properties and binding to serum albumin upon desulfonation was identified. In polar solvents, these soluble compounds are strongly fluorescent, however become less fluorescent when the sulfonate groups are cleaved by the enzyme to form the corresponding straight chain alkylaldehyde derivatives. In this study we first have characterized a new class sulfonated heptamethine dyes for this purpose. We have further successfully *in vitro* photo-reduced riboflavin mononucleotide (FMN) with a glucose/ glucose-oxygenase oxygen scavenging system. The reduced FMN serves as a key substrate in the enzymatic desulfonation. NIR Laser Induced Fluorescence (LIF) detected CZE was utilized to detect the sulfonated and de-sulfonated dyes. Once the separation optimization was successfully achieved, the lower fluorescence quantum yield of the less water soluble alkylaldehyde was detected. The lower fluorescence intensity can be significantly increased by adding HSA that binds the alkylaldehyde NIR dye. This change in fluorescence can be used to quantitatively determine the alkylaldehyde dye. This new approach can simplify enzymatic activity measurements as no volatile products are generated.
This presentation gives examples of these specific applications illustrating additional utility of carbocyanines.

(355) **Surface Enhanced Photothermal Induced Resonance (SE-PTIR): A New Method to Image near Field Hot Spots and Dark Plasmonic Modes**

Andrea Centrone[1,2]; [1]National Institute of Standard and Technology; [2]University of Maryland

PTIR is a new technique that combines the chemical specificity of IR spectroscopy with the lateral resolution of Atomic Force Microscopy (AFM). PTIR uses a tunable pulsed laser for sample illumination in ATR configuration and an AFM tip in contact mode to measure the sample instantaneous thermal expansion induced by light absorption. The AFM tip acts as a spatial filter to extract the local chemical composition with a lateral resolution several times smaller than the diffraction limit of IR wavelengths. The recent development of plasmonic nanostructures with resonances in the mid-IR has generated considerable interest in Surface-Enhanced Infrared Absorption (SEIRA) Spectroscopy due to chemical detection limits in the zeptomolar range. SEIRA "hot spot" engineering is the subject of intense research mostly relying on theoretical modeling, but the diffraction of the long IR wavelengths (2-16 μm) has prevented nanoscale SEIRA investigations. In this work the PTIR technique is applied for the first time to map the local absorption enhancement of polymethylmethacrylate (PMMA) coated on asymmetric split ring resonators (A-SRRs), revealing hot spots with local enhancement factors up to ≈ 30 at 100-nm lateral resolution. A-SRRs are plasmonic nanostructures, composed by two metallic arcs with different length sharing a common center of curvature. In A-SRRs, the diameter size allows tuning the plasmon resonance across the whole IR spectral range to match the vibrational absorption resonances of target analytes while the degree of asymmetry controls the electrical dipolar coupling of the A-SRRs dark mode to the propagating waves. The low scattering losses of the dark mode result in a narrower resonance and potentially stronger enhancement. Additionally the PTIR technique was used to provide direct proof and visualization of the dark-mode in plasmonic structures. We name the technique described here Surface-Enhanced PTIR (or SE-PTIR) and we demonstrate its utility for engineering plasmonic nanomaterials towards their technological applications.

(356) **Mid-infrared Vibrational Nanospectroscopy via Direct Molecular Force Detection**

Feng Lu[1], Mingzhou Jin[1], Mikhail Belkin[1]; [1]Univ. of Texas at Austin

In this talk, we report by far the most sensitive mid-infrared (mid-IR) absorption spectroscopy technique with nanometer spatial resolution, which may open new avenues of nanoscale research in chemistry, material and life sciences. Only about 300 molecules contribute to the spectral signal and we expect the current setup is capable of detecting as few as 30 molecules. Rather than counting on photon detection as used in traditional mid-IR spectroscopy, light absorption in our scheme was measured in an opto-mechanical way via reading an atomic force microscope (AFM) cantilever's deflection amplitude caused by mechanical forces exerted on the tip by molecules excited with infrared radiation. This technique is therefore termed as *molecular force spectroscopy*. We demonstrated that high-quality mid-IR spectra can be obtained from sub-monolayer sample substantially thinner than 1 nm. Better than 25 nm spatial resolution was achieved either by measuring mid-IR spectra at different sample locations or by performing chemical mapping. Our method is based on photoexpansion spectroscopy (or 'AFM-IR' technique) originally developed by Alexandre Dazzi and colleagues, which is used for bulk material measurement. In order to achieve monolayer sensitivity, we proposed and implemented two ways of improvement. Firstly, we utilized the local electrical filed intensity enhancement in the nano-gap between a sharp gold-coated tip and a flat gold substrate. This not only increases the optical absorption by molecules below the tip apex, thus increases the interaction between molecules and tip, but results in high spatial resolution as well which is effectively limited by the tip 'hot spot' region. Secondly, the laser pulse repetition rate was moved in resonance with one of the bending modes of the AFM cantilever. In this case the cantilever deflection amplitude can be amplified by its quality factor. For this purpose, a semiconductor based compact-sized broadly tunable quantum cascade laser (QCL) was used as the light source in the experiments.
The mid-IR nanospectroscopy we developed features a simple and robust experimental setup without using any infrared detector, which is friendly to users outside of optical labs. With further improvement, this technique could potentially lead to single-molecule mid-IR spectroscopy in ambient conditions. This work was supported by the Welch Foundation grant F-1705 and STTR program from the DOE.

(357) **Infrared Nanoscopy Applied to Microbiology and Cellular Biology**

Alexandre Dazzi[1], Ariane Deniset-Besseau[1], Delphine Onidas[1], Marie-Joelle Virolle[2]; [1]LCP, University of Paris-Sud, France; [2]IGM, University of Paris-Sud, France

We have developed an innovative infrared microspectroscopy technique, called AFM-IR, based on the coupling between a tunable

infrared laser and an AFM (Atomic Force Microscope). This coupling allows us to perform ultra-local infrared spectroscopy and chemical mapping at the nanometer scale. The principle [1] is based on detecting the local thermal expansion of the sample, irradiated at the wavelength of its absorption bands. This expansion is detected by the AFM tip in contact mode. As the duration of expansion and relaxation of the sample is always shorter than the response time of the cantilever in contact, the excitation transmitted to the cantilever acts as an impulse function, exciting oscillations at resonant frequencies of the cantilever. The technique can create nanoscale IR absorption spectra by recording the amplitude of these oscillations as a function of wavelength and chemical maps by measuring the oscillation amplitude as a function of position. We have validated this technique by comparing the infrared spectrum of a single E.coli bacterium and the corresponding FTIR spectrum, and showing the possibility to perform chemical mapping with sub-wavelength spatial resolution (50 nm) [2]. Later, similar outcomes have been obtained in nanophotonics (20 nm resolution) [3]. Our work is now mainly focused on microbiology [4] systems and cell imaging [5]. For example, we are now interested by the production optimization of bio-polymer (PolyHydroxyButyrate) done by a photosynthetic bacteria, Rhodobacter sphaeroides. The AFMIR technique allows us to easily detect the polymer (PHB) vesicles inside the bacterium due its specific absorption band (ester carbonyl at 1740 cm-1) that is different from those of the bacterium. Similar studies are also provided on different bacteria like Streptomyces to optimize the production of bio-fuel precursor (triacylglycerols).

1. A.Dazzi et al, Opt. Lett. 30, Issue 18, 2388-2390 (2005).
2. C. Mayet et al Analyst 135, 2540-2545 (2010).
3. J.Houel et al, Phys. Rev. Lett. 99, 217404 (2007).
4. C. Mayet et al, Biothechnology advances, vol.31, issue 3, 369-374 (2013).
5. C. Policar et al, Angewandte Chemie International Edition,Vol 50, Issue 4, 860–864, (2011).

(358) **Nano-FTIR: From Nano-Spectroscopy to Quantitative Determination of Dielectric Properties and Thickness Profiling**

Alexander Govyadinov[1], Stefan Mastel[1], Martin Schnell[1], Florian Huth[1, 2], Scott Carney[3], Rainer Hillenbrand[1, 4]; [1]CIC Nanogune Consolider, Donostia-San Sebastian, Spain; [2]Neaspec GmbH, Martinsried, Germany; [3]ECE Dept. and Beckman Institute, U. of Illinois at Urbana-Champaign, Urbana, IL; [4]IKERBASQUE, Basque Foundation for Science, Bilbao, Spain

Scattering-type scanning near-field optical microscopy (s-SNOM) is a powerful optical technique for nondestructive spectroscopic imaging with deep subwavelength resolution [1]. In s-SNOM the information about dielectric properties of a sample is acquired by introducing a sharp probe into the near zone of the sample, subject to an external illumination. The field scattered by the probe depends on the dielectric properties of the sample, therefore providing means for its optical investigation. By detecting this scattering while scanning the sample with the probe, the nanoscale-resolved optical imaging of the sample can be performed. Nano-FTIR is the s-SNOM based technique that utilizes broadband illumination to provide an additional spectroscopic degree of freedom to the sample analysis [2]. We have recently demonstrated that nano-FTIR absorption spectra can be directly compared to the far-field FTIR databases for samples composed of weak oscillators (polymers, biological matter, etc.), therefore allowing for the identification of chemical composition of sample surface with unprecedented spatial resolution [3]. In this work we demonstrate the ability of s-SNOM and nano-FTIR to *quantitatively* measure local optical constants (such as complex-valued permittivity, absorption coefficient, etc.) of thin films [4]. Our approach constitutes a direct inversion of the s-SNOM data based on a perturbative description of s-SNOM scattering process. We further show for the first time that in addition to the dielectric function, the film thickness can also be recovered from the s-SNOM data, i.e. s-SNOM is able to provide the same information as far-field ellipsometry, but (in contrast to ellipsometry) with nanometer-scale spatial resolution. Our work lays the foundation for the quantitative optical imaging and spectroscopy of materials on the nanometer scale. It opens new frontiers for chemometrics, materials and biosciences and presents an important advance towards complete three-dimensional near-field tomography.

References:

[1] T. Taubner, R. Hillenbrand, and F. Keilmann, Appl. Phys. Lett. 85, 5064 (2004)
[2] F. Huth, M. Schnell, J. Wittborn et al, Nat. Mater. 10, 352 (2011)
[3] F. Huth, A. Govyadinov, S. Amarie et al, Nano Lett. 12, 3973 (2012)
[4] A. Govyadinov, I. Amenabar, F. Huth, et al, J. Phys. Chem. Lett. 4, 1562 (2013)

(359) **Thermal Infrared Near-Field Spectroscopy: Coherence, Heat-Transfer, Optical Forces, and Chemical Nano-Imaging**

Markus Raschke[1]; [1]University of Colorado

One of the most universal physical processes shared by all matter at finite temperature is the emission of thermal radiation. Its experimental characterization and theoretical description was a cornerstone in the development of modern physics with the groundbreaking contributions from Gustav Kirchhoff and Max Planck to far-field blackbody radiation. With its origin in thermally driven fluctuations of the charge carriers, thermal radiation reflects the resonant and non-resonant dielectric properties of media, which is the basis for far-field thermal emission spectroscopy. However, associated with the underlying optical source polarization are fundamentally distinct spectral, spatial, resonant, and coherence properties of the evanescent thermal near-field. These properties have been recently predicted theoretically and characterized experimentally for systems with thermally excited molecular, surface plasmon polariton (SPP), and surface phonon polariton (SPhP) resonances. We discuss our recent work on the optical and spectroscopic characterization of distance dependence, magnitude, spectral distribution, and coherence of evanescent thermal fields. Scattering scanning near-field microscopy proved instrumental as an enabling technique for the investigations of these fundamental thermal near-field properties. We discuss the basic theoretical models of the thermal near-field based on the fluctuation-dissipation theory and in terms of the electromagnetic local density of states (EM-LDOS). We introduce the use of thermal infrared near-field spectroscopy (TINS) for broadband chemical nano-spectroscopic imaging, where the thermally driven vibrational optical dipoles provide their own intrinsic light source. We conclude with an outlook on the possibility of intrinsic and extrinsic resonant manipulation of optical forces, and control of nano-scale radiative heat transfer with optical antennas and metamaterials,

(360) **Expanding Applications for AFM-based Infrared Nanospectroscopy**

Craig Prater[1], Qichi Hu[1], Michael Lo[1], Curtis Marcott[2], Kevin Kjoller[1]; [1]Anasys Instruments; [2]Light Light Solutions

Atomic force microscope-based infrared spectroscopy (AFM-IR) has been developed in recent years providing extremely high spatial resolution chemical characterization and imaging. The technique is based on the combination of a tunable infrared laser with an atomic force microscope that can locally map and measure thermal expansion of nanoscale regions of a sample resulting from the absorption of infrared radiation. Because the AFM probe tip can map the thermal expansion on very fine length scales, the AFM-IR technique provides a robust way to obtain interpretable IR absorption spectra at spatial resolution scales well below the diffraction limit.

The technique also provides simultaneous and complementary mapping of mechanical properties and has been widely and successfully applied to applications in polymers and the life sciences. Most previous AFM-IR measurements have been performed using total internal reflection illumination from below the sample, generally requiring samples to be prepared as thin sections transferred to an IR transparent prism. We have recently extended the AFM-IR technique to work in a "top side illumination" configuration. The top side illumination enables a much broader range of samples to be measured and can in some cases dramatically simplify sample preparation. Using top side illumination we have been able to measure samples including semiconductors, metal films, geological samples and others. One additional challenge associated with top side illumination is that the AFM cantilever probe is also in the illumination path and can contribute an unwanted background. We have developed and demonstrated techniques to automatically separate and remove the probe absorption background.

(361) **The Things You Learn Deploying LIBS in Heavy Industry**

Arel Weisberg[1], Joseph Craparo[1], Robert De Saro[1]; [1]Energy Research Company

Energy Research Company (ERCo) has installed or demonstrated LIBS systems in aluminum, glass, titanium, and superalloy plants and at coal-fired electric power stations. LIBS is a unique analytical technology in that it lends itself to in-situ installations because of the ability to collect data via fiber optics and standoff telescopic optics. Also the fact that little or no sample preparation is needed and that LIBS can analyze liquids and solids, all translate to great potential for LIBS as a process control sensor technology in industrial settings.

What are often overlooked are the practical issues involved in realizing this potential utility in an industrial plant. ERCo has learned valuable lessons from working in industrial plants that are essential to a successful project. These lessons range from technical hurdles when collecting LIBS spectra in adverse environments, to the very human, unexpected, and even unimagined, issues that must be overcome for a successful installation.

(362) **Laser-Induced Breakdown Spectroscopy: A Versatile Technique for the Real Time / On-line Analysis of Materials**

Paul Bouchard, Mohamad Sabsabi, François Doucet, André Moreau, René Héon, André Hamel, Francis Boismenu, Lütfü Özcan, Aïssa Harhira; [1]National Research Council Canada

The LIBS technique consists in producing a plasma from a target material with an intense laser pulse and analysing the light emitted by the plasma to obtain atomic composition. This technology has the advantage of being applicable remotely to solids, liquids and gases, without any sample preparation. These qualities are rapidly making it a technology of choice for real time monitoring of chemical composition during materials processing. Since a few years, there has been a renewed interest in the method for a wide range of applications. This is due to the result of significant technological developments in the components used in LIBS instruments as well as emerging needs to perform measurements under conditions to which conventional techniques cannot be applied and where field portable technologies are sought. Extensive studies have been carried out investigating the influence of the parameters affecting the analytical signal to improve the LIBS performances. We will present some approaches to improve the LIBS sensitivity developed in our laboratory and elsewhere, such as double pulse mode, laser induced fluorescence coupled to LIBS, resonance enhanced LIBS, resonant ablation, etc. Recently, high irradiance laser beams have been generated using the "master-oscillator power amplifier" architecture. In this presentation we will report their use for LIBS analysis. Also, we will give an overview about LIBS applications for on-line measurements such as molten materials, metal ore processing, effluents, slurries, liquids and LIBS for the nuclear industry.

(363) **LIBS Analyzers in Mining Industry**

Michael Gaft[1], Lev Nagli[1], Yoni Groisman[1]; [1]Laser Distance Spectrometry

Laser Distance Spectrometry (LDS) was the first to propose LIBS for on-line evaluation of bulk minerals on a moving belt conveyer. We developed the technology, built a machine and proved its viability to provide on-line analyses for raw ores in field conditions. The industrial LIBS machines were successfully installed for on-belt evaluation of phosphate rock measuring Mg, Fe, Al, Bone Phosphate Lime (BPL), Insoluble phase and Metal Impurity Ratio (MER) in CF and Mosaic (Florida, USA), sintering mix basicity stabilization measuring Ca and Si in Novolipetsk Steel (Russia), magnesite crushed ore quality control (Magnezit Group, Russia) and sylvinite product quality control (Solikamsk, Russia). The central issue in an industrial online system using LIBS is to transform the spectral information into quantitative analytical data. In industrial online applications the spectral line intensity depends not only on corresponding element concentration, but also on sample geometry, its distance from the laser source and detecting system, moisture level, physical and chemical matrix effects and so on.

The critical issue for new device acceptance by any industry is its "accuracy". For proper accuracy evaluation, strong attention has to be paid for statistical representatives of the laboratory control sampling. The control samples have to be collected by several persons from conveyer belt simultaneously and analyzed as "unknowns" by the same laboratory or by different laboratories. It was proved that the absolute difference between LIBS machine and control analyzes is approximately the same as between two laboratory analyzes of the different samples taken simultaneously from conveyer belt. Besides, it has to be kept in mind that the main application of such device is process control and the accuracy judgment has to be done according to the correctness of the technological decision which has been made based on online device data. In all industrial installations, LIBS analyzers provided accuracy required for technological process control. With frequent elemental data from a LIBS system, process engineers have the tools to best optimize the process. These processes could be minerals blending and separation to meet customer specifications, monitoring and controlling the efficiency of a minerals process.

(364) **Application of Laser Induced Breakdown Spectroscopy (LIBS) in Monitoring CO2 Storage in Deep Saline Formations**

Christian Goueguel[1], Dustin McIntyre[2], Jinesh Jain[2], Jagdish Singh[3], Athanasis Karamalidis[1]; [1]Carngie Mellon University; [2]USDOE National Energy Technology Laboratory; [3]Mississippi State University

The U.S. Department of Energy's carbon capture and sequestration (CCS) program goals to reduce the emission of CO2 from anthropogenic sources will entail a great amount of cost and efforts and deep saline formations have great potential for geologic CO2 sequestration. To ensure the success of the program it is important that the carbon dioxide that is injected underground remains there (99% permanence over 1000 years). A number of CO2 monitoring techniques have been employed since the inception of the CCS program. The methods range from the injection of tracers, micro-seismic monitoring techniques, satellite imaging, aerial monitoring with gas sensors, and various optical techniques. We propose the use of laser induced breakdown spectroscopy (LIBS) analytical technique for evaluating potential leaks (i.e., CO2 and brine leakage) from the storage sites. The chemical composition of brines varies greatly by location and typically sodium is the most abundant element making 70% to 90% of total cation mass. We are using LIBS to examine the effects of sodium chloride (NaCl) molar concentration on the LIBS signals of calcium and potassium. Solutions of two salts (NaCl/CaCl2 and NaCl/KCl) were prepared by varying the molar concentration of NaCl in each solution ranging from 0 to 3 M. A Q-switched Nd:YAG

laser with a 9 ns pulse length operating at 1064 nm was used to produce plasma in bulk solutions. The plasma emission was spectrally analyzed and the signals from the Ca I 422.67 nm and K I 766.49 lines were investigated. The study has implications in developing LIBS technique for examining changes in brine composition resulting from interaction of CO2 with saltwater reservoirs.

(365) **Towards Optimal Stand-Off LIBS Detection of Various Geochemical Reference Materials at Low Laser Energy**

Soo-Jin Choi[1], Kang-Jae Lee[1], Jack J. Yoh[1]; [1]Seoul National University

Laser-induced breakdown spectroscopy (LIBS) is an atomic emission spectroscopy using a highly irradiated pulse laser focused onto target surface to produce plasma. We obtain the spectroscopic information from this microplasma and determine the chemical composition of the sample based on its elemental and molecular emission peak. We configured a stand-off LIBS technique to analyze the efficiency of remote sensing of various geochemical reference materials. Using a commercial 8 inch Schmidt-Cassegrain telescope (Meade Corp.), our stand-off LIBS system is positioned at 5 m distance from the four USGS geochemical samples that include Granodiorite, Quartz Latite, Shale-Cody and Diabase, which are selected in the interest of the planetary exploration. Prepared samples were mixed with paraffin binder, containing only hydrogen and carbon, and were pelletized for experimental convenience. A Q-switched Nd:YAG laser (Surelite I, Continuum) operating at 1064 nm, pulsed at 10 Hz with the energy of 19.2 ~ 160 mJ/pulse was used to obtain signals, which showed that the geochemical samples were successfully detected by the present stand-off detection scheme. Low laser energy in general results in decrease of signal intensity while the energy efficiency can vary for samples and elements of various types. We successfully identified the minimum laser energy for stand-off detection by tight focusing of the light detecting part of the LIBS setup and by using a larger aperture telescope with a focal reducer. As a result, the optimal conditions for detecting minor elements of the reference materials are determined.

(366) **Simulating Chromatography with MS ExcelTM : An X-ray Vision into a Column: Made into Reality**

Purnendu Dasgupta[1], Brian Stamos[1], Akinde Kadjo[1]; [1]Univ Texas Arlington

An instinctive feeling for how chromatography works will be invaluable to the novice. Although numerous chromatographic software exist, the inner algorithm is rarely transparent. In contrast Microsoft ExcelTM is universally available and basic algebraic operations are self-evident. Simple repetition of an equilibration process at each plate (a spreadsheet row) followed by discrete movement of the mobile by a row, easily automated by a "Macro", readily simulates chromatography and is readily understood by a novice. Isocratic or linear/multistep gradients are easily simulated. The versatility of a transparent platform enables the simulation of complex scenarios nonlinear isotherms, active sites, column overloading, on-column analyte degradation, etc. The 4-bit color gradation of numerical values permits visualization of a band. Majority of these simulations make one very wistful to look at the separation as it develops – not with an end-column detector, like Tswett saw his chlorophyll bands move down his column, except to have a quantitative vision. Attempts have been made towards whole column imaging in optical detection, especially in fluorescence based isotachophoretic systems. We present dynamic conductivity imaging of an open tubular column that quantitatively images the temporal development of ionic separations

(367) **Advances in High Speed and High Resolution Ion Chromatography**

Charles Lucy[1], M. Farooq Wahab[1]; [1]University of Alberta

Traditionally, separation speeds and efficiencies in ion chromatography (IC) have lagged behind those of HPLC and UHPLC. Most IC columns were based on 7-13 μm particles. In recent years, dramatic strides have been made in reducing separation times and increasing efficiency in IC by using particles as small as 2 μm. This presentation will review technological developments such as higher pressure PEEK flow components, new eluent generators and membrane suppressors with increased pressure and lower volumes that enable faster separations. But the heart of a faster IC separation lies in the use of smaller ion exchange particles. Such particles allow shorter columns to be used with correspondingly faster separations, or if packed in longer columns yield higher efficiency columns. However use of small IC particles come with challenges such as increased back pressure, greater demands on extra column components and overcoming the colloidal nature of the particles when packing columns. Means of overcoming these challenges will be discussed. Finally recent investigations of new materials for IC separations will be presented.

(368) **Amino Acid Containing Column Materials for Transition Metal and Drug Separations**

Roger Harrison[1], Na Li[1], Tayyebeh Panahi[1], Lucy Wang[1], John Lamb[1]; [1]Brigham Young University

Amino acids provide a variety of functional groups including polar acid groups and nonpolar alkyl groups. Column materials based on amino acids, mainly the carboxylic groups, have been used for ion separations. [1] Ion chromatography has also been aided by amino acid containing packing materials to separate metal ions and larger molecules such as proteins. [2] We have designed and synthesized molecules based on resorcinarenes which have amino acid groups on one face and $-C_{11}H_{23}$ alkyl chains on the other. The hydrophobic alkyl chains adhere to styrene divinylbenzene packing resin, leaving the amino acid groups exposed to the eluent and anylites. Columns prepared with these new packing materials are able to separate transition metal cations with the aide of eluent additives such as oxalic acid. [3] Also, a set of guanidine containing drugs have been separated by the a similar packing material, but that contains a different amino acid.

1. S. R. Costa, M. J. Bonifacio, J. A. Queiroz, L. A. Passarinha, *J. Chromatogr. B*, **2011**, *879*, 1704.
2. B. Paull and P. N. Nesterenko, *Analyst*, **2005**, *130*, 134.
3. N. Li, L. J. Allen, R. G. Harrison, J. D. Lamb, *Analyst*, **2013**, *138*, 1467-1474.

(369) **High-Pressure Ion Chromatography – A New Platform for High Resolution or High Throughput Separations of Ionic Compounds**

Joachim Weiss; [1]Thermo Fisher Scientific GmbH

One of the most topical subjects in conventional HPLC is the increase of sample throughput without sacrificing resolution by utilizing UHPLC techniques. This is typically achieved by packing separator columns of shorter length and smaller internal diameter with separation materials of smaller particle sizes. However, even at optimal flow rates the resulting back pressure often exceeds the pressure tolerance of traditional HPLC hardware. Therefore, we currently witness the development of HPLC instruments with significantly improved back pressure tolerance well above 80 MPa. Although the stress on wear parts is very high at these high pressures, this development is facilitated with working materials in pumps and valves based on stainless steel. Since ion chromatography is part of liquid chromatography, it is not surprising that a similar solution for IC is demanded as well. The fundamental difference in instrument design, however, is the fact that the fluidic pathways in ion

chromatography instruments are made of metal-free components with a significantly lower pressure tolerance which excludes the use of particle sizes of around 2 µm (or smaller) typically employed in UHPLC separations. While particle sizes of common ion-exchange materials used in analytical IC are typically around 8.5 µm, so-called fast ion-exchange columns do exist, featuring 5 µm particle sizes in smaller column formats (150 mm × 3 mm ID). Thus, the analysis times for anion and cation profiles could be decreased by 50% as compared with conventional ion exchangers. But even under these conditions, typical anion or cation profiles are characterized by a run time of around eight minutes. One possibility for further decreasing analysis times in IC is a flow rate increase beyond the van Deemter optimum, which goes along with a loss of resolution due the relatively large particle size of the ion-exchange material. Thus, this approach is only feasible for samples with a simple analyte composition and little or no matrix contamination. Doubling the linear velocity of the mobile phase through the separator column cuts the analysis time in half, while keeping the back pressure of the separator column well below the maximum pressure tolerance of the system. Another approach for increasing sample throughput in IC is the general trend in separation science towards polymeric monoliths, well known today for separating bio-relevant macromolecules such as proteins, peptides, and oligonucleotides. Using monolith columns, the separation of bio-molecules can be achieved at elevated linear velocities with little or no loss of resolution. There are a number of challenges to be resolved in order to design monolith columns specifically for conventional ion chromatography. For example, one of the challenges is a selection of a suitable column wall material with broad range pH stability and pressure robustness. However, the most critical challenge is an elimination of void space between the monolith and the column wall. Traditionally, capillary scale monoliths are prepared with covalent attachment to the wall to avoid formation of an annular void at the capillary wall. In the case of fused silica capillaries, attachment to the wall is usually accomplished via a silyl methacrylate. However, this is not a practical solution for ion chromatography applications due to the susceptibility of the silane to hydrolysis under normal operating conditions. The way out of this dilemma is a covalent attachment of monolithic structures to a PEEK capillary, providing the necessary pH stability for the new family of IonSwift™ columns. The latest development in ion chromatography hardware design is the expanded pressure tolerance of electrolytic eluent generation in capillary and analytical IC systems up to 34.5 MPa (5000 psi). This allows the use of higher linear velocities of the mobile phase in conventional ion exchangers or the use of separator columns packed with a resin of smaller particle size (4 µm). On the other hand, it also facilitates high resolution separations of complex samples through the use of longer conventional or 4 µm separator columns with standard length. Besides the two major detection techniques for ion chromatography (conductivity and amperometry), a new type of detection mode based on charge measurements will be presented showing increased sensitivity and linear calibration behavior for weakly dissociated anions and cations.

(370) **High Performance Ion Exchange Chromatography of Small and Large Molecules using Monolithic Stationary Phases**

Emily Hilder[1], Paul Haddad[1], R. Dario Arrua[1], Mohammad Talebi[1], Nathan Lacher[2]; [1]University of Tasmania; [2]Pfizer BioTherapeutics Pharmaceutical Sciences

Since their introduction more than 20 years ago, polymer monoliths have been shown to provide excellent separation performance for the separation of large biomolecules. However, the question still remains whether their performance for separations of a wider range of molecules can compete with particle packed columns. This presentation will introduce a range of approaches that we have explored to improve both the separation efficiency and selectivity of separations of both small and large molecules using polymer monoliths. These include new synthetic approaches such as incorporation of nanoparticles into the monolithic structure or synthesis using cryopolymerisation approaches, as well as approaches to extend the operating conditions for these column types, particularly through the use of very high temperature gradients or rapid pulses. The focus will be on separations in ion exchange modes, where polymeric monolithic columns have been shown to offer superior performance for a range of ions, from inorganic and small organic ions to large biomolecules (e.g. monoclonal antibodies).

(371) **Stable Isotope- and Mass Spectrometry-based Metabolomics as Tools in Drug Metabolism**

Andrew Patterson[1]; [1]The Pennsylvania State University

The field of metabolomics is rapidly growing and there have been many noted advances in instrumentation and in the development of tools for the collection of high dimensional, large-scale data and its analysis. Unfortunately, there has been less emphasis and effort into standardizing and optimizing the extraction, separation, and identification of both endogenous and xenobiotic metabolites. Here a stable isotope- and mass spectrometry-based metabolomics approach that captures both drug metabolism and changes in the endogenous metabolome in a single experiment is described. The antioxidant drug tempol (4-hydroxy-2,2,6,6-tetramethylpiperidine-N-oxyl) was chosen because its mechanism of action is not completely understood and its metabolic fate has not been studied extensively. Furthermore, its small size (MW = 172.2) and chemical composition (C9H18NO2) make it challenging to distinguish from endogenous metabolites. Mice were dosed with tempol or deuterated tempol (C9D17HNO2) and their urine was profiled using ultraperformance liquid chromatography coupled with quadrupole time-of-flight mass spectrometry. Principal component analysis of the urinary metabolomics data generated a Y-shaped scatter plot containing drug metabolites (protonated and deuterated) that were clearly distinct from the endogenous metabolites. This study underscores the power of a stable isotope- and mass spectrometry-based metabolomics in expanding the view of drug pharmacology.

(372) **Source Induced Dissociation as a Means for Polymer Structure Characterization and Quantitation**

Peifeng Hu[1], Christopher Jones[1], Liqiong Fang[1]; [1]Baxter Healthcare Corporation

Heterogeneity and polydispersity are common structural characteristics of many functional polymers found in nature (such as heparin) or made by synthesis (poloxamer). These features in structure often limit the usefulness of mass spectrometric analysis of these polymers. Either the compositional complexity prevents the true component profile from being obtained by MALDI analysis or the convolution of the multiply charged signals from the components completely eliminates the possibility for the detection of individual components by electrospray-based methodology including LC-MS. Despite their compositional complexity many functional polymers have repeating units or statistically unique building block ratios. These polymers, upon analysis by electrospray, produce multiply charged ions that can easily be dissociated into small oligomers via source-induced fragmentation. The patterns of the fragments (m/z values and relative abundances) are characteristic of the parent molecule structure, and can easily be recorded by any mass spectrometer. In this presentation source-induced fragmentation of heparin related polysaccharides and its application in qualitative and quantitative analysis will be reviewed as a prelude to an example of real live problem solving. Poloxamer is a triblock polymer with a PEG-PPG-PEG pattern. It is used as a cell culture component for its effect of enhancing cell's resistance to shear. Polymeric impurities are found in technical grade of poloxamer. The detection of an impurity in poloxamer and the eventual determination of the impurity

structure with source-induced fragmentation as the critical tool will be described.

(373) **High Resolution Mass Spectrometry for Low Level Unknown Identification in Drug Product: From Small Molecules to Large Peptides**

Wendy Zhong[1]; [1]Merck Research Laboratories

Impurity and degradation product identification are very critital to late stage pipeline support. According to regulatory guidelines, any impurity above 0.1% needs to be identified. LC/MS and MS/MS have become routine techniques for obtaining molecular weight information and fragmentation patterns. With the advancement of high resolution mass spectrometry, LC/MS and MS/MS with accurate mass measurement can provide the molecular formulae of unknown impurities and degradation products for both molecular ions and their fragments. Compared to other accurate mass MS instruments such as Orbitrap and TOF instruments, a Fourier transform ion cyclotron resonance (FT-ICR) mass spectrometer with ultra high mass resolution and high mass accuracy capability is particularly powerful in both determining isotopic fine structures of unknown impurities and studying stable, isotopically-labeled compounds. High mass accuracy leads to the unambiguous assignment of elemental composition for unknown molecules or fragment ions, which facilitates the impurity ID process and provides higher confidence in the data analysis. Several case studies will be presented to demonstrate the unique capabilities of ultra high resolution mass spectrometry in the structure elucidation of degradation products of small molecules as well as large peptides. In addition, an example of using CASI (Continuos Accumulation of Selected Ion) technology coupled with ECD (Electron Capture Dissociation) to determine isomeric structures for a degradation product in large peptides using a top down approach will also be presented.

(374) **The Addition of Atmospheric Pressure Chemical Ionization GC-MS to the Structure Elucidation Toolbox**

Christopher Jones[1], Edward Chess[1], Peifeng Hu[1]; [1]Baxter Healthcare Corporation

Ionization in a GC-MS experiment is typically performed under vacuum by electron impact (EI) or chemical ionization (CI). EI provides extensive fragmentation, making it highly robust and easily amenable to library searching, but the lack of molecular ion often hinders the identification of unknown compounds. Recent commercialization of atmospheric pressure CI sources for GC-MS (GC/APCI-MS) has removed the vacuum restrictions of traditional CI, allowing for fully optimized GC separations and more easily accessible soft ionization. The use of this ionization source on a QTOF platform allows it to be combined with high resolution mass spectrometry and MS/MS for complete structure elucidation. This technology has been explored in a pharmaceutical R&D setting for the identification of unknown compounds. All GC/APCI-MS analyses were conducted on an Agilent 7890A GC coupled to a Waters Synapt G2 QTOF. A variety of compounds with different functional moieties were analyzed to assess the effectiveness of ionization and the utility of this technique for structural determination. Several protic solvents (water, methanol, formic acid) were introduced into the ionization chamber to promote protonation, and consistent with recent literature, found to provide sensitive and selective control over the ionization process.

In addition, selective ion-molecule reactions have been observed in the ion source that can be exploited for structure elucidation purposes. For example, carboxylic acid moieties reacted to form esters when methanol was used as the proton transfer reagent. Carbonyl-containing compounds subject to silylation, a commonly used derivatization reagent in GC-MS, were prone to form carbonyl-trimethylsilyl (TMS) adducts. This reaction was previously noted in the literature, but the structural basis for its occurrence has been further investigated here leading to a proposed mechanism of TMS-carbonyl adduct formation. Such reactions can assist not only in the unambiguous determination of the molecular ion, but also identify the presence of specific functional groups within an unknown molecule.

Finally, GC/APCI-MS has been applied in several extractables and leachables studies, including the analysis of extracts from pharmaceutical packaging and biopharmaceutical filters. It has proven to be a valuable complement to traditional GC/EI-MS and LC-MS and a valuable addition to our collection of structure elucidation tools.

(375) **Effects of Nucleobase Identity, the 2′-Hydroxyl Group, and Modifications on Glycosidic Bond Stability: Energy Resolved CID Studies of Protonated Nucleosides**

Mary T. Rodgers[1], Ranran Wu[1], Yanlong Zhu[1], Lin Fan[1]; [1]Wayne State University

Nucleosides are N-glycosides of ribose and 2'-deoxyribose, the basic building blocks of nucleic acids: ribonucleic acid (RNA) and deoxyribonucleic acid (DNA). Reactions leading to glycosidic bond cleavage are of great interest for a variety of reasons; in particular, they are amongst the most common reactions involved in DNA repair and nucleobase salvage. Upon protonation, the nucleobase becomes a better leaving group thereby facilitating cleavage of the glycosidic bond. Thus, protonation of the nucleobase is generally involved in the enzymatic processes leading to glycosidic bond cleavage in biological systems. The mechanisms for glycosidic bond cleavage of protonated nucleosides, and the effects of the nucleobase identity, the 2′-hydroxyl group of the ribose moiety, and modifications on glycosidic bond stability are not well understood. In this work, we used energy-resolved collision-induced dissociation (CID) experiments carried out in both guided ion beam (GIBMS) and quadrupole ion trap mass spectrometers (QITMS) to examine the energy dependence of the observed CID pathways. In almost all cases, glycosidic bond cleavage resulting in elimination of the protonated nucleobase is the dominant CID pathway at all energies. Glycosidic bond cleavage resulting in loss of the neutral nucleobase is also observed as a minor CID pathway. Very minor water loss and sequential dissociation pathways are also observed at elevated energies. Experimental studies are complemented by theoretical electronic structure calculations to map out the potential energy surfaces, i.e., relative energetics of reactants, transition states, intermediates, and products, for both glycosidic bond cleavage reactions. Comparative survival yield analyses of the QITMS data provide a relatively high throughput assessment of the relative energetics for glycosidic bond cleavage in these systems. Rigorous GIBMS and theoretical studies are more time consuming, but provide mechanistic details and absolute activation energies for glycosidic bond cleavage. Systematic investigations of the common DNA and RNA nucleosides as well as a wide variety of modified nucleosides provide insight into the effects of nucleobase identity, the 2′-hydroxyl group of the ribose moiety, and modifications on glycosidic bond stability. The detailed mechanistic and thermodynamic gained here also provides insight into functional differences between DNA and RNA and the roles that modifications play.

(376) **Hydrophobic Trapping of Molecules in Nanopores**

Lei Geng[1]; [1]University of Iowa

In vivo diagnosis and therapeutics involve the delivery of sensing molecules and therapeutic payloads to the disease site. A requirement of the delivery is to trap and enclose the drug molecules inside the nanopores during the transport. When the nanoporous particles reach the target site, the drug molecules are released, triggered by environmental changes. A number of elegant approaches have been devised to chemically synthesize, or to mechanically fabricate caps that can block the pore opening during transport. In this talk, we present an approach that hydrophobically traps molecules in the

nanopores, without the need of cap synthesis and fabrication. The new approach is simple and robust, achieving 100% loading efficiency and 100% trapping efficiency. The loading and trapping of an anti-cancer drug, doxorubicin will be discussed.

(377) **Luminescent Probes for High Resolution Chemical Sensing Through Tissue**

Jeffrey Anker[1], Hongyu Chen[1], Fenglin Wang[1]; [1]Clemson University Chemistry Department and Center for Opical Materials Science and Engineering Technology (COMSET)

Fluorescence-based chemical sensing techniques are highly sensitive and versatile, but their utility is limited for *in vivo* imaging because tissue autofluorescence creates spectral interference and optical scattering dramatically reduces the spatial resolution of imaging. In order to circumvent these problems, we introduce X-ray scintillators into the tissue and irradiate them with X-rays to generate local light sources at positions defined by the X-ray beam. This light then serves as a source for chemical sensing based on the absorption spectrum of indicator dyes on the scintillators. These probes provide high resolution chemical measurements, limited by the width of the X-ray beam because only probes within the beam emit light. We show sub-millimeter, low background spectroscopic measurements through 1 cm of tissue. Applications include bacterial detection via pH changes on the surface of implanted medical devices, detection of dissolution of silver nanoparticles on implanted surfaces, and detection of drug release from drug-loaded hollow nanophosphors.

(378) **Surface Enhanced Spectroscopy in the Short-Wave IR**

Jon Camden[1]; [1]University of Tennessee

The intersection of higher-order spectroscopies with the emerging field of plasmonics is an unexplored frontier; therefore, we are exploring the ability of plasmonic nanostructures to drive nonlinear spectroscopies, such as hyper-Raman. Surface enhanced hyper-Raman scattering (SEHRS) demonstrates a method to probe the properties of nonlinear chromophores. It also provides a means for signal upconversion, which allows for surface enhanced spectroscopy to be extended into the short-wave IR.

(379) **Molecular Imprinted Polymers for Raman-based Nanosensors**

Anna Volkert[1], Michael Boller[1], Amanda Haes[1]; [1]University of Iowa

Molecular imprinted polymer (MIP) integration into biosensors is becoming increasingly popular because of their improved stability and detection selectivity vs. traditional recognition agents. Herein, methacrylate-based aspirin, acetaminophen, and caffeine MIPs are synthesized, characterized, and used to selectively detect and quantify the amount of the drugs present in complex mixtures. Briefly, polymerization is first carried out in the presence of aspirin, acetaminophen, or caffeine. Next, these template molecules are extracted thereby leaving a polymer with specific drug imprint sites. The MIPs are characterized using dynamic light scattering (DLS), bright field microscopy, and normal Raman spectroscopy. Finally, the materials are used for quantitative and selective drug detection using normal and surface-enhanced Raman scattering. Integration of nanomaterials into MIP devices will be shown to provide direct and selective detection of drug molecules in complex sample matrices. Better methods for detecting drugs in complex sample matrices is critical in achieving quantitative nanosensors.

(380) **Surface Enhanced Spectroscopy on Infrared Transparent Substrates**

David E. Thompson, Emily N Miller, Dustin C Palm, Deepthika De Silva, Asish Parbatani, Adam R. Meyers, Darren L. Williams; [1]Sam Houston State University

Due to their differing selection rules, surface enhanced infrared (IR) and Raman spectroscopies often provide complementary data. Surface enhanced nonlinear spectroscopy experiments can incorporate both visible and infrared probe beams. Thus, it is advantageous to have the ability to prepare noble metal nano or microparticles that are capable of enhancing, and surface enhancing substrates that exhibit transparency at both the relevant IR and visible frequencies. Evaporative self-assembly of nano and micro spheres was employed as a method to prepare sphere masks on calcium fluoride surfaces and on glass micro scope cover slips under conditions of controlled head space partial pressures. Gold films were deposited over the spheres on both substrates. By varying the diameter of spheres in the sphere mask, LSPR's were generated that are tunable across the IR. IR microscope extinction spectra and Surface Enhanced Raman spectra were collected for gold enhancing surfaces prepared using the same spheres on glass and Calcium Fluoride surfaces. These spectra are compared to highlight the effect of substrate on enhancement in different spectral regions.

(381) **Stable Isotope-Labeled Raman Microspectroscopy: Shedding New Light on Cellular Metabolism**

Shinsuke Shigeto[1], Hemanth Nag Noothalapati Venkata[1]; [1]Department of Applied Chemistry, National Chiao Tung University

As cells are more and more perceived as systems in current biology, system-wide approaches such as proteomics have been used to understand the molecular mechanisms that underlie diverse cellular processes. In those approaches, instead of targeting specific cellular components, proteins or other metabolites (e.g. lipids) need to be globally analyzed. It is thus crucial to measure a large set of proteins and lipids simultaneously and their intracellular dynamics in a spatiotemporally resolved manner. Here we show using fission yeast as a model organism, that Raman microspectroscopy and imaging coupled with stable isotope labeling is a powerful tool to trace and visualize cellular metabolism *in vivo*. In our experiments, we cultured yeast cells with ^{13}C-glucose as the primary carbon source, and examined how the isotope label is incorporated and assimilated into proteins and lipids by looking at ^{13}C-isotope shifts of several characteristic Raman bands. The results of ensemble measurements (n = 25) reveal that complete ^{13}C incorporation requires about 24 h for cytoplasmic proteins and 30 h for lipids, reflecting the difference in turnover time. We also performed time-lapse Raman spectral imaging on a single living yeast cell and found an interesting phenomenon of colocalization of a newly synthesized proteome (labeled with ^{13}C) and lipid droplets. This finding provides direct evidence for the dynamic interplay between lipid droplets and proteome. We will also present our most recent efforts in extending this method to isotope mixtures (^{12}C and ^{13}C) as well as to other isotopes such as deuterium.

(382) **Super-resolution SERS Imaging**

Katherine Willets[1]; [1]University of Texas at Austin

Noble metal nanoparticles can support localized surface plasmons, which lead to enhanced electromagnetic fields at the nanoparticle surface and allow for a host of surface-enhanced spectroscopies, such as surface-enhanced Raman scattering (SERS). While extensive theoretical calculations have predicted how these enhanced electromagnetic fields are distributed on the nanoparticle surface, experiments that reveal how the enhanced electromagnetic fields interact with molecules on the surface of nanoparticles are extremely difficult due to the diffraction limit of light. Because the metal nanoparticles are smaller than the wavelength of light, they appear as diffraction limited spots in optical images, obscuring the local electromagnetic field enhancements and the molecule-metal interactions. This talk will describe how super-resolution imaging can be used to probe enhanced electromagnetic fields in SERS as well as map the size and shape of plasmonic nanostructures.

(383) **Fast and Objective Histopathology by Optical Spectroscopy**

Ioan Notingher[1], Kenny Kong[1], Chris Rowlands[1], Sandeep Varma[3], Ian Leach[3], Alexey Koloydenko[2], Hywel Williams[1]; [1]University of Nottingham; [2]University of London; [3]Nottingham University Hospital NHS Trust

Histopathology based on tissue sectioning and staining has been the gold-standard for diagnosis of cancers for more than a century. However, its use during cancer surgery has been limited mainly by the time-consuming tissue preparation steps (1-2 hours) and diagnosis variability caused by subjective interpretation of images. We have developed a new optical technique based on molecular spectroscopy that overcomes these limitations. The technique relies on a selective sampling rather than raster scanning and uses multimodal spectroscopy and multivariate spectral classification models to establish quantitatively the diagnosis for tissue samples as large as 15mm. Using a laboratory-based instrument, quantitative diagnosis of basal cell carcinoma was achieved in only 25-40 minutes for skin tissues removed during Mohs micrographic surgery. This study demonstrates the potential of this technique to revolutionise cancer surgery by providing a simple and objective way of checking during surgery whether all tumour cells were removed or not.

(384) **Applications of Gold Nanoparticles in SERS Imaging of Fungi**

Kathleen Gough[1], Fatemeh Farazkhorasani[1], Susan Kaminskyj[2]; [1]University of Manitoba; [2]University of Saskatchewan

We are developing various high spatial resolution methods to assess the physiology of growing cells in filamentous fungi, in order to achieve better analysis of fungal biochemical composition. Whole colony methods cannot capture the details of physiology and organism environment interaction, in part because the structure, function and composition of fungal hyphae vary within individual cells and are dependent on their distance from the growing apex. For several years, we have explored Surface Enhanced Raman Scattering (SERS), since it can provide chemical information on materials that are in close contact with appropriate metal substrates, such as nanopatterned gold surfaces and gold nanoparticles (AuNPs). We have tried several methods from growing hyphae across nanopatterned gold substrates to NP synthesized *in vitro* by the growing fungi. More recently, we have experimented with separate preparations of fungal colonies and AuNP. The pre-formed NP are incubated for a short period with the fungal colonies, in monosodium glutamate (MSG) solution, with the intent of allowing the NP to coat the hyphal walls. SERS imaging is then used to explore compositional differences between normal and mutant hyphae that differ in cell wall composition and structure. Results of this on-going research, including NP synthesis, characterization and SERS analyses, will be presented and the different strategies will be compared.

(385) **Raman Microscopy in Clinics - What are the Potentials and Limits?**

Juergen Popp[1,2], Petra Roesch[1], Christoph Krafft[2], Karina Weber[1, 2], Dana Cialla[1, 2], Christian Matthaeus[1, 2], Ute Neugebauer[2, 3], Benjamin Dietzek[1,2], Michael Schmitt[1]; [1]Friedrich-Schiller University, Institute of Physical Chemistry and Abbe Center of Photonics, Jena, Germany; [2]Institute of Photonic Technology, Jena, Germany; [3]Center for Sepsis Control and Care, Jena, Germany

Within the last years a rapid increase of applications of Raman spectroscopy to address biomedical questions has been observed. New concepts of cancer diagnostics as well as a rapid identification of sepsis pathogens were among the most important questions answered by innovative Raman approaches. Here we describe briefly some of our latest results concerning the application of linear and nonlinear Raman microspectroscopy for clinical diagnosis. We will start with highlighting the potential of Raman microspectroscopy for an online / on-site identification of microorganisms that is of great relevance for an efficient medical diagnosis (e.g. rapid identification of pathogens in urine samples) or air- and soil monitoring (e.g. identification of anthrax endospores embedded in complex matrices). The implementation of Raman spectroscopy and optical traps in a microfluidic chip allows for Raman activated cell sorting which offers large potential for an automated classification of cells like e.g. circulating tumor cells. Besides single cells whole tissue sections like biopsy specimens can be characterized by means of Raman-microspectroscopy. The processing of the specific Raman-maps via mathematical approaches enables an objective evaluation of the tissue samples for an early disease diagnosis like e.g. cancer. Besides these ex-vivo tissues Raman studies first steps towards in-vivo Raman spectroscopy that is Raman endospectroscopy will be presented. By doing so novel Raman fiber probes for an intravascular monitoring of the artheriosclerotic plaque in living rabbits will be presented. The low Raman scattering cross section results in long acquisition times. However, the acquisition times can be reduced by utilizing non-linear Raman approaches like CARS (coherent anti-Stokes Raman scattering) and allows recording Raman images of single characteristic Raman bands in real time. In order to further improve the diagnostic result CARS microscopy can be easily extended by the two other non-linear contrast phenomena second harmonic generation (SHG) and two-photon fluorescence (TPF). Overall we will present the development of a compact CARS/SHG/TPF multimodal nonlinear microscope in combination with novel fiber laser sources for use in clinics. The diagnostics potential of this compact multimodal microscope as compared to conventional histopathological images has been demonstrated for the examples of atherosclerosis and cancer.

(386) **Uncertainties in Clustering and Classification of Multivariate Geochemical Data**

Steven Brown[1], Liyuan Chen[1]; [1]Univ. of Delaware

Identification of classes of localized geochemical data is an area that has a long history in chemometrics. One early study on the geochemical effects of strip mining was reported by Brown, Skogerboe and Kowalski. Extending assignments of classes to a specific geographical location of a sample on the basis of the chemical signature of that sample is far less common, as is the estimation of uncertainty of the results.

This presentation reports some results of our recent focus on assigning water samples to a specific watershed, based only on the results of trace metal and isotopic analyses. Some of the challenges inherent in environmental data will be considered. Results of classification and clustering studies will be presented and a route to estimating uncertainties in the results will be reported.

(387) **The Errors of My Ways: Maximum Likelihood PCA Seventeen Years after Bruce**

Peter Wentzell; [1]Dalhousie University

Maximum likelihood principal components analysis (MLPCA) describes a general framework for incorporating measurement error information into multivariate data analysis. The foundations of this methodology were established during a sabbatical period that this presenter spent with Bruce Kowalski in 1996, and the interactions established during that time were key to breakthroughs and developments of many derived methods from that point forward. The fundamental principles of MLPCA have been applied to diverse problems ranging from multivariate calibration and signal preprocessing to curve resolution and exploratory data analysis. This talk will reflect on some of the more personal aspects associated with the origins and genesis of this methodology and Bruce's role in it, and also briefly review some of the applications of MLPCA that have evolved over the years.

(388) **Are O-PLS Models Really More Interpretable?**

Barry M. Wise[1], Jeremy M. Shaver[1]; [1]Eigenvector Research, Inc.

Orthogonal PLS, introduced originally by Trygg and Wold in 2002 [1], is a patented algorithm that has received much attention for its perceived ability to simplify model interpretation. Since its introduction, it has been shown by Ergon [2] and Kemsley and Tapp [3] that results identical to the original O-PLS formulation can be obtained by post-processing conventional PLS models in a non-patented way. This demonstrated, unequivocally, that O-PLS models have predictive properties identical to their non-rotated versions. The authors did not, however, consider the interpretability of the models at length. Exploration of the method, using both synthetic and real data sets, shows that O-PLS does in some cases recover simpler factors that are closer to the true underlying response. However O-PLS factors appear to more sensitive to chance correlation problems than traditional PLS factors.

References:
[1] J. Trygg and S. Wold, "Orthogonal Projections to Latent Structures (O-PLS)," J. Chemo, 16, 119-128, 2002.
[2] R. Ergon, "PLS post-processing by similarity transformation (PLS+ST): a simple alternative to OPLS," J. Chemo, 19, 1-4, 2005.
[3] E.K. Kemsley and H.S. Tapp, "OPLS filtered data can be obtained directly from non-orthogonalized PLS1," J. Chemo, 23, 263-264, 2009

(389) **Assessing Multivariate Calibration Trade-Offs to Select Model Tuning Parameters**

John Kalivas[1]; [1]Idaho State University

Common methods used to form multivariate calibration models are partial least squares (PLS), principal component regression (PCR), and ridge regression (RR). There are many aspects to forming a "good" calibration model including sample design, outlier removal, data preprocessing method, variable selection, and for spectroscopic data, using full wavelengths or select wavelengths (bands and/or individual for sparse models) as well as the method used to select wavelengths. New calibration approaches have been developed that do not require reference samples. Regardless of the calibration method, a key step is determining "good" values of respective meta-parameters (tuning parameters). In most situations, the common approach is usually some form of cross-validation and the resultant root mean square error of cross-validation (RMSECV) values are evaluated. The RMSECV values can be thought of as a prediction accuracy (bias) measure and does not isolate variance information. The methods of PLS, PCR, RR (and others) are biased regression methods and hence, there is a bias/variance tradeoff that should be considered in determining tuning parameter values. Presented in this paper are new combinations of model accuracy and fit that can be plotted with a model variance indicator for selecting appropriate tuning parameter values. For the data sets evaluated, these new combinations appear to remove ambiguities that can occur in RMSECV plots. The data sets include spectroscopic, industrial, and quantitative structure activity relationship (QSAR). Essentially, the user's preference for the degree of balance between bias and variance ultimately decides the tuning parameter selection. Because analytical instrumental data is often utilized, the tradeoff is also characterized by a tradeoff in selectivity and sensitivity.

(390) **Applying ARSE to Classification and Calibration**

Karl Booksh[1], Josh Ottaway; [1]University of Delaware

In many cases Adaptive Regression by Subspace Elimination (ARSE) enables accurate prediction in the presence of uncalibrated interferents with multivariate data. Wavelet transformations are exploited to generate multiple pseudo-variables, each describing a facet of information contained within the spectra. An improved algorithm has been developed to identify which variables in 'wavelet space' are contaminated by uncalibrated interferents. These variables are removed and the calibration model is rebuilt with the remaining variables. Thus the regression model adapts to the presence of the interferent and the contaminated subspace is eliminated. A more accurate prediction is realized at the expense of increased variance. ARSE is applied to quantitative determination of hydrocarbon mixtures with IR spectroscopy and classification of cooking oils with Raman spectroscopy.

(391) **Hyphenated Instrumentation: Developments to Date and Future Prospects**

Charles Wilkins[1]; [1]University of Arkansas

This presentation will briefly review the status of hyphenated analytical chemistry instrumentation from its inception to the present. The factors that facilitated the development of modern analytical systems will be discussed. The possibilities conferred by present day computer, data storage, and electronics capabilities have significant implications for analytical chemical instrumentation in the future. The prospects for those future developments will be considered.

(392) **Surface-Enhanced Infrared absorption Spectroscopy: Arguments Against a Plasmonic Origin**

Peter Griffiths[1]; [1]University of Idaho

Since the first report of surface-Enhanced Infrared absorption (SEIRA) by Hartstein et al in 1980, many practitioners have attributed the enhancement to a similar mechanism to the electromagnetic mechanism of surface-enhanced Raman scattering (SERS). In this talk I will attempt to summarize several of the theories that ascribe SEIRA both to plasmonic and non-plasmonic mechanisms. The observation that SEIRA enhancements are very similar for all metals and that the band-shapes in SEIRA spectra become distorted when the percolation limit is exceeded mitigate strongly against a plasmonic mechanism. In practice, SEIRA spectra can be accurately modeled using the appropriate form of effective medium theory.

(393) **Distance-of-Flight Mass Spectrometry with a Low-Cost Imaging Detector**

Gary Hieftje[1], Alexander Graham[1], Steven Ray[1], Elise Dennis[1], Christie Enke[2], David Koppenaal[3], Charles Barinaga[3]; [1]Indiana University; [2]University of New Mexico; [3]Pacific Northwest National Laboratory

Distance-of-flight mass spectrometry (DOFMS) is a new sort of mass spectrometry that is similar in architecture to time-of-flight mass spectrometry (TOFMS). Like TOFMS, DOFMS has no upper mass range, so is attractive for biomolecule analysis, and offers very high repetition rates, so can be employed for detection of species that have been separated by high-speed chromatography or electrophoresis. In DOFMS as in TOFMS, ions are accelerated to a mass-dependent velocity. In TOFMS, the mass-to-charge ratio (m/z) of those ions is then determined from the time they reach a fast detector positioned at the end of a field-free region. In contrast, in DOFMS, ions are not allowed to emerge from the field-free region but are pushed sideways onto a spatially selective detector stationed part way down the region. A single detector is therefore not required to measure different m/z values, signal integration is simplified, and high-speed electronics are not needed. In recent work, DOFMS detection was achieved by means of a detector array. Unfortunately, such an array is relatively expensive and, at present, is not available in large format, which constrains the mass range that can be measured at one time. To address this problem, we have substituted for the detector array a simple position-sensitive detector fashioned from a microchannel-plate stack and a phosphor screen. The resulting DOFMS was then equipped with an inductively coupled plasma ion source to enable it to be used for elemental and isotopic analysis. Somewhat to our surprise, the figures of merit of the new combination were impressive and compete favorably with those of sequentially scanned

spectrometers. The design of the new system and its performance will be described in this presentation.

(394) **Spectroelectrochemistry as a Strategy for Improving Sensor Selectivity**

William Heineman[1], Samuel Bryan[2]; [1]University of Cincinnati; [2]Pacific Northwest National Laboratory

Spectroelectrochemistry enhances selectivity for sensors by electrochemically modulating the optical signal associated with the analyte. The sensor consists of an optically transparent electrode (OTE) coated with a thin film for preconcentrating the target analyte. The OTE serves as an optical waveguide for attenuated total reflectance (ATR) spectroscopy, which detects the analyte by absorption spectroscopy. Alternatively, ATR can provide the excitation light for fluorescence detection, which is generally more sensitive than absorption. The analyte partitions into the film, undergoes an electrochemical redox reaction at the OTE surface, and absorbs or emits light in its oxidized or reduced form. The change in the optical response associated with electrochemical oxidation or reduction at the OTE is used to quantify the analyte. Absorption sensors for metal ion complexes such as [Fe(CN) 6] 4- and [Ru(bpy) 3] 2+ and fluorescence sensors for [Ru(bpy) 3] 2+ and the polycyclic aromatic hydrocarbon 1-hydroxypyrene have been developed. The sensor has been demonstrated to measure analytes in complex samples such as nuclear waste and natural water.

(395) **Fourier Transform Ion Cyclotron Resonance Mass Spectrometry: 40 Years and Counting**

Alan Marshall[1]; [1]Florida State University

When Charles Wilkins entered the field of FT-ICR MS, the magnetic field was 3 tesla, and applications were limited to electron ionization of gaseous analytes at low pressure. This presentation will review advances at the front end (various atmospheric pressure ionization sources), ion external accumulation and transmission to the ICR cell, ion trapping/excitation/detection, magnet technology, signal processing, and applications ranging from petroleum crude oil to large protein complexes. Work supported by NSF Division of Materials Research through DMR-11-57490, NSF CHE-1016942, CHE-1019193, BP/The Gulf of Mexico Research Initiative, the Florida State University Future Fuels Institute, and the State of Florida.

Marshall, A. G.; Hendrickson, C. L.; Jackson, G. S. "Fourier Transform Ion Cyclotron Resonance Mass Spectrometry: A Primer," Mass Spectrom. Rev. 1998, 17, 1-35.

Marshall, A. G.; Rodgers, R. P. "Petroleomics: Chemistry of the Underworld," Proc. Natl. Acad. Sci. U.S.A. 2008, 105, 18090-18095.

Nyadong, L.; Quinn, J. P.; Hsu, C. S.; Hendrickson, C. L.; Rodgers, R. P.; Marshall, A. G. "Atmospheric Pressure Laser-Induced Acoustic Desorption Chemical Ionization Mass Spectrometry for Analysis of Saturated Hydrocarbons," Anal. Chem. 2012, 84, 7131-7137.

Podgorski, D. C.; Corilo, Y. E.; Nyadong, L.; Lobodin, V. V.; Robbins, W. K.; McKenna, A. M.; Marshall, A. G.; Rodgers, R. P. "Heavy Petroleum Composition 5: The Compositional and Structural Continuum of Petroleum Revealed," Energy & Fuels 2013, 27, 1268-1276.

Valeja, S. G.; Kaiser, N. K.; Xian, F.; Hendrickson, C. L.; Rouse, J. C.; Marshall, A. G. "Unit Mass Resolution for an Intact 148 kDa Therapeutic Monoclonal Antibody by FT-ICR Mass Spectrometry," Anal. Chem. 2011, 83, 8391-8395.

Noble, A. J.; Zhang, Q.; O'Donnell, J.; Hariri, H.; Bhattacharya, N.; Marshall, A. G.; Stagg, S. M." A Pseudoatomic Model of the COPII Cage Obtained from Cryo-Electron Microscopy and Mass Spectrometry," Nature Struc. Mol. Biol. 2013, 20, 167-174.

(396) **Capabilities and Limitation of RF-PGD-TOFMS: An Emerging Technique for Near-Surface Analysis**

Jorge Pisonero[1], Cristina González[1], Nicole Tibbetts[2], Katharine Dovidenko[2], Denise Anderson[2], Dustin Ellis[2], Alfredo Sanz-Medel[3], Nerea Bordel[1]; [1]Department of Physics, University of Oviedo, Mieres, Spain; [2]General Electric Global Research, Niskayuna, NY; [3]Department of Physical and Analytical Chemistry, University of Oviedo, Oviedo, Spain.

In many fields of Industry and Science, the development and characterization of innovative materials, for instance those based on thin-coatings, require the use of direct-solid analytical techniques able to provide high depth resolution, high sensitivity and elemental/molecular information. A group of well-established analytical techniques have been extensively used for direct surface analysis and for depth profiling of ultra-thin layers (e.g. nm-layers). These techniques include, among others, Auger electron spectroscopy (AES), X-ray photoelectron spectroscopy (XPS), and secondary ion mass spectrometry (SIMS). For example, SIMS (e.g. cryo-TOF-SIMS) has been used for bioimaging applications that include analysis of layered organic materials and tissues. Nevertheless, the cost of ownership and maintenance of these techniques is high, and they require analysis of the samples to be performed under ultrahigh vacuum conditions. Furthermore, for analysis of thicker layers (e.g. >hundreds of nm), these techniques are combined with high-energy (>keV) Ar ion beams that might induce surface roughness as a result of preferential sputtering directions. In addition, analysis time is relatively long (e.g. from minutes to hours), resulting in low sample throughput. On the other hand, glow discharges (GDs) have gained increasing importance as atomization, excitation, and ionization sources for depth-profiling analysis, and constitute a useful complementary technique. In particular, the pulsed GD (PGD) mode applies less thermal stress to samples, making it easier to analyze thin coated materials such as glasses or polymers. The pulsed glow discharge is a dynamic plasma with different major ionization processes (i.e. electron-ionization, charge-transfer, Penning collisions) along the temporal distribution of power that define different time domains, for example the “prepeak”, the “plateau”, and the “afterpeak” (or “afterglow”). Suitable combination of PGD with a time-of-flight mass spectrometer (TOFMS) enables time-gated detection of ions along the whole GD pulse period, and, thus, selection of the integration time window that provides the highest analyte signal with minimum spectral interference. In this work, the capabilities and limitations of radiofrequency-PGD-TOFMS are evaluated for the direct solid analysis of ultra-thin layers, paying particular attention to photovoltaic materials. Moreover, distributions of major, minor and trace elements are investigated combining positive and negative ion detection modes.

(397) **A Comparative Study of CCD Array Detector and PMT Signals during Thin Layer Compositional Depth Profile Analysis**

Kim Marshall[1], Greg Schilling[1], Scott Chrispell[1]; [1]Leco Corporation, Saint Jospeh Michigan

Glow discharge spectrometry (GDS) has proven to be a very capable "bulk" analysis technique. However, it is the analysis of surface layers, also known as compositional depth profiling (CDP), where GDS truly excels. Historically, CDP capable glow discharge instruments have utilized multichannel photomultiplier (PMT) based detection. This is because solid-state CCD detectors have been considered either too slow or too insensitive for these types of analyses. This is particularly true when such analyses involve so-called “thin layers”, as for example, in the case of measuring the magnetic layers of a computer hard disk. The required detection speeds for such analyses depend not only on the sample’s structure but on the analysis conditions and, subsequently, the resulting material sputter rates. Previous work [1] has indicated that the data band-width requirements are less than 200Hz for even the most

demanding thin layer applications. The necessary data acquisition rates are quite feasible with modern solid-state detectors. In addition, the dynamic range possible with modern spectroscopic CCD arrays is impressive. These two factors make it feasible to design a CDP capable system utilizing solid-state CCDs. In the work presented here, the bandwidth requirements of various layered materials will be considered. The bandwidths and dynamic ranges observed utilizing both traditional PMT based instruments and CCD based detection systems, as well as other important attributes of these two approaches, will be compared and contrasted. Finally, the CDP analysis of thin layer materials such as the magnetic layers of hard drives will be presented and these results compared.

1) K. Marshall and S. Chrispell, invited paper, International Glow Discharge Spectroscopy Symposium, Albi France (2010)

(398) **Ultrafast Elemental Mapping of High-throughput Screening Samples via Pulsed Glow Discharge Optical Emission Spectroscopy**

Gerardo Gamez[1], Gaurav Mohanty[1], Johann Michler[1]; [1]Swiss Federal Laboratories for Materials Science and Technology, EMPA

The discovery of novel functional materials has been greatly accelerated by the use of combinatorial and high-throughput techniques. Thin film composition spreads are particularly useful for studying numerous materials properties. However, understanding of the behavior of the system of interest can only be reached by knowing the spatially resolved composition. Traditional techniques require several hours to tens of hours or more for determining the compositional landscape of such large area samples (e.g. a full wafer). It follows that much faster elemental mapping techniques are needed to prevent the composition analysis step from being the bottleneck in the high-throughput screening process. Herein, exploratory results will be presented pertaining to the applicability of GDOES elemental mapping to combinatorial and high-throughput screening samples. It will be shown that qualitative analysis images can be obtained in a matter of seconds. Also, quantitative information will be demonstrated through the use of reference materials. The figures-of-merit of GDOES elemental mapping will be compared to alternative techniques.

(399) **Automatable On-Line Generation of Calibration Curves and Standard Additions with Solution-Cathode Glow Discharge Optical Emission Spectrometry**

Andrew Schwartz[1], Steven Ray[1], Gary Hieftje[1]; [1]Indiana University

The solution-cathode glow discharge (SCGD) has emerged in recent years as a promising alternative source for optical emission spectrometry (OES). The SCGD offers a number of advantages over conventional plasma sources such as the inductively coupled plasma (ICP); it boasts simple, inexpensive design, requires no compressed gasses or sample-solution nebulizer, operates at low DC power (~70 W), and produces detection limits comparable to and, in some cases, better than ICP-OES. Regrettably, the SCGD suffers more from matrix interferences than does the ICP. As a consequence, analysis of real samples typically necessitates use of standard addition in order to obtain accurate results. Unfortunately, standard additions are normally tedious, time-consuming, and reduce sample throughput. Methods that automate or increase the speed at which standard addition analyses can be performed are therefore highly desirable for SCGD-OES.

Here, two methods will be described that enable on-line generation of calibration standards and standard-addition samples. One method employs a gradient high-performance liquid chromatography pump to perform on-line mixing of a stock standard, sample, and dilution medium to achieve a desired solution composition. The second method makes use of simpler system of three peristaltic pumps to perform the same function of on-line solution mixing. Both methods can be computer-controlled and automated, and thereby enable both simple and standard addition calibrations to be easily performed on-line. Performance of the on-line methods will be critically compared to that of traditional methods of sample preparation, with emphasis on comparison of calibration curves, signal stability, accuracy, and limits of detection. A potential drawback to the on-line methods (time lag between changes in solution composition) will also be addressed. The new on-line methods are not limited in application to only SCGD-OES—any instrument that samples from flowing solution streams (flame atomic absorption spectrometry, ICP-OES, ICP-mass spectrometry, etc.) could benefit from them.

(400) **Investigation of Outgassing of Volatile Compounds in GD-OES**

Arne Bengtson[1], Mats Randelius[1]; [1]Swerea KIMAB AB

A number of well known artefacts in Glow Discharge Optical Emission Spectroscopy (GD-OES) are due to outgassing of adsorbed volatile compounds in the early stage of the discharge. This results in background signals from gaseous and other light elements, as well as transient emission from several molecular species. The molecular emission in turn interferes with several elemental emission lines. In addition, the excitation mechanisms of the glow discharge are influenced by primarily hydrogen, but possibly also by other light elements. Substantial work has been done in order to compensate for these unwanted effects in the data evaluation algorithms, but in order to improve analytical accuracy the best approach is to reduce both the adsorption and the outgassing of volatile compounds. Experimental work is presented, providing insight into the origin of the volatile compounds and the mechanisms by which they are introduced into the glow disharge lamp. Further work to reduce the amount of outgassing by different procedures prior to the lamp ignition are presented and discussed.

(401) **Process Patent Protection: Protecting Intellectual Property via Ambient Stable Isotopes**

John Jasper[1], Martin Pavane[2], Dean Eyler[3], Ila Sharma[4], Albert Lee[4]; [1]Nature's Fingerprint®/Molecular Isotope Technologies, LLC; [2]Cozen O'Connor, New York, NY; [3]Gray Plant Mooty, Minneapolis, MN; [4]Chemir Analytical Services, St. Louis, MO

The ambient distribution of light stable isotopes in biopharmaceutical synthetic pathways permits the identification and differentiation of potentially-infringing pathways. After reviewing three cases of product identification, we examine three cases of process authentication: one of false advertising and two of process patent infringement. The three cases of product authentication demonstrate the dynamic range of the light stable isotopes in differentiating sources of pharma-ceutical materials. The false-advertising case was substantially a product case because the green-tea L-Theanine and the client- and competitor L-Theanine were markedly different in carbon- (~15‰) and nitrogen isotopic (~10‰) composition. The competitor L-Theanine process was revealed from court documents and chemical-isotopic insight. The competitor was accused of falsely advertising the source of their L-Theanine. The second case of process patent infringement was a straightforward case of infringement. An infringer used synthetic intermediates that were readily available on the market to produce the infringing product. When confronted with the isotopic evidence of process infringement, an out-of-court, business resolution was reached. The third case of process infringement was a case of wrongful accusation of infringement. The carbon-isotopic records of both the product and process studies show that (i) the products are of different origins and (ii) the defendant had in fact used a different synthetic pathway so that he was not infringing the patent of the plaintiff.

(402) **Assessment of a Handheld Raman Device in Potential Use to Detect Counterfeit and Substandard Medicines**

Mustapha Hajjou[1]; [1]United States Pharmacopeia

The spread of counterfeit substandard medicines remains a serious threat worldwide. Hardest hit are countries with limited resources often due to the lack of adequate regulatory strategies. The United States Pharmacopeial Convention (USP) strives to help under-resourced countries combat substandard and counterfeit medicines by building local capacity. It has established programs to monitor the quality of medicines in over 22 countries around the globe, such as collecting and screening medicines in the field. Results collected from monitoring activities provide evidence-based data on quality trends of essential medicines in the market. Screening a relatively large number of samples reduces the burden on the national laboratory and the country's resources. There is a strong need for easy and rapid detection of counterfeit and substandard pharmaceuticals throughout the supply chain. Spectroscopic methods and tools have gained increasing interest. USP scientists evaluated the performance of a handheld Raman device for potential use as a screening tool in evaluating medicines quality. The device is likely to detect counterfeit medicines lacking API or containing the wrong API, however, it is not reliable in detecting substandard medicines. The advantages and shortcomings of the use of portable Raman device in monitoring the quality of medicines will be discussed.

(403) **Performance Validation of Handheld Raman Spectrometers for Counterfeit Screening**

Robert Brush[1], Robert Green[1], Craig Gardner[1], Wayne Jalenak[1]; [1]Thermo Fisher Scientific

The scientific response to the global fake medicine epidemic continues to be redefined by the perpetual emergence of new technologies which are easier to use, smarter and faster. Specific differentiation of pharmaceutical materials in turnkey fashion requires technical foreknowledge of measurement boundaries to be truly successful. Automated analyses which transform data into decisions, such as pass or fail, must follow distinct implementation protocols for development and validation if one expects definitive confidence in the result. In this paper we present an experimental assessment of performance and analytical selectivity achieved with a portable analyzer for pharmaceutical material verification. Advanced applications focused upon counterfeit screening will be presented highlighting recent hardware and algorithm enhancements for Raman spectrometry.

(404) **The USP Spectal Library Project**

Bei Ma[1]; [1]U.S. Pharmacopeial Convention

As the leading global standard-setting organization for medicines, foods and dietary supplements, USP is expanding and enhancing its activities to fight counterfeit and substandard food and drug substances and products. USP Spectral Library project is to establish a food and drug informatics database, which could provide the public with the most authoritative and comprehensive spectral information of medicines. Every food and pharmaceutical ingredient and formulated product, together with its packaging materials has a set of unique physical and chemical properties, and generates characteristic signals or leaves "a fingerprint" within various regions of the electromagnetic spectrum of wavelengths that can be probed and captured using appropriate analytical instrumentations and advanced informatics. A vast collection of spectral "fingerprints", also called a "spectral library," can aid regulatory authorities, law enforcement agencies, hospitals, pharmacies, manufacturers and distributors worldwide to screen for potential counterfeit and substandard food and drug substances and products in any part of the world via internet access. To fully characterize a substance, USP has adopted the orthogonal methodology for the development of the library, which is to use multiple analytical technologies including, but not limited to, gas chromatography-mass spectrometry (GC-MS), near infrared spectroscopy (NIR), NMR, XRD/XRF and Raman technology to gather spectral information. USP has begun working with involved stakeholders with a goal of providing the public with the most authoritative and most comprehensive spectral information for material identification. USP envisions that the spectral library will also capture any known or likely adulterants and contaminants for drugs and foods. Industries, pharmacopoeias, government agencies and other stakeholders interested in learning more about USP's Spectral Library project may contact Ms. Bei Ma at bm@usp.org or +1 301 230 6356.

(405) **Don't Always Assume Natural Is Safe: Screening of Supplements for the Presence of Undeclared Drugs**

Connie Gryniewicz-Ruzicka[1], Jamie Dunn[1], Laura Mecker-Pogue[1], Jason Rodriguez[1]; [1]US Food and Drug Administration

Dietary supplements and herbal—or natural remedies are increasing in popularity all over the world due to the widespread belief that natural products are safer and healthier than synthetic ingredients. Natural supplements are widely available and claim to benefit consumers by treating various health conditions as well as promoting general wellbeing. One of the major concerns related to the safety of dietary supplements is their adulteration with undeclared synthetic drug products in order to enhance the claims stated on the label. To ensure the safety of the American consumers, the FDA has begun an initiative to develop rapid and reliable screening methods to assess the quality of food and drug products. This presentation will evaluate the potential of Raman, near infrared, and ion mobility spectroscopies as screening techniques for the detection of undeclared drugs in dietary supplements. We will highlight the capability of each technique to identify drug adulterants in a broad spectrum of natural products.

(406) **Practical Colorant Identification Applied to Forensic Casework**

Christopher Palenik[1], Skip Palenik[1]; [1]Microtrace LLC

Forensic microscopy and trace evidence analysis are usually conducted by means of comparative examinations: for example, hair comparisons, fiber comparisons, paint comparisons, glass comparisons, etc. While this is a necessary and pragmatic approach, the full extent of information that microscopical analysis can provide is often overlooked, particularly in an era of certifications and accreditations, where SOPs tend to discourage thoughtful and creative analytical approaches to problem solving. For example, many laboratories that operate under such constraints will not even open a package of evidence unless a potential source (i.e., comparison sample) is submitted in parallel.

While the analysis of samples without comparative material can be more time consuming and requires a greater understanding of the material being studied, a great deal of factual and investigative information can be elucidated from such samples by applying the scientific approach in a thoughtful manner. While there are many types of evidence that can be exploited through such investigative (as opposed to comparative) study, this talk will focus specifically on the types of investigative information that can be obtained through the characterization of colorants (dyes and pigments) and their surrounding media, be they paint, food, cosmetics, art, or even an industrial tool. Through the presentation of casework based examples that represents the cutting edge of practical colorant analysis and identification through microscopy, spectroscopy, and microchemistry, this talk will illustrate the types of information that can be obtained from a ubiquitous, but generally overlooked component of trace evidence: the colorant.

(407) **The Ultimate Challenge For Forensic Science**

John Reffner[1]; [1]John Jay College, CUNY

Analytical chemistry plays an important role in providing the courts scientific data and expert testimony to assist judges and jurors in adjudicating justice. Perhaps Archimedes (287-212 BC) was the first forensic scientist. The story of how Archimedes uncovered fraud in the manufacture of a golden crown is legendary. Hiero II, the king of Syracuse, commissioned a goldsmith to make a crown of pure gold. Suspecting that the goldsmith replaced some gold an equal weight of silver, Hiero ordered Archimedes to determine if the wreath was pure gold. Since the crown was to be dedicated to the gods, Archimedes could not disturb it in any way. (In today's terms, he was to perform nondestructive testing). This was a challenging problem for Archimedes. The solution occurred to him while he was taking a bath. Archimedes observed that the bath water's level would rise and overflow as he immersed himself into the bath. Eureka! He found a solution. He put a solid block of pure gold equal to the weight of the crown in water and measured the volume of water it displaced. When the crown was be immersed in water he compare its displacement to that of the pure gold. If the crown were pure gold, then the crown would displace the same volume of water as the pure gold. Since silver's density is lower than gold's, if silver was an impurity it would displace more water. The fraud was detected. Today's problems in forensic science are similar to those faced by Archimedes. Evidence can be anything in our environment, naturally occurring or synthetic materials. The challenge is determining its origin or history. Did the fiber found on a suspect originate from the victim's clothing? In a hit-and-run accident investigation, can analysis of paint transferred onto the victim determine the make and model of motor vehicle that left the scene? Civil actions, intellectual property disputes and legal actions arising from violating a governmental regulation may require the scientific analysis of evidence and expert testimony. The analytical challenges are diverse and the results of analyses have important consequences.

(408) **Detction of Fuel Fraud by Surface Enhanced Raman Scattering (SERS) Spectroscopy**

Peter White[1], Timothy Wilkinson[1]; [1]DeCipher Pte Ltd

Theft, smuggling, counterfeiting and product diversion of goods and services across all market sectors lead worldwide to lost revenues estimated at over $800 billion annually. This amounts to about 7% of world trade, with fraudulent practices in the fuel sector contributing significantly to these losses. To detect and discourage these malpractices some countries have set up fuel control programs in which markers are added to fuels with the markers being detected by a variety of analytical techniques. Although only developed less than three years ago, a novel SERS method with a portable Raman instrument for use in the field has been selected in several countries as their lead technology for detecting fuel fraud and already resulted in successful prosecutions. Hence, this is believed to be the first major successful, commercial and forensic application of SERS technology. The rapid acceptance followed successful pilot studies and also from these, the advantages of SERS over other detection methods eg, cost, speed of analysis, sensitivity, qualitative and quantitative analysis of multi-markers etc., were established. These advantages, supported with examples from use of this SERS system in the field, are presented. These examples will also highlight the demanding requirements of the analytical system. Critical to the success of this SERS method was the availability of a stable and reproducible silver colloid. Over fifteen years ago the first potential forensic applications of SERS were published but deemed impractical due to the lack of a commercially available silver colloid with the desired properties. The ability to resolve this problem was when one of the authors (PW), who conceived and developed the concept of this novel SERS application, had also been able to develop and patent [1] a method for producing a silver colloid with very reproducible SERS properties and a very long shelf-life. Since this colloid plays a vital role in this particular commercial application and the prospect of other potential commercial applications of SERS, the unique properties of this colloid will also be presented.

[1]. P.C. White and J. H. Hjortkjaer. "Preparation of Metal Colloids", International Patent Application, PCT WO 2009/081138 A1, 2009. (Patent owned by the University of Lincoln).

(409) **Wooden Stick Matches as Evidence in Forensic Casework: Not All matches are 'Equal'**

Marianne Stam[1]; [1]California Criminalistics Institute

To a casual observer, wooden stick matches may seem mundane and uninteresting; however, upon closer evaluation these matches often exhibit variability in their physical appearances as well as their chemical compositions, and this variability can be of value when these matches are encountered as evidence in forensic cases. There are two types of wooden stick matches: Strike-On-Box' (aka 'safety matches'), and 'Strike Anywhere' matches. These differ in the chemical composition and physical appearance of their match heads. Safety matches include those made for weather-related functions. Wooden stick matches consist of a match head and a wooden stick, with the match head being the most chemically variable component. Match heads are composed of various inorganic substances within an organic matrix. Both the inorganic composition and organic matrix of a match head can vary. The variability in the organic matrix is usually due either to the function of the match (e.g. waterproof, windproof, weatherproof matches vs. matches produced for non-weather related functions), or the geographical distribution of the matches (e.g. matches produced for distribution to humid geographical regions vs. arid regions). The variability in the inorganic composition of the match heads is usually a result of the inert fillers that are added during manufacturing. Case examples involving the examination of wooden stick matches using microscopy, infrared microspectroscopy, and scanning electron microscopy with an energy dispersive x-ray detector will be presented to illustrate the potential variability in match head composition, and the physical and chemical features that are most discriminatory will be discussed. This presentation will also cover the value of added information to the interpretation of analytical results that can be obtained via industry contacts and the work of investigators.

(410) **Revisiting the Elemental Analysis of Bullet Lead**

Peter De Forest[1], Brooke Kammrath[1, 2]; [1]Forensic Consultants; [2]University of New Haven

Elemental analysis has long been used as a comparative technique with a range of forensic science physical evidence types. The demands this general need or application places on instrumental techniques are formidable. Ideally, the technique employed should be able to non-destructively analyze small samples for multiple elements simultaneously, with extreme sensitivity, excellent quantitative accuracy and great precision. It should also have good inter-laboratory reproducibility. Forensic science has a long history of evaluating instrumentation for the general problem of source attribution by elemental analysis, starting with the emission spectrograph and progressing through a succession of refined instrumental techniques. All have been found wanting. Unfortunately, the ideal instrument or technique for dealing with this demanding problem does not exist. To compound matters further, in the application to certain evidence types, problems arise in addition to the limitations of the instrumentation. For comparative analysis with any evidence type, some information in the form of a database is necessary for proper interpretation. A finding that a "known" and a "questioned" sample are indistinguishable with a given elemental analysis technique means very little without knowledge derived from a database and an understanding of the nature of the sample.

Inhomogeneity and other intra-sample variations lessen the value of a positive comparison. The discrimination value of the comparison is enhanced when the selected instrumental technique offers a high degree of sensitivity coupled with good quantitative accuracy and reproducibility, while the variation of composition within the overall sample population is relatively large as demonstrated by previously generated database information. The controversy surrounding the use of inductively coupled plasma/optical emission spectroscopy (ICP/OES) by the FBI laboratory to characterize bullet lead will be the focus of this presentation. Case examples illustrating the application of the ICP/OES technique to the bullet lead problem and its limitations will be discussed.

(411) **A New *in vivo* Raman Probe for Enhanced Applicability to the Body**

Paul Pudney[1], Eleanor Bonnist[1], Peter Caspers[2], Jean-Philippe Gorce[1], Chris Marriot[1], Gerwin Puppels[2], Scott Singleton[1], Martin van der Wolf[2]; [1]Unilever Discover; [2]RiverD International

This lecture describes a new *in vivo* Raman probe that allows investigation of areas of the body that are otherwise difficult to get access to. It is coupled to a previously described commercially available *in vivo* Raman spectrometer which samples the skin through an optical flat. In the work presented here the laser light emerges from a smaller pen shaped probe. It thus works on the same principles as the original spectrometer with its relative performance in terms of signal to noise of the spectra and spatial resolution obtained being only slightly diminished. It allows the window to be placed against the subject in more curved and recessed areas of subject's body and also for them to be more comfortable whilst the measurements take place. Results from three areas of the body that have been very difficult to study before are described, these being the mouth, axilla and scalp. Results from the scalp and axilla strata cornea (SC) show significant differences from the 'normal' SC of the volar forearm. For instance the scalp is observed to have lower amounts of natural moisturising factors (NMF) compared to the volar forearm within the same subjects. Also for both the axilla and scalp the lipids show a change in order as compared to the lipids in the volar forearm and also differences from each other. The potential significance of these observations is discussed. Further we show how we can probe the mouth, in this case observing the presence of the astringent tea polyphenol epigallocatechin gallate within the oral mucosa.

(412) **Isotopic Analysis at Atmospheric Pressure in Laser Plasmas**

R.E. Russo[1,2]; [1]Lawrence Berkeley National Lab; [2]Applied Spectra, Inc.

High pulsed laser power incident on a sample creates a plume of hot atoms and ions. The measurement of optical emission from these species is the basis of analytical spectrochemical analysis known as LIBS (Laser Induced Breakdown Spectroscopy). LIBS has become a popular technology because it allows rapid analysis of any sample type, requires no sample preparation or consumables, can be performed at atmospheric pressure, and is suitable for remote analysis; a system is currently on Mars (ChemCam). The classical LIBS approach has been to measure elemental analysis; only a nominal amount of research has addressed the laser plasma for isotopic analysis because of the small splitting (shift) in emission spectral lines from atomic and ionic transitions. By measuring molecular emission spectra as the plasma cools, a new technology named LAMIS (Laser Ablation Molecular Isotopic Spectroscopy) provides isotope ratio measurements in these same plasmas – a mass spectrometric measurement without a mass spectrometer. We developed LAMIS to date by demonstrating its ability to measure B, C, H, D, Sr and other isotopes, in some cases with precision < 0.5%. LAMIS also is used to study the temporal and spatial chemical behaviour of atoms and ions in the plasma as the plasma expands and cools into the atmosphere. A significant body of research has been established for physical properties of the laser plasma like temperature, electron density, shock and others. However, a critical parameter to success of laser plasma spectrochemical analysis is the chemistry in the plasma. This talk will describe fundamental aspects of the laser-matter interaction that drive the performance of laser plasma spectrochemical analysis, isotope analysis in laser plasmas at atmospheric pressure, and how these data can be coupled with LIBS and ICP-MS for complete elemental and isotopic analysis.

(413) **Inductively Coupled Plasma Gradient Flow Analysis**

Willis Jones[1], George Donati[1], Bradley Jones[1]; [1]Wake Forest University

Gradient Flow Analysis (GFA) is a new calibration method that corrects for matrix interferences and signal fluctuations in the inductively coupled plasma. The method combines the benefits of the classic standard addition method with those of the internal standard method. Gradient Flow Analysis is performed by preparing two mixtures, each containing 50% sample solution. For mixture #1, the sample is simply diluted 1:1 with water. For the mixture #2, the sample is diluted 1:1 with a standard solution containing several analytes and internal standards at known concentrations. The analysis begins by aspirating the second mixture into the ICP using the normal peristaltic pump. Once the signal levels are constant, an aliquot of mixture #1 is added to mixture #2 as it is continually aspirated. Since each mixture contains the same amount of sample, only the analytes from the standard solution in mixture #2 are diluted. This produces a negative gradient in emission signal for each element with time. The concentration of the analyte in the sample is determined from a plot of the ratio of the analytical signal to the internal standard signal (S_A/S_{IS}) on the y-axis, versus the inverse of the concentration of the internal standard ($1/C_{IS}$) on the x-axis. The entire analysis is performed using just these two mixtures in a single run that takes approximately 3 minutes. The GFA method provides detection limits equal to or better than those observed for traditional calibration techniques, even in complex samples. Precision is often better than 1% relative standard deviation. Accuracy is better than 3% error. The technique has been tested with Cd, Cr, Cu, Fe, and V using Sc and Y internal standards. Results for a variety of sample matrices will be reported.

(414) **Development of High-Power Pulsed Microplasma AES System for Analysis of Small Amount Samples**

Kensuke Okumura[1], Takahiro Iwai[1], Ken Kakegawa[1], Hidekazu Miyahara[1], Akitoshi Okino[1]; [1]Department of Energy Sciences, Tokyo Institute of Technology

Recently, target of elemental analysis has shifted to smaller amount samples such as bio-cells or nanoparticles. Inductively coupled plasma (ICP) has been widely used as excellent ionization or excitation source for elemental analysis. However, it consumes large amount sample solution (~1 mL/min) because of low introduction efficiency and sample diffusion into large size plasma (about 3 mL). Therefore, conventional ICP system is not suitable for analysis of small amount samples. To realize high sensitive analysis of small amount samples, high-power pulsed microplasma source has been developed. A micro hollow cathode structure plasma was used as ionization/excitation source. This plasma is generated in a cylindrical hole of a molybdenum-glass-molybdenum sandwich structure. The hole size is 1 mm in diameter and 1 mm in depth thus this plasma source has small plasma volume of 0.78 μL. The peak electric input power up to 10 kW can be applied and so, the emission intensity was enhanced 1,500 times compared with usual a few W DC plasma. In this study, our droplet direct injection nebulizer (D-DIN) system was hyphenated to the microplasma source. In this system, sample solution is not nebulized but injected into the microplasma as a single droplet using a piezoelectric actuator. By synchronizing pulsed

plasma generation and droplet sample introduction into the plasma, sample elements should be effectively ionized/excited. The droplet volume was 30 pL. Individual analysis of bio-cell or particle will be realized by containing the samples in a droplet. To evaluate the analytical performance, droplets of 100 ppm standard solution was introduced to the plasma and the emission was measured using a multi-channel spectrometer (Ocean Optics, HR4000). With introduction of 30 pL single droplet, strong emission of sodium (Na I 588.99, 589.59 nm) was observed and the limit of detection was 550 fg (10^{-15} g). However, when igniting the plasma, droplet introduction decreased plasma stability due to the solvent load so we developed and tested a droplet desolvation system. Detail of the microplasma, fundamental analytical properties and effect of desolvation system will be presented.

(415) **LA-ICP-oTOF-MS for the Mining Industry: An Investigation**

Andrew Saint[1]; [1]GBC Scientific Equipment Pty. Ltd

ICP-oTOF-MS and laser ablation are becoming widely recognized as very compatible techniques for ultra-trace element analysis. The rapid multi-element, simultaneous data collection of time-of-flight analysis allows the analyst to take full advantage of the transient nature of laser ablation sample introduction.

There are certain applications in the mining industry where LA-ICP-TOF-MS can be utilised to provide accurate, high quality data. Minerals prospecting entails the identification of geological anomalies. These anomalies are represented by high concentrations of elements in the earths crust at a certain location. The precious metals can then be extracted at an economic price.

This poster will discuss some of the applications of LA-ICP-TOF-MS to minerals analysis and prospecting.

(416) **An Examination of Matrix Effects of Carbon and Iron Mixtures in LIBS Spectra, Experimental and Numerical Approaches**

Leon Taleh[1], Poopalasingam Sivakumar[1], Yuri Markushin[1], Jeremie Lasue[2, 3, 4], Noureddine Melikechi[1]; [1]Optical Science Center for Applied Research, Department of Physics and Engineering, Delaware State University, Dover, DE; [2]Université de Toulouse, UPS-OMP, IRAP, 9 Av. Colonel Roche, Toulouse cedex 4, France; [3]ISR, MS D466, Los Alamos National Laboratory, Los Alamos, NM; [4]Lunar and Planetary Institute, Houston, TX

A fundamental problem in LIBS lies in better understanding the analyte response that occurs when the composition and/or property of a sample's matrix is altered. The combined effects of all components of the sample other than the analyte on the LIBS spectra are generally referred to as *matrix effects*. We report on a study of the behavior of atomic and ionic lines emitted by a nanosecond laser-induced plasma as a function of the atomic number densities of the constituents of a binary mixture formed of carbon (C) and iron (Fe). To achieve this, we recorded the LIBS spectra of samples with a known and carefully controlled ratios of the concentrations of C and Fe. This study reveals two critical observations. First, we find that the intensities of Fe neutral atomic lines behave differently than those of the ionic ones particularly at and above concentrations of 75% - 80% Fe embedded in C matrix. Unlike the emission from neutral Fe, those from ionic Fe yield a very sharp decrease followed by an equally strong increase of the emission lines over a relatively small range of relative concentration of C and Fe. Second, we observe stronger shot-to-shot variations of the intensities of iron emission lines than those from carbon. We suggest that the morphology and more specifically the *packing density* of the binary carbon-iron mixture greatly affects the relative standard deviation (RSD) of the laser-induced plasma emission lines. To better understand these results, we simulate the laser-target interaction using a two dimensional (2D) random close packing (rcp) model of disks distributed in a confined geometry. This work suggest that it may be possible to use of the fluctuations of LIBS spectra to determine the size of particles interrogated in various fields including the characterization of soils and rocks on Earth and other planets.

(417) **Effects of Axial and Transverse Magnetic Fields on Laser Produced Plasmas**

Faisal Odeh[1], Niral Shah[1], Nick Mckenna[1], Prasoon Diwakar[1], Filippo Genco[1], Sivanandan Harilal[1], Ahmed Hassanein[1]; [1]Center for Materials Under Extreme Environment, School of Nuclear Engineering Purdue University, West Lafayette, Indiana

The plasma hydrodynamic expansion properties and emission features can be controlled by external magnetic field. We investigated the effect of the magnetic field on both confinement and collimation of laser-produced plasmas. An Nd:YAG pulsed laser (λ:1064 nm and FWHM:6 ns) was used for generating laser ablation plumes. A magnetic trap was designed with nearly uniform magnetic field strength of 0.8T. The magnetic field strength can be varied by changing the distance between the magnets. The generated plasma was allowed to expand onto either a transverse magnetic field or onto an axial magnetic field. Various target samples were used in this study that included carbon, aluminum, magnesium, silicon, brass, and tungsten. All experiments were undertaken in vacuum. Three different plasma diagnostics were used to study the dynamics of the transient plasma. First, Faraday cup was used to determine the velocity (kinetic energy) and ion flux. It was observed that low-Z materials undergo more than 50% reduction in velocity in the presence of the magnetic field. Second, fast photography was performed using an intensified charged coupled device (ICCD) to study the plume dynamics. In the presence of transverse magnetic field, the plume expansion was confined and travelled a shorter distance as compared to free expanding plasma. In axial magnetic field, collimation of the plume was observed. Finally, optical emission spectroscopy was used to determine the temperature, electron density, and ionization rate of the plasma plume. In the presence of transverse magnetic field, enhancement in the emission of some ionic lines was observed along with a slight reduction in electron density. Comparison between plasma emission intensity in the transverse and axial magnetic fields will also be discussed.

(418) **CO2 Removal Using a Falling-Film Column in the Analysis of Organic Samples with Inductively Coupled Plasmas**

Farzaneh Moradi[1], Helmar Wiltsche[1], Günter Knapp[1]; [1]Graz University of Technology, Institute of Analytical Chemistry and Food Chemistry, Graz, Austria

The direct determination of trace elements in volatile organic matrices using inductively coupled plasma optical emission spectrometry (ICP-OES) is often challenging and requires procedures substantially different from those used for aqueous samples e.g. cooled spray chamber, high RF power, addition of oxygen to the nebulizer and / or auxiliary gas flow. Direct online-combustion of the volatile organic samples in the presence of oxygen and subsequent removal of the CO2 from the sample gas stream prior to the introduction into the ICP is a novel strategy to overcome the aforementioned problems. The results presented in this contribution focus on the removal of CO2 from the gas stream leaving the combustion oven. CO2 is known to affect the excitation conditions of the ICP. For the instrument used in this work 3.4% CO2 (v/v) is the maximum concentration which plasma can tolerate. In order to reduce the CO2 concentration after the combustion process, a thin film column absorber based on the chemical reaction of CO2 with an alkaline solution (NaOH) was designed. The effect of CO2 concentration in the carrier gas flow on the absorption efficiency of CO2 was investigated. It was found that the ICP was entirely stable at CO2 concentrations up to 7% v/v in the nebulizer gas stream. In the presented system the absorption efficiency was dependent on the

CO2 concentration. With increasing CO2 concentration in the carrier gas flow a decrease in the absorption efficiency was encountered.

(419) **Study of S0→S3 Transition for Liquid Benzene and Mono-Substituted Benzenes by Using Far-Ultraviolet Spectroscopy and Quantum Chemical Calculations**

Yuuki Uematsu[1], Yuusuke Morisawa[2], Masahiro Ehara[3], Yukihiro Ozaki[1]; [1]Department of Chemistry, Kwansei Gakuin University; [2]Department of Chemistry, Kinki University; [3]Institute for Molecular Science

Benzene and its derivatives are basic chemical compounds. Though their photoabsorption is relevant to understand the electronic structure and photochemistry, only the gas phase spectrum in far-ultraviolet (FUV) region (120 ~ 200 nm) has been studied.[1] In the present study, the FUV spectra of benzene and its derivatives in liquid phase are examined by an attenuated total reflection far-ultraviolet spectrophotometer (ATR-FUV) which was recently developed by our research group. [2] Different concentration solutions (1.0 M ~ neat) of benzene and eight mono-substituted benzenes (toluene, chlorobenzene, bromobenzene, anisole, benzyl alcohol, acetophenone, nitrobenzene, aniline) were prepared in cyclohexane. The ATR-FUV spectra of the sample solutions were measured in the wavelength from 145 to 300 nm. After applying the Kramers-Kronig transformation to derive the absorption coefficients for the benzene solutions, the intense $S_0 \rightarrow S_3$ transition bands were observed around 185 nm due to π-π* (HOMO-LUMO) transition. As the benzene concentration increases from 1.02 to 11.3 M, (1) the positions of $S_0 \rightarrow S_3$ band maxima are red-shifted from 183.4 to 186.4 nm and (2) the molar absorption coefficients (ε) decrease from 4.46×10^4 to 1.52×10^4 L $mol^{-1}cm^{-1}$. Those spectral changes with the sample concentration are derived from the inter-molecular interaction of benzene molecules. The characteristic π-π stacking and T-shaped structures were reported for the solid state of benzene. [3] To examine how the inter-molecular interaction among benzene units affects the $S_0 \rightarrow S_3$ transition, the electronic spectra of chlorobenzene molecules for monomer, dimer and trimer with π-π stacking configuration were calculated by quantum chemical calculations with a time-dependent density functional theory (TD-DFT) method. Theoretical results show that the ε values decrease in the order of monomer, dimer and trimer, which would partly explain the experimental observation. We will also examine the electronic spectra of other possible interacting configurations of chlorobenzenes.

[1] E. Pantos, J. Philis, and A. Bolovinos, *J. Mol. Spectrosc.*, 1978, **72**, 36-43

[2] Y. Ozaki, Y. Morisawa, A. Ikehata, N. Higashi, *Appl. Spectrosc*., 2012, **66**, 1-25

[3] E. G. Cox, *Reviews of Modern Physics*, 1958, **30**, 159-162

(420) **The Determination of Si in RM 3475 Silicon Nanoparticles**

Savelas Rabb[1], Vytas Reipa[1]; [1]National Institute of Standards and Technology

The National Institute of Standards and Technology is developing a Si nanoparticle reference material for the validation of physical and chemical properties of Si nanostructures used in the biotechnology, electronics and energy sectors. The Si concentration in colloidal systems is typically determined using absorption measurements. However, the extinction coefficient for these measurements is unknown, thereby making it difficult to provide accurate Si determinations for these suspensions. As a result, inductively coupled plasma optical emission spectroscopy (ICP-OES) was utilized for the Si measurements in this analysis. Method development for the ICP-OES experiment involved digestion of the Si nanoparticle suspensions using tetramethylammonium hydroxide, heating the samples to near dryness to remove the toluene matrix, and then reconstituting with water. Accurate Si measurements were conducted using the method of standard additions. The observed Si concentration in the reference material was 6.43 ± 0.31 μg/g. These measurements could potentially be used to establish a relationship between the Si concentration in the nanoparticle suspensions and the observed Si absorption signal.

(421) **Quantification of the Centimetre-scale Heterogeneity of Human Cortical Bone Composition**

Kevin Buckley[1,2], Jemma G. Kerns[2], Anthony W. Parker[1], Allen E. Goodship[2], Pavel Matousek[1]; [1]Science & Technology Facilities Council; [2]University College London

It is well known that the complex and heterogeneous nature of bone limits the conclusions that can be drawn from individual point spectra about the bulk composition of bone, and thus many studies now report spectral maps scanned over tens, or hundreds, of micrometres.[1] Here, we report the presence of centimetre scale heterogeneities in long bones which could be missed when mapping millimetre (or smaller) scale areas; we investigate compositional variation of bone across several centimetres of mid-shaft human tibiae cortical bone with a spatial resolution of ~2 mm. The results reveal a large variation, of 8%, in the phosphate to amide I intensity ratio (a widely used measure of mineral to collagen ratio) and a variation of 5% in the phosphate to carbonate intensity ratio (used to assess the bone mineral), across the ten centimetre section of bone. An understanding of the natural variation in bone tissue composition will result in an improvement in the sampling accuracy analogous to that obtained by switching from point spectra to spectral-images and will reduce the possibility of natural heterogeneity obscuring, or being mistaken for, experimental signal.

[1] Morris MD (2010) Raman spectroscopy of bone and cartilage. Chapter 14 of: Matousek P, Morris MD (eds) Emerging Raman applications and techniques in biomedical and pharmaceutical fields. Springer, New York, pp 347–364

(422) **Use of a Simultaneous Mattauch–Herzog Inductively Coupled Plasma-Mass Spectrometer for Analysis of Cerebrospinal Fluid from Alzheimer's Patients**

Esperanza García-Ruiz[1], Luis Rello[2], Frank Vanhaecke[3], Martín Resano[1]; [1]University of Zaragoza; [2]Hospital Miguel Servet; [3]Ghent University

Alzheimer's disease (AD) is the most common form of dementia. It is a degenerative disease for which there is no known cure. Moreover, AD develops in a different way for every patient, making it difficult to diagnose. Although there are some common symptoms, these are easily mistaken with age-related issues or stress indicators. Owing to the high social and economic cost of this disease, any effort devoted to better understand its mechanism, which could eventually lead to earlier detection or to new treatment procedures, is certainly welcome. Some works have investigated the relation between AD and the intake of some metals, particularly of Aluminum, Zinc and Copper, although the results obtained so far are not considered as conclusive. In order to investigate this relation between metals and AD, sampling of cerebrospinal fluid (CSF) seems to be a logical choice, because the brain and CSF are protected from fluctuations in plasma metal concentrations by the blood–brain barrier. Obviously, the amount of CSF available per patient is typically very low. Thus, the use of an instrument allowing simultaneous monitoring of the whole inorganic mass spectrum would be desirable, instead of restricting the investigation to a few elements only. It is the purpose of this work to develop a method for the fast elemental and isotopic analysis of CSF, in an attempt to develop a pattern that could permit to differentiate AD patients from patients suffering from other brain-related illnesses. For this purpose, the use of a fully simultaneous Mattauch–Herzog inductively coupled plasma-mass spectrometer (ICP-MS) will be evaluated.

(423) **Integrating Second Harmonic Generation and Two-Photon Ultraviolet Fluorescence into an X-ray Diffraction Beamline for Protein Crystal Centering**

Christopher Dettmar[1], Jeremy Madden[1], Justin Newman[1], Scott Toth[1], Michael Becker[2], Robert Fischetti[2], Garth Simpson[1]; [1]Purdue University; [2]GM/CA @ APS, Argonne National Labs

An instrument has been developed for integrating second harmonic generation (SHG), and two-photon excited ultraviolet fluorescence (TPE-UVF) imaging into a synchrotron X-ray diffraction (XRD) beamline. The goal of this instrument is to rapid screening for protein crystals and centering them for XRD analysis. In SHG, two photons of infrared light combine to form one photon of visible light at twice the frequency. The symmetry requirements of this process make it sensitive to non-centrosymmetric crystalline order, including the large majority of protein crystals and excluding most common salts, cryo-protectants, solvents, and aggregated protein. In TPE-UVF, the simultaneous absorption of two photons of visible light, the energy equivalent of one photon of UV light, results in emission of a photon in the near UV to blue range. The wavelengths used are sensitive to aromatic amino acid residues, particularly tryptophan, making ~80% of proteins detectable through a mechanism unique and complementary to SHG. These imaging methods are sensitive to micron-sized crystals, including those grown in the lipidic mesophase that are otherwise difficult to visualize. Positioning by nonlinear optical imaging may reduce or eliminate the need for large area X-ray raster scanning thereby reducing X-ray induced radiation damage and increasing throughput of synchrotron x-ray diffraction. Integration with the synchrotron beam line allows a sample to be mounted on the goniometer, imaged, crystal centered and ready for diffraction in just a few minutes.

(424) **Effects of Local Environment on UV–VIS Spectra of Zinc Porphyrins: Protein & Solvent**

Hannah E. Wagie[1], Jorg C. Woehl[1], Peter Geissinger[1]; [1]University of Wisconsin - Milwaukee

We are interested in how a protein's three-dimensional structure might generate a directional electric field to influence its active site and achieve the specificity with which these macromolecules perform their biological tasks. An experimental method has been developed for use with heme proteins to measure this internal electric field with a UV–VIS technique, hole-burning Stark spectroscopy. Here, the method along with preliminary data is presented in the study of myoglobin with zinc protoporphyrin IX, a heme analog that has more experimentally friendly emission qualities. In addition, a more detailed characterization of the influence of protein matrix and solvent on the UV– VIS spectra of various zinc porphyrins is given. The molecule's immediate surroundings influence its electron distribution and thus its electronic transitions. This environment can be well-defined, like a protein, or isotropic, like a solvent continuum. Experimental absorption and fluorescence excitation spectra provide points of comparison for both types of environment. Then, theoretical values for state energies and oscillator strengths, calculated with the Gaussian09 computational package and a time-dependent density functional theory method, are shown to depend on the way the environment is modeled. Here, we explore the notions of discrete point-charge distribution versus dielectric constant in mimicking the protein matrix's electric field.

(425) **Exploiting Human Fingernail as a Surrogate Marker of Fracture Risk in Postmenopausal Women**

J Renwick Beattie[1], Olive O'Driscoll[2], Niamh Cummins[3], Mark Towler[4]; [1]Crescent Diagnostics Ltd; [2]Cork Institute of Technology; [3]University of Limerick; [4]Ryerson University

Fracture risk is high among post-menopausal women, with 30-40% lifetime risk . Currently the gold standard method used to test bone health is Dual X-ray Absorptiometry (DXA), which measures the mineral density of a selected area of the skeleton. Patients with a bone mineral density less than 2.5 standard deviations below the mean for a cohort of healthy 25 year old women are diagnosed as osteoporotic [1]. Typically only 30-40% of low-impact fractures occur within the context of an osteoporotic diagnosis [2]. Anecdotally, osteoporosis patients have reported increased fingernail strength following pharmaceutical treatment. Raman spectroscopy was used to analyse fingernail clippings taken from 633 postmenopausal women presenting for a DXA scan at 6 hospitals across the UK and Ireland. The DXA results from these patients were recorded. Samples from 4 centres were used to design processing and analysis algorithms, with the remaining 2 centres used to validate. The Area Under the Curve (AUC) for DXA (osteoporoisis diagnosis) against fracture was 56%, which was not significantly different from random chance ($p>0.05$). The Raman spectra led to an AUC of 60% which was significantly better than random chance ($p<0.05$). The validation set demonstrated the model is very stable, with sensitivity and specificity maintained. Using a fingernail clipping Raman spectroscopy was able to identify patients at risk of fracture better than DXA. Because a fingernail is a much simpler sample to analyse than placing a whole person in a DXA scanner the approach offers a significant benefit for screening bone health in postmenopausal women.

[1] WHO 2007; Assessment of Osteoporosis at the Primary Health Care Level

[2] Bone 2008; 467-475

(426) **Spectral Characterization of Carbonated Apatites and Computation of NMR Spectra**

Mary Tecklenburg[1], Barbara Pavan[1]; [1]Central Michigan University

Carbonated hydroxyapatite (CAp) is the dominant solid mineral phase within skeletal and dental tissue of vertebrates. The bio-mineralization of bone tissue is a complex process and it has been proposed to occur through a progression of mineral phases. The extent of carbonation controls biomineral properties such as crystallinity and solubility. Synthesized carbonated apatite is commonly used to model the mineral phase of hard tissues and explore its properties as a function of substitution site and level of carbonate in apatite. Spectral methods (IR, Raman, NMR) are ideal for characterization of types of mineral phases, crystallinity, and interaction between ions, in bone or in model materials. We report here the variation in carbonate incorporation into the hydroxyapatite structure $Ca_{10}(PO_4)_6(OH)_2$ and the changes in composition necessitated by charge compensation when carbonate replaces a phosphate (B-type) or hydroxide (A-type) or both. Interpretation of experimental results was augmented by computation of equilibrium structures of carbonated apatites. Calculated NMR chemical shifts compared favorably with experimental values and indicated which nuclei are most sensitive to structural changes in apatite upon carbonation.

(427) **Principal Component Analysis of Phenolic Acid Spectra**

Ronald Holser[1]; [1]Russell Research Center

Phenolic acids are common plant metabolites that exhibit bioactive properties and have applications in functional food and animal feed formulations. The ultraviolet (UV) and infrared (IR) spectra of four closely related phenolic acid structures were evaluated by principal component analysis (PCA) to develop spectral models for their rapid detection. Results demonstrated that UV and IR spectra could discriminate between each of the phenolic acids in overall models. Calculation of model scores and loadings showed derivative UV spectra accounted for 99% variation with 2 principal components (PC) while derivative IR spectra required 3 PCs. Individual PCA models were developed for ferulic acid and p-coumaric acid using derivative UV spectra for detection and classification by soft independent modeling of class analogy (SIMCA). The application of

this spectral technique as a classification model is expected to promote the use of agricultural residues as a source of these phenolic compounds.

(428) **Parallel Factor Analysis of Multi-Excitation UV Resonance Raman Spectra for Protein Secondary Structure Determination**

Olayinka Oshokoya, Renee JiJi[1]; [1]University of Missouri-Columbia

Studies pertaining to protein or peptide structure, dynamics or function fundamentally require a method for secondary structure measurement. The structurally sensitive protein vibrational modes (amide I, II, III and S) in deep-ultraviolet resonance Raman (DUVRR) spectra resulting from the backbone C-O and N-H vibrations make DUVRR a potentially powerful tool for studying secondary structure changes. Experimental studies reveal that the position and intensity of the four amide modes in DUVRR spectra of proteins are largely correlated with the varying fractions of α-helix, β-sheet and disordered structural content of proteins. Employing multivariate calibration methods and DUVRR spectra of globular proteins with varying structural compositions, the secondary structure of a protein with unknown structure can be predicted. A disadvantage of multivariate calibration methods is the requirement of known concentration or spectral profiles. Second-order calibration methods, such as parallel factor analysis (PARAFAC), do not have such a requirement due to the "second-order advantage."

An exceptional feature of DUVRR spectroscopy is that DUVRR spectra are also dependent on excitation wavelength as they are on secondary structure composition. Thus, higher order data can be created by combining protein DUVRR spectra of several proteins collected at multiple excitation wavelengths. Here, PARAFAC has been used to analyze DUVRR data collected at multiple excitation wavelengths on several proteins to determine secondary structure content.

(429) **Spectroscopic Discernment of Seed Cotton Trash**

Gary Rayson, Elizabeth Gámez[1], Fengshan Jiang[1], Surja Ghale[1], S. Hughes[2], Dean Anderson[3]; [1]New Mexico State University; [2]USDA-ARS Southwest Cotton Ginning Research Laboratory; [3]USDA-ARS Jornada Experimental Range

Detection and identification of foreign material in harvested seed cotton is required for efficient removal by ginning. Trash particles remaining within the cotton fibers can detrimentally impact the quality of resulting textile products. Luminescence has been investigated as a potential tool for such determinations. Specifically, excitation-Emission luminescence spectra of basic phosphate buffer solution extracts were used to distinguish among botanical components of trash within seed cotton. Each targeted material was separated from whole plants which were removed from a field in southern New Mexico. Following removal of Rayleigh scattering signals, application of unfolded principal component analysis (U-PCA) enabled distinction of seeds, stems, bracts and leaves as trash material. Model robustness was tested using replicate data sets. Additionally, parallel factor analysis (PARAFAC) was applied to these spectra and revealed three spectral factors enabling trash identification. Elucidated excitation and emission spectra of these factors exhibited excitation wavelengths of maximum intensity of 295, 320, and 400 nm and respective emission wavelengths of 348, 435, and 473 nm. The implications of these findings on the utility of luminescence spectroscopy for cotton trash identification will be discussed.

(430) **Image Analysis and Machine Learning for the Recognition of Chain-Forming Phytoplankton**

Shawna Tazik, Joseph Swanstrom[1], Tammi Richardson[1], Timothy Shaw[1], Michael Myrick[1]; [1]University of South Carolina

Phytoplankton contribute significantly to the global carbon cycle through photosynthesis. This effect varies by species and class. We have previously demonstrated the use of an imaging multivariate optical computing (IMOC) system for the classification of phytoplankton based on fluorescence excitation. This system and the related analysis algorithms work well for single cells travelling through the image plane. However, some classes of phytoplankton tend to form chains of cells. In this case, it becomes more difficult to extract the desired spectral information. The use of Fourier methods and machine learning for the recognition of chain-forming phytoplankton when imaged by the IMOC system will be discussed.

(431) **Net Analyte Signal Geometry Facilitates Model Selection for Multivariate Calibration with Ridge Regression and Partial Least Squares**

Jonathan Palmer[1], John Kalivas[1]; [1]Idaho State University

Typical multivariate calibration approaches include some method of tuning parameter selection. Tuning parameters are selected in effort to stabilize an inverse as with ridge regression, or to select an optimum number of latent variables as with partial least squares, or for any other purpose which yields a collection of prediction models to choose from. The researcher may undertake exhaustive manual procedures to select the appropriate tuning parameter value. For example, cross validation procedures can be employed by leaving one or many samples out of the calibration set for model post-validation. The myriad of selection methods discussed in literature is vast and constantly evolving. Net analyte signal (NAS) multivariate calibration seeks a method of tuning parameter selection that bypasses exhaustive cross validation procedures while still delivering results comparable to other leading methods. Direct comparison of NAS derived geometric merits efficiently highlights accurate prediction models among a collection. Certain NAS related merits also demonstrate great promise toward the goal of automatic selection without the need for a human observer to interpret the results. Presented are results from several chemically distinct data sets analyzed using various NAS-derived angles and Euclidean distance measures.

(432) **Chemometric Assessment of Airborne Silica Dust in Mines by Infrared Spectrometry**

Andrew Weakley[1], Arthur L. Miller[2], Peter R. Griffiths[3], Emanuele G. Cauda[2], Pamela L. Drake[2]; [1]University of Idaho; [2]National Institute of Occupational Safety and Health (NIOSH); [3]Griffiths Spectroscopic Consulting LLC

The efficacy of accurately predicting the quantity of filter-deposited respirable silica dust (< 4 μm dia.) by measuring the mid-infrared transmission spectra of mine dust samples has been demonstrated. These spectra, collected from diverse mining operations on an appropriate filter, were analyzed by partial least-squares (PLS) regression. Previous univariate methods had relied on the α-quartz doublet absorbing between 750 and 850 cm-1. In this work, wavelength selection using a modified Monte Carlo unimportant variable elimination (MCUVE) procedure improved prediction performance, reduced the size of the PLS factor space, and identified alternative absorption bands for the assessment of airborne silica. This approach limits the influence of amorphous silica and common clay confounders on quantitative analysis. By incorporating these chemometric approaches with portable FT-IR instrumentation, end-of-shift quantification of respirable silica is realizable.

(433) **Applying Multivariate Curve Resolution Analysis techniques to NIR Reflectance Hyperspectral Images**

Howland Jones[1], Lam Nguyen[1], Eli Margalith[1]; [1]OPOTEK Inc.

Hyperspectral imaging combined with multivariate analysis techniques, such as multivariate curve resolution (MCR), is a proven and powerful imaging tool for detecting and quantifying known and unknown chemical compounds in a variety of sample images. Near-infrared (NIR) reflectance hyperspectral imaging is becoming a

useful technique for many applications including: pharmaceutical inspections, detection of food product adulteration, counterfeit detection and forensic investigations. It can be quite challenging to separate the overlapping spectroscopic signatures within a NIR reflectance image, and therefore obtaining interpretable quantitative images is often problematic. MCR can provide quantitative analyses of hyperspectral image data without the need for standards by discovering the independently varying absorbing spectral components present in the image data, even those for which there is no *a priori* information. Once these spectral components have been identified by MCR, they can be stored in a spectral library and used for subsequent analyses. These spectral components can either be used to initialize the MCR analyses or applied to the image data using Classical Least Squares methods to estimate the pixel intensities of each component. We have applied MCR algorithms developed and licensed from Sandia National Laboratories to hyperspectral images obtained from our HySPEC^{TM} NIR reflectance imaging system. This unique imaging system incorporates a tunable laser rather than a traditional broadband light source and spectrometer to collect spectral images. The system has several advantages over traditional imaging systems. First, there is flexibility in which spectral data are collected. Specific wavelengths (1000-2400 nm) can be collected instead of the entire wavelength region. Spectral resolution also can be specified. This flexibility allows for tailoring the imager to specific applications. Second, the field of view can be adjusted to be as low as a few mm to greater than 20 cm. Finally, there are no spectral smile and keystone distortion artifacts that are sometimes associated with a spectrometer, and there is no sample heating. We will describe our approach for applying MCR to the NIR reflectance hyperspectral images and demonstrate our MCR analysis applied to several food and pharmaceutical sample images using the HySPEC^{TM} system.

(434) **Limits of Detection from the Viewpoint of Statistical Hypothesis Testing**

Kaylee R. McDonald[1], Molly R. Burnip[1], Scott J. Hoy[1], Stephen L. Morgan[1]; [1]University of South Carolina

The limit of detection (LOD) is one of the most fundamental performance measures of an analytical chemical method; its impact extends also to numerous societal implications (1). We present an overview of decision limits as described by standards and accreditation organizations in view of shortcomings that impede practical interpretation and comparisons. Typically, a detection threshold is defined in the signal domain and extrapolated to the equivalent amount or concentration domain. However, ambiguity often exists in the choice of measurement uncertainty as a basis for the LOD (replicate blank measurements, residuals from the calibration relationship, etc.). Few sources discuss assumptions made with different choices (normality of data distribution, homoscedasticity of variance, absence of outliers), and validation testing is rarely mentioned. The statistical basis for LOD variants is also often not clear to practitioners and the reporting of multiple types of decision limits, particularly in regard to false positive and negative detection probabilities can be confusing. We summarize these issues and present comparisons of alternative approaches for estimation of detection limits along with appropriate validations tests. Finally, we present the application of statistical tolerance intervals to LOD estimation to provide a statistical basis for uncertainty estimates related to LODs. Based on sample statistics rather than assumed known population parameters, a tolerance interval specifies the range of concentrations that include a specific proportion of the entire population of results around the estimated LOD. This approach allows for statements to be made concerning false positive and negatives with a stated degree of confidence.

(435) **Single Molecule Counting in Nanopores**

Yan Hu[1,2,3], Lei Geng[1, 2, 3, 4]; [1]University of Iowa; [2]Department of Chemistry; [3]The Optical Science and Technology Center; [4]The Nanoscience and Nanotechnology Institute and the Center for Biocatalysis and Bioprocessing

We report a comprehensive analytical method for probing molecular transport in nanopores of silica with confocal single molecule spectroscopy. The method provides time resolution for microsecond kinetic processes including diffusion and adsorption, spatial resolution for locating diffusing molecules into ellipsoidal shells of nanometer thickness, and molecular resolution to record the distributions of physicochemical properties of the nanopores. Molecules diffusing through the probe volume emit bursts of photons while adsorbed molecules emit constant photon counts during its residence on the nanopore surface. Coefficient of clustering of photon bursts signifies the random arrival of single molecules across the probe volume. The burst heights scale linearly with the excitation power but not with molecular concentration. Instead, the molecular concentration is analyzed through single molecule counting. The noise in single molecule counting follows shot noise distribution that is reduced when more molecules are counted. The strengths of the photon bursts correlate with the trajectory of molecules with the ones diffusing closer to the center of the Gaussian beam emitting stronger bursts while ones crossing the peripheral of the beam emitting weaker bursts. Probability distribution functions are derived for the localization of molecules into super-resolution ellipsoidal shells that exhibit equal photon counts. Diffusing coefficients are evaluated through the autocorrelation function and the adsorption events are analyzed for their desorption times. Single molecule analysis has shown that the nanostructures in the particle are uniformly distributed within the probe volume of ~ 400 nm and that there are no large obstacles in the molecular diffusion. There is a Gaussian distributed population of diffusion coefficients inside the nanopores, indicating a distribution of pore sizes and/or pore architecture.

(436) **Multi-Modal Imaging Platform for Nanomaterials Characterization**

Emmanuel Leroy[1]; [1]HORIBA Scientific

Multi-modal imaging is a trend already well established in the microscopy field. Scanning probe microscopy also offers many possible measurement modes from a modular platform. Multi-techniques spectroscopy platforms are also fairly common, however less so in micro-spectroscopy. We're presenting a multi-modal platform combining scanning probe microscopy and micro-spectroscopy, optimized for near field optical spectroscopy and nano-spectroscopy: surface physical characterization combined with molecular identification without interference.

(437) **Identification of Liquids and Solids by Infrared Hyperspectral Imaging**

Sergey Shilov[1], Roland Harig[1], Samer Sabbah[1], René Braun[1], Jörn Gerhard[1], Peter Rusch[1]; [1]Bruker Optics

Remote sensing by Fourier-transform infrared spectrometry allows identification and quantification of unknown chemicals from long distances. While the quality of the spectra of systems of this type is high, missing spatial information limits the significance of findings because the compounds that are to be analysed may be present in a highly inhomogeneous spatial distribution such as liquid droplets on a surface. In contrast, imaging spectrometers allow the analysis of highly inhomogeneous distributions of compounds. In addition, spatial and spectral information may be combined in order to improve the performance of analysis methods. In order to exploit these advantages, scanning systems that combine a Michelson interferometer with a single detector element, and imaging Fourier-transform spectrometers that employ a focal plane array detector have been developed. The analysis of samples is performed using a source

of infrared radiation illuminating the sample from short distances or in a passive mode. The remote sensing systems, data analysis methods and methods for identification of solid materials and mapping of liquids on surfaces will be presented. Application examples will include remote imaging of surfaces including art objects.

(438) **Individual and Simultaneous Determination of Oxytetracycline and Florfenicol in Salmon Muscle and Skin by Fluorimetry**

M. Ines Toral[1], Patricia Gaete[1], Jose Moncada[1], Patricio Carreño[1], Pablo Richter[1]; [1]University of Chile

Florfenicol (FLOR) and oxytetracycline (OTC) are antibiotics widely used in aquaculture worldwide. This paper presents a study of the spectral behavior of both analytes with the aim of developing methods for individual or simultaneous determination of both antibiotics. Considering the classical spectra of FLOR and OTC in $1x10^{-2}$ M NaOH in methanol, were selected the following excitation wavelengths (λ_{exc}): 220, 224, 263, 280, 300, 360 and 378 nm with a 10 nm excitation and emission slit were taking for fluorometric measure. The OTC fluorescence emission spectra presents bands in all λ_{exc}, however, FLOR significantly reduces the fluorescence as λ_{exc} approaches to infrared, disappearing, which makes it possible to determine OTC in presence of FLOR. This determination is made at λ_{exc} 378 nm where OTC presents a high and well-defined band at 492 nm. However, 520 nm was used as λ_{anal}, since at this wavelength FLOR not present fluorescence.Later 6 portions of 100 mg of salmon were weighed, 2 were used as a blank, 2 were enriched independently with OTC, and 2 with FLOR, then 20 mL of NaOH $1x10^{-2}$ M in methanol, were added. Blanks and samples were agitated by 60 min and then centrifuged at 5000 rpm for 15 min. The extracts were evaluated by fluorimetry, in the optimized conditions, being found a bathochromic effect as product of the matrix. For this reason, was chosen to perform calibration curves using enriched salmon with FLOR and OTC, equation is as follows IF = $1.0x10^{6}$C (mol / L) +2.3, the detection and quantification limits were $3.7x10^{-8}$ M and $1.2x10^{-7}$ M (11µg/Kg) respectively, The method was applied to OTC salmon samples with different concentrations of FLOR, the found percent recovery was 97 ± 5%. Moreover, with λ_{exc} 224 nm OTC and FLOR present between 260-380 nm and 530-600 nm of overlapped fluorescence bands, being possible its simultaneous determination in first derivative mode with 100 amplification, obtaining recoveries near to 100% with a RSD of 4%, at this time is being applied to salmon muscle. The authors thank FONDECYT Project 1100103.

(439) **Fluorescence Correlation Spectroscopy and Time Resolved Fluorescence Anisotropy Decay Measurements for Structures and Dynamics of Room Temperature Ionic Liquids**

Robert Shaw[1], Jianchang Guo[1], Shannon Mahurin[1], Gary Baker[2], Patrick Hillesheim[1], Sheng Dai[1]; [1]Chemical Sciences Division, Oak Ridge National Laboratory; Oak Ridge, TN; [2]Department of Chemistry, University of Missouri-Columbia, Columbia, MO

Room-temperature ionic liquids (RTILs) have desirable properties such as negligible volatility, high electrochemical and thermal stability, and high ionic conductivity. To fully exploit the potential of RTILs an understanding of their liquid structure and microscopic dynamics in the bulk and in nano-confinement is essential. Our goal has been to understand the relationship between the local structures of ionic liquids and the diffusional/rotational dynamics of dissolved ions and molecules, and how these change at interfaces. Fluorescence correlation spectroscopy (FCS) and time-resolved fluorescence anisotropy decay (TRFAD) were used to investigate solute diffusional and rotational dynamics toward elucidating local ionic liquid structures. The existence of self-aggregation in RTILs has been a subject of intense interest. We provide new experimental evidence for chain length-dependent self-aggregation in RTILs using FCS. In studying a homologous series of N-alkyl-N-methylpyrrolidinium bis(trifluoromethylsulfonyl)imide, [CnMPy][Tf2N], RTILs of varying alkyl chain length (n = 3, 4, 6, 8, and 10), biphasic solute diffusion dynamics were observed; both the fast and slow diffusion coefficients decrease with increasing alkyl chain length, with the relative contribution from slower diffusion increasing for longer-chain [CnMPy][Tf2N]. We propose that the biphasic diffusion dynamics originate from self-aggregation of the nonpolar alkyl chains. We have employed TRFAD to probe fluorescent rhodamine dyes in the RTIL. A specific interaction of the R6G cation and [Tf2N]- anion was identified, resulting in near-stick boundary condition rotation for R6G. We have studied the effect of solute charge on the rotational dynamics of rhodamine dyes. The rotational dynamics of negatively charged sulforhodamine (SR640) are in the stick boundary condition regime and those of neutral rhodamine B (RhB) fall between slip and stick boundary conditions, suggesting a strong electrostatic interaction for SR640 and hydrogen bonding for RhB and the ionic liquid. * Research supported by the Fluid Interface Reactions, Structures, and Transport (FIRST) Center, an Energy Frontier Research Center funded by the U.S. Department of Energy, Office of Science, Office of Basic Energy Sciences. G.A.B. and P.C.H. were supported by the Division of Chemical Sciences, Geosciences, and Biosciences, Office of Basic Energy Sciences, U.S. Department of Energy.

(440) **Emerging Trends in F19 & P31 NMR Spectroscopy**

Abhishek Gupta[1,2]; [1]Indian Institute of Technology, Delhi, India; [2]Daiichi Sankyo India Pharma Pvt.Ltd- Gurgaon, India

Phosphorus-31 & Fluorine-19 NMR spectroscopies are analytical techniques based on the detection of 31P & 19F nucleus. Because of high natural isotopic abundance and a relatively high magnetogyric ratio, these nucleuses are highly responsive to NMR measurements and hence are being used as one of the more routine NMR techniques. The 31P & 19F nucleus also have a spin of ½, making spectra relatively easy to interpret. Phosphorus & Fluorine both are commonly found in drugs, biological samples & prodrugs. Current poster reviews the few 31P & 19F applications which can be widely utilized in modern research. As a first example of 19F -NMR spectroscopy, its application to the identification of metabolites of fluorine containing drugs is discussed while 2nd example of 19F NMR presents the methodology of using this nucleus to study the structure & dynamics of DNA-Carcinogen adducts. As an example of 31P-NMR spectroscopy, its usefulness to assign structures of phosphorus-containing prodrugs is discussed because these signals are well resolved and often occur at characteristic frequencies.

(441) **Rapid Spectrophotometric Determination of Nitrite across 5 Orders of Magnitude using a Single Set of Experimental Conditions**

Mya Porche[1], Benoit Lauly[1], Jonathan Scaffidi[1]; [1]Miami University

The linear dynamic range (LDR) of most spectrophotometric determinations extends across ~ 3 orders of magnitude under any single set of experimental conditions due to fundamental instrumental limitations. This limitation can be overcome through use of complexing agents possessing multiple analyte-specific absorption bands with greatly differing molar absorptivities. We demonstrate this concept through spectrophotometric detection of nitrite in water via reaction with captopril. Two concentration-dependent absorption bands appear at ~332nm and ~547nm when captopril is nitrosylated under acidic conditions. The molar absorptivities of these bands differ by a factor of ~500 (ε = 1020 M-1 cm-1 and ε = 20 M-1 cm-1, respectively), and allow nitrite determination at concentrations from < 1 micromolar to > 75 millimolar under a single set of experimental conditions. Interference by various environmentally relevant cationic and anionic species was found to be minimal, highlighting the

potential for this spectrophotometric assay to be applied to real-world nitrite determination.

(442) **A Comparative, Experimental Approach to Teaching Analytical Methods**

Maury Howard[1]; [1]Virginia Wesleyan College

This project originally took the form of a typical undergraduate research project related to oyster restoration, but has found new perspective and utility in course-related projects. The initial work focused on water quality monitoring that was later supplemented by trace metal analysis. The results proved to be intriguing, but continuing the work meant finding ways to incorporate the analysis into coursework during the academic year. The prospect of using field test kits for fast analysis, requiring little lab experience was appealing, but led to questions about the accuracy and precision of the test kits which was unknown, and in some cases questionable. Thus, last Fall, these questions were integrated into Analytical Chemistry by implementing multiple mini-research projects comparing the performance of field test kits to in-lab spectrometric methods. Students were challenged to work in groups to 1) research the kits and find/adapt comparable spectroscopic methods, 2) prepare and analyze standards and real samples by both methods, and 3) apply quality control measures to compare the results in terms of accuracy and precision. Our objectives in implementing this curriculum change were two-fold: First, improve the capabilities of our chemistry graduates to design and implement good experimental design to answer a scientific question; second, to discover whether the use of test kits was actually a viable means to continue data collection for the oyster restoration project.

(443) **3D Tomographic FTIR Spectrochemical Imaging for Assessment of Nutrients in Arctic Sea-Ice Diatoms**

Catherine Liao[1], Alexandra Ciapala[1], Peter Trokajlo[1], Julia Sedlmair[3, 4], Carol Hirschmugl[2, 3], C. J. Mundy[1], Kathleen Gough[1]; [1]University of Manitoba, Winnipeg, Manitoba, Canada; [2]University of Wisconsin - Milwaukee, WI; [3]Synchrotron Radiation Center, University of Wisconsin - Madison, WI; [4]USDA Forest Service, Forest Products Laboratory, Madison, WI

We demonstrate the use of FTIR for evaluation of the composition of single, whole and intact diatoms at low and high resolution, in 2D and 3D. To this end, data import, Radon transform and 3D model export algorithms in MatLab™ were adapted for reconstruction of FTIR tomographic data. FTIR spectrochemical imaging allows detailed analysis of the distribution and abundance of compounds inside a single diatom on a sub-cellular level. Targets are selected individually, permitting species-specific examination, without need for laboratory culture.

In keeping with the adage “out of sight, out of mind”, the impact of microscopic organisms on life on Earth can easily be overlooked. Despite this, they play a major role in Earth’s ecosystems, and are critical to our understanding of the environment. Of particular interest are sea ice pennate diatoms, the dominant taxa during the vernal Arctic ice algae bloom. Ice algae provide the primary food source during early spring and are thus a key component of the Arctic ice-covered ecosystem, an ecosystem currently undergoing rapid change associated with climate warming. High spatial resolution images were collected at the InfraRed ENvironmental Imaging (IRENI) beamline (Synchrotron Radiation Centre, University of Wisconsin-Madison). A Bruker Hyperion 3000 IR microscope equipped with 128x128 pixel FPA and 74x objective, Vertex 70 spectrophotometer, gives a geometric pixel size of 0.54x0.54 μm². For comparison, our in-house Agilent 670 IR spectrophotometer equipped the 620 IR microscope and 64x64 pixel Focal Plane Array (FPA) detector was used for thermal source imaging, with a pixel size of 5.5x5.5 μm². Attenuated Total Reflection (ATR) FTIR images were collected using a slide-on Ge crystal, for a nominal pixel size of 1.1x1.1 μm². The advent of FTIR tomography brings a new dimension to infrared spectrochemical imaging technology (Nature Methods DOI:10.1038/nmeth.2596). The first ever 3D FTIR diatom images were created from a total of 160 FTIR images, captured at 1.5 degree intervals, from a single goniometer-mounted diatom sample, processed by integration at every angle, and reconstructed to form micron-scale 3D images of component distribution. This allows a never-before-seen view into the cellular distribution of organic and inorganic materials within these important organisms.

(444) **Imaging of Nanoparticles and Nano-structual Features Using a Home-built Near-field Scanning Optical Microscope**

Taher Ababneh, Jorg Woehl[1]; [1]University of Wisconsin-Milwaukee

Near-field scanning optical microscopy (NSOM) is a powerful method for the nanoscale imaging of surfaces with a resolution down to the nanometer scale. By using a very small light source with a diameter much smaller than the wavelength of the light, resolutions better than the diffraction limit can be achieved. The probe must be very close to the surface; much closer than the wavelength of the light. This region is the "Near-Field" and hence the name of the technique. We demonstrate the construction of a near-field optical module for a confocal microscope. Several hardware requirements are implemented in order to bring the tip into the general vicinity of the sample (coarse approach), fine position the tip using a piezoelectric scanner, attain the proper tip-sample working distance using shear-force feedback and maintain the vertical position of the tip using a feedback loop control system. In addition to the hardware requirements, a computer system drives the scanner, measures date and converts the data into an image is used. The details of the technique, optimal experimental parameters and imaging results will be discussed.

(445) **Quantitative Imaging of Powder Samples using NIR Reflectance Hyperspectral Imaging with a Tunable Laser**

Howland Jones[1], Lam Nguyen[1], Gregory Israelson[2], Eli Margalith[1]; [1]OPOTEK Inc.; [2]Nestle Purina PetCare

Adulterated food products can be dangerous to the health of the consumer and can cause numerous and expensive recalls for the food manufacturers. Examples of food adulteration can range from melamine intentionally added to infant formula and animal feed to insects accidentally ground into flour food products. Therefore, developing a robust imaging technique that has the ability to quickly detect and quantify trace levels of potential adulterants in powder food products (human food or animal feed) would be beneficial to both the consumer and manufacturer. Near-infrared (NIR) reflectance hyperspectral imaging can provide both the sensitivity and specificity necessary to detect food adulterants. We have developed a hyperspectral imaging system (HySPEC™) that relies on an optical parametric oscillator tunable laser rather than a traditional broadband light source and spectrometer to collect spectral images. The advantage this system has over traditional imaging systems is in its ease and flexibility to collect the hyperspectral data based upon the specific imaging application. The collected wavelength region as well as the spectral resolution (as high as 1 nm resolution) can be adjusted depending on the application. This flexibility allows the user to optimize the hyperspectral image collection and analysis for speed, sensitivity and specificity which is critical when developing screening techniques for food product applications. This system is also flexible with respect to its spatial resolution and field of view (FOV) with FOVs ranging from a few mm to greater than 20 cm. To analyze and quantify the amount of adulterants in our powder samples, we use fast and efficient multivariate curve resolution algorithms developed and licensed from Sandia National Laboratories. These algorithms extract the pure spectral components (absorbing species) and the corresponding quantitative intensities for each pixel within the image. MCR can be a powerful technique for

food adulterant detection and quantification because it can discover all independently varying spectral species present within the image data, including unknown adulterants. For this presentation, we will demonstrate the sensitivity and specificity of this imaging technique by investigating several known concentrations of adulterants prepared in flour samples. We will then extend this demonstration on real-life applications.

(446) **Evaluation of the Inhomogeneity of Crystallinity on the Polymer by Using Wide Area NIR Imaging Camera (Compovision)**

Daitaro Ishikawa[1], Takashi Nishii[1], Fumiaki Mizuno[2], Yukihiro Ozaki[1]; [1]Kwansei Gakuin University; [2]Sumitomo Electric Industries, Ltd.

Crystalline polymers such as poly lactic acid (PLA) and PHB should have different crystallinity depending on the annealing conditions and the spatial distribution within the sample is also affected by the difference in the conditions. Thus, the quest for homogeneity of crystallinity of these polymers is a main concern for the quality evaluation. The NIR imaging which can be non-destructive and non-contact monitoring has been used for the detail investigation of the spectra behavior of these polymers. Although wider area image with high speed is an integral part to apply NIR technique to the polymer industrial situation, an NIR imaging instrument with their advantages is still under development. A new NIR Camera (Compovision) developed for high speed measurement under various practical situations by Sumitomo Electric Industries, Ltd. The innovative characteristics of Compovision are to measure two dimensional spectra of the 150 × 250 mm wide area with 2 - 5 seconds high speed. Thus, Compovision has a high efficiency for application of practical monitoring tools. However in many cases, the wavelength resolution of the instrument for wide area high speed monitoring become relatively lower, so that the predictive accuracy using original absorbance and/or second derivative spectra is rather lower than the general monitoring results. The present paper, therefore, the quantitative accuracy of crystallinity of PLA and its concentration in the blend with PHB were investigated. The results obtained by using the SNV (standard normal variate) spectra yielded the best prediction with the smallest RMSE and the highest for the crystallinity and the concentration. The NIR image for crystallinity developed by SNV spectra clarified the inhomogeneity of crystal evolution in the wide area. This result has revealed that Compovision and its NIR image are very useful for the quality evaluation of polymer such as crystallinity.

(447) **Applied Brewery Quality Control Curriculum for Analytical Chemistry Course**

Daniel Kool, Katie Martin, Andrew McDonald, Nicholas Rothfus, Yuan Yuan, Dale LeCaptain; [1]Central Michigan University

Numerous approaches for senior undergraduate/graduate level analytical chemistry are practiced. The most common and classic instrumental analysis world-wind tour is week 1 is AA; 2. ICP; 3. FTIR; 4. UV-Vis; 5. Fluorescence; 6. GC; 7. HPLC; 8. MS; 9. take a breathier; 10. Let's hyphenate GC-MS; 11. Etc. To effectively navigate the instrument-a-week format labs are 'canned', outcomes will test parameters, and students will write reports. This effectively exposes students to most analytical instruments (or at least everything in the chemistry department) and defaults the students to the instrument operator perspective. In the end, does it teach analytical problem solving? What happens when equipment is broken, are labs dry-run? Skipped? Their "customer" is an instructor who has seen many a varied student response and can read between the lines, is this effective for the student? Presented her is the work in progress from the student perspective of experiencing a laboratory curriculum that is quality control for the local micro-brewery. The problem identification, analysis, solutions, and communication aspects are explored.

(448) **LabVIEW programming of a Multimode Thermal Infrared Imaging for Forensic Applications**

Nicholas D. Boltin[1], Brianna M. Cassidy[1], Zhenyu Lu[1], Michael L. Myrick[1], Stephen L. Morgan[1]; [1]University of South Carolina

Multimode thermal imaging aids in visualizing and distinguishing blood stains and other features important in forensic investigations. A previous generation of instrumentation used an asynchronously-modulated light source to measure reflectance images, and a camera with a nonstandard interface and only 12-bit readout, with data analysis performed on a separate computer. LabVIEW™ was used to collect images, but all processing was performed in Matlab. We have recently introduced light sources that can be synchronously modulated, as well as a lower-cost FLIR camera with 16-bit readout and digitally-controllable I/O ports with a gigabit ethernet interface and an electronically controllable focus. This poster will describe how the LabVIEW language was used to program this instrument for AC reflectance and thermal re-emission imaging, how the tendency of the camera to produce striations, focus improperly, and to interrupt data acquisition for internal calibration were minimized by processing and low level control, and will show example data acquired and processed with the new control software. We will also show how the focus is assured through a computer controlled pointer laser system, and how thermal marks are created on real images so that visible light and infrared images can be aligned.

(449) **Greek and Roman Unguentaria: Fingerprinting Ancient Perfumes by ICP-MS and FT-IR**

Jenna Mortensen[1], Bettina Arnold[1], Joseph H. Aldstadt[2]; [1]Dept. of Anthropology, Univ. of Wisconsin-Milwaukee; [2]Dept. of Chemistry & Biochemistry, Univ. of Wisconsin-Milwaukee

We will describe our recent work in the characterization of residues from the interiors of unguentaria (clay and glass vessels) from the Milwaukee Public Museum collections. Funerary perfume vessel contents can serve as a proxy for reconstructing particular olfactory atmospheres associated with mortuary rituals as a means to explore one of the typically ephemeral aspects of the past. The 27 vessels that were studied showed evidence of original contents and a comparison of our results to other studies of unguentaria residues, as well as historical written sources from the Late Greek and Early Roman periods related to this vessel form, will be presented. The chemical characterization of the inorganic and organic contents of these bottles relied upon the application of ICP-MS and FT-IR. ICP-MS results and preliminary results from the FT-IR studies will be discussed as well. Comparing the chemical analyses of the contents with contemporary and ethnographic written documentation, in which scented unguents, oils, perfumes, creams, and cosmetics are described, allows one to test the archaeological classifications of this vessel category and to provide a better understanding of the extent to which olfactory elements were involved in mortuary rituals within Classical contexts.

(450) **Selective Fabrication of SERS-active Ag Nanoparticles by Near-Field Photo-Reduction and *in situ* AFM Measurement**

Yasutaka Kitahama[1], Takuya Ikemachi[1], Toshiaki Suzuki[1], Yukihiro Ozaki[1]; [1]Kwansei Gakuin University

For surface-enhanced Raman scattering (SERS) measurements, noble metal nanostructures have been fabricated by various methods. It is important to control the size and shape of the nanostructure. Conventional photo-reduction of a metal ion forms only a single or many metallic nanoparticles at a laser focal point on a glass in a solution containing the metal salt. In the present study, a metallic nanoparticle was fabricated by near-field photo-reduction using an apertured cantilever coupled with an atomic force microscope (AFM). The near-field photo-reduced nanostructure can be selectively fabricated and observed *in situ* by the same apertured cantilever coupled with the AFM.

The near-field photo-reduction was performed by an AFM setup which is combined with a reflection mode Raman microscope. The laser beam (λ = 514 nm, 5 mW) for the near-field photo-reduction was focused onto a crystal of $AgNO_3$ through the aperture of the cantilever (200 nm in diameter) by an objective lens. Before and after the near-field photo-reduction, topographic images of the crystal surface were observed by the same apertured cantilever coupled with the AFM. Then, 4,4′-bipyridine in acetone (100 mM) was dropped on the crystal. After evaporation, a SERS spectrum was measured by focusing the laser beam (0.1 mW) onto the crystal not through the apertured cantilever by the same objective lens.

After the near-field photo-reduction, a nanoparticle was observed on a smooth surface of $AgNO_3$. The lengths of long and short axes of the nanoparticle were similar to the diameter of the aperture of the cantilever. The Ag nanoparticle can be arranged at a desired position by the near-field photo-reduction. In the case of the single nanoparticle, a SERS peak appeared at around 1026 cm^{-1}, which is assigned to the ring-breathing mode of metal complex of 4,4′-bipyridine. From a dimer of the nanoparticles, the SERS peak was observed at around 1000 cm^{-1}, which is due to polycrystalline 4,4′-bipyridine in a gap of the dimer.

(451) **Plasma-Induced Enhancement of Azo Dye SERS Intensity on ZnO**

Szetsen Lee[1], Chih-Sheng Liu[1], Bing-Han Li[1]; [1]Department of Chemistry, Chung Yuan Christian University

Surface–enhanced Raman scattering (SERS) spectra of azo dyes (methyl orange and methyl red) were observed using ZnO as a substrate. Hydrothermally synthesized ZnO nanoparticles were calcined at 550 °C. The composition and morphology of ZnO nanoparticles were characterized by powder X-ray diffraction and X-ray photoelectron spectroscopy. The further enhancement of SERS intensity by plasma treatment on was investigated. Oxygen plasma showed significant enhancement, whereas hydrogen plasma had little effect on SERS intensity. The enhancement of the azo dye SERS intensity was found to be related to the shift of the ZnO band gap induced by plasma treatment.

(452) **Gold Clusters as SERS Substrates**

M. Fernanda Cardinal[1], Richard P. Van Duyne[1]; [1]Northwestern University

In this work, we investigate the synthesis and performance of silica-coated gold nanoparticles assemblies as Surface-enhanced Raman spectroscopy (SERS) substrates. Our work is motivated in the fabrication of tunable and robust SERS substrates [1]. The ensemble SERS response of gold clusters for different Raman probes is investigated with a commercially available portable Raman equipment.

Gold nanospheres were synthesized through the seeded growth method [2] and/or through the Turquevich method [3]. Subsequently, the gold nanoparticles were washed and functionalized with a linker, a Raman probe and a silane coupling agent. After silica coating, the samples are washed and characterized with UV-visible spectroscopy and transmission electron microscopy (TEM). In Figure 1, we observed the spectra of the gold nanospheres before and after triggering their assembly and with TEM images we can confirm clusters formation.

Finally, the optical enhancing properties of gold clusters is measured with a 785 nm laser line and the enhancement factor is estimated.

References

[1] Kleinman, S. L.; Frontiera, R. R.; Henry, A.-I.; Dieringer, J. A.; Van Duyne, R. P., PCCP 2013, 15 (1), 21-36.

[2] Rodríguez-Fernández, J.; Pérez-Juste, J.; García de Abajo, F. J.; Liz-Marzán, L. M., Langmuir 2006, 22 (16), 7007-7010.

[3] Bastus, N. G.; Comenge, J.; Puntes, V., Langmuir 2011, 27 (17), 11098-105.

(454) **Evaluation of Matrix Effects During SERS-based TNT Determination in Fresh Water**

Marc Wadsworth[1], Benoit Lauly[1], Jon Scaffidi[1]; [1]Miami University

Typical SERS-based approaches to TNT detection rely on formation of charge-transfer complexes that enhance the intensity of pre-existing Raman bands via resonance Raman effects. Unfortunately, TNT-independent aggregation of nanoparticles in complex real-world matrices can produce similar increases in SERS intensity. We have developed TNT-sensitive, SERS-active nanoparticles with a built-in internal standard that allows straightforward "self-normalization" to correct for aggregation-induced changes in SERS intensities. Previously tested in distilled water, we have now extended this self-normalization approach to determination of TNT in tap water and spiked environmental samples. Low ppb limits of detection have been achieved in a variety of freshwater matrices, thereby demonstrating the versatility of this technique for real-world TNT detection.

(455) **Direct Measurement of Electric Fields from Plasmon Excitation**

James M. Marr[1], Zachary D. Schultz[1]; [1]University of Notre Dame

The excitation of plasmon resonances creates local electric fields that increase sensitivity in chemical sensing. The vibrational Stark effect has been used to investigate local electric fields that are present in biological and interfacial systems. To that extent, little has been done in the way of determining the electric fields associated with localized surface plasmon resonances by Stark chromophores. The enhancement factor in surface enhanced (SERS) and tip enhanced (TERS) Raman spectroscopy is inferred from the changes in Raman intensity. The vibrational Stark Effect provides a direct measurement of the electric field experienced by molecules. It was previously reported that the stark shift associated with tip enhanced Raman was very weak. We have found that improved overlap between the CN stretch Raman frequency and the excited plasmon resonance can produce a large Stark shift from probe molecules in the enhanced electric field. We have been able to show this through SERS from micro-electrodes which show a blue shift in the cyanide peak that correlates with an increased SERS intensity of co-deposited thiophenol. TERS results show even more dramatic shifts, suggesting enhancement factors on the order of 10^{13} in these experiments.

(456) **Simple Approach to Realize Flexible SERS Sensor Platforms on Microfluidic Device**

Donghyuk Kim[1]; [1]University of Minnesota

Herein, a proof of concept microfluidic platform that is capable of chemical recognition by surface-enhanced Raman scattering (SERS) is described. High-throughput, real-time detection of chemical mediators from biological samples is a daunting task as the analytes are usually limited in amount, and the biological systems are usually complex and dynamic. Thus, one aim of biosensor development is in

the realization of simple detection schemes, without extrinsic labels, on a platform that can provide control over samples in dynamic environments while facilitating real-time, high-throughput analysis. Microfluidics is a powerful technique that provides the ability to work with small amount of samples without excessive dilution, enabling real-time and high-throughput sample analysis when coupled with a proper detection scheme. SERS is known for enabling detection of the unique intrinsic vibrational signatures of various biochemical molecules; as such, we bring these techniques together and enable a simple SERS sensor platform on a microfluidic device. The microfluidic platform is fabricated in polydimethyl siloxane (PDMS) in which gold nanoparticles are dispersed. The PDMS layer with embedded gold nanoparticles is dry-etched to ensure nanoparticle protrusionfrom the PDMS layer, making them available for plasmonic enhancement of nearby molecules. Both 1,2-bis(4-pyridyl)ethylene (BPE) and benzenethiol (BZT), well-known SERS-active molecules, have been tested in the developed platform and show strong SERS signatures. In addition, the microfluidic platform is designed to establish serial dilution of a solution so that multiplexed detection and/or limit-of-detection (LOD) experiments can be performed in one shot, and the on-chip recorded data confirm that the device operates as desired. For quantitative analysis, SERS frequently requires introduction of an internal standard, but on this platform, the device media, PDMS, has multiple SERS-active modes and acts as a standard. Also, while assembling a SERS detection platform with a microfluidic platform has historically suffered from issues relating to alignment and sealing between the PDMS channel layer and SERS substrate, this developed platform does not require any extra effort for alignment or sealing. The complete sensor platform is transparent and flexible, making it potentially useful in many biosensing applications.

(457) **Tip-enhanced Raman Scattering (TERS) Study of Local Structure in Ethylene Propylene Diene Terpolymer (EPDM) Rubber/Multiwall Carbon Nanotubes Nanocomposites**

Ryohei Hinaga[1], Toshiaki Suzuki[1], Yukihiro Ozaki[1]; [1]Kwansei Gakuin University

In recent years, polymer/carbon nanotubes (CNT) nanocomposites have been interesting to reinforce mechanical and conductive properties of polymer. Their properties are caused by distribution and dispersion of CNT. Raman spectroscopy is one of the most powerful methods to investigate intermolecular interaction between polymer and CNT. However, spatial resolution of Raman spectroscopy is determined by diffraction limit. Tip-enhanced Raman scattering (TERS) can be observed in less than 100 nm regions. In this study, we try to reveal the intermolecular interactions at the interface of polymer and filler in ethylene propylene diene terpolymer (EPDM) rubber/CNT nanocomposites using TERS. EPDM/CNT nanocomposites that contained 1phr and 5phr CNT are measured in these experiments. The unit "phr" stand for parts per hundred of rubber by weight. A bulk silver needle was used as the TERS tip needle, which was attached to a quartz tuning fork. The 514 nm line from an Ar ion laser was used for excitation light. A TERS spectrum was calculated by subtracting the spectrum observed under the tip-retracted condition from the spectrum observed under the tip-approaching condition. In the Raman spectra, both CNT and EPDM signals were always observed at each point. However, in TERS spectra, the intensity of the signals assigned to the CNT are changed at each point. In some TERS spectra, CNT signals were not appeared at all. These differences can be explained by the distribution of fillers in the polymer nanocomposites. Moreover, in the spectra without CNT there were changes of intensity at CH_2 symmetric stretching and CH_2 antisymmetric stretching. It is expected that the intensity change of CH_2 signals reflect the structure change or orientation change of nanocomposites.

(458) **Towards Tip-Enhanced Raman Scattering (TERS) Investigation of Nanoscale Architectures**

Kirsty F. Gibson[1], Jennifer A. Dougan[1], Sergei G. Kazarian[1]; [1]Imperial College London

Tip-enhanced Raman scattering (TERS) spectroscopy is an emerging and powerful technique that combines Raman spectroscopy and scanning probe microscopy (SPM) to provide detailed chemical and spatial information. TERS utilises a metal-coated tip which results in the confinement of a large electromagnetic field about the tip that greatly enhances Raman scattering from any Raman-active molecules which are in close-proximity to the tip. This technique is ideally suited to the investigation and characterisation of nanomaterials. TERS has been used by a number of groups to analyse a wide range of samples. In our research group, we have previously used TERS to image single walled carbon nanotubes in both inverted (1) and upright (2) configurations. Our recent research examines the use of TERS for the investigation and understanding of nanoscale architectures. TERS is not limited by optical diffraction and so can be used to spatially resolve areas of enhanced Raman intensity in the nanometer size regime. This makes TERS a valuable technique for correlating the confined areas of large Raman enhancement (hot-spots) in surface enhanced Raman scattering (SERS)-active structures to the substrate architecture. The TERS data collected can be used to elucidate the relationship between sample topography and SERS activity in nanostructures which can in turn be applied to further developing highly enhancing SERS-active substrates.

1. K. L. A. Chan and S.G. Kazarian, Nanotechnology, 2010. 21 445704.

2. K. L. A. Chan and S.G. Kazarian, Nanotechnology, 2011. 22 175701.

(459) **Self-normalizing SERS-based Determination of Heavy Metals**

Benoit Lauly[1], Jenny DeJesus[1], Jon Scaffidi[1]; [1]Miami University

Strong interest in environmental monitoring of metal ions is driven by their widespread occurrence and their toxicity. Unfortunately, most sensitive, selective metal-detection instrumentation is poorly suited to on-site application. We have developed and tested a simple, potentially field-portable SERS-based assay for rapid determination of various heavy metals. The strong affinity between the carboxylic acid group of para-mercaptobenzoic acid (pMBA) and heavy metal ions changes the frequencies and relative intensities of several pMBA vibrational bands upon pMBA-metal interaction. Taken together, these spectral frequency shifts and changes in intensity allow both identification and quantitation of Pb2+, Hg2+, Cu2+, Cd2+, Co2+ and Zn2+ at environmentally-relevant concentrations. Spectral normalization using metal-independent peaks in the pMBA spectrum additionally reduces the effects of aggregation-related artifacts.

(460) **The Multiresonant Family of Coherent Multidimensional Spectroscopy**

John Wright[1]; [1]University of Wisconsin-Madison

The discovery of optical analogues of multidimensional NMR that use phase matching and phase cycling has opened the new field of coherent multidimensional spectroscopy (CMDS). In analogy to NMR, the full power of this field rests on the ability to create and manipulate multiple quantum coherences (MQCs) between a wide variety of electronic and vibrational states. MQCs are formed by exciting multiple quantum states quickly enough to insure that the quantum mechanical phase oscillations of each state are maintained and reemit beams of light at all of the frequency differences between the states composing the MQCs. MQCs are only formed between states that are coupled so excitation of one affects all of the others. Multiresonant CMDS is a particularly interesting approach because it is a frequency domain method that only requires phase coherence between the excitation beams during the creation of the MQCs. That

freedom allows the use of different excitation frequencies to create MQCs containing any mixture of electronic and vibrational states. This approach provides enhanced multidimensional resolution, line narrowing, isolation of coupled states, elimination of background, and coherent and incoherent dynamics. This talk will show examples of how the different multiresonant methods are used to resolve individual vibrational and electronic quantum states and their dynamics in molecular spectroscopy and nanostructure applications

(461) **2DIR and IR Pump-Probe Studies of Ion Dynamics**

Minhaeng Cho[1]; [1]Korea University

Water structure ad dynamics are strongly affected by the presence of ions. One of the specific ion effects is known as the Hofmeister effect on protein stability. Depending on the chaotropic or kosmotropic nature of ions in aqueous protein solutions, the stability of tertiary structure of protein is affected by either making the hydrogen-bond network structure change or forming direct electrostatic interaction of ions with proteins. One of the well-known and widely used denaturizing agents is thiocyanate. We first studied the ion pair formation dynamics of thiocyanate with lithium cation in aprotic solvents using chemical exchange two-dimensional IR spectroscopy of thiocyanate CN stretch mode. The ion pair formation and dissociation time constants are on the order of a hundred picoseconds. To study thiocyanate vibrational dynamics in liquid water, we carried out a series of IR pump-probe studies of thiocyanate in highly concentrated aqueous solutions. To avoid self-attenuation problem in femtosecond IR pump-probe measurements, we focused on the vibrational dynamics of ^{13}C-labeled thiocyanate whose frequency is shifted towards low frequency region, while the total concentration of thiocyanate is adjusted by adding unlabeled thiocyanate to the solution. Analysing the population and rotational relaxations of thiocyanate ion in water, we found that the ions tend to form large ion aggregates at a high concentration. To elucidate possible ion-aggregation effects on water dynamics, the IR pump-probe studies of OD stretch mode of HOD in water were performed with varying potassium thiocyanate concentration. Using two-component analyses of the experimentally measured dispersed IR pump-probe spectra, we could separate the pump-probe spectrum of HOD molecules in bulk-like water and that of those interacting with thiocyanate ions. Since the two OD stretch modes have sufficiently different frequencies, it was possible to extract quantitative information on their rotational times and peak frequency shifts for varying ion concentration. The nonlinear dependence of the OD stretch frequency indicates that there is a critical concentration separating free ion phase and ion aggregate phase.

(462) **Moving from 2D Spectroscopy to 3D Spectroscopy: What are the Potential Advantages of Adding One More Dimension?**

Peter Chen[1]; [1]Spelman College

When applied to gas phase samples, high resolution coherent 2D spectroscopy can distribute peaks across 2D space, thereby improving resolution and reducing rotational congestion. It can also sort peaks into readily identifiable patterns, even for molecules that yield spectra that otherwise appear patternless. However, severe congestion can make parts of the 2D spectrum difficult to analyze. This problem can be addressed by adding a third dimension in a way that not only improves resolution but also provides selectivity. Results from carrying out high resolution coherent 3D experiments will be presented, and the relationship between coherent 2D and 3D spectroscopies will be discussed.

(463) **Directly Probing Changes in the Intermolecular Solvent Spectrum during Chemical Reactions**

David Blank[1], Matthew Ammend[1], Benjamin Fitzpatrick[1]; [1]University of Minnesota

When considering chemical reaction dynamics in solution, the intermolecular motions constitute what is commonly referred to as the solvent bath. The bath often plays a critical, dynamic role in the chemistry, providing a source/sink for energy, and in the case of electron transfer serving as the primary reaction coordinate. Using third-order electronically non-resonant Raman spectroscopy as a probe, we report direct measurements of the changing intermolecular solvent spectrum following electronic excitation of a solute. Recent experimental advances have allowed the full signal field to be resolved at the amplitude level, and the signal phase information provides insight into previous reports that appeared to conflict. Our results demonstrate that the spectrum of the bath is different around the reactant and the product, and that the spectrum of motions local to the reaction evolves over a wide range of time scales in response to the changes in solvent-solute interactions. Finite-field molecular dynamics simulations show agreement with the experiments and provide a molecular level interpretation of the changing intermolecular spectrum.

(464) **Quantitative Analyses for Coal Application using Laser Induced Breakdown Spectroscopy**

Zhe Wang; [1]Tsinghua University

Spectrum standadization and dominant factor based PLS mothod were disscussed for measurement precision and accuracy improvement. The application of these motheds on coal application were also discussed in the presentation.

(465) **Artificial Neural Networks Applied to LIBS Spectra for Both Quantification and Classification of Soil Samples**

Josette EL Haddad[1,2], Lionel Canioni[1, 2], Bruno Bousquet[1, 2]; [1]Univ. Bordeaux, LOMA, Talence, France ; [2]CNRS, LOMA, Talence, France

Quantitative LIBS for soil samples analysis have been demonstrated with both univariate and multivariate analysis methods. Soils being complex and heterogeneous samples related to continuously varying matrices, their quantification by univariate analysis is almost impossible. To overcome the matrix effects, artificial neural networks (ANN) were applied to on-site LIBS spectra as an advanced nonlinear method for on-site quantification. Different campaigns of on-site LIBS analysis of soils were achieved and all the samples were also measured by ICP-AES in order to get reference values to calibrate the LIBS data. In this paper, we demonstrate as a first step that quantitative LIBS for soil samples was impossible by using the usual univariate approach and then as a second step that ANN was perfectly adapted to overcome the matrix effects. We report here relative errors of prediction of the ANN smaller than 20% for both trace elements in the mg/kg range of concentrations and major elements in the range of tens of g/kg. We point out that the performance of the ANN models strongly depends on the input data. Moreover, we demonstrate that a single 3-layer ANN is not able to predict concentrations over a wide range of concentrations from mg/kg to tens of g/kg. A solution was found to overcome this problem. It consisted in classifying the samples into two sets and then in applying a separate ANN model to each set. Thus, a separate ANN model designed for decision-making allowed to perform the classification. Finally, all the process, namely classification and quantification, was demonstrated in the case of lead into soil samples.To address the question of matrix effects, another ANN model was exploited for semi-quantitative purpose in order to separate the soil samples into three major categories of soil, namely rich in calcium, in aluminum/silicon and in ores. This allows us to classify correctly unknown samples and then to apply the best ANN

model for quantification.Moreover, the performances of different ANN models for classification or quantification were evaluated from different figures of merit commonly used in chemometrics.

(466) **Elemental Analysis (LA-ICP-MS and LIBS) and Multivariate Comparison of Soils: Tape as an Alternative to Pellets for Small Forensic Specimens**

Sarah C. Jantzi[1], José R. Almirall[1]; [1]IFRI, Florida International University

Elemental analysis of soil is a useful application of both laser ablation inductively-coupled plasma mass spectrometry (LA-ICP-MS) and laser-induced breakdown spectroscopy (LIBS) in geological, agricultural, environmental, archaeological, planetary, and forensic sciences. In forensic science, the question to be answered is often whether soil specimens found on objects (e.g., shoes, tires, or tools) originated from the crime scene or other location of interest. Elemental analysis of the soil from the object and the locations of interest results in an elemental profile of each specimen, consisting of the amount of each element present. Because multiple elements are measured, multivariate statistics can be used to compare the elemental profiles in order to determine whether the soil specimen from the object is similar to one of the locations of interest. Previous work involved milling and pressing ~0.5 g of soil into pellets before analysis [1]. However, forensic examiners prefer techniques that require less sample, are less time-consuming and less destructive, allowing for future analysis by other techniques. An alternative sample introduction method was developed to meet these needs while still providing quantitative results suitable for multivariate comparisons. The tape method involved deposition of a thin layer of a few milligrams of soil onto double-sided tape. A comparison of tape and pellet method performance is presented for both LA-ICP-MS and LIBS. Calibration standards and reference materials, prepared using the tape method, were analyzed by LA-ICP-MS and LIBS. As with the pellet method, linear calibration curves were achieved with the tape method, as well as good precision and low bias. Soil specimens from Miami-Dade County were prepared by both the pellet and tape methods and analyzed by LA-ICP-MS and LIBS. Principal components analysis (PCA) and linear discriminant analysis (LDA) were applied to the multivariate data. Results from both the tape method and the pellet method were nearly identical, with clear groupings and correct classification rates of > 94 %.

[1] S.C.Jantzi, J.R.Almirall, Characterization and forensic analysis of soil samples using laser-induced breakdown spectroscopy (LIBS), Anal. Bioanal. Chem. 400 (2011) 3341-3351.

(467) **Chemometric Analysis of LIBS Based Aluminum Measurements**

Dahu Qi[1], Steven Buckley[1], Chris Stipe[2]; [1]TSI Inc.; [2]University of Seattle

Laser induced breakdown spectroscopy (LIBS) has attracted a lot of attentions for its straightforward and process-free measurements, and rapid results with rich elemental level information. However limitations and challenges remain in applying chemometrics to interpreted LIBS spectrum. Due to matrix effect, the observation is usually nonlinear to the chemical content. The dimensionality of a typical LIBS spectrum is high (10e4 or higher), and both prior knowledge and training data are very limited. Due to these, many times the un-attended chemometric results are either inaccurate or invalid. In this study, we put theoretical and statistically learned constraints on data and regression process to establish accurate and reliable modeling. Both quantification and classification results were improved compared to direct analysis. The results were also compared to univariate analysis.

(468) **Application of Laser-Induced Breakdown Spectroscopy for Origin Assessment of Uranium Ore Refining Process Intermediates**

François R. Doucet[1], Paul Bouchard[1], Mohamad Sabsabi[1], Rick Kosierb[2]; [1]National Research Council Canada, Energy, Mining and Environment; [2]Canadian Nuclear Safety Commission, Directorate of Security and Safeguards

The International Atomic Energy Agency (IAEA) has the mandate to safeguard the use of uranium, plutonium and thorium worldwide, as nuclear fuel for civil uses, avoiding their diversion use in weapons of mass destruction or explosive devices. Terrorist and proliferation activists are employing more sophisticated means than those used in the past to achieve their objectives. Border security services, first responders and regulators need to adapt to this challenge and to seek technologies that can provide quick and accurate information, in order to prevent clandestine activities or initiate rapid responses to them. Laser-Induced Breakdown Spectroscopy (LIBS) technique has several advantages, the most relevant are real-time measurement, contact with the sample is not necessary, and analysis can be made at a distance avoiding contamination by radioactive materials. LIBS and Partial Least Square – Discriminative Analysis (PLS DA) were used for the origin assessment of uranium ore refining process intermediates for real-time nuclear forensics. A PLS-DA model was built to assess the origin different process intermediate samples. The results obtained suggest the applicability of LIBS to identify the origin of uranium ore refining intermediate. The correctly classified rate for external validation set is better than 96% for the blind validation set. The results obtained with the transportable LIBS unit clearly show the usefulness of this approach for real-time onsite nuclear forensics.

(469) **Attempts to Overcome Some of the Challenges in Molecular Weight Characterization of Polymers by Gel Permeation Chromatography**

Erick Soto-Cantu[1], David Yarusso[1], Richard Ross[1], Karl Benson[1]; [1]3M Company

The molecular weight of polymeric materials often influences a number of their physical and performance properties. Analytical methods such as osmometry and nuclear magnetic resonance (NMR) spectroscopy have the ability to measure molecular weight (MW) of polymers but their accuracy diminishes as MW increases. These methods also do not provide information about MW distribution. A widely used technique for measuring MW and its distribution in polymers is gel permeation chromatography (GPC), also known as size exclusion chromatography (SEC). Some of the challenges include:

•Analysis of samples that interact chemically with the stationary phase.

•Analysis of polymeric samples that are (chemically) crosslinked.

•Measurement of accurate or absolute molecular weights (i.e. not relative to molecular weight standards) of high molecular weight polymers.

Attempts to overcome these challenges will be discussed in this presentation.

(470) **Bridging the Gap in Polymer Characterization: Single- and Multi-detector SEC**

Amandaa Brewer[1]; [1]Tosoh Bioscience LLC

Since its inception the principle use of size-exclusion chromatography (SEC) has been to determine the molar mass averages and distributions of natural and synthetic polymers. In general these properties have been characterized through the application of calibration curves via a single-detector instrumental set-ups e.g. SEC-refractive index (RI). Over the years, as the complexity of polymers has increased the ability to obtain accurate and precise distributions of both their physical and chemical

properties have piloted a new era of polymer analysis: multi-detector SEC. Here, we will discuss polymer characterization via single- and multi-detector SEC namely, the coupling of SEC to various combinations of RI, UV-Vis, multi-angle light scattering (MALS), and differential viscometry (VISC). A dual detector system composed of two concentration-sensitive detectors allows for chemical composition determination of copolymers. While, the addition of a MALS detector to a single-detector SEC system allows for the determination of not only the absolute, calibrant-independent, molar mass and molar mass distributions but also provides size information. When coupled to the SEC-MALS-RI a viscometer can provide molar mass averages and distributions via universal calibration in addition to the intrinsic viscosity and macromolecular size of the analyte. Lastly, we will provide an overview of both multi-detector technologies as well as applications of natural and synthetic polymers.

(471) **Analyzing complex Polymers Using 2D-chromatography**

John McConville[1,2], Thorsten Hofe[1], Peter Kilz[1], Peter Montag[1], Derek Lohmann[2]; [1]PSS Polymer Standards Service GmbH, Mainz, Germany; [2]PSS USA Inc., Amherst, MA

Advances in polymer synthesis have resulted in a variety of new complex polymers with predetermined chemical composition, functionality and architecture. The task of characterizing these polymeric materials has become challenging, as no single analytical technique provides adequate information regarding all the different distributions. As a result, hyphenated techniques such as two-dimensional liquid chromatography (2D-LC) in which two liquid chromatography methods are combined to achieve selective separations according to the various distributions, have been established. PSS has commercially developed a unique software package that has the capability of performing 2D-LC analysis and allows data acquisition and control of fraction transfer between two liquid chromatographic systems.

After a short introduction of the basic concepts of HPLC and GPC the setup of a system and data acquisition and processing is discussed, outlining the advantages of 2D-chromatography and showing practical examples.

(472) **Online Coupling of SEC-MR-NMR**

Derek Lohmann[4], Markus Cudaj[1], Gisela Guthausen[2], John McConville[4], Thorsten Hofe[3], Manfred Wilhelm[1]; [1]Institute for Chemical Technology and Polymer Chemistry, Karlsruhe Institute of Technology (KIT), Karlsruhe, Germany; [2]Institute of Mechanical Process Engineering and Mechanics, Karlsruhe Institute of Technology (KIT), Karlsruhe, Germany; [3]PSS Polymer Standards Service GmbH, Mainz, Germany; [4]PSS USA-Inc., Amherst, MA

Hyphenation of size exclusion chromatography and medium resolution nuclear magnetic resonance (SEC-MR-NMR) has shown to be one solution to solving the problem of chemically sensitive detection in liquid polymer chromatography. The use of a combination of SEC and a specially designed table-top 20MHz NMR spectrometer using a permanent magnet, enables the acquisition of online 1H NMR spectra of the generated SEC fractions. With digital and mechanical improvements, a substantial increase in sensitivity and chemical selectivity has been achieved. 1H NMR spectra of PMMA and PS homo-polymers as well as PS-PMMA block-copolymers were of sufficient quality to enable detection and deformulation of unknown polymer compounds. 1H NMR spectra of acceptable resolution and S/N ratio were collected online during the chromatography. The SEC separation online with the NMR measurements performed well and resulted in the proof of principle of the SEC-MR-NMR combination. We will present method and challenges, as well as data generated utilizing the coupling of SEC-MR-NMR.

(472B) **Online Polymerization Monitoring with and without GPC**

Wayne Reed, Tulane University

The ability to monitor polymerization reactions as they occur offers advantages in both the fundamental understanding of reaction kinetics and mechanisms and the possibility of reaction control. Among the desired characteristics to be monitored are polymer molar mass and intrinsic viscosity distributions, monomer conversion kinetics, composition drift in copolymer reactions, residual monomer amounts, etc. GPC has been used at-line frequently to obtain such data with varying degrees of success. One alternative to GPC is the use of in-situ optical, rheological, and other types of sensors. While such approaches often work well in small molecule reactions they can experience difficulties within a polymer reactor environment. Another alternative is automatic continuous online monitoring of polymerization reactions (ACOMP). This involves continuous withdrawal of a small stream from the reactor, with dilution and conditioning, followed by multiple analytical measurements such as light scattering, viscometry, UV/visible absorption, polarimetry, refractivity, etc. This yield cumulative and instantaneous values of reaction characteristics, rather than complete distributions, but yields a continuum of points and steady, non-pulsed instrumentation flows. Examples from a wide variety of reactions will be presented; free radical and controlled radical copolymerization, reactions in heterogeneous phase, such as emulsions and inverse emulsions, grafting, and post-polymerization modifications, and phase change processes, such a coil-globule transitions and monoclonal antibody aggregation.

(473) **Thermoelectric Fabrics**

David Carroll[1]; [1]Wake Forest University

Carbon nanotube/polymer composite thin films for use as thermoelectrics has become of interest recently due to their favorable properties. The combined high electrical conductivity of the nanotubes and low thermal conductivity of the polymer, along with Seebeck coefficients reaching 40 μV/K, lead to an improved figure of merit (ZT) over that of either material individually. This is due to the ability to slightly decouple the relationship between the thermoelectric parameters because of the heterogeneous structure. Single film ZT values reach 0.005, while the best thermoelectrics, including bismuth telluride (Bi2Te3), have ZT values of 1. Although ZT for the nanotube/polymer films is low, these materials have favorable production and structural properties over Bi2Te3 including ease of production and lower cost with a light weight, flexible, and durable physical structure. Further, these single films can be combined and layered into multilayered thin film thermoelectric devices called Z-modules by using an alternating p-type/n-type layering structure. This allows for the addition of the magnitude of the voltage generated by each film since they are arranged in series. The thermoelectric voltage output is proportional to the number of layers in the module, and is limited only by the heat source available. The Z-modules can then be coupled together in a number of geometries to create an array of modules that can meet the specified power demands. These Z-module arrays are most suitable for portable low power applications where waste heat is readily available.

(474) **Synthesis and Properties of Nitrogen-doped Carbon Nanotube Cups**

Alexander Star[1]; [1]University of Pittsburgh

In this talk, I will describe an effective methodology for synthesizing nitrogen-doped carbon nanotube cups (NCNCs), which have a hollow multiwall graphitic structure with one end sealed and the other open. We have previously shown that nitrogen doping is essential for bestowing the unique morphology and properties of NCNCs. [1] In particular, we have demonstrated that NCNCs possessed excellent electrocatalytic properties toward oxygen reduction reaction (ORR)

which was comparable to platinum; therefore, this nanomaterial can be used as novel electrode material for fuel cell and electrochemical sensing applications.[2] Most recently, we have demonstrated[3] that by applying intense ultrasonication stacked NCNC fibers, which were prepared by the chemical vapor deposition (CVD) technique, can be greatly shortened to afford individual NCNCs in an efficient yield. Microscopic and spectroscopic characterization confirmed the cup-shaped hollow structure of isolated NCNCs and showed their robust chemical reactivity due to amine groups that are preferentially distributed at the open rims of the cups. Using these nitrogen functionalities as reactive sites, we managed to cork the nanocups with commercial gold nanoparticles (GNPs).[3] Furthermore, we found that by reducing GNPs from $HAuCl_4$ solutions using sodium citrate as the reducing agent the efficiency of the corking interaction was greatly increased. We are currently working to control the detachment of the GNP corks from the NCNCs as a potential trigger to release internalized cargo and have found that in the presence of H_2O_2 the enzyme, myeloperoxidase (MPO), could not only effectively degrade the nanocups, but also trigger the release of GNPs at the early stages of the degradation process. As a result of these promising findings, these self-enclosed nanocups may represent ideal nanoscale containers for drug delivery applications.

1. Allen, B. L.; Kichambare, P. D.; Star, A. Synthesis, characterization, and manipulation of nitrogen-doped carbon nanotube cups. *ACS Nano* **2008**, *2*, 1914–1920.
2. Tang, Y.; Allen, B. L.; Kauffman, D. R.; Star, A. Electrocatalytic activity of nitrogen-doped carbon nanotube cups. *J. Am. Chem. Soc.* **2009**, *131*, 13200–13201.
3. Zhao, Y.; Tang, Y.; Chen, Y.; Star, A. Corking carbon nanotube cups with gold nanoparticles. *ACS Nano* **2012**, *6*, 6912–6921.

(475) **Nano Materials for Photo-Mechanical Actuators**

Hongrui Jiang[1]; [1]University of Wisconsin - Madison

Actuators are critical components for microelectromechanical systems (MEMS). Recent development of materials that can be driven by light and provide photo-mechanical response have caught much attention since they have great potential to form actuators that can be remotely controlled by light. Of these materials, nanocomposites incorporating nanomaterials in polymer matrices are especially promising. In this talk, I will present our work on light-responsive hydrogels and liquid crystal elastomers, utilizing gold nanoparticles, carbon nanotubes and graphene oxide. I will also describe some applications of thus formed actuators in tunable liquid microlenses, endoscopy, and autonomous light tracking.

(476) **Nanostructured Photovoltaics: Limits and Unique Opportunities**

Richard Lunt[1]; [1]Michigan State University

Nanostructured and organic semiconductors offer new opportunities for low-cost photovoltaics (PV) and provide prospects for unique solar harvesting applications. In the first part of this talk, I will outline the upper limit of realistic efficiencies with these new technologies to give a clear perspective on the potential market viability for large-scale energy generation and outline the challenges necessary to overcome this threshold. The potential of "Third Generation" concepts accessible to nanostructured PVs (e.g. multi-exciton generation) will be discussed for their potential in reducing thermal losses that can subsequently impact cost structures. In the second part of the talk, I will introduce our pioneering work on developing of a light-weight transparent PV technology that creates a new paradigm for building integrated photovoltaics and that is specifically enabled by the manipulation of near-infrared excitonic semiconductors. I will outline the thermodynamic and practical limits to this class of devices and show our experimental demonstrations aimed at approaching these limits.

(477) **Nanostructured Electrode for Spectroelectrochemistry Studies and Charge Storage**

Shanlin Pan[1]; [1]The University of Alabama

We present a multifunctional nanostructured electrodes of TiO2 doped with carbon or decorated with Au nanoparticles (NP) for investigating their charge storage, and spectroelectrochemistry (e.g., electrogenerated chemiluminescence, ECL, and Raman) enhancement capabilities. For spectroelectrochemical studies, we use N3 dye (cis-[Ru (4, 4′-COOH-2, 2′-bpy)2(NCS)2]) as probe molecule for understanding the electrochemical and optical enhancement capability of this nanostructured electrode. Double layer charging capacitance and ECL of carbon doped nanostructured electrode are investigated. The SERS enhancement of gold sensitized electrode is determined by surface coverage and particle size of Au NPs, and the surface self-assembly configuration of N3 on this new nanostructured electrode. Our studies suggest that these modified TiO2 electrodes can serve as a new spectroelectrochemistry platform and charge storage media.

(478) **Histology and Ultrastructure of the Diabetic Kidney**

Suman Setty[1], Vishal Varma[1], Michael Walsh[1], Sanjeev Akkina[1]; [1]University of Illinois at Chicago

Long standing diabetes is associated with end-organ damage and includes nephropathy, neuropathy and retinopathy. In the kidney of diabetics, dysfunction of nephrons result from structural alterations to the glomeruli and tubules and additionally blood vessels are also affected. Characteristic glomerular changes include an increased deposition of matrix in the mesangium and basal lamina. The extent of these alterations is associated with glycemic control and the duration of diabetes and is also influenced by genetic and epigenetic characteristics of the individual. Electron microscopy is a tool which facilitates the diagnosis of early glomerular and tubular alterations in nephropathy and in quantitating glomerular and tubular basal lamina and mesangial changes when assessing the impact of clinical intervention. We are studying native and transplanted kidneys from diabetics by light and ultrastructural studies.

(479) **IR Spectroscopic Imaging for the Monitoring of Diabetic Renal Transplant Patients**

Michael Walsh[1], Vishal Varma[1], Alexandru Susma[1], Sanjeev Akkina[1], Andre Kajdacsy-Balla[1], Suman Setty[1]; [1]University of Illinois at Chicago

The leading cause of renal failure leading to kidney transplant is due to diabetes. To assess the status of transplanted patients, protocol biopsies are acquired every 6 months to examine for any complications such as organ rejection or recurrent diabetic nephropathy. The current gold standard is for biopsies to be stained and examined by an experienced pathologist to identify changes associated with disease, however this is difficult due to histological changes often being unspecific. Infrared (IR) spectroscopic imaging is an emerging approach to measure biochemical changes in tissue biopsies from transplant patients in a label-free and non-destructive fashion. IR spectroscopy has been shown to be a potentially powerful tool to identify biochemical changes associated with transplantation complications. In this study, we show some of the advances in using IR spectroscopy towards identifying biochemical changes associated with diabetes and the identification of biomarkers associated with transplant complications.

(480) **Raman Spectroscopic Perspective on Long-Term Glycemic Markers**

Narahara Chari Dingari[1], Rishikesh Pandey[1], Jaqueline Soares[1], Gary Horowitz[1], Ramachandra Rao Dasari[1], Ishan Barman[1]; [1]Massachusetts Institute of Technology

Glycemic control refers to the typical levels of blood sugar in a person with diabetes mellitus. Much evidence suggests that many of

the long-term complications of diabetes, especially the microvascular complications, result from many years of hyperglycemia. Long-term glycemic control has become an important goal of diabetes care and in the development of therapeutics for diabetes. The essential examination that has usually been performed in a clinical chemistry laboratory is the measurement of blood HbA1c and fructosamine levels as a functional metric of glycemic control over the past two to three months and three weeks, respectively. In my talk, we present the first demonstration of non-enhanced Raman spectroscopy as a novel analytical method for qualitative and quantitative detection of HbA1c and glycated albumin. Using the drop coating deposition Raman (DCDR) technique, we observe that the non-enzymatic glycosylation of these proteins results in subtle, but consistent, changes in vibrational features, which with the help of multivariate classification techniques can be used to distinguish the glycated proteins from their unglycated variants with 100%. The acquired Raman spectra demonstrate excellent reproducibility of spectral characteristics at different locations in the drop and show a linear dependence of the spectral intensity on the analyte concentration. Furthermore, the developed multivariate calibration models show a high degree of prediction accuracy even at substantially lower concentrations than those typically encountered in clinical practice. The excellent accuracy and reproducibility accomplished in this proof-of-concept study opens substantive avenues for basic investigations of glycated proteins as well as in high-throughput glycemic marker sensing in multi-component mixtures and potentially even in serum and whole blood samples. Finally, we also discuss the caveats in determining these two glycemic markers in patients with diabetic complications and how they correlate with the development of diabetic complications. We believe that the proposed approach can provide a uniquely powerful tool for glycemic marker determination in routine clinical diagnostics in the near future.

(481) **Fluorescent and Electrochemical Proximity Immunoassays for Quantifying Hormone Secretions in Small Volumes**

Christopher Easley[1], Joonyul Kim[1], Subramaniam Somasundaram[1], Jessica Brooks[1], Kennon Deal[1], Jean Negou[1], Lauren Hoepfner[1], Robert Judd[1]; [1]Auburn University

It is understood that acute insulin secretion is altered or abolished in the disease states of obesity, insulin resistance, and diabetes. However, much less is known about the acute endocrine function of adipose tissue (fat), since current methods are insufficient to interrogate dynamics. Petri dish or well-plate sampling systems still require relatively large volumes that make it difficult to impossible to accomplish time-course studies on small animal models such as mice or rats, or even from *in vitro* measurements on primary tissue. Our goal is to replace these larger-scale sampling methods with simple microfluidic systems that can interrogate much smaller samples of tissue. To maintain assay compatibility with these smaller volumes, we have concurrently developed small-volume proximity immunoassays such as proximity FRET assays (pFRET) and the electrochemical proximity immunoassay (ECPA). We show that both of these assay formats are uniquely suited for interrogating hormone secretion from small samples of endocrine tissue, namely murine pancreatic islets and adipocytes. When combined with droplet microfluidics for sampling, pFRET enables second-scale temporal resolution of insulin secretion quantitation from pancreatic islets; and ECPA permits hormone quantitation at the femtomolar level in secreted samples or in unspiked mouse serum. When combined, microfluidics and proximity immunoassays should open the door to a wide range of novel experiments on small animal models or on small samples of endocrine tissue for applications ranging from dietary studies to high throughput drug screening.

(482) **Metabolomics of Diabetic Aorta using Capillary LC-MS**

James Edwards[1]; [1]Saint Louis University

The detection, identification and quantification of the collection of small organic molecules in a biological sample are broad and deep analytical challenges. Given the vast number of metabolites and the wide ranges of their concentrations, current methods of untargeted analyses cannot hope to analyze the entire metabolome. Rather our approach will be to extract specific classes of molecules from the remaining metabolic milieu. This is expected to enhance the sensitivity of those classes of molecules believed to be relevant to the biological system. Specific classes of molecules will be tagged based on functionality for analysis by mass spectrometry (MS). Multiple tags have been synthesized and utilized to both extract these specific classes of metabolites as well as enhance ionization efficiency. Coupling high efficiency capillary liquid chromatography to MS analyses proves critical to resolving structural isomers and differentiating subclasses of extracted metabolites. Isotope and isobaric tagging in addition to extraction tags will be discussed. Three approaches will be undertaken: Untargeted analysis of metabolites in both positive and negative mode nESI-LC-MS; 2) targeted analysis of amine metabolites and 3)semi-targeted analysis of carbonyl metabolites. Samples analyzed using these methods will be aorta from db/+ and db/db mice.

(483) **Spectroscopic Analysis of Consumer Products: A Forensic Approach**

Richard Brown[1], Mary Miller[1]; [1]MVA Scientific Consultants

Foreign material in consumer products is of great concern to the manufacturer, the supplier and ultimately, the consumer. This overall problem may result in costly delays due to quarantined product, manufacturing line or plant shut-downs, or delays of a critical ingredient necessary for a formulated product. Recalls are also costly, not only from an economic standpoint, but a company's reputation may also be impacted. Although many types of foreign materials in products may be considered to be an aesthetic problem if a harmless substance is identified, numerous materials which may pose a potential health hazard have been reported. Identification of the material and determining the root cause is approached using many of the same techniques applied in forensic analyses, and has been coined 'industrial forensic investigations' or 'industrial forensic analysis' in recent years. This is particularly true for the regulated food, drug, cosmetic and healthcare products. Ultimately the key goal for the manufacturer of a product is identification of the source of the foreign material. Much like establishing connections from trace evidence collected at a crime scene, with foreign material in a consumer product, it is important to identify the party responsible (manufacturer or supplier) for the problem and associated costs. Microscopical and micro-spectroscopy techniques are especially useful for analysis of foreign materials in consumer products such as beverages, food products, and pharmaceutical products due to the small amounts of material available for analysis. Several examples of the combined application of light microscopy, infrared spectroscopy, and scanning electron microscopy with energy dispersive x-ray spectrometry are presented that highlight the diverse nature of foreign materials and provide information about their possible sources.

(484) **Applications of Micro-Spectroscopy to Forensic Trace Evidence**

John Reffner[1]; [1]John Jay College, CUNY

The discovery and analysis of trace evidence is frequently a pivotal part of forensic investigations. When microscopy and spectroscopy techniques are united, the analysis of trace evidence has increased value. Analyzing forensic evidence uses standard analytical methods; however the questions to be answered are unique. The infrared or Raman spectrum of a fiber can easily identify its

composition as being nylon-6,6. If this fiber was evidence recovered from a suspect, then the important forensic question is: could this fiber oringated from a garment worn by a victim? Clearly more information is needed to address this critical issue. New questions are raised. Was the fiber dyed? If so can a visible light spectrum be collected to provide additional information that may be used to exclude or include this fiber evidence? Is the dyed fiber dichroic? Can its dichroic spectrum the recorded? Micro-spectroscopy plays an important role in evaluating this evidence.

In all major categories of trace evidence in criminal investigations, such as soil minerals, glass, fibers, paints and drugs, micro-spectroscopy is applied to provide scientific data for forensic investigations and litigation. Forensic science continues to benefit by the advances in micro-spectroscopy. Elemental analysis using scanning electron microscopes with energy dispersive x-ray spectrometers are used routinely for gunshot residue identification and to determine the elemental composition of particulates. Molecular spectra, using infrared or Raman microprobes, provide data from paint transfers in hit-and-run cases that may classify the make and sometimes the year of a vehicle involved in the accident. The contributions of micro-spectroscopy to forensic science have an established history and continue to advance.

(485) **Forensic Spectroscopic Chemical Fingerprinting of Fingerprints**

David Wetzel[1], Mark Boatwright[1, 2], Jarrod Bechard[2]; [1]Microbeam Molecular Spectroscopy Laboratory, Kansas State University, Manhattan, KS; [2]Department of Biochemistry and Molecular Biophysics, Kansas State University, Manhattan, KS

The art of lifting human fingerprints and their utility in forensic science is legend. The potential of linking the chemical deposition of the fingerprint with prior topical environmental contact has not yet been fully realized. The prevalent use of skin treatment via health and beauty products if detected may reveal the nature of the unintended deposition. We chose skin treatment contact to illustrate this feature because each particular pharmaceutical company has its own formulation that may leave a distinctive infrared chemical fingerprint. A library of various commercial products was established using transmission reflection transmission from a polished stainless plate or an infrared reflecting glass microscope slide. From a thin coated surface, a transfer of the product to the finger was completed. The fingerprint ridge deposited on a clean hard surface was subjected to infrared microspectroscopy to obtain the mid-infrared spectrum to reveal the chemical identity of the residue remaining on the finger. Initial classification of the library spectra was by the prevalence of the carrier solvent type by prominent stretching vibrations and their individuality was recognized by the pattern of the finger region. Discriminant analysis algorithms were employed to enable objective matching of the spectrum obtained from the actual fingerprint with a particular cosmetic or health care product. This modest effect is intended to demonstrate the potential of the IMS forensic approach. Spectra are presented to illustrate the utility of infrared microspectroscopic fingerprinting.

(486) **Simultaneous Determination of Geographical Origin and Quality Characteristics of Agricultural Products from the Alpine Area Based on Near Infrared Spectroscopy (NIRS)**

Christian Huck[1], Matthias Schmutzler[1], Oliver Lutz[1], Lorenzo De Benedictis[1]; [1]Institute of Analytical Chemistry and Radiochemistry, CCB – Center for Chemistry and Biomedicine, Leopold-Franzens University, Innsbruck, Austria

Reliance in quality control and the demand for highest standards in the field of food analytics are topics of increasing importance due to the claims of the customers. Although current regulations are already rigorous, negative headlines revealing frauds occur repeatedly, impairing the customers trust in the food industry. Therefore the willingness to accept higher prices in order to have the assurance that the product originated from a local premium producer is apparent in the market's high price segment. This demands an affordable and reliable analytical method, which is readily applicable outside a chemical laboratory, enabling the determination of the agricultural products' geographical origin in a fast and non-destructive way. Approaching this scientific challenge, an Interreg IV project called OriginAlp, funded by the European Union, has been initiated. The goal of this cross-border cooperation between Austria (northern and eastern Tyrol) and Italy (southern Tyrol) is the establishment of an efficient and fast analytical platform, focusing on the simultaneous determination of critical quality parameters of regional alpine foods such as milk, cheese, butter, apples and meat. The OriginAlp consortium consists of three scientific partners (University of Innsbruck, Austria; University of Bolzano, Italy; Research Center Laimburg, Italy) and three commercial partners (Agrar Marketing Austria; Southern Tyrolian Alpine Dairy Association; Transidee) [1] . For the quality control of milk, cheese and meat, near-infrared measurements of different samples from Northern Tyrol, Southern Tyrol and foreign countries have been performed. Additionally, a titanium dioxide based casein extraction procedure has been established, being verified via multivariate partial least squares regression (PLSR). The milk, cheese and meat samples have successfully been separated according to their origin via principal component analysis (PCA). In order to improve sensitivity, a number of meat samples were lyophilized prior to PCA analysis. Concerning the apple module, 160 Golden Delicious (GD) apples from 16 locations in the Alpine area (northern and southern Tyrol) and 120 GD samples from 12 foreign countries were collected. A specialized surface-scanning technique has been developed, facilitating accessibility to chemical information contained in the peel of apples. Therefore, an automatic sample rotation tool was constructed, allowing for easy hyphenation to any common NIR spectrometer with a fiber optic probe. PCA clustering attempts led to a significant differentiation between the Alpine area and other geographical origins [2]. In addition to spectroscopic approaches, stable isotope analysis for carbon (δ13C) and nitrogen (δ15N) in combination with classification models based on linear, quadratic and decision tree methods have been developed for the determination of the products' geographical origin. Modern GCMS, HPLC, and IC techniques are utilized for reference analytical purposes. Moreover, in order to facilitate interpretation of the complex near-infrared spectral data, ab initio correlated quantum mechanical frequency evaluations are employed, supporting the experimentally available data [3]. Reproducible in-field measurements are a crucial step in the realization of the project goals. Thus, an InGaAs diode array detector equipped miniaturized near-infrared spectrometer has been extended by a tailor made transflection measurement cell, utilizing the integrated low-power tungsten light source. A spherical gold mirror was found to serve as a reflector superior to conventionally employed polytetrafluorethylene, improving the quality of the measurements significantly. Alongside, the reflector serves as an internal reference unit, minimizing the influence of thermal sensor drift. The incorporation of a thermoelectric cooling appliance aided by means of further improving the signal to noise ratio as well as by ensuring thermostatic measurement conditions, thus facilitating a wide range of quantification tasks. The suitability of NIRS for both qualitative and quantitative determinations of the mentioned products will be discussed by several selected examples.

References:

1 De Benedictis, L. et al. Near infrared spectroscopy as a tool for quality control of food of the alpine region—A short report about a cross-border project. NIR news 23, 11-14 (2012).

2 Schmutzler, M. & Huck, C. W. Automatic sample rotation for simultaneous determination of geographical origin and quality

characteristics of apples based on near infrared spectroscopy (NIRS). unpublished work (2013).
3 Lutz, O. M. D. et al. A Combined Ab Initio Computational and Infrared Spectroscopic Study of the Cis and Trans Bis(Glycinato)copper(II) Complexes in Aqueous Environment. The Journal of Physical Chemistry Letters 4, 1502–1506 (2013).

(487) **Profiling Caramel Colour in the Scotch Whisky Industry using Mid-infrared Spectrometry with an Attenuated Total Reflectance Probe**

Megan Holden[1], Alison Nordon[1], David Littlejohn[1], Ian Goodall[2], Craig Owen[2], Walter Johnstone[1], Gary Colquhoun[3]; [1]University of Strathclyde; [2]Scotch Whisky Research Institute; [3]Fibre Photonics

The natural colour of Scotch whisky originates during the maturation stage of production, where colour components are extracted from the oak casks in which the spirit is stored. The particular colour that results is dependent on the history of individual casks and so legislation permits the addition of E150a caramel, to achieve consistency of colour in the final product. The composition of caramel is very complex and so there is currently very little knowledge of its exact chemical profile. The work undertaken in this research has therefore aimed to gain an understanding of the chemical profile provided by E150a (and other colorant materials) to provide information that could be beneficial to the Scotch whisky industry in terms of colour stability, product integrity and product authenticity. This study has investigated the use of mid-infrared (MIR) spectrometry for profiling caramel colour, using an attenuated total reflectance (ATR) probe incorporating polycrystalline silver halide optical fibres. All caramels were initially dissolved in 40% ethanol to mimic the conditions of a typical Scotch whisky. Spectra dominated by colour components were then obtained by inverting the probe head and drying samples onto the ATR crystal, so as to remove the contributions of the major volatile constituents. This approach was used to profile a selection of different caramel materials including an example of each caramel class recognised by the European Union (E150a, E150b, E150c and E150d). The spectral profiles obtained were compared using principal component analysis (PCA) and it was demonstrated that these products could be clearly differentiated between using ATR-MIR spectrometry. When the same caramel materials were dissolved in the more complex matrix of Scotch whisky, separation between classes was maintained, indicating the potential for counterfeit whiskies to be identified based on the colour additive they contain.

A variety of legally permitted E150a caramels, each produced using different substrates and manufacturing conditions, were also analysed in this work. PCA again demonstrated the potential to differentiate between these products, indicating the possibility for E150a manufacture to be controlled in the future to create a distinctive signature profile for the positive identification of authentic Scotch whisky samples.

(488) **Detection and Thermal Stability of Home-Made Explosives: A Comprehensive Study of Fuel-Oxidizer Mixtures**

Ilana Goldberg[1], Joseph Kozole[2], Harry Rose[3], Luther Schaeffer[3], Jack Stephenson[4], Jason Stairs[4]; [1]The Johns Hopkins University Applied Physics Laboratory; [2]Dupont; [3]Nova Research; [4]Department of Homeland Security

The use of non-conventional explosives is an emerging threat to homeland security and of particular interest to the explosive detection community. Among non-conventional explosives of interest are fuel-oxidizer (FOx) mixtures such as sugar with hydrogen peroxide (HP). The study of their thermal properties and detection characteristics is of utmost importance to test and evaluation in order to prevent harm from these threats. However, a detailed understanding of these properties for sugar-HP mixtures has yet to be undertaken. In this work the thermal properties of mixtures of HP with different sugars was examined using differential scanning calorimetry (DSC), and hot-stage microscopy (HSM). Kinetic parameters were determined using both "model-free" and model-based fitting methods. It was found that sugar-HP mixtures have very complex, multi-step decomposition processes. Additionally, the detection properties of sugar-HP mixtures was examined by atmospheric pressure ionization (API) with ion mobility spectrometry (IMS) or mass spectrometry (MS) using a commercial-off-the-shelf (COTS) IMS instrument interfaced to a triple quadruple mass spectrometer [1] and the relevant gas phase ion chemistry was elucidated. The response of sugar-HP was found to be discernible from the pure materials providing a starting point for the development of detection algorithms. The combination of these analyses has led to the identification of possible reaction pathways based on the inherent chemistry of the mixture. This work has formed the basis for establishing protocols for the improved detection of these materials, and for their safe storage, handling, and disposal in support of test and evaluation.

[1] Kozole, J.; Stairs, J. R.; Cho, I.; Harper, J. D.; Lukow, S. R.; Lareau, R. T.; DeBono, R.; Kuja, F. Analytical Chemistry 2011, 83, 8596.

(489) **Taming Peroxide Explosive**

Jimmie C. Oxley[1], James L. Smith[1], F. Lucus Steinkamp[1], Joseph Brady, IV[1]; [1]URI

Homemade explosives exploiting the oxidizing power of hydrogen peroxide will be discussed. Various aspects of these materials will be presented from preventing HP concentration to safe dog training aids of TATP. Mechanisms for TATP/DADP syntheses and decomposition will be proposed as well as a protocol for gentle digestion of up to one pound TATP. Acid catalyzes the formation of triacetone triperoxide (TATP) from acetone and hydrogen peroxide, but acid also destroys TATP, and, under certain conditions, converts TATP to diacetone diperoxide (DADP). Addition of strong acids to TATP can cause an explosive reaction while reaction with dilute acid reduces the decomposition rate so drastically that gentle destruction of TATP is impractical. However, the combined the use of dilute acid with slightly solvated TATP made gentle destruction of TATP feasible. Variables including acid type, concentration, solvent and ratios thereof have been explored, along with kinetics, in an attempt to provide a field-safe technique for gently destroying this homemade primary explosive. The preferred method is moistening TATP with an alcoholic solution (aqueous methanol, ethanol or i-propanol) followed by addition of 37wt% hydrochloric acid. Preliminary experiments have shown the technique to be safe and effective for destruction of hexamethylene triperoxide diamine (HMTD).

(490) **Novel Capillary Microextraction Coupled to Gas Chromatography Mass Spectrometry**

Jose Almirall[1], Wen Fan[1]; [1]Florida International University

A newly developed sorbent-coated microfiberglass preconcentration device for use as a non-contact sampler of explosives and volatiles associated with the presence of explosives is reported for the first time. The new configuration overcomes some of the practical limitations of the widely used solid phase miroextraction (SPME) device by significantly increasing the surface area of the sampler while retaining the small size and compatibility with the inlet of a GC-MS injection port. The new configuration is also compatible with dynamic sampling of open systems requiring sampling times of less than 1 minute to preconcentrate the volatiles from targets as low as 10 mg of explosives. Nitroglycerin, 2,4 DNT and Diphenylamine, indicators of the presence of smokeless powders (10 mg), were detected using a commercial off-the-shelf GC-MS after a 30 s dynamic extraction in containers as large as 14 L. The new capillary microextraction of volatiles (CMV) device is inexpensive to

manufacture and can therefore be deployed for field sampling and subsequent analysis by GC-MS. The sorbent chemistry can be configured for specific target polarities and molecular sizes when the target compounds are known, the sorbent can also be configured for universal sampling or stacking of a variety of sorbents within the same CMV device when the target compounds are not known.

(491) **Chemometric Analysis of Multi-Channel Fused Datasets to Improve Source Attribution of Prevalent Homemade Explosives**

Joseph Chipuk[1], Myles Gardner[1], Carolyn Mazzitelli[1], Julie Wilkerson[1], Melissa Reaves[1], Alan Smith[1], Jamie Patterson[1]; [1]Signature Science

Trace level chemical attribution signatures go beyond the detection of explosives, and aim to distinguish the source of the materials used in the production, routes used in the synthesis, and other manufacturing conditions. When combined with other biometric and physical evidence these trace level signatures can provide key information in investigations of both pre and post blast scenarios. In particular, chemical attribution signatures can support trends analysis and enhance intelligence reporting via the elucidation of reagent sources and techniques used to manufacture the energetic components of the improvised explosive device (IED). The field of chemical forensics is expanding and evolving with the application of new techniques and technologies. Contemporary detailed investigations require synthetic and analytical chemistry expertise, as well as rigorous test planning and execution, structured data management, detailed statistical evaluation, and innovative computational analysis to provide robust and defensible signatures. This presentation will summarize the system used at Signature Science for the discovery of chemical attribution signatures, and illustrate the methods and techniques used by discussing example cases involving homemade explosives (HME). A majority of IEDs employ HME main charges, and many employ improvised boosters and initiators. The most prevalent oxidizers used to manufacture HMEs are ammonium nitrate (AN) and potassium chlorate (PC), while the most readily synthesized secondary explosives include nitrate esters such as erythritol tetranitrate (ETN), nitroglycerin (NG), ethylene glycol dinitrate (EGDN), and nitrocellulose (NC). Here, common AN- and PC-based HMEs such as AN-aluminum (ANAL), AN-sugar (ANIS), PC-aluminum, and PC-sugar were prepared using a variety of over-the-counter materials. Likewise, ETN samples were prepared using a variety of methods, reaction conditions, and reagent sources. Samples were analyzed by inductively-coupled plasma – mass spectrometry (ICP-MS), gas chromatography – mass spectrometry (GC-MS), and liquid chromatography – mass spectrometry (LC-MS). Composite datasets were evaluated using chemometric methods (PLS-DA and HCA) to develop classification models that ultimately attribute each sample to specific material sources, or other synthetic variables. Unlike other methods that identify a single chemical as the chemical attribution signature (CAS), this approach utilizes a multi-dimensional composite signature as the CAS, resulting in a more powerful technique that is analogous to a fingerprint investigation.

(492) **Total Internal Reflection Raman Spectroscopy**

Colin Bain[1]; [1]Durham University

Total internal reflection (TIR) Raman spectroscopy has been developed as a surface-sensitive technique for studying the adsorption of surfactants, organic molecules, polymers, biological lipids and inorganic ions at solid-liquid interfaces.[1] The short penetration depth of the evanescent wave (typically ~100 nm) allows the discrimination of adsorbed species from those in the bulk. The combination of TIR Raman spectroscopy with chemometric methods allows the acquisition of spectra in seconds, even in multicomponent systems, without the use of SERS or resonance enhancement. When coupled with a wall jet flow cell, TIR Raman spectroscopy can be used to study the kinetics of adsorption and desorption with one-second time resolution. The well-defined hydrodynamics of the wall jet permit quantitative modelling of kinetics. Recently, we have coupled the flow cell to a continuous stirred tank, which allows the determination of complete adsorption isotherms in a few hours provided that the adsorption kinetics are sufficiently fast. If the substrate of interest is transparent, it can be used as incident medium for the pump laser light and molecules of interest adsorbed directly onto the substrate. More generally, thin films of other materials, such as cellulose or haematite, can be deposited on an optical prism and adsorption studied at the interface of the thin film with a liquid.

[1] Woods, D. A., Bain, C. D., "Total Internal Reflection Raman Spectroscopy" *Analyst*.**2012**, *137*, 35.

(493) **Breaking the Mould: Raman Optical Activity as a Structural Tool Beyond Biology**

Christian Johannessen[1]; [1]University of Antwerp

The main research focus of Raman optical activity (ROA), particularly in the last twenty years, has been within structural biology. The reason for this focus, in addition to the scientific interests of the main groups involved in the development of ROA, has been the intrinsic sensitivity of ROA towards structural changes in highly chiral biomolecules, and the advantage of measuring Raman scattering in aqueous solution, making the method ideal for studying highly soluble biomolecules in solution. To date, impressive advances have been made in developing ROA as a tool in structural biology, both with respect to instrumental development and in tackling the complexity of predicting the ROA spectra of large biomolecules. One potential downside of this focus of ROA towards structural biology is of course pigeon-holing, branding ROA as only suitable for the analysis of biomolecules in aqueous solution. In this presentation, we demonstrate the state-of-the-art of ROA as a structural analysis tool well beyond the realm of structural biology. Examples of ROA analysis from the realms of material science, polymer science and solid-state catalysts highlight the general applicability of ROA as a structural tool. In fact, exchanging water for apolar solvents combined with the smaller conformational heterogeneity of many materials in many cases sharply decreases the complexity of the detailed structural analysis made by combining experimental and theoretical ROA, thus making the method much more accessible as a quick analysis tool. Hence, we show that ROA can be employed to a much broader range of characterisation studies than the current focus on structural biology indicates.

(494) **MCR Augmented Ordinary Least-Squares Models for Improved *in-vivo* Raman Spectroscopy**

Thomas Hancewicz[1], Chunhong Xiao[1, 2], Shuliang Zhang[1], Manoj Misra[1]; [1]Unilever R&D; [2]Perkin-Elmer

In-vivo confocal Raman spectroscopy has become the measurement technique of choice for skin health and skin care related communities as a way of measuring functional chemistry aspects of skin that are key indicators for care and treatment of various skin conditions. The technique has proven to be a rapid and effective method for quantifying component penetration in skin for topically applied skin care formulations. The benefit of such a capability is that non-invasive analytical chemistry can be performed in-vivo in a clinical setting, significantly simplifying studies aimed at evaluating product performance. The standard analysis method used by most researchers for in-vivo Raman data is ordinary least-squares (OLS) regression. The focus of work described in this talk is the applicability of OLS for in-vivo Raman analysis with particular attention given to use for non-ideal data which often violates the inherent limitations and deficiencies associated with proper application of OLS. We then describe a newly developed in-vivo Raman spectroscopic analysis methodology called multivariate curve resolution augmented ordinary least-squares (MCR-OLS), which is a relatively simple route to addressing many of the issues with OLS. The method is compared

with the standard OLS method using the same in-vivo Raman data set, and using both qualitative and quantitative comparisons based on model fit error, adherence to known data constraints, and performance against calibration samples. A clear improvement is shown in each comparison for MCR-OLS over standard OLS. This suggests that that the methodology is more readily adaptable to a wide range of component systems and is thus more generally applicable than standard OLS.

(495) **Applications of Confocal Raman Spectroscopy in Dermal Drug Delivery**

Majella Lane[1]; [1]UCL School of Pharmacy, London, United Kindom

Confocal Raman Spectroscopy (CRS) has been used in the personal care industry for many years to analyse the thickness of the stratum corneum in humans *in vivo*. CRS has also been used to profile the *in vivo* skin disposition of actives commonly found in cosmetic products. The aim of this presentation is to highlight the potential of CRS for determining drug disposition in skin following topical application, as exemplified by recent work from our group. Initially, we have used CRS to examine topical delivery to the skin in humans following application of the model drug, ibuprofen, in simple formulations. The skin profiles obtained from CRS compared very well with conventional methodology to determine drug levels in skin *in vivo*. In addition the application of CRS in the development of *in vitro - in vivo* correlations for skin permeation has been explored. As we have previously demonstrated that the fate of the drug in skin is a function of the vehicle or carrier in which it is formulated, CRS analysis of specific vehicles used to deliver the drug to the skin were also investigated. Encouragingly, the amount of drug permeated through skin *in vitro* was linearly proportional to the intensity of the drug signal determined in the stratum corneum *in vivo*. Moreover, excellent correlations were obtained for selected vehicles and drug signal intensities *in vivo*. Finally, the use of CRS to assess topical bioequivalence of different pharmaceutical formulations *in vivo* will be discussed.

(496) **FTIR Spectroscopy and Imaging Studies of Skin and Hair**

David Moore[1]; [1]Rutgers University

Over the last 15 years we have utilized biophysical FTIR molecular and imaging spectroscopic methods to study *in vitro* and ex vivo models of human skin and hair. The first part of this presentation will highlight recent work using FTIR spectroscopy to qualitatively and quantitatively characterize inter- and intra-molecular membrane lipid organization in isolated stratum corneum (SC) - the outer layer of the epidermis). SC lipid organization is directly associated with skin health therefore FTIR measures of lipid organization changes provide a useful tool to characterize skin barrier changes induced by external and intrinsic factors. Examples from recent studies using kinetic and thermal FTIR spectroscopy methods to characterize changes in skin lipid organization will be presented. The second part of this presentation will highlight some recent work utilizing FTIR imaging spectroscopy to characterize human hair and will demonstrate the utility of spectroscopic imaging in providing spatially resolved information on the location within the hair fiber changes in hair chemistry and protein structure induced by consumer behaviors including applying chemical treatments and heat to hair.

(497) **From Explosives to Lipids: Coupling Ambient Ionization to Miniature Mass Spectrometers for *in-situ* Detection and Real-Time Chemical Analysis**

Paul I. Hendricks[1], Jacob T. Shelley[2], Jon K. Dalgleish[1], Jason S. Duncan[1], Matt T. McNicholas[3], Linfan Li[4], Tsung-Chi Chen[4], Chien-hsun Chen[4], Zheng Ouyang[4], R. Graham Cooks[1]; [1]Department of Chemistry, Purdue University, West Lafayette, IN; [2]Institute for Inorganic and Analytical Chemistry, University of Muenster, Muenster, Germany; [3]Department of Electrical and Computer Engineering Technology, Purdue University, West Lafayette, IN; [4]Weldon School of Biomedical Engineering, Purdue University, West Lafayette, IN

Miniaturized and portable mass spectrometers are the subject of increasing attention due to their potential utility for in-field detection of illicit drugs, explosives, environmental contaminants, therapeutic drugs, and more recently, the characterization of biological tissues. A key to achieving chemical analysis on time scales relevant for in-situ detection and real-time analysis is the successful coupling of ambient ionization sources to miniature instruments. Based on multiple earlier versions, the Mini 12 mass spectrometer represents a top down approach to instrument design whereby individual instrument systems are identified and targeted for miniaturization. The result of this effort is an instrument that has miniaturized electronics, vacuum system, mass analyzer, and ion detection system. Interestingly, this instrument can be deployed in one of two form factors: a backpack portable instrument, capable of mobile in-situ field analysis, or a compact desktop instrument. Both instrument models have tandem MS capabilities, can detect positive and negatively charged ion species, and support integrated ambient ion sources, i.e. low temperature plasma (LTP) and paper spray (PS), as well as classical ion sources such as nano-electrospray (nESI) and atmospheric chemical ionization (APCI). Utilization of ambient ionization sources with a miniature mass spectrometer allows for in-situ analysis of a wide range of different chemical compounds. Illicit drugs (methamphetamine), chemical warfare simulants (mipafox), explosives (TNT), environmental contaminants (PAHs), and therapeutic drugs have been detected. Target analytes are analyzed at nanogram levels, or lower, and have been detected directly from surfaces containing complex matrices such as human fingers, paper, and cloth. Recently, advancements to the RF system for the Mini 12 have increased the available mass range from 925 to 1225 Th while maintaining mass resolutions of 1-2 Th (FWHM) thus, making it possible to complete direct analysis of lipids from brain tissue and subsequently differentiate between tissue types using standard discriminant analysis techniques. Furthermore, a novice user interface has been developed and implemented on these instruments to facilitate instrument startup and shutdown, instrument status, data acquisition, and compound detection / identification based upon MS library matching.

(498) **Enabling Access to Ambient Ionization in a Simpler Mass Spectrometer**

Brian Musselman[1], Joseph Tice[1], Joseph LaPointe[1], Randall Pedder[2]; [1]IonSense, Inc.; [2]Ardara Technologies

Access to ambient ionization mass spectrometry (AIMS) has been limited to laboratories utilizing LC/MS and LC/MS/MS systems. Those advanced systems are invariably expensive and due to the need for extreme cleanliness objections are made to their use with often complex samples of interest to AIMS users. Reconfiguration of an Agilent 5975 GC/MS for use as an AIMS detector has been completed in our laboratory. A two stage atmospheric pressure inlet (API) has been added to the MS analyzer with little modification of the commercial instrument. Implementation of the both DART and nanospray permit demonstrate the utility of hte instrument for both ambient and normal operation. As the instrument can be implemented using used GC/MS units we have utilized it for more rapid

determination of samples typically analyzed using GC/MS. These samples include; supplements containing polyols and the use of different derivatization schemes as potential methods for their quality control as required in the FDA modernization act of 2011.

(499) **Halo-FAPA, an Angelic Source for Solid, Liquid and Gaseous Sample Volatilization and Ionization**

Kevin P. Pfeuffer[1], J. Nik Schaper[2], Jacob T. Shelley[3], Steven J. Ray[1], Gary M. Hieftje[1]; [1]Department of Chemistry, Indiana University; [2]Institute for Inorganic and Analytical Chemistry, Johannes Gutenberg University Mainz; [3]Institute of Inorganic and Analytical Chemistry, University of Munster

Sample introduction is often viewed as the Achilles heel of modern analytical techniques. Ambient mass spectrometry addresses this problem by avoiding sample introduction altogether. However, sample introduction methods are often ingrained in routine analyses and sometimes provide superior analytical capabilities. Overall, the ability to couple a wide variety of sample-introduction methods to a source capable of ambient mass spectrometry would be ideal. A new-geometry FAPA source, dubbed the halo-FAPA or h-FAPA, has been developed to address this need. The h-FAPA, so called because of its shape, employs two concentric electrodes with a fully annular plasma generated between them. Two separate gas flows are utilized, an outer helium flow that sustains the discharge and an inner flow for cooling and sample introduction. The inner electrode (central channel) can be used to introduce samples for analysis while the afterglow from the h-FAPA can be used for ambient MS analysis of samples. The h-FAPA has proven capable of analyzing vapor, liquid and solid samples. Headspace from an organic solvent was analyzed as a gas sample. Individual and bulk droplets from a droplet generator and nebulized sample were introduced through the central channel to demonstrate liquid-sample analysis. Finally, aerosol particles generated from a solid sample by laser ablation were analyzed. The h-FAPA will be compared with the original FAPA source for ambient ionization; in general, it offers comparable sensitivity, but lower spatial resolution. Additionally, a new geometry is shown in which the central electrode/capillary is replaced by a capillary inlet to a mass spectrometer. This configuration allows geometry-independent analysis, as a sample need only be placed near the inlet. A pharmaceutical tablet was analyzed for its active ingredient and spatial resolution was evaluated by imaging a TLC plate for three analytes. Additional applications utilizing the central channel will be shown as well as fundamental examinations into mass-transfer phenomena with the h-FAPA and with the central channel as the inlet to the mass spectrometer.

(500) **Compact Laser Ablation - Atmospheric Pressure Glow Discharge System for Elemental Analysis by Optical Spectrometry**

Jhanis Gonzalez[1,3], Benjamin Manard[2], Meirong Dong[1], Arnab Sarkar[1], Jose Chirinos[1], Xianglei Mao[1], Ken Marcus[2], Rick Russo[1,3]; [1]Lawrence Berkeley National Laboratory, Berkeley, California; [2]Department of Chemistry, Clemson University, Clemson, South Carolina; [3]Applied Spectra, Inc. Fremont, California

The need for compact instruments with low operating costs associated with low consumption of consumables (e.g., working gases, power demand, and cooling water) is one of the most important motivations for developing and miniaturizing analytical measurement systems. These miniaturized plasmas offer the prospect for field portability and adaptability to on-line analyses. Some other advantages of these excitation/ionization sources like the Atmospheric Pressure Glow Discharge (APGD) hold true for not only for characteristics like low cost, analysis in ambient conditions, low power, and miniaturized footprint, but also, the APGD source has great versatility in sample analysis (solids, liquids, gases, laser ablated (LA) particles). Recent collaborations with Dr. Marcus at Clemson University have focused on utilizing the APGD source as a secondary excitation source following LA. This combination, LA-APGD, has been shown to be qualitatively comparable to LA-ICP-MS and can excite particles produced from a nanosecond pulsed laser. In this study we present the first LA-APGD system, featuring complete integration, small footprint, plus performance metrics for the analysis of ablated particulate.

(501) **Levitated Droplets in Mass Spectrometry**

Jens Riedel[1], Arne Stindt[1], Carsten Warschat[1], Andreas Bierstedt[1], Ulrich Panne[1, 2]; [1]BAM Federal Institute for Materials Research and Testing, Berlin, Germany; [2]Humboldt University, Berlin, Germany

Ultrasonic levitation valuably supports the field of microfluidics and analytical chemistry. It allows the contactless handling of microliter samples and therefore minimizes contamination and sample consumption as well as adhesion or nucleation processes on the walls of reaction vessels. Even though optical spectroscopy and X-ray scattering are widely used in combination with ultrasonic levitation the coupling to mass spectrometry (MS) is still in its initial stage. In the present work, a combined approach of IR laser desorption and low temperature plasma ionization is introduced to interrogate both, the droplet contents as well as its volatile surroundings. The droplets were levitated in a homebuilt ultrasonic trap positioned in front of the inlet of a time of flight mass spectrometer. The evaporation process and ionization step were accompanied by high speed shadowgraphy experiments, stroboscopic visualization of ballistic microdroplets and spectroscopic characterization of the transient ions in the gas phase. The presented experimental results show a soft ionization method directly from levitated droplets. For the first time the gas phase in the direct vicinity of the droplets is also considered. The presented data shines light on the underlying ionization mechanism as well as the gas-phase kinetics during the transfer into the mass spectrometer.

(502) **Use of Biophysical Testing in Biosimilar Development**

Bryan Bernat[1], Asok Sen[1], Yangshang Wei[1], Jenny Gao[1]; [1]Hospira

Biosimilars offer wider access to life-saving medicines throughout the world. Biosimilar development requires a full analytical assessment of the test and reference products. Part of the analyses requires biophysical testing to understand the secondary, tertiary and quaternary structure of the protein. Several biophysical methods have been used to assess the structure of the reference products. These techniques provide important information to direct and confirm process development activities when developing a biosimilar.

(503) **Denaturation of Therapeutic Proteins Studied by Deep UV Resonance Raman Spectroscopy**

Liwei Yuan[1], Sergey Arzhantsev[1], Vincent Vilker[1], John Kauffman[1]; [1]US Food and Drug Administration

The number of protein based therapeutics entering the US market is increasing rapidly, and the degradation of therapeutic proteins is one of major concerns of biopharmaceutical industry. To assure the safety and quality of therapeutic protein products, it is important to develop rapid analytical methods to screen for the change of secondary structure of protein drug products. Deep ultraviolet resonance Raman (DUVRR) spectroscopy is a good alternative to techniques such as NMR, IR, UV and Circular Dichroism for determination of secondary structure of the protein. The resonance excitation provides high selectivity and sensitivity to secondary structure compared to non-resonance Raman spectroscopy and other vibrational spectroscopies. DUVRR spectra are dominated by protein vibrational modes that are coupled to the amide electronic state, including C-O and N-H vibrations that are extremely sensitive to secondary structure. This presentation will describe the application of DUVRR spectroscopy to screen the change of secondary structure of protein drug products. The chemometric analysis of DUVRR spectra of known secondary structure proteins enables us to predict secondary

structure of proteins with unknown structure. A chemometric model has been built based on DUVRR spectra of 18 well characterized proteins. DUVRR spectroscopy was applied to forced denatured protein samples and results of this study will be discussed.

(504) **Raw Material Characterization for Biopharmaceutical Process Development: Adaptation Drivers and Measurement Approaches**

Maureen Lanan[1], Amr Ali[1], Jessica Mondia[1], Pavel Landsman[1]; [1]Biogen Idec

Multiple biopharmaceutical companies are focusing on methods to understand and control the impact of raw material variation on cell-culture processes; however implementation and methods are not mature at this time. This presentation will expand on the vision of "Quality-by-Design for Raw Materials in Biologics" and present a simple strategy building on the process analytical chemistry literature for biopharmaceuticals. Data fusion techniques showing examples of outer-product analysis and combination vectors applied beyond NIR and NMR as well as twists on current analytical techniques such as XRF analysis and water activity will be discussed. Finally, approaches to set raw material specifications that balance business and regulatory risks while taking full advantage of improved raw material characteristics are addressed.

(505) **Raman Spectroscopic Characterization of Protein Structure in Lyophilized States**

Yemin Xu[1], Christopher Carpenter[1], Rina Dukor[2], John Carpenter[3], Theodore Randolph[1]; [1]University of Colorado Boulder; [2]BioTools; [3]University of Colorado Denver

Maintaining protein high order structure integrity is critical for developing protein pharmaceuticals. Mis-folding or unfolding of protein pharmaceuticals may cause reduced efficacy, altered pharmacokinetics and/or severe immune-responses. Thus, it is important to develop fast and accurate methods to routinely monitor the protein structure within pharmaceutical formulations. Currently, one third of all therapeutic proteins are stabilized in sugar-based glasses (i.e. prepared by lyophilization), wherein the proteins generally exhibit slower degradation kinetics than those observed in liquid formulations. It has been proposed that retention of native-like protein structure is critical for minimizing protein degradation in the glassy state. In order to more rationally design formulations to reduce degradation rates in glassy states, it is desirable to develop an accurate and quick method to monitor protein structure with high resolution in glassy state formulations, without reconstitution. Here, we employed Raman spectroscopy to characterize protein structure (secondary structure, aromatic residue environment, disulfide bond stretch, etc.) in glassy state formulations. The extent of structural perturbation observed upon lyophilization and during incubation was well-correlated with the rate of aggregation measured after reconstitution. Raman spectroscopy could be a quick and reliable way to predict protein stability and high order structure integrity in lyophilized states.

(506) **Probing Higher-Order Structure in Protein Pharmaceuticals using Infrared and Raman Vibrational Optical Activity**

Laurence A Nafie[1,2], Rina K Dukor[2]; [1]Syracuse University; [2]BioTools, Inc.

Protein structure is traditionally classified using the descriptors primary, secondary, tertiary and quaternary. These levels apply to individual proteins with well-defined structure. With the advent of commercial protein pharmaceuticals, further descriptors of protein structure have become necessary that are collectively called higher-order protein structure (HOS). These HOS variables predominantly involve glycolytic appendages to the protein and affect its *in situ* action and therapeutic effectiveness. Variations in HOS, which occur from one cell line to another, modify protein-protein interactions in a number of ways. The development and production of biopharmaceuticals, most of which are protein-base products, requires monitoring the conformation to ensure that various forms of degradation, aggregation or denaturation have not occurred during production, formulation, transportation and storage prior to human administration. In addition, as various biopharmaceutical products come off patents held by originator companies, so-called bio-similar products, the same biopharmaceutical but produced with different cell lines, are coming to market but differing in HOS effects that may cause differing side effects or immune responses compared to the original biopharmaceutical. Due to its well-established high sensitivity to stereo-conformation in biomolecules, ROA and VCD are now being used not only as a test for secondary structure and stability, but also for subtle differences in HOS [1,2] Recently, a number of conferences have been organized to develop methods for monitoring, evaluating and controlling HOS in protein based pharmaceuticals [3] Examples of the use of vibrational spectroscopy, including FT-IR, Raman, VCD and ROA, for probing biopharmaceuticals and HOS will be described.

[1] "Application of Vibrational Spectroscopy to the Structural Characterization
of Monoclonal Antibody and its Aggregate" Cynthia H. Li and Tiansheng Li, Current Pharmaceutical Biotechnology, 2009, 10, 391-399.

[2] "Characterization of Protein Higher Order Structure Using Vibrational Circular Dichroism Spectroscopy" Radhika P. Nagarkar, Brian M. Murphy, Xiaotong Yu, Mark Cornell Manning andWasfi A. Al-Azzam, Current Pharmaceutical Biotechnology, 2013, 14, 199-208.

[3] "Higher Order Structure 2013: 2nd International Symposium on Higher Order Structure of Protein Therapeutics" Baltimore, February 11-13, 2013. https://m360.casss.org/event.aspx?eventID=37952

(507) **Tunable High-Resolution Atomic and Molecular Spectroscopy Inside and Outside the Laboratory -- At Ranges to 80 km**

Marc Klosner, Andrew Grimes, Gary Chan, Chunbai Wu, John Walling, Donald Heller; [1]Light Age, Inc.

We discuss recent advances in narrow-band, wavelength-tunable pulsed laser technology. These developments provide high pulse energies, excellent beam quality, and transform-limited linewidths with MHz frequency precision and stabilization. Used in conjunction with non-linear wavelength conversion techniques, these systems enable a variety of spectroscopy applications at UV, Visible, and IR wavelengths. Such systems are being routinely used in highly demanding applications including characterization of the earth's upper atmosphere and laboratory-based atomic and molecular spectroscopy. In this presentation, we describe the capabilities of these high-precision, tunable narrowband pulsed laser systems; we review performance specifications that have been demonstrated; we summarize research and commercial applications that have been enabled by this technology, and we discuss its potential.

(508) **Fluorescence Correlation Spectroscopy Used to Study Confinement-Induced Anomalous Macromolecular Transport in Nanochannels**

Dane Grismer[1], Sneha Polisetti[1], Paul Bohn[1]; [1]University of Notre Dame

As lab-on-a-chip technology continues to transition from fluidic manipulations in two-dimensional planar geometries to three-dimensional stacked geometries, the need for a more comprehensive understanding of nanoscale behavior becomes apparent. Of particular interest are the effects of confined environments on molecular transport, specifically, in rectangular nanochannels of approximately attoliter volume. Confinement occurs when the container size is of

the same magnitude as important scaling lengths of macromolecules. Translational diffusion in this restricted space results in an increased frequency of wall collisions, Ω_W, and the corresponding cumulative effect on surface adsorption events can no longer be discounted when modeling molecular motion. As optically-accessible vessels, horizontally-aligned nanochannels of nanometric height are ideal structures to study confinement effects on macromolecular transport. A Fluorescence Correlation Spectroscopy (FCS) setup is used to take precise *in situ* measurements of the translational diffusion rates. As a platform for single-molecule studies, the need for averaging from ensemble data is eliminated. Varying the degree of confinement and relating it to subsequent changes in molecular motion adds valuable insights into our understanding of transport at the nanoscale. Of particular significance are the subdiffusive tendencies of large, flexible molecules compared to small molecules, which show little to no deviation from bulk behavior. Consideration is taken when using the autocorrelation function to analyze data, as confined diffusion approximates two-dimensional diffusion, rather than the traditional three-dimensional free diffusion assumption.

(509) **Simultaneous Determination of Concentration and Extinction Coefficient by All-Optical Methods**

David Jonas[1], Byungmoon Cho[1], Vivek Tiwari[1]; [1]University of Colorado at Boulder

Absolute molecular number concentration and extinction coefficient are simultaneously determined from linear and nonlinear spectroscopic measurements. As in gravimetric and coulometric determinations of concentration, no standard samples are needed for calibration. This new photonumeric method is based on measurements of absolute photon numbers for femtosecond pump probe signals. Accounting for pulse propagation, we present a closed form expression for molecular number concentration in terms of absorbance, fluorescence, absolute pump probe signal, and laser pulse parameters (pulse energy, spectrum, and spatial intensity profile); all quantities are measured optically. The extinction coefficient can then be determined from the absorbance spectrum and the concentration. For fluorescein in basic methanol, the optically determined molar concentrations and extinction coefficients match gravimetric determinations to within 10% for concentrations from 0.032 to 0.540 mM, corresponding to absorbance from 0.06 to 1. In principle, this new photonumeric method is extensible to transient chemical species for which other methods are not available.

(510) **Cleaning, Replicating and Protecting Diffraction Gratings with First Contact Polymer**

James Hamilton[1]; [1]Photonic Cleaning Technologies

First Contact Polymer solutions have been developed that dry to a resilient peelable film and can clean dust and fingerprints from many types of diffraction gratings from various vendors. Data will be presented on replicated aluminum gratings such those from Edmund Optics as well as as a 12 inch grating for one of the Keck Telescope detectors and a fused silica phase mask by Ibsen in Denmark. Optical, Electron and Atomic Force Microscopy scans as well as light scattering and X-ray photoelectron spectra show that not only are the gratings clean afterward, but such surfaces also are left with no residue.

(511) **A Novel Hydrogen Peroxide Biosensor based on Adsorption of Horseradish Peroxidase onto a Nanobiomaterial Composite Modified Glassy Carbon Electrode**

Nana Agyei, Mambo Moyo[2], Jonathan Okonkwo[2]; [1]University of Limpopo; [2]Tshwane University of Technology

Composite materials resulting from the combination of carbon nanotubes with biomaterials have been used in recent years as immobilization matrices for redox enzymes; this is a subject of considerable interest in chemical, environmental and biological applications. In this study a novel hydrogen peroxide biosensor was fabricated by using a maize tassel - multiwalled carbon nanotube (MT-MWCNT) composite to adsorb horseradish peroxidase (HRP) onto the surface of a glassy carbon electrode (GCE). The morphology and structure of the products were characterised by SEM, FT-IR and UV/visible spectroscopy. Voltammetric and amperometric methods were used to evaluate the electrochemical and analytical performance of the HRP/MT-MWCNT/GCE biosensor. Cyclic voltammetry (CV) showed that HRP was successfully immobilized on the MT-MWCNT composite, and amperometry yielded a linear response range of 9 μM to 1 mM H2O2 (R= 0.9978) and a detection limit (S/N = 3) of 4.0 μM. The biosensor also exhibited good stability and reproducibility.

(512) **A New Technique for Surfaces and Interfaces: 2D SFG Spectroscopy**

Martin Zanni[1]; [1]University of Wisconsin-Madison

Multidimensional spectroscopies in the infrared and visible spectral regions are now established techniques for studying molecules structures and electronic energy transfer, among many other topics. In this presentation, I will present our work extending these technologies into the realm of interfaces and surfaces via sum-frequency generation (SFG) spectroscopy. SFG spectroscopy is perhaps the most utilized non-linear spectroscopy. By adding a mid-IR pulse shaper to a standard SFG setup, we are able to generate 2D data sets that correlate vibrational modes in analogy to 2D IR spectroscopy but with surface/interface specificity. We show that we can probe a single monolayer of carbon monoxide on a Pt electrode, from which we uncover the structural heterogeneity of the system, which has been miss assigned for decades, and we will present data on a peptide monolayer. In the same way that 2D IR spectroscopy improves upon FTIR spectroscopy, 2D SFG contributes to the information content of SFG through couplings, lineshapes and dynamics.

(513) **Ultrafast Infrared Spectroscopy of Charge Generation, Trapping, and Transport in Emerging Photovoltaic Materials**

John Asbury[1], Ryan Pensack[1], Kwang Jeong[1]; [1]Pennsylvania State University

Two applications of ultrafast infrared spectroscopy to examine electronic processes in organic and colloidal quantum dot photovoltaic materials are described. In the first application, we examine archetypal classes of electron acceptors in organic photovoltaic materials and reveal how their molecular structures determine whether hot charge transfer state dissociation can influence the dynamics and yield of photo-generated electrons and holes. In the second application, we discuss the surface chemistry of ligand-nanocrystal interactions and how they impact the states involved in minority carrier transport in colloidal quantum dot photovoltaic materials. In both cases, the ability to link underlying molecular structure with electrical properties provides unique insights that lead to new design rules in support of continued materials development efforts.

(514) **Dual-Frequency Two-Dimensional Infrared Spectroscopy of Conjugated Molecular Vibrations**

Nien-Hui Ge, Hiroaki Maekawa[1], Soohwan Sul[1]; [1]University of California, Irvine

Coherent dual-frequency 2D IR spectroscopy is a powerful approach to study coupling and correlation between vibrational modes of very different frequencies. In this talk we will report our recent application of three-pulse photon echo, single- and dual-frequency 2D IR to the ester C=O and diazo N=N stretching modes in ethyl diazoacetate (EDA). The two modes exhibit different vibrational dynamics and 2D lineshape, which are well simulated by frequency-frequency correlation functions (FFCFs) with two decaying components. Although the FTIR spectrum shows a single C=O band, single-

frequency 2D IR nonrephasing spectrum displays spectral signatures supporting the presence of an equilibrium mixture of *cis* and *trans* conformations. The dual-frequency 2D IR spectrum exhibits cross-peaks that are tilted toward the anti-diagonal. This behavior indicates that the frequency fluctuations of the modes are anticorrelated. Because the two modes are connected through conjugated π electrons, solvent and structural fluctuations can cause EDA to adopt a different mixture of resonance structures and give rise to anticorrelated change in the bond orders. The effects of cross FFCF on the cross-peak line shape will be discussed.

(515) **Vibrational Energy Transfers in Condensed Phases**

Junrong Zheng[1]; [1]Rice University

Inter-molecular resonant and nonresonant vibrational energy transfers in liquids and solids at various temperatures were investigated with nonlinear IR techniques. It was discovered that the currently dominant theories based on the Fermi golden rule are not sufficient to describe vibration/vibration couplings and transfers. The vibrational dephasing induced coherence breakdown which is not considered by the Fermi golden rule is necessary to properly describe the one-donor-to-one-acceptor vibrational energy transfer process.

(516) **Fully Coherent Hybrid Raman-IR Multidimensional Spectroscopies**

Erin Boyle[1], Nathan Neff-Mallon[1], Andrei Pakoulev[1], John Wright[1]; [1]UW - Madison

Coherent Multidimensional Spectroscopies (CMDSs) such as 2D-IR are becoming increasingly useful tools for extracting greater structural and dynamical information than one-dimensional techniques such as infrared and Raman spectroscopy can provide. Here we present a lesser-known class of mixed electronic/vibrational CMDS which takes advantage of both infrared and Raman transitions, and can probe the coupling between those states over time. Doubly Vibrationally Enhanced and Triple Sum Frequency - Four Wave Mixing (DOVE and TSF-FWM) each probe vibrational states via the interaction of two infrared lasers and one visible beam that induces a Raman output that is spectrally resolved from all input frequencies. The different quantum pathways of the two techniques result in DOVE and TSF spectra that are complementary in their parity selection rules. This is demonstrated cleanly with a model system with an inversion center, benzene. Progress toward the multidimensional analogue of resonance Raman will also be discussed.

(517) **Laser-Induced Breakdown Spectrometry (LIBS) for the Determination of Macro- and Micronutrients in Plants**

Francisco José Krug[1], Dário Santos Jr[2], Lidiane Cristina Nunes[1], Marcelo Guerra[1], Gabriel Carvalho[1], Marcos Gomes[1, 3]; [1]Centro de Energia Nuclear na Agricultura-Universidade de São Paulo, Brazil; [2]Centro de Ciências Exatas e da Terra-Universidade Federal de São Paulo; [3]Departamento de Química, Universidade Federal de São Carlos, Brazil

In the last years, it has been demonstrated the ability of LIBS to interrogate plant samples in the form of pressed pellets [1] for the determination of macro (P, K, Ca, Mg), micronutrients (B, Cu, Fe, Mn, Zn) and beneficial elements (Si). To achieve this goal, there are boundary conditions for appropriate quantitative analysis, which are associated with the test sample presentation, with the quality of the test sample and with the calibration itself. In addition, one must pay attention to the complex nature of the laser-sample interaction processes, which depends upon both laser characteristics and sample properties, and to the plasma-particle interaction processes, that may affect the results due to corresponding matrix effects. A common approach to quantitative analysis relies on the use of calibration curves prepared with certified reference materials (CRMs). However, in practice, the similarity of physical and chemical properties of CRMs, including the corresponding similarity of pellets properties, are often rare when compared to the corresponding test samples, impairing their commutability. In this review, strategies for overcoming this common drawback for obtaining appropriate calibration curves will be presented. Quantitative analysis can be successfully carried out, for example, by selecting calibration and validation samples from test samples with similar chemical and physical matrix composition, with the aid of chemometric tools. Alternatively, it is possible to prepare matrix-matched standards from laboratory samples. This novel strategy proved to be useful to extend the range of the calibration curves towards lower concentrations.

[1] D. Santos Jr, L. C. Nunes, G. G. A. Carvalho, M. S. Gomes, P. F. Souza, F. O. Leme, L. G. C. Santos and F. J. Krug. Spectrochim. Acta, Part B, 2012, 71-72, 3-13.

Acknowledgments: Processos 2010/16379-0, 2010/17158-8, 2012/16203-5 Fundação de Amparo à Pesquisa do Estado de São Paulo (FAPESP), and Conselho Nacional de Desenvolvimento Científico e Tecnológico (CNPq) Processos 578728/2008-7, 140926/2009-7, 305913/2009-3, 309800/2011-0, 482500/2011-5.

(518) **Laser Induced Breakdown Spectroscopy for the Quantitative Analysis of Microdrops and Aerosols**

Erica Cahoon[1,2], Jose Almirall, Ph.D.[1]; [1]Florida International University; [2]High Purity Standards

Laser Induced Breakdown Spectroscopy (LIBS) demonstrates to be an effective technique for the quantitative analysis of ultra-low volume solution analysis using aerosols and microdrops. This study investigated single-pulse and collinear double-pulse LIBS using a 532 nm dual head laser coupled to a spectrometer with an intensified charge coupled device (iCCD) detector. The aerosols were generated using a micro-nebulizer, conditioned inside a concentric spray chamber, and discharged through an injector tube with a diameter of 1 mm. The LIBS plasma was formed ~2 mm from the exit of the tube to atomize and ionize the aerosol. The microdrops were formed by an inkjet printing system. The inkjet printing system was utilized to deliver single microdrops containing picoliter volumes for LIBS analysis. Multielement calibration solutions and continuing calibration verification (CCV) standards were prepared and analyzed for both aerosol and microdrop systems to calculate the precision, accuracy, and limits of detection (LOD). The correlation coefficients produced for both systems were R^2 values > 0.99. The determined precision, accuracy, and LOD in aerosol LIBS were ~3.8% RSD, 3.1% bias, 0.7 µg/mL, for the emission lines of Sr II (421.55 nm), Mg II (279.80 nm), Ba II (493.41 nm), and Ca II (396.84 nm), respectively. A 90 pL microdrop, containing a mass of 45 pg was dispensed into the space where a LIBS plasma was generated. The single microdrop LIBS experiment achieved a precision of 13% RSD and a bias of 1% for the Al I (394.40 nm) emission line. The absolute LOD detection for single microdrop LIBS for the emission lines Al I (394.40 nm) and Sr II (421.5 nm) were approximately 1 pg, and Ba II (493.41 nm) produced an absolute detection limit of approximately 3 pg. In conclusion, for a single 90 pL microdrop, LIBS performance resulted in precision, accuracy, and absolute LOD of ~14% RSD, 6% bias, and 1 pg for the elements Sr II (421.55 nm), Al I(394.40 nm), Mg II (279.80), and Ba II (493.41 nm).

(519) **Forensic Applications of Laser Induced Breakdown Spectroscopy (LIBS)**

Tatiana Trejos[1], Jose Almirall[1], Kiran Subedi[1]; [1]Florida International University

Laser Ablation Breakdown Spectroscopy is an emerging technology for direct in-situ micro-sampling of materials. The intrinsic advantages of LIBS are very attractive for forensic analysis, especially for its micro-destructive nature, the elimination of the need for chemical procedures for dissolution, ultrafast analysis and good discrimination potential. This presentation describes the development

and application of LIBS methods for the elemental profiling of a variety of matrices such as ink and paper for document examinations and chemical taggants for theft-deterrent products. A critical evaluation of the parameters of forensic interest is discussed in detail, including the analytical performance of the technique, discrimination potential (when comparing samples), homogeneity of the samples at the micro-scale, reproducibility, sampling strategies, calibration strategies and interpretation of results. The physical and chemical characteristics of paper, writing inks and printing inks can be used to differentiate documents printed from different sources or to associate documents that originated from the same printing or writing source. In this presentation the discrimination capability of LIBS of over 200 printing ink and paper samples is discussed. In addition, the analytical performance of LIBS is compared to other elemental analysis methods such as SEM-EDS and LA-ICP-MS. LIBS was also used for the characterization of traceable chemical tagging systems. These taggants are now commercially available in the USA (SmartWater CSI, LLC TM) therefore is anticipated to reach the US courts soon. In this study, the scientific foundation of these products was evaluated. The analytical performance of the LIBS method was evaluated and compared to LA-ICP-MS in terms of repeatability, reproducibility, bias and limits of detection. A total of 150 coding samples were measured as "unknown specimens" in order to evaluate the discrimination potential and error rates of the method. Mock cases were also received as part of the validation study.

(520) **Fundamental Understanding of the Dependence of the LIBS Signal Strength on the Complex Focusing Dynamics of Femtosecond Laser Pulses Either Side of Focus**

Craig Zuhlke[1], John Bruce III[1], Troy Anderson[1], Dennis Alexander[1], Christian Parigger[2]; [1]University of Nebraska-Lincoln; [2]University of Tennessee

In this work, we interrelate the complex focusing dynamics of 50 femtosecond laser pulses to the laser induced breakdown spectroscopy (LIBS) signal strength for research conducted on silicon samples where the sample surface is located at various locations relative to "true" focus. A comprehensive description is provided for the LIBS signal strength as a function of focusing dynamics including: concentric ring shaped variations in the electric fields before focus (prefocus), resulting from lens aberrations, and non-symmetry between the pre and post-focus beam profile as a result of continuum generation, occurring around focus. This research helps explain why the LIBS data reported by different researchers can vary if experimental conditions are not controlled tightly. Comparisons are made of the LIBS signal observed versus sample location relative to "true" focus using both an achromatic aspherical lens and a plano-convex spherical lens, each with a 40 mm focal length. Work was conducted for both atmospheric and vacuum conditions, yielding very different LIBS signal trends attributed to a lack of continuum generation in vacuum. In an attempt to understand lens aberrations effects on the LIBS signal strength, the electric field distribution of pulses focused using both the plano-convex spherical lens and the achromatic aspherical lens were further studied. Through the use of high resolution scanning electron micrographs of the silicon surface after ablation, along with theoretical simulations, the subsequent electric field patterns around focus are presented at numerous locations along the LIBS intensity curve. With ultrashort laser pulse ablation the energy is deposited in such a short timeframe that the surface of silicon quickly freezes once the pulse is over and material melt occurs. Thus the subsequent silicon surface melt pattern mimics the resulting applied electric field intensity distribution. The results from this research explain many of the confusing results that have been obtained in the LIBS community. The results are also important to the LIBS community for understanding how to make LIBS measurements more quantitative. This research represents a breakthrough in the fundamental understanding of the basic Physics of ultrashort laser interaction with materials and the resulting LIBS signal obtained.

(521) **Sparse Bayesian Inference of LIBS Spectra for Elemental Analysis**

Peter Torrione[1], Leslie Collins[1], Kenneth Morton[1]; [1]Duke University

A primary goal in analysis of LIBS spectra (and chemometrics in general) is to determine the chemical composition of the sample under interrogation. Often this is accomplished by expert analysts making use of their expertise and prior information (i.e., "human-in-the-loop" processing). However manual interpretation of spectra is time-consuming, and different experts may disagree about the correct interpretation of a particular spectra. This work presents a novel, automated technique for automatic inference of chemical composition from LIBS spectra that simultaneously infers the number of elements present and which spectral peaks are due to each element. Our approach fits in a Bayesian probabilistic framework which enables principled trade-offs between model accuracy and simplicity, and also allows for straightforward incorporation of prior information. Our results on both simulated and real data illustrate the efficacy of the technique, and show significant promise for automated interpretation of spectra.

(522) **Innovative Strategies for the Analysis of Pharmaceutical Compounds**

Davy Guillarme[1], Szabolcs Fekete[1], Aurelie Periat[1], Alexandre Grand-Guillaume Perrenoud[1], Serge Rudaz[1], Jean-Luc Veuthey[1]; [1]University of Geneva

High performance liquid chromatography has strongly evolved during the last years, to meet some requirements from different areas in terms of i) high throughput or elevated resolution, through the use of innovative stationary phases and instruments ii) selectivity by using alternative modes of separation and iii) sensitivity, thanks to the efficient coupling of HPLC with modern mass spectrometers (MS) devices.

Since 2004, the use of columns packed with fully porous sub-2µm followed by core-shell sub-3µm particles has strongly expanded in both academic laboratories and industries. Numerous providers propose today such columns together with instruments able to withstand pressures up to 1300 bar allowing separations in less than 1 min or plate count beyond 50000, while maintaining reasonable analysis times. It is therefore possible to separate in RPLC mode a large number of compounds, from small drugs toward large biomolecules (i.e. proteins and monoclonal antibodies). Some alternative modes of separation to RPLC have also been developed, to deal with difficult separations. For instance, hydrophilic interaction liquid chromatography (HILIC) appears as a suitable strategy to retain polar compounds, attain orthogonal selectivity with ionisable compounds and improve MS sensitivity, thanks to the high proportion of acetonitrile required to elute the compounds of interest. A recent regain of interest for supercritical fluid chromatography (SFC) has also been noticed thanks to the commercialisation of new stationary phases and more reliable instruments. This approach has indeed some evident benefits as it appears as a green technology, easy to transfer at the preparative scale and allowing excellent kinetic performance as well as selectivity for a wide range of compounds with diverse polarity. Finally, some significant progresses were also made in MS during the last decade, to achieve high sensitivity thanks to user-friendly, robust and fast instruments. The new generation of low resolution (quadrupole-based instruments or ion trap) and high resolution instruments (TOF/MS, QqTOF/MS or orbitrap) can be coupled with RPLC, HILIC and SFC, to further improve sensitivity. Advantages and limitations of these separation techniques will be discussed for the analysis of several pharmaceutical compounds and MS sensitivity will be compared between these three chromatographic modes.

(523) **A Novel Optimization Strategy for Multi-Segment Gradient Method Development Based on the One-Segment-Per-Component Strategy**

Gert Desmet[1], Eva Tyteca[1], Kim Vanderlinden[1]; [1]Vrije Universiteit Brussel

Compared to the conventional linear gradient programs, multi-segment gradient programs are only scarcely used, despite their intrinsically larger separation power. This lack of use is mainly due to the difficulty of the instruments to comply to the imposed complex gradient program, as well as to the lack of good search strategies to find the best multi-segment program among the innumerous possible combinations. Because the gradient-conformity of the latest generation of instruments has greatly improved, a renewed interest in more complex multi-segment gradient LC can be expected in the future, raising the need for better performing gradient design algorithms.

The present study has been set up to explore the maximal gain in separation selectivity that can be expected from multi-segment gradient algorithms. This was done by making the hypothesis that a maximal selectivity can be expected when designing the gradient program such that the gradient slope is adjusted after the elution of each individual component of the sample, thus offering a maximal degree of flexibility to the program. Different "one-segment-per-component" gradient design strategies were developed and applied to find the best possible gradient program The different strategies were applied to real as well as to in silico samples. For the real samples (mixtures of drugs most commonly found in waste water, API's and their impurities, …), a good predictability of the retention times could be observed (taken into account the non-LSS behavior [1] of the compounds), and a significant gain compared to a single or three- or four-segmented linear gradient could be demonstrated. The in silico-study demonstrated the enhanced selectivity of the "one-segment-per-component" gradient programs over a statistically significant amount of different samples and also pointed out that the approach allows to develop faster search algorithms compared to the conventional methods.

[1] Neue and Kuss, 2010, J. Chrom. A, 1217, 3794-3803

(524) **Technological Improvements Enabling New Levels of Efficiency in UHPLC: 1.3 µm Core-Shell Particles**

Jason Anspach[1], A. Carl Sanchez[1], Tivadar Farkas[1]; [1]Phenomenex

The last 10 years of chromatographic innovation has seen great strides in the next generation of chromatographic efficiency. The first enabling technology was the use of sub 2 µm fully porous particles. The next innovation saw the use of 2.6 – 2.7 µm core-shell particles. The core-shell particles demonstrated 30% higher efficiency than fully porous particles of the same size, which allowed for sub 2 µm efficiency at significantly lower backpressure. This core-shell technology was then extended to 1.7 µm particles. While these particles did provide 30% higher efficiency than fully porous particles, they did not provide double the efficiency that has typically been associated with the next generation of HPLC materials. Recently, 1.3 µm core-shell particles have been introduced. These particles do exhibit nearly double the efficiency of a fully porous sub 2 µm particle, representing the next generation of HPLC performance. In this presentation we will discuss some of the features of core-shell materials that allow them to provide high levels of performance. It is shown that frictional heating considerations are of little concern, whereas perhaps with fully porous particles they are

(525) **Genotoxic Impurities Analysis and Control Strategies in Pharmaceutical Development**

Archana Kumar[1], Kelly Zhang[1], Larry Wigman[1]; [1]Genentech Inc.

Genotoxic or carcinogenic impurities belong to a class of compounds that interact with DNA causing mutations. Regulatory guidelines for the control of these impurities in pharmaceutical compounds pose a significant challenge. EMA as well as FDA guidances suggested an approach based on a threshold of toxicological concern (TTC) and no more than 1.5 mcg/person/day, which corresponds to 15 ppm in a 100mg daily dose of drug. These limits are well below the ICH Q3A reporting levels and trace level analytical methods are needed to analyze these impurities. Effective analytical strategies are required to develop selective and sensitive trace level methods and physical properties of the GTIs need to be considered such as volatility, presence of UV chromophore, ionizable groups, presence of derivatizable functional groups. API method may be used with high column loading strategy if the analyte has a strong UV chromphore. However, this poses its own challenge due to interference with the matrix and presence of other process related impurities at a comparatively higher level. Some well known genotoxic impurities such as alkyl chlorides, sulfonic acid esters and hydrazines lack UV chromophores and achieving the required quantitation limits can be challenging. Derivatization/LC-UV approach may be followed or using GC-MS (SIM) can increase sensitivity. A number of case studies utilizing various analytical techniques such as high column loading, derivatization/LC-UV, GC-SIM, GC-FID, CAD in determining trace level GTIs and the control strategies will be presented.

(526) **Chemical Imaging of Pharmaceutical Cocrystals Using Terahertz Spectroscopy**

Katsuhiro Ajito[1], Jae-Young Kim[1], Danielle M. Charron[1], Yuko Ueno[1]; [1]NTT Microsystem Integration Laboratories

Terahertz (THz) spectroscopy is a promising technique for distinguishing pharmaceuticals of similar molecular composition but differing crystal structures, since molecular networks based on noncovalent bonds have resonant frequencies in the THz region. Physicochemical properties, such as bioavailability, are manipulated by altering the crystal structure of an active pharmaceutical ingredient through methods such as cocrystalization. Cocrystals are molecular complexes whose crystal structures differ from those of their pure components. The demonstration of chemical imaging of pharmaceutical cocrystals using a THz spectroscopic system is presented. Since THz spectral peaks of pharmaceuticals are broad at room temperature, a cryostat was added to the system to cool the tablets and enable multicomponent chemical analysis in them. Using the system, the cocrystal distributions in the tablets were clearly identified with 0.3−1.3% w/w error. This result broadens the prospective applications of THz spectroscopy in pharmaceutical chemical imaging and offers researchers and drug developers a new analytical tool.

(527) **Terahertz Spectroscopy on Condensed Phases; Molecular Crystals, Proteins, and Aqueous Solutions**

Keisuke Tominaga[1,2], Ohki Kambara[1,2], Feng Zhang[3], Jun-ichi Nishizawa[1,3], Tetsuo Sasaki[1,4], Houng-Wei Wang[4], Michitoshi Hayashi[2,4], Naoki Yamamoto[2], Haruka Iguchi[2], Atsuo Tamura[2]; [1]Shizuoka University; [2]Kobe University; [3]Sophia University; [4]National Taiwan University

We have studied low-frequency spectra of molecular systems in condensed phases such as molecular crystals, proteins, and aqueous solutions by terahertz radiation spectroscopy. As for the molecular crystals, the low-frequency spectra of normal anthracene and anthracene-d10 in the solid state were measured. We observed the isotope shift of the vibrational frequency in the THz frequency region at 5 K. The vibrational mode assignment was performed based on the DFT calculation for the isolated species and observed isotope shifts. We also conducted the solid state DFT calculation using CRYSTAL09 to confirm the mode assignment. The correlation field splitting for the intramolecular mode due to the dipole-dipole interaction is quantitatively discussed. The hydration water molecules around the hydrophobic probe in an aqueous solution were also

studied by using tetraalkylammonium cation as a probe and terahertz time-domain spectroscopic technique. The phenomenon, called dynamical transition, has been known to be universally observed among proteins and polypeptides. In this work we investigated temperature and hydration dependence of low-frequency dynamics to clarify relationships between the dynamical transition and protein structures, and its functional states. We also mention general behaviors of the low-frequency spectra of globular proteins.

(528) **The Role of Spectrally Resolved Measurements in THz Medical Imaging**

Zachary Taylor[1], Shijun Sung[2], Neha Bajwa[1], James Garritano[1], Bryan Nowroozi[4], Sophie Deng[3], Jean-Pierre Hubschman[3], Erik Dutson[4], Warren Grundfest[1]; [1]UCLA Bioengineering; [2]UCLA Electrical Engineering; [3]UCLA Ophthalmology; [4]UCLA Sugery

Medical imaging has been the subject of much interest in the THz community recently due to promising results obtained in *ex vivo* and *in vivo* tissues. The dielectric properties of water and other tissue constituents at THz frequencies are quite unique and significant contrast can be generated with THz illumination that is unavailable to currently accepted medical imaging modalities. The majority of research in THz medical imaging and sensing is carried out with THz time domain spectroscopy (TDS) which illuminate the sample with broad band pulses and use coherent, synchronous detection schemes to produce spectrally resolved data. While significant spectral resolution is possible with TDS, few characteristic narrow band resonances have been identified in physiologic material. This is most likely due to the liquid water background present in most tissues. This talk covers conventional applications of THz spectroscopy to medical imaging followed by a number of newer applications that offer potentially lower barriers for translation.

(529) **Investigations of Crystallinity by THz 2D Correlation Spectroscopy and Heterospectral Spectroscopy**

David Heaps[1], Xiao Hua Zhou[1], Richard McKay[1], Mark Sullivan[1], Eiji Kato[1], Edward King[1], Akiyoshi Irisawa[2], Motoki Imamura[2]; [1]Advantest America, Inc.; [2]Advantest Corporation

In this presentation, results obtained from the application of two-dimensional correlation spectroscopy (2DCOS) to terahertz (THz) spectral analysis will be discussed. Lower wavenumber or THz bands are due to intermolecular interactions, crystal lattice along with other low energy vibrational modes. Some of the intermolecular interactions investigated are dipole-dipole, hydrogen bonding and van der Waals. These interactions and vibrational modes give unique information about the system that is being measured. Utilization of 2DCOS and Heterospectral correlation spectroscopy aids in the ability for elucidation of the system. Principal component analysis (PCA) will also be used to identify the interesting portion of the dynamic system for analysis by 2DCOS. This study will use a wide band THz spectrometer that has a spectral range of 0.2 to 7 THz (0.67 to 233 cm-1) and Raman spectroscopy.

(530) **Chemometrics as a Tool to Explore Hydration Shell of Molecules with Terahertz Spectroscopy in a Microfluidic Device**

Ludovic Duponchel[1], Simon Laurette[2], Anthony Treizebre[2], Bertrand Bocquet[2]; [1]LASIR, University of Lille (France); [2]IEMN, University of Lille (France)

Hydration is the interaction between water and other molecules in aqueous solutions. Understanding the hydration mechanisms is essential because they are involved in many biological phenomena. For exemple, previous works have demonstrated that solvated-proteins dynamics and expression is highly correlated to the solvent dynamics. Considering a non-charged molecule solvated in water, hydration is made through weak bonds such as hydrogen ones. As a consequence, the behavior of water molecules at the vicinity of the solvated molecule is changed. These molecules are called ”bound water” and forms the hydration shell of the molecule. Far from the molecule, the so-called ”bulk water” behavior is the same as pure water. Although many studies have been done on such molecular structures, many questions remain concerning the hydration shell extent [1, 2]. This work presents a fruitful example of lab-on-chip/chemometrics combination with the example of subterahertz hydration probing of ethanol/water solutions in a chip. A multivariate curve resolution algorithm (MCR-ALS) is used to extract the contributions of all chemical compounds [3]. Contrary to the well-etablised classical model, chemometrics results highlight a two bound-water layers in the hydration shell. As will be seen, molecular dynamics simulations will also validate these results.

Refs :

[1] S. Ebbinghaus, S. J. Kim, M. Heyden, X. Yu, U. Heugen, M. Gruebele, D. M. Leitner, M. Havenith, Proceedings of the National Academy of Sciences of the United States of America 104(52), p 20749 (2007).

[2] T. Arikawa, M. Nagai, K. Tanaka, Chemical Physics Letters 457(1-3), p 12 (2008).

[3] A. de Juan, R. Tauler, Critical Reviews in Analytical Chemistry 36(3-4), p163-176 (2006).

(531) **Battlefield to Bench: Understanding the Role of Technology in Clinical Decision Making**

Eric Elster[1,2]; [1]Uniformed Services University of Health Sciences; [2]Naval Medical Research Center

In recent years, the Naval Medical Research Center (NMRC) and the Uniformed Services University (USU) has demonstrated that local and systemic cytokines and chemokines are objectively associated with acute war wound healing. In addition, we have hypothesized that acute wound failures are a consequence of a dysregulated systemic and local inflammatory response to traumatic injury. Finally, an algorithm has been developed for objective wound closure based on cytokine and chemokine biomarker expression using probabilistic (Bayesian) modeling. This approach towards clinical decision-making has broad applications in critically ill patients.

(532) **Current Models of Burn Injury and the Development of Novel Characterization Modalities for Burn Wounds**

Jonathan Peterson[1], Katherine Cilwa[2], Francis Esmonde-White[2], Benjamin Levi[1], Stewart Wang[1], Michael Morris[2]; [1]Department of Surgery, University of Michigan Medical School; [2]Department of Chemistry, University of Michigan

Burn wounds represent a leading cause of injury and death world-wide with over 11 million burns necessitating medical treatment in 2004. The establishment of specialized burn care centers, rapid patient evacuation protocols, and a focus on the early and aggressive treatment of burn wounds are contributing to reducing rates of morbidity and mortality. A central dogma to these improved guidelines is the recent establishment of early excision and grafting of burn wounds in acute therapy. However, distinguishing salvageable tissue from dead tissue necessitating surgical removal is difficult during early time-points following burn injury. Even experienced surgeons are able to make correct prognostic decisions only 75% of the time. Complicating this crucial period is a lack of adequate, objective diagnostic tools to aid physicians treating burn victims. Here we describe current research models of burn injury, including scald, flame, and chemical burns in rodent and swine models. Wounds of various sizes and depth are created to mimic different burn categories and treatment requirements. Severity of a burn wound and the recommended treatment course are dependent primarily on the depth of a burn wound. Biochemical and physiologic changes define the depth of burn injury and include blood vessel destruction, cell rupture, and collagen denaturation. While several technologies have been employed to assist surgeons including laser Doppler imaging, indocyanide green

videoangiography, and near-infrared spectroscopy, a reliable, quick diagnostic tool that can be employed at the earliest stages of burn treatment is still lacking. By better understanding the research models and chemical changes in burn injury, strides can be made towards the new application of chemical and spectroscopic modalities which hold promising potential to aid in the early identification of viable tissue in burn injuries.

(533) **Toward Non-Invasive Raman Spectroscopy of Pathological Mineralization in Diabetic Foot Wounds**

Karen Esmonde-White[1], Francis Esmonde-White[2], Michael Morris[2], Blake Roessler[1]; [1]University of Michigan Medical School; [2]University of Michigan

Raman spectroscopy has potential for early-stage disease identification based on molecular risk factors even before imaging or clinical symptoms manifest. Translation of Raman spectroscopy for transcutaneous measurements of musculoskeletal tissues is an ongoing avenue of research in the Roessler and Morris laboratories. In one study, we are translating Raman spectroscopy for intra-operative measurements of osteomyelitis (infected bone) in diabetic foot wounds. Discrimination of infected bone from healthy bone during surgical removal of osteomyelitic bone represents a significant challenge because incomplete removal leads to further infection. Current clinical imaging tests to diagnose early-stage diabetic osteomyelitis are inadequate, and not applicable in intra-operative environments. In a clinical study, Raman microspectroscopy (785 nm excitation) was used to define chemical composition of diabetic osteomyelitis bone fragments and normal healthy toe tissue. Fiber-optic measurements (□-785nm) were collected from human bone fragments in the clinical trial, human cadaveric feet and mouse tibiae to test the feasibility of transcutaneous Raman spectroscopy in a clinical setting. Initial tests demonstrated feasibility of transcutaneous measurements on plantar surfaces. We also identified anatomic features which may present a challenge to future transcutaneous measurements which include a thick layer of overlying tissue and multiple photon scattering from fat and tendon.

(534) **Optical Spectroscopy Devices for Assessing Wound Healing and Formation**

Joshua Samuels[1], Michael Weingarten[2], Michael Neidrauer[1], Leonid Zubkov[1], Peter Lewin[1]; [1]Drexel University-School of Biomedical Engineering; [2]Drexel University- College of Medicine, Surgery

With diabetes rates on the rise in the United States, diabetic foot ulcers have become increasingly prevalent, resulting in nearly 75,000 annual cases at a cost of $5 billion. A key component to this cost is due to expensive wound therapies which can exceed $1,800 per week. Wound size reduction has been the standard benchmark for determination of efficacy for these treatments, but due to inter-clinician error and difficulty measuring irregular wound shapes, this method is unreliable with a positive predictive value of less than 60%. Diffuse Near-Infrared Spectroscopy (DNIRS) uses 70-MHz modulated light in the diagnostic window (650-900nm) non-invasively to quantify levels of oxy- and deoxy-hemoglobin in the wound bed, which when measured over time, can show a trend towards or away from healing based on the changes in oxy-hemoglobin concentration from week to week. In this study, DNIRS was used to monitor 24 human diabetic foot ulcers longitudinally over the course of 20 weekly or bi-weekly measurement sessions. In just four weeks, the DNIRS system has a 91% positive predictive value (sensitivity of 0.9 and specificity of 0.86; $p<0.002$). These data indicate that it could be possible to objectively predict healing in 4 weeks using DNIRS and make decisions to cease or continue expensive treatments based on physiological conditions and health of the underlying tissue, not solely on the estimated size of the wound. Discontinuing ineffective treatments after 4 weeks could have potentially saved over $12,600 per patient, based on the treatment regimen of patients in this study. The use of similar optical technologies, including Diffuse Correlation Spectroscopy methods, could also be used to predict pressure ulcer formation by optically characterizing severity of deep tissue injury and different depths. Work on this topic is currently underway by the Drexel Wound Healing Team. Overall it is felt that optical technologies provide additional information regarding wounds not visible from the surface and can be applied bedside and be read in real-time. These characteristics will prove themselves invaluable to the future of wound healing.

(535) **Stand off Chemical Detection of Contaminated Skin using IR Hyperspectral Imaging**

Oliver Payne[1], Christopher Howle[1], Benjamin Alexander[1], Linda Lee[1], Rhea Clewes[1], Phillippa Spencer[1]; [1]DSTL

Recent advances in spectroscopic technologies have made possible the stand-off detection of low volatility chemical warfare agents (CWAs). Maximising the distance between detector and sources of hazardous contamination is most desirable as this reduces the potential for cross-contamination. The Negative Contrast Imager (NCI) is an infra-red (IR) hyperspectral imaging detector that can locate, classify and potentially identify surface deposited chemicals. The NCI is based upon an optical parametric oscillator (OPO) source comprising a Q-switched intracavity magnesium oxide (MgO): periodically poled lithium niobate (PPLN) crystal with a fanned grating design. Wavelength tuning is achieved by moving the crystal through the 1064 nm pump beam. This enables the generation of shortwave and midwave radiation (1.5 μm - 1.8 μm and 2.6 μm - 3.8 μm respectively) which is rapidly scanned across any scene of interest. Any materials of interest within the scene containing absorption features corresponding with the wavelength of incoming radiation will attenuate the intensity of the returned radiation. This process results in dark pixels within the acquired images. Most recently the NCI system has been used in the shortwave infrared (SWIR) spectral region to locate and detect the presence of a variety of liquid CWAs upon human and porcine skin. A non-CWA chemical; N, N-Diethyl-meta-toluamide (DEET) was also investigated. Results of these investigations, conducted at a stand-off distance of approximately 2m, are presented here.

(536) **Aptamer-Enabled SERS Detection of Staphylococcus Aureus.**

Peter Vikesland[1], Weinan Leng[1], Maria Virginia Prieto Riquelme[1], Amy Pruden[1]; [1]Virginia Tech

Staphylococcus aureus is the causative agent for ever growing numbers of disease outbreaks both within the United States as well as worldwide. Although transmission of this organism has historically been associated with hospitals, recent environmental outbreaks of resistant forms such as methicillin resistant *S. aureus* (MRSA), as well as its detection in wastewater effluent, have inaugurated *S. aureus* as an emerging environmental pathogen of concern. Unfortunately, existing protocols for detection of *S. aureus* are slow and not readily translatable to field applications. Herein we describe a method for the rapid detection of S. aureus that couples highly specific aptamer-functionalized gold nanoparticles (Apt-AuNPs) with sensitive surface enhanced resonance Raman spectroscopy (SERRS). Apt-AuNPs were prepared by conjugating gold nanoparticles with a *S. aureus*-specific aptamer and the Raman reporter malachite green isothiocyanate (MGITC). Raman XY images of *S. aureus* and four negative controls demonstrate the specificity and sensitivity of the probes and their capacity for detection of whole *S. aureus* cells. Apt-AuNP facilitates identification of individual *S. aureus* cells due to the agglomeration of large numbers of nanoparticles on the cell surface and the resultant amplification in SERRS spectral intensity relative to free Apt-AuNPs in solution. *S. aureus* cells can be quantitatively identified based upon the collected Raman images.

(537) **A Quantitative TERS Bioassay for Protein at the Tip of an AFM Cantilever**

Jean-Francois Masson[1], Rita Faid[1], Helene Yockell-Lelievre[1], Felix Lussier[1], Maxime Couture[1], Hugo-Pierre Poirier-Richard[1]; [1]Universite de Montreal

We have recently achieved a tip-enhanced Raman scattering (TERS) assay for human IgG using a secondary nanoparticle amplification stage. The pyramidal tip of an AFM cantilever was gold-coated and derived with 16-MHA and functionalized with anti-human IgG. Capture of IgG was confirmed with the specific Raman bands of the protein using 633 nm laser excitation. Then, the quantitative signal for IgG was obtained by a secondary detection stage of Au-NPs functionalized with a Raman reporter (DSNB) and a secondary antibody selective for IgG. The shape and size of the nanoparticle was optimized for sensitivity and minimal nonspecific interaction with the tip of the cantilever. Specifically, Au nanospheres, nanoraspberries and nanostars were compared for the detection of IgG. The sensor showed a dynamic range in the ng/mL range, comparable to other sensing platform for IgG reported in the literature. Dark-field microscopy of the AFM tip allowed the investigation of the plasmonic properties of the sensor and SEM images afforded identification of the surface density of AuNP on the tip opf the AFM cantilever. The broad applicability of this sensing scheme to a variety of proteins is promising for quantitative nano-analytical sensors.

(538) **Quantification of Xenobiotics and Their Metabolites using SERS**

Roy Goodacre[1], Omar Alharbi[1], Graham Kenyon[1], Samuel Mabbott[1,2], David Cowcher[1], Yun Xu[1], Elon Correa[1]; [1]University of Manchester; [2]University of Strathclyde

The detection and quantification of xenobiotics and their metabolites in man, and indeed other biological systems, is important for drug dosing, therapy and for substance abuse monitoring where longer-lived metabolic products from illicit materials can be assayed after the drug of abuse has been cleared from the system. Raman spectroscopy offers unique specificity for molecular characterization and this usually weak signal can be significantly enhanced using surface enhanced Raman scattering (SERS). Using judicious design of experiments we have recently demonstrated excellent detection and quantification for a range of drugs and biomarkers using SERS [Levene et al. (2012) Analytical Chemistry 84, 7899-7905; Mabbott et al. (2013) Analytical Chemistry 85, 923-931; Cowcher et al. (2013) Analytical Chemistry 85, 3297-3302]. In this presentation we have further developed our SERS with chemometric and machine learning methods for multiplexed quantification of drugs and their metabolites. We shall also demonstrate how SERS can be used to follow dynamic cellular processes.

(539) **Dynamic Raman Scattering: Studying Anomalous SERS effects**

Keith Carron[1,2], Brandon Scott[2]; [1]Snowy Range Instruments; [2]University of Wyoming

Since its discovery in the early 1970's SERS has eluded a theoretical explanation that is widely accepted. There has been some convergence that the predominant source of enhancement is electromagnetic and it is still believed that certain species can produce a resonance Raman like chemical enhancement. The most recent addition to the explanation of SERS enhancements is the "gap" theory which states that anomalously large enhancements (hotspots) for species located where two (or more) nanoparticles are in close proximity.

One of the challenges for the experimental SERS scientist in providing SERS theorists with data to support their efforts is the nanoscopic nature of SERS. It is difficult to study individual nanoparticles with respect to their morphology and their enhancement. Additionally the process of preparing SERS active nanoparticles for vacuum surface analysis or electron microscopy changes their native environment. SERS is often used in nanoparticle solutions where the SERS behavior of individual particles in the large ensemble of nanoparticles becomes averaged by conventional Raman spectroscopy. We will present the method of Dynamic Raman Scattering (DRS) to study anomalous SERS behavior in solutions and on surfaces. This method collects a large data set of spectra and analyzes it for the average result (conventional Raman spectroscopy) and for statistical aberrations in the data set. The statistical aberrations have been found to represent SERS anomalies that can be related to species in unusual morphological locations. This is demonstrated by 4-mercaptopyridine and anomalous behavior with respect to access to protonation. Additional material will be presented about Principal Component Analysis (PCA) as a method to located unusual SERS components in ensemble spectral data sets. It will be demonstrated that a data set from a large collection of SERS active particles can be analyzed by PCA to produce subsets of anomalous particle spectra. Finally, we will present data where the frame of reference has been changed from the stationary laser beam and moving particles to a stationary surface and a moving laser beam.

(540) **SERS Analysis in Blood**

Christy Haynes[1], Antonio Campos[1]; [1]University of Minnesota

Surface-enhanced Raman scattering (SERS) is employed herein for label-free detection of protein species in complex media. This is accomplished by employing high enhancement factor SERS substrates modified with aptamer-based affinity agents. Unlike antibody affinity agents, the aptamer Raman features don't interfere with the target protein bands. Excitation with infrared wavelengths allows detection of the protein target, ricin in this case, even when it is presented in whole blood. The SERS detection method allows concentration quantitation following data treatment with either principle component analysis or hierarchical cluster analysis. Further, the detection method is easily adapted for use within a microfluidic platform where multiple targets can be detected in parallel using relatively small blood samples.

(541) **Enhancing Process Understanding in the Pharmaceutical Industry through Chemometric Data Analysis**

Allyson McIntyre[1], Richard Hart[1], Nicholas Pedge[1]; [1]AstraZeneca

Process analytical technologies (PAT) have been widely implemented in the pharmaceutical industry for analysis and understanding of drug manufacturing processes. Some examples include release of starting materials for manufacture and analysis of chemical processes, through to blend monitoring and uniformity of content in final product tablets. However, implementation of process analytical technology and subsequent data interpretation can prove challenging in many situations. The former is true at AstraZeneca, with a change in the business model involving more acquisitions or in-licensed projects there are fewer opportunities to gain long term process understanding using PAT. In addition, much of AZ manufacturing is completed by contract research organisations (CROs) which can present added difficulties in providing PAT support. An example of the PAT challenges of a late phase in-licensed project where the API manufacture was outsourced to a CRO will be discussed. The process stage was complicated and had a number of issues including variable reaction rates as well as the production of an impurity which had to be controlled. Therefore, better process understanding was required to ensure consistent manufactures with acceptable levels of this impurity. *In situ* UV/vis spectroscopy was used to monitor the reaction chemistry along with chemometric techniques such as principal component analysis, partial least squares and multivariate curve resolution (MCR) to build up knowledge and understanding of the process and develop a model

which could be transferred for use in the manufacture at the CRO. A suitable qualitative model was developed and successfully transferred to the CRO and used in the manufacture. Additionally, fundamental understanding of the process was obtained that would otherwise not have been observed had PAT and MVA/Chemometrics not been utilised.

(542) **Monitoring Plutonium Reprocessing Despite Disproportionation and Complexation: Uni- and Multivariate Approaches**

Robert Lascola[1], Edward Kyser[1], Patrick O'Rourke[1]; [1]Savannah River National Laboratory

Several operations in plutonium reprocessing at the US DOE's Savannah River Site are controlled by absorption measurements using colorimeters (filter photometers). Process conditions include large swings in nitric acid concentration, altering the distribution of Pu(IV) nitrate complexes. Each complex has a unique and complicated absorption spectrum, and the combined spectra overlap considerably. Despite these challenges, with appropriate filter selection univariate instruments measure Pu within 8-10%, meeting process requirements. Expansion of the monitoring scope has led to new acidities, where not only is the nitrate complexation different, but significant disproportionation of Pu(IV) to Pu(III) + Pu(VI) occurs. Negative measurement biases occur not only from loss of Pu(IV) but interference from Pu(III). Using full multivariate analysis, one can follow the disproportionation as a function of time, temperature, and acidity. Not only does this allow more accurate reporting of total Pu for process control, but it allows a study of the kinetics and equilibria of disproportionation.

(543) **Improving Confidence in FT-IR Analysis by Using Multiple Spectral Techniques**

Steve Lowry[1], Garry Ritter[1]; [1]Thermo Fisher Scientific

Modern FT-IR spectrometers make it very easy to acquire not only traditional mid infrared spectra but also high quality Near Infrared and Raman spectra in a few minutes. While it may be easy to acquire multiple spectra at the push of a button, productively managing and using the large amounts of data resulting from these instruments can be daunting. In this presentation we will describe the results of our research into applying spectral searching and chemometric techniques to multi-range data. We will discuss the challenges in: 1) data acquisition, 2) file formats/data scaling and 3) some approaches to creating combined reference spectra for libraries and multivariate statistical analysis . We will conclude with a discussion of scaling and weighting functions which are a key consideration when linking multiple spectral ranges for a single analysis.

(544) **Applying Process Analytical Technology (PAT) Tools to Early Active Pharmaceutical Ingredient (API) Development**

Shelly Li[1], Tasneem Patwa[1], Mengtan Zhang[1], Shane Eisenbeis[1], Michael Coutant[1]; [1]Pfizer Inc

Traditional Analytical support for early API synthesis process development has mainly relied on off line techniques such as chromatography. Off-line Analysis does not allow real-time insight into what is occurring in a chemical reaction and is often not amenable to reactions with unstable or transient intermediates. In recent years, spectroscopy based Process Analytical Technology (PAT) tools such as FTIR and Raman have proven to be valuable for real time monitoring of reactions involving reactive/unstable intermediates, critical endpoints, high energy reagents, high pressure, high temperature or cryogenic reactions. In Pfizer Groton, a multidisciplinary team is charged with providing online monitoring support during early API development. The team also serves as technical experts, training chemists and ***ysts on the use of the PAT tools and championing the development and adaptation of new PAT tools. To date, the core team has applied the PAT tools to a large variety of chemical processes across multiple project teams. In this presentation, we will discuss the reaction monitoring work flow, instrument capabilities, and several recent examples where PAT tools have been successfully applied during enabling work and API manufacture for process understanding and optimization, as well as in-process control.

(545) **Methods for Weighted Outlier Detection**

Mark Dewar, Suresh Thennadil[1], Alison Nordon[1], Craig Herdsman[2], Edo Becker[2]; [1]Strathclyde University; [2]BP Hull

The combination of spectroscopic analysis with chemometric modelling can be a powerful technique to enable prediction of sample properties of interest much more quickly and cheaply than standard laboratory reference analysis techniques. Due to the speed of these spectroscopic analysis techniques they have been applied online for safety, environmental and process optimisation applications within the petrochemical and other industries for over 20 years. However there still remain some issues related to chemometric modelling which must be overcome for these spectroscopic analysis techniques to be fully realised. These issues can include subjective decision making, recalibration scheduling and a large resource drain for the end user. For example there is a requirement for specialists to make subjective decisions regarding whether an observation is an outlier. This decision is usually guided by statistical measures but ultimately the final decision lies with the specialist. Different specialists will regard different samples as outliers causing variation in the chemometric models that are produced. Also the system can drift over time causing chemometric models to fail. The causes of drift are often due to instrumental variations or new process conditions. Deciding when to schedule recalibration is again subjective. Finally the task of building chemometric models can be very resource intensive. This resource drain can be a major burden on an organisation when specialist knowledge is in high demand. This project purposes to reduce the problem of required specialist knowledge and subjective decision making through the development smart auto-calibration algorithms including a robust outlier detection system. This is to be achieved through a battery of tests each with set confidence limits, providing objective standards for what constitutes an outlier. This way the system also removes the need for further resources.

(546) **High-resolution Laser Absorption Spectroscopy of Isotopes in Atmospheric-Pressure Laser Induced Plasmas**

Mark Phillips[1], Nicholas Taylor[1]; [1]Pacific Northwest National Laboratory

We present recent results using tunable diode laser spectroscopy to measure isotope-specific absorption spectra of atoms and ions in laser-induced plasmas. Differential laser absorption techniques are used to reduce noise and allow measurements to be performed at atmospheric pressures, under ambient conditions, and with low concentration samples or on transitions with low oscillator strength. These techniques are applied to characterize the time-resolved evolution of absorption lines of elements including uranium, and to determine pressure- and Stark-broadening and shifts for the observed transitions. In one example, small pressure-broadening contributions leads to observed absorption linewidths as low as 2.2 GHz (5.4 pm) for the uranium 861 nm atomic transition, in a laser-induced plasma under ambient conditions.

(547) **A Computer Simulation Study for Improving Isotopic Determination of Uranium by Atomic Emission Spectrometry**

George Chan[1], Xianglei Mao[1], Inhee Choi[1], Arnab Sarkar[1, 2], Richard Russo[1]; [1]Lawrence Berkeley National Laboratory, Berkeley, CA; [2]Bhabha Atomic Research Centre, Mumbai, India

Since the early days of the development of Bohr's atomic model, it has been recognized that atomic transitions of the same element but

from different isotopes emit light at slightly different wavelengths. Such shift is referred to as isotopic splitting and allows the different isotopes to be analyzed by means of atomic optical spectrometry. Of the various optical spectroscopic techniques, only atomic emission spectroscopy has the capability to measure a pool of multiple lines simultaneously. In addition, the ability to perform standoff or remote analysis is one great advantage of photon-emission based measurement (e.g., laser induced breakdown spectrometry) over other analytical techniques (e.g., mass spectrometry). It is well known that the two most common naturally occurring U isotopes, ^{235}U and ^{238}U, have distinctly different nuclear properties. Thus, the isotopic analysis of U is very important to nuclear industry, nuclear safeguards, regulatory agencies, forensics, national defense and related fields. Uranium is a line-rich element and its isotopic information is contained in many different emission lines. However, the U II 424.437 nm line was almost exclusively employed for isotopic analysis, particularly in atomic emission measurements.

In this work, a list of uranium emission lines that are potentially useful for isotopic analysis was experimentally screened, checked for additional potential spectral interference from database and compiled. Analytical performance of isotopic analysis of uranium in LIBS was investigated through computer simulation, with experimentally determined source-flicker, photon-shot and detector-read noises incorporated.

In this presentation, this computer simulation model will be described in detail. In addition, potential advantages of the use of multiple emission lines in isotopic analysis of uranium will be assessed.

(548) **Femtosecond and Nanosecond Laser Ablation Molecular Isotopic Spectrometry of Nuclear Materials**

Igor Jovanovic, Phyllis Ko[1], Jessica McNutt[1], Kyle Hartig[1]; [1]Pennsylvania State University

Laser-produced plasmas offer exceptional opportunities for detection of a wide range of materials in both laboratory and field conditions. While most of the applications of laser-induced breakdown spectroscopy require only elemental detection or quantification, there is a growing interest in extending and improving the techniques that also allow the isotopic composition to be obtained from laser-produced plasmas. It has been recognized recently that such developments could help address a variety of needs in the field of nuclear science and engineering, including nuclear forensics, nuclear fuel cycle monitoring, verification, and nuclear security. Detection of both nuclear materials and ancillary materials that offer information about the associated nuclear activities is desirable. Both elemental and isotopic characterization is needed, with some applications being conducted in the field or at a large standoff. Laser ablation molecular isotopic spectrometry, a technique closely related to laser-induced breakdown spectroscopy, has been recently proposed and demonstrated, exhibiting considerably greater isotopic shifts that can be detected even with low to moderate resolution spectrometers. This is of particular interest in characterization of nuclear materials such as uranium and plutonium, where the isotopic shifts are relatively small and difficult to measure. We describe our recent work on femtosecond and nanosecond laser ablation molecular isotopic spectrometry. We demonstrate by measurement on boron that accurate isotopic measurements are possible using this method even without the use of fast time gating detectors. We discuss the use of spectral pre-filtering and multivariate calibration and show that the accuracy of the reconstruction of isotopic composition is strongly dependent on the data analysis.

(549) **Carbon Isotope Separation and Molecular Formation in Laser-Induced Plasmas by Laser Ablation Molecular Isotopic Spectrometry (LAMIS)**

Meirong Dong[1,2], Xianglei Mao[1], George Chan[1], Jhanis Gonzalez[1], Jidong Lu[2], Richard Russo[1]; [1]Lawrence Berkeley National Laboratory, University of California, Berkeley, CA; [2]School of Electric Power, South China University of Technology, Guangzhou, Guangdong, China

Laser Ablation Molecular Isotopic Spectrometry (LAMIS) recently was reported for rapid isotopic analysis by measuring molecular emission from laser-induced plasmas at atmospheric pressure. This research utilized the LAMIS approach to study C2 and CN molecular formation from laser ablation of carbon isotopic samples. The isotopic shift for the Swan system of the C2 $\Delta v=1$ band and the violet system of the CN $\Delta v=-1$ band were chosen for carbon isotope analysis. Firstly, the temporal and spatial resolved measurements of 12C2, 12C13C, and 13C2 show that C2 forms from recombination reactions in the plasma. A theoretical simulation was used to determine the temperature from the molecular bands and to extract the isotopic ratio of 12C/13C derived from 12C2, 12C13C, and 13C2. Then the LAMIS was utilized for the carbon isotopic samples with the same aromatic ring (C=C) structure to study the CN formation which was based on the similar plasma conditions (temperature and electron density) of carbon isotopic samples. Temporal and spatial resolved measurements of 12C/13C were, respectively, derived from C2 and CN isotopic bands. The results show that there exists opposite relationship between CN and C2. The same source C for the chemical reaction to form CN and C2 would be the main reason. Our measurements provide the understanding of the chemical processes and analytical improvement in the laser induced plasma.

(550) **Laser Ablation Molecular Isotopic Spectrometry for Rare Isotopes of the Light Elements**

Alexander A. Bol'shakov[1], Xianglei Mao[2], Arnab Sarkar[2], Dale L. Perry[2], Richard E. Russo[1, 2]; [1]Applied Spectra, Fremont, CA; [2]Lawrence Berkeley National Laboratory, Berkeley, CA

Laser Ablation Molecular Isotopic Spectrometry (LAMIS) is a technique that uses optical spectra of transient molecular species produced in ablation plumes in air or buffer gases for rapid isotopic analysis of solid samples. This technique is similar to LIBS but optical emission spectra in LAMIS are measured at longer delays after an ablation pulse than used in LIBS. Molecular spectra are advantageous for isotopic analysis because the isotopic shifts in molecular emission are considerably larger than in atomic spectra. Molecules are generated effectively when the ablation plume cools down, resulting in an increase of the molecular emission in the plasma afterglow. We demonstrated detection of rare isotopes of H, B, C, N, O and Cl using LAMIS. Isotopic ratios of these elements are particularly variable in nature because of chemical reactivity and high solubility and volatility of the associated with them compounds. All of these elements are ubiquitous in nature as well as in practice, with carbon being the basis of many millions of compounds. Variation of the natural isotopic ratio $^{13}C/^{12}C$ in different materials ranges from 1.147% to 0.963%, which includes specific biological fractionation. Rare isotope ^{15}N is often used as a marker, particularly to track the efficiency of fertilizers in agronomy. Alteration of the $^{37}Cl/^{35}Cl$ ratio is distinctive in microbial reduction of anthropogenic chlorinated compounds. Heavy water nuclear reactors require deuterium enrichment 99.85%. Water-^{18}O is used as a precursor in the radiopharmaceutical industry. Deuterated drugs and stable isotopic tracers are increasingly used in the fields of medicine, pharmacology, nutrition and physiology for tracing biochemical processes. Boron isotope ^{10}B is essential in radio-chemotherapy, nuclear technology and neutron detection. To assess quality, specifications or aging of these materials, their isotopic homogeneity or distribution, and a degree of isotopic enrichment can be rapidly tested by LAMIS in

open air or inert gas flush, without using laborious and expensive mass spectrometry. Multiple applications of LAMIS are anticipated in the nuclear power industry, medical diagnostics and therapies, forensics, carbon sequestration, and agronomy studies.

(551) **Nanoscale and Surface Characterization of Biomaterials**

Greg Haugstad[1]; [1]University of Minnesota

Visualizing structures down to the nanometer scale, probing chemical composition, and measuring physical behaviors (e.g., friction) in relevant environments are at the core of biomedical research, particularly in considering biomaterial surfaces. Indeed, the materials utilized by biomedical technologies generate a long list of research questions related to characteristics at or near surfaces. These include the near-surface segregation of polymers and small molecules in drug-eluting biomedical (e.g., stent) coatings; crystalline versus amorphous states and near-surface mobility in pharmaceuticals (impacting drug activity); the location and activity of agents in nanoparticle-based drug delivery (e.g., for cancer therapy); the tribological behavior of inserted biomedical (e.g., catheter) surfaces; and much more. Scanning probe microscopy (SPM) is a tool known primarily for its ability to produce digital maps of surface topography. It does this by sensing nanonewton-regime, distance-dependent forces between a sharp physical stylus and a material surface. But this method of "finding" a surface can simultaneously characterize the physicochemical properties and behavior of the material surface. This presentation will overview AFM capabilities and provide vignettes on both imaging and physical property characterization using state-of-the-art AFM modes and methodologies.

(552) **Depth Profiling of OLED Materials by Cluster Ion Beams**

Sankar Raman[1], John Moulder[1], Scott Bryan[1], John Hammond[1], Nicholas Erickson[2], Russell Holmes[3]; [1]Physical Electronics; [2]Department of Electrical and Computer Engineering, University of Minnesota; [3]Department of Materials Science, University of Minnesota

The past few years have witnessed a paradigm shift in the use of cluster ion beams for the sputter depth profiling of organic materials in conjunction with the surface analysis techniques of XPS and TOF-SIMS. Today the use of low-energy monatomic ion beams such as Ar^+ for depth profiling has been replaced with cluster ions such as C_{60}^+ and Ar gas cluster ion beams for a wide range of organic materials, including multi-layer organic thin films and organic light emitting diodes (OLEDs). The improvements in the efficiencies for OLED structures have recently focused on the incorporation of more effective organic materials and the development of novel structures for arranging these organic materials. Multi-layer devices, graded composition devices and novel electrical contact layers to the organic materials are all being rapidly developed. The need for analytical techniques to elucidate the organic thin film structures as a function of device fabrication and lifetime studies is becoming extremely important. In combination with gas cluster ion beam (GCIB) sputtering, XPS and TOF-SIMS can now be used for quantitative chemical as well as molecular depth profiling techniques for OLED structures. The presentation will briefly review the XPS and TOF-SIMS techniques and the generation of gas cluster ion beams. The capability to provide quantitative compositional depth profiling of OLEDs will be illustrated from the XPS depth profile analysis of graded composition multilayer OLED films. Finally, TOF-SIMS in conjunction with GCIB depth profiling will be used to characterize unused and used blue phosphorescent OLED devices. The TOF-SIMS depth profiling data will be shown to provide molecular information on the degradation pathways for these used OLED devices.

(553) **A Multi-Technique Analytical Approach to Designing the Surface of a Hydrogel Biomaterial for Ophthalmic Applications**

Daniel Hook[1]; [1]Bausch + Lomb

There are many well accepted techniques that allow polymer chemists to formulate bulk properties such as modulus, oxygen transmission and water content into hydrogel biomaterials that are ultimately implanted into the body. All of these bulk property formulation "tricks" are amenable to large scale, high speed manufacturing lines and are widely practiced in the ophthalmic industry. Relative to bulk polymer formulations there are relatively fewer methods for tailoring surface properties that are scalable and do not impact manufacturing speed or cost negatively. Data will be presented summarizing a different approach for modifying the surface of a hydrogel biomaterial that involves using polymerizable surfactants as device forming co-monomers. The use of these monomers in conjunction with the information gained from surface analytical methods such as contact angle, X-ray Photoelectron Spectroscopy (XPS) and Time of Flight Secondary Ion Mass Spectrometry (TOF-SIMS) enable the selection of specific surface properties that are suited to the ocular physiological environment.

(554) **Investigation of Inhalation Ordered Mixtures using Time-of-Flight Secondary Ion Mass Spectrometry (TOF-SIMS)**

Mark Nicholas[1], Marja Savolainen[1], Carl Roos[1], Mats Joseflson[1], Magnus Fransson[1], Kyrre Thalberg[1]; [1]AstraZeneca R&D

INTRODUCTION Ordered mixtures are widely used as dry powder inhalation formulations [1]. Ordered mixtures consist of micronized drug and excipient particles attached to the surface of larger (50-100μm) carrier particles.

Time-of-flight secondary ion mass spectrometry (TOF-SIMS) is a novel sub-micron chemical imaging technique for the analysis of ordered mixtures. It has previously been used to characterize surface properties of a coated lactose carrier [2] and the distribution of drugs and excipients in controlled release formulations [3].

EXPERIMENTAL Ordered mixtures of budesonide (BUD) and beclomethasone dipropionate (BDP) with lactose fines (d50=2.9 μm) and carrier (Respitose SV003, d50=57 μm) were prepared using high shear mixing. Three different formulation compositions were manufactured: 2% w/w and 10% w/w drug as well as 2% w/w drug with 8% w/w lactose fines.

The formulations were analyzed by acquiring TOF-SIMS images of the carrier particle surfaces. In addition, a next generation pharmaceutical impactor (NGI) with pre-separator was used to separate the carrier particles from the inhalable particles, and TOF-SIMS imaging was done of the inhalable particles. Multivariate image analysis was used to compare degree of drug coverage and homogeneity.

RESULTS TOF-SIMS imaging of the blends shows that the drug distribution pattern on the carrier surface is dependent on the nature of the drug, the amount of the drug, and the presence of absence of lactose fines. For 2% drug and carrier, the drug was distributed over the carrier surface without extensive agglomeration. The degree of coverage was higher for the 2% BUD compared to 2% BDP. At 10% drug load, a 'crust' of agglomerated fine particles was formed, and the degree of coverage was highest for both drugs. The 2% drug and 8% lactose fines displayed a more complicated pattern. The TOF-SIMS analysis of the samples collected from stage three of the NGI indicates that the inhalable size fraction contains aggregates that consist of both the drug and lactose fines.

REFERENCES

1. Iida, K, et. al. Chem Pharm Bull 2003, 51 (12), 1455-1457.
2. Zhou, QT, et. al. J Pharm Sci 2011, 100, 3421-3430.
3. Belu, AM, et. al. Anal Chem 2000, 72(22), 5625-5638.

(555) **Application of Surface Characterization Techniques in Pharmaceutical and Biopharmaceutical Development**

Xia Dong; [1]Eli Lilly and Company

Surface characterization techniques have been increasingly utilized for the drug development due to their ability to provide insight into the composition and performance of drug products. These techniques, such as TOF-SIMS, XPS, SEM/EDS, etc, have their own strength and limitations, and combination of multiple techniques usually provide complimentary information. This presentation will focus on the use of surface characterization techniques for root cause analysis of undesirable performance related to drug products and packaging materials. The combination of chemical identification and imaging capabilities of surface characterization techniques makes them powerful tools for foreign materials analysis and particle characterization. The strengths and limitations of various surface techniques (chemical and physical) will also be discussed.

(556) **Evaluation of an Ultra-compact NIR Spectrometer for Pharmaceutical Product and Process Monitoring**

Dongsheng Bu[1], Boyong Wan[1], Gary McGeorge[1], Doug Both[1]; [1]Bristol-Myers Squibb

Ultra-compact, lightweight, fast and cost effective Near Infrared (NIR) spectrophotometers have the potential to change the way we use spectrophotometers in the pharmaceutical industry. The promise of low-cost NIR spectrophotometers is that they provide the opportunity for on-line, multi-point, rapid analyses or multi-point deployment with a high ROI. Besides the obvious size advantages, compact NIR devices could have trade-offs and may suffer from poor spectral resolution, low signal-to-noise or poor instrument stability, limiting their usefulness in some pharmaceutical applications. It is, therefore, important to understand measurement performance in comparison to other types of NIR instruments. This paper presents our evaluation results on a Micro NIR device. Three basic and distinct evaluations will be presented. Firstly, USP Chapter 1119 provides a standardized platform by which to evaluate instrument stability, noise, wavelength accuracy and photometric linearity. Secondly, feasibility results will be presented from an application to measure tablet hardness which showed good correlation between spectral slope and sample hardness. A third demonstration will illustrate the utility of measuring the water content of cellulose. Finally a commentary will be provided on the future use of these innovative NIR spectrophotometers.

(557) **Optimization of FT-NIR Instrument Parameters on the Performance of a Content Uniformity Method: A Multivariate Figure of Merit Study**

Zhenqi Shi[1], Greg Doddridge[1]; [1]Eli Lilly and Company

Ever since near infrared spectroscopy was introduced to the pharmaceutical industry, a tremendous amount of effort was to leverage the power of chemometrics to extract out the best possible signal to correlate with the analyte of the interest. In comparison, only a few studies address the potential impact of instrument parameters, such as resolution and co-adds, on the method performance. In this study, a multivariate figure of merit approach was used to evaluate the effect of the instrument parameters of a FT-NIR spectrometer on the performance of a content uniformity method. A Bruker MPA FT-NIR spectrometer was used for the investigation of five combinations of resolution and co-adds, including 32cm-1 and 16 co-adds, 32cm-1 and 256 co-adds, 8cm-1 and 32 co-adds, 4cm-1 and 16 co-adds and 4cm-1 and 256 co-adds. Given the balance among underlying chemistry, instrument parameters, chemometrics and measurement time for the intended purpose as a CU method, 8cm-1 and 32 co-adds in combination with appropriate 2nd derivative preprocessing was found to be the best choice. The consideration for optimizing instrument parameters in order to maximize the method performance for the intended purpose for future NIRS method development will also be addressed.

(558) **Monitoring, Online and in Real Time, the Coating of an Active Solution onto Tablets by Near Infrared Spectroscopy**

Benoit Igne[1], Hiroaki Arai[2], Hanzhou Feng[1], James Drennen[1], Carl Anderson[1]; [1]Duquesne University; [2]Daiichi Sankyo Co., LTD

Tablet coating is primarily employed in the pharmaceutical industry to give solid dosage forms an aesthetic appearance, mask undesirable taste, and control the rate of drug release. It can also be used to coat an active ingredient onto a tablet core when a specific release pattern is required or to enhance stability. Typically, a polymer solution/suspension is sprayed onto tablets in a fluidized-bed or a pan-coating system. The coating unit operation is traditionally monitored by performing at-line measurements of quality attributes such as tablet weight gain. More recently, near-infrared spectroscopy has been used to perform at-line and on-line tablet quality measurements, consistent with a process analytical technology paradigm. In this study, the coating of acetaminophen onto tablet cores in a pan coater was monitored in real-time by near infrared spectrometry. Processing parameters were set according to a design of experiment where spray speed, active concentration, and the coating solution polymer concentration were varied. Near-infrared measurements were performed on-line as well as off-line and UV measurements were used to develop models and confirm results. Online near-infrared spectroscopy was demonstrated to effectively monitor the coating of the active ingredient and allowed the control of the process, in real time. The accuracy of online measurements was confirmed by off-line spectroscopic evaluations and UV analysis.

(559) **Regulatory View of NIR Implementation in Pharmaceutical Industry**

Bogdan Kurtyka[1]; [1]Food and Drug Administration

Near-Infrared Spectroscopy has been successfully used in pharmaceutical manufacturing for quality control and process control. Together with implementation of Quality by Design and Real Time Release Testing, NIR has provided new opportunities and challenges to both the pharmaceutical industry and regulators regarding how to implement and evaluate the novel methods. The presentation will discuss scientific and regulatory aspects of NIR for monitoring and control of pharmaceutical processes, including consideration for method development, validation, submission, and maintenance.

(560) **Finished Product Identity Testing of a Pharmaceutical Dosage Form with API at a Low Concentration Using Reflectance Near Infrared Spectroscopy**

Jerry Jin[1]; [1]Actavis

The identity of a finished product is probably the most important specification the pharmaceutical industry has to test prior to product release for commercialization or clinical trials. The United States Pharmacopeia lists infrared spectroscopy, thin-layer chromatography and ultraviolet light absorption as the analytical methods for finished product identity testing. These traditional methods require tedious sample preparation and are therefore time and resource consuming. We presented an alternative analytical method, near infrared (NIR) spectroscopy, for rapid and cost-effective identity testing of a pharmaceutical tablet product that contains a highly potent API with a concentration as low as 0.2% (w/w). Due to its weak light absorption, NIR is however generally considered not suitable for trace analysis. We explored the limit of detection of such a low-dosage form afforded by a grating-based NIR spectrometer in reflectance measurement mode. Placebos of this tablet product were prepared following its master formula. Different amounts of API were added to the placebos to make synthesized samples with API concentration ranging from 0% to 0.2%. NIR spectra of these

samples were pretreated by the 2nd derivatives, and partial least-squares discriminant analysis was used to develop a classification model for discriminating the synthesized dosage forms from the placebo. We found that while samples of lower concentrations 0.03% and 0.05% cannot be differentiated from the placebo, samples of higher concentration 0.1% and 0.2% are well differentiated from the placebo. A limit of detection at least 0.1% can be established for this dosage form. This finding supports the application of the NIR spectroscopy for identity verification of the finished product with 0.2% API. The practicability of this NIR method is further substantiated by the ability of this method to discriminate among four 0.2% APIs each having a similar chemical structure to the target API. All of the sample discriminations were achieved without wavelength selection, as opposed to the common concept that spectral features specific to API have to be selected for identifying low-dosed tablets.

(561) **Towards Stimulated Raman Scattering for Cell Type Differentiation**

Matthew Kole[1], Matthew Schulmerich[1], Sarah Holton[1], Rohit Bhargava[1, 2, 3]; [1]Department of Bioengineering and Beckman Institute for Advanced Science and Technology, University of Illinois at Urbana-Champaign, Urbana, IL; [2]Department of Electrical and Computer Engineering, University of Illinois at Urbana-Champaign, Urbana, IL; [3]University of Illinois Cancer Center, University of Illinois at Urbana-Champaign, Urbana, IL

Stimulated Raman scattering (SRS) has emerged as a powerful rapid-imaging microscopy tool which derives contrast from a specimen's chemistry without the use of external dyes or labels. Recently, SRS has been used to identify a cell's nucleus and cytoplasm, demonstrating the first step towards the use of this technique for optical histopathology. Here, we evaluate the possibility for developing SRS instrumentation to differentiate between cell types or other functional characteristics. A key component of this is improving the ability to measure low-wavenumber Stokes shifts ($<=1500\ cm^{-1}$). We compare models and results to existing optical methods which allow for cellular differentiation, including Fourier transform infrared (FT-IR) and spontaneous Raman imaging, and highlight the potential impact of the advantages that SRS can provide.

(562) **Application of Terahertz Chemical Imaging to Pharmaceutical Coating: Evaluation of a Tableted Immediate Release Dosage**

Thomas Hall[1], Dawn Herrick[1], Kristine Beaulieu[1], Charles Kish[1]; [1]Pfizer Consumer Healthcare

Pharmaceutical tablets are commonly produced with a nonfunctional cosmetic coating that serves to refine their aesthetic qualities (e.g., color, texture, taste, gloss, aroma) and to improve ease of swallowing. These coatings usually do not significantly impact the pharmacological properties or chemical stability of the tablet over time. Here we report an unusual case where properties of a cosmetic film coat did have a negative influence on product appearance over time. Chemical imaging in the terahertz (THz) region was employed to investigate the properties of the tablets' film coat and to provide evidence regarding the cause of the undesirable phenomenon. The same technology was used in conjunction with statistically designed experiments to show that a modified coating process intended to resolve the issue was effective. Finally, THz image analysis was used to verify that laboratory scale experiments had been reliably scaled-up for use in the manufacturing plant. In the course of this work it was shown that THz chemical imaging data could be correlated with *in vitro* dissolution performance of the dosage form. The possibility of using THz data to predict dissolution and other properties of immediate release dosages is discussed

(563) **Quality by Design and Spectroscopy: A Perfect Match**

John Wasylyk[1], Ming Huang[1], Robert Wethman[1], Daniel Hallow[1], Douglas Mcleod[1]; [1]Bristol-Myers Squibb Co.

In the Pharmaceutical Industry, Quality by Design (QbD) serves as a means for the transformation of how drugs are discovered, developed, and commercially manufactured. Spectroscopy plays a key role in enhancing process knowledge by gaining key information that allows the research scientist to establish critical design spaces. We have utilized in-line and off-line spectroscopy tools that enable rapid analyses with minimal sampling. We will present examples which include in-line Raman Spectroscopy for following the progression of reactions during the process development phase that not only define design space limitations but also provided valuable kinetic information. In addition, we utilized off-line spectroscopy techniques to facilitate rapid evaluation of process steps during the screening and evaluation stages. Both in-line and off-line spectroscopy techniques played a key role in defining not only the knowledge transferred to manufacturing but also provided insight as to if specific in-line spectroscopy methods were critical in manufacturing.

(564) **Twists and Turns: VCD Chiral Assignment of Atropisomers in Drug Discovery**

Steven Wesolowski[1], Don Pivonka[2]; [1]AstraZeneca; [2]Incyte

Atropisomers exist when axial chirality is present as a result of conformationally restricted rotation around a single bond. The interconversion rate of the individual atropisomers is critical to the assessment of chiral stability of a drug throughout scale-up, development, production, and storage as well as *in vivo* pharmacokinetics. We describe the application of vibrational circular dichroism spectroscopy coupled with quantum mechanics simulations to assign the absolute axial chirality and measure the racemization half-life of a series of potential anxiolytic drugs that act as γ-aminobutyric acid modulators.

(565) **Infrared and Raman Analysis of Polymorph Content in Early Development**

Don Pivonka[1], William Rocco[1]; [1]Incyte Corporation

Vibrational spectroscopy has evolved as one of the premier analytical techniques for the analysis of polymorphism in both "drug substance" and formulated drug product. This lecture will present a case study of polymorph analyses throughout the progression in pharmaceutical development to include: initial analysis of the synthetic API, polymorph stability under elevated temperature and humidity and excipient compatibility. Within the development process, vibrational spectroscopy was used to identify and understand the extreme dependence on polymorphic form on exposure of formulations dosed in animals. The ability of infrared and Raman spectroscopy to identify kinetics of conversion from thermodynamically less favorable forms, which produced good exposure, to a form with greater thermodynamic stability, which exhibited little to no exposure, proved extremely valuable throughout the formulation and dosing process.

(566) **Exciton and Biexciton Dynamics in CdSe/ZnS Nanoparticles by Two-Dimensional Kinetics**

Mark Berg[1], Kalyanasis Sahu[1], Haorui Wu[1]; [1]Department of Chemistry and Biochemistry, University of South Carolina

Previously, MUPPETS (multiple population-period transient spectroscopy) has been used to measure two-dimensional kinetics in two-level systems. This work is the first to extend MUPPETS to a multilevel, excitonic system. As in two-level systems, a 2D experiment can measure the extent of heterogeneity in the exciton decay. In an excitonic system, it can also distinguish biexciton dynamics from the rapid exciton decay of photoproducts, and it can detect correlations in between biexciton and exciton decay

mechanisms. We show that the biexciton decay is strongly dispersed (nonexponential) in contradiction to the predictions of simple Auger-recombination models. The exciton signal has a large and highly dispersed decay before the radiative relaxation time. Contrary to expectations, the results do not support a subpopulation of defective particles, but do support a surface relaxation in response to the formation of the exciton. No evidence is found for a correlation between the exciton and biexciton decays. The fluence-dependence of the measurements has been measured and modeled to show that no higher excitons are involved. An external calibration of the relative size of effects from solvent heating show them to be too small to affect the results. The methods demonstrated here can be applied to other excitonic systems, including dye aggregates, photosynthetic systems and conjugated polymers. Based upon work supported by the National Science Foundation under CHE-1111530

(567) **Water on the Edge: Hydrogen Bonding through the Eyes of Vibrational Spectroscopy**

Alexander Benderskii[1]; [1]University of Southern California

We will review the surface-selective vibrational sum frequency generation (VSFG) spectroscopy as a probe of the hydrogen bond network at the air-water interface. Water's two intrinsic vibrational modes, stretch and bend, both report on the hydrogen bonding but in different ways. VSFG measurements of the stretch and bend spectra of the air/water interface will be presented and the lineshapes analyzed in terms of their information content. In particular, we focus on the "free OH" species of water molecules straddling the interface, which probe hydrogen bonds in the first monolayer of waters, and compare these with bulk water H-bonds.

(568) **Ballistic Energy Transport in Oligomers**

Igor Rubtsov[1], Natalia Rubtsova[1], Zhiwei Lin[1]; [1]Tulane University

Energy transport on molecular level is investigated using dual-frequency relaxation-assisted two-dimensional infrared spectroscopy. The transport is initiated by vibrational excitation (relaxation) of a localized terminal vibrational mode and probed by influence of the excess energy on the frequency of another mode localized at another end. Very efficient energy transport is found in molecules with repeating units (oligomers), which occurs with a constant speed, suggesting a ballistic transport mechanism. Such transport regime was observed in compounds featuring two types of molecular backbones, polyethylene glycol (PEG) and perfluoroalkane; a faster speed was found via PEG chains where it is ca. 500 m/s (5 Å/ps). The experiments were performed in several solvents and in a solid phase. Interplay between the diffusional and ballistic transport mechanisms is discussed.

(569) **The Effect of Ion Pairing on the Dynamics and Spectroscopy of the Strong Electrolyte Solutions**

Wei Zhuang[1]; [1]Dalian Institute of Chemical Physics

We carried out series of spectral modeling based on the molecular dynamics simulation to help understanding the dynamic events in the ionic solution systems. By calculating different ionic solution spectra based on the same simulation trajectory ensemble, we achieved a better understanding of the underlying physics. Simulation suggests that ion pairing is the reason of various spectroscopic features. Spectroscopy provides vivid microscopic evidences for the existence of ion pairing.

(570) **Ultrabroadband Two-Dimensional Electronic Spectroscopy of Coupled Semiconducting Carbon Nanotube Thin Films**

Thomas McDonough[1], Randy Mehlenbacher[1], Maksim Grechko[1], Meng-Yin Wu[1], Michael Arnold[1], Martin Zanni[1]; [1]University of Wisconsin-Madison

We report ultrabroadband two-dimensional electronic spectroscopy (2D ES) of bandgap-selected semiconducting carbon nanotubes in coupled thin films suitable for photovoltaics. Previous transient absorption and anisotropy measurements indicate that energy transfer proceeds from large to small bandgap tubes via a fast, long-range process followed by a slow, short-range process. However, these methods are unable to discern whether transfer occurs sequentially from large to small bandgap tubes or whether transfer can occur non-sequentially but the rate of transfer decreases with increased difference in bandgap. In 2D ES, the evolution of distinct crosspeaks between the interband optical transitions (E_{ii}) of different bandgap nanotubes as a function of waiting time maps out the energy transfer pathway. Furthermore, we employ a supercontinuum pump and probe spanning a 500-1500 nm range, generated by focusing several μJ of 800 nm fundamental into an undoped yttrium aluminum garnet (YAG) crystal. Utilizing a supercontinuum allows us to collect 2D electronic spectra over a much broader frequency range than is possible with the output of an optical parametric amplifier. Thus, we are able to access both the E_{11} (1050-1350 nm) and E_{22} (650-750 nm) interband optical transitions of each of the film's five different bandgap tubes. These results on the energy transfer dynamics of nanotube films inform future efforts to tailor film morphology in nanotube photovoltaic devices, in which efficient exciton diffusion to the heterojunction interface is key to efficient charge separation.

(571) **Laser Ablation-Laser Induced Breakdown Spectroscopy (LA-LIBS) for the Measurement of Total Elemental Concentration in Soils**

Alejandro Molina[1], Jhon Pareja[1], Sebastian López[1], David W Hahn[2], Daniel Jaramillo[1]; [1]Universidad Nacional de Colombia - Sede Medellín; [2]University of Florida

The performances of traditional laser-induced breakdown spectroscopy (LIBS) and laser ablation-LIBS (LA-LIBS) were compared by quantifying the total elemental concentration of potassium in highly heterogeneous solid samples, namely soils. Calibration curves for a set of fifteen samples with a wide range of potassium concentrations were generated. The LA-LIBS approach produced a superior linear response than the traditional LIBS scheme. The analytical response of LA-LIBS was tested with a large set of different soil samples for the quantification of the total concentration of Fe, Mn, Mg, Ca, Na and K. Results showed an acceptable linear response for Ca, Fe, Mg and K while poor signal responses where found for Na and Mn. Signs of remaining matrix effects for the LA-LIBS approach in the case of soil analysis were found and discussed.

(572) **Effect of Solid Substrates on Reproducibility of LIBS Measurements**

Sergey Mozharov[1], Brian Marquardt[1]; [1]University of Washington

Laser-Induced Breakdown Spectroscopy is a widely used analytical technique that provides rich information about the chemical elements present in the sample. Despite many advantages of LIBS such as high speed of data generation or the convenience of remote non-contact measurements that can be performed with no sample preparation, this method has relatively low reproducibility that makes it difficult to use LIBS for quantitative analysis. We studied different ways to analyze liquid samples with LIBS and found that sensitivity and reproducibility of measurements were improved when the samples were dried on a solid substrate prior to the measurements. In this presentation, we present the analysis of these observations and discuss factors that influence the metrological characteristics of LIBS when applied to liquid samples.

(573) **Comparative Study of Laser Induced Breakdown Spectroscopy (LIBS) and Laser Ablation Molecular Isotopic Spectroscopy (LAMIS)**

Krishna Kanth Ayyalasomayajula[1], Herve Sanghapi[1], Bader Alfarraj[1], Fang Yueh[1], Jagdish Singh[1, 2], Dustin McIntyre[3]; [1]Institute for Clean Energy Technology, Mississippi State University, Starkville, MS; [2]JPS Advanced Technology LLC, Starkville, MS; [3]U.S. Department of Energy, National Energy Technology Laboratory, Morgantown, WV

Laser induced breakdown spectroscopy (LIBS) is a laser spectroscopic technique that is widely used in various fields such as material science, forensic science, biological science and chemical and pharmaceutical industries. Laser Ablation Molecular Isotopic Spectrometry (LAMIS) is an emerging technique to perform optical isotopic analysis of different types of samples. The goal of this study is to compare the limit of detection (LOD) of LIBS and LAMIS using spectra of SrO in Al_2O_3 matrix. LIBS and LAMIS measurements were performed in binary mixtures to understand the matrix effects on the performance of the LAMIS technique. The LIBS analysis was performed using radiative transitions from the Sr atomic emission. The LAMIS analysis was performed using radiative transitions from the SrO molecular band emissions. In this study we have collected LIBS and LAMIS spectra by varying various parameters such as laser energy, gate delay and gate width to optimize the LIBS and LAMIS signals. Calibration models were developed to quantify the Sr concentration in a binary matrix by applying a simple linear regression data analysis to LIBS and LAMIS spectra. The LAMIS plasma and electron temperature values were measured and subsequently used to optimize the Sr molecular band emission for concentration measurement.

(574) **Mechanisms Leading to Signal Enhancement in NIR fs-fs and NIR ns-ns Double-Pulse Laser-Induced Breakdown Spectroscopy**

Prasoon Diwakar[1], Sivanandan Harilal[1], Ahmed Hassanein[1]; [1]Center for Materials Under eXtreme Environment, School of Nuclear Engineering, Purdue University

Emission properties of collinear NIR femtosecond-femtosecond and NIR nanosecond-nanosecond double-pulse laser induced breakdown spectroscopy are discussed. In particular, the role of excitation energy, inter-pulse delay times, and energies of the reheating pulses on LIBS sensitivity improvements are studied. Significant emission intensity enhancement was noticed for both fs-fs and ns-ns DPLIBS schemes, however laser ablation as well as the signal enhancement mechanisms differ for both the cases. Our results show that the significant signal enhancement noticed in fs-fs double pulse scheme is strongly dependent on characteristic electron-ion relaxation time and hence inter-pulse delays. Spectroscopic excitation temperature analysis showed that the improvement in signal enhancement is caused by efficient reheating of the pre-pulse generated plume by the delayed pulse. The signal enhancement in fs-fs DPLIBS schemes is also found to be related to the upper excitation energy of selected lines; more enhancements noticed for line originating from higher excitation energy levels. A dual peak in signal enhancement was observed for different inter-pulse delays for ns-ns DPLIBS scheme, which is explained based on temperature measurement and shockwave expansion phenomenon.

(575) **Characterization of Single and Double Pulse LIBS with Nd:YAG and CO2 lasers for Improving Signal-to-Noise Ratio**

Justin Freeman[1], Prasoon Diwakar[1], Sivanandan Harilal[1], Ahmed Hassanein[1]; [1]Purdue University

Laser-induced breakdown spectroscopy (LIBS) is a technique used to identify elemental constituents from unknown samples. Despite several advantages such as *in situ* analysis, minimal sample preparation, and real-time results, LIBS suffers from limited sensitivity and limits of detection that are often several orders of magnitude lower than other mass detection based analytical laboratory techniques. In order to improve sensitivity, LIBS research has investigated various laser and collection system parameters, such as laser wavelength, pulse duration, collection gate delay, and gate width, all in an effort to optimize signal-to-noise ratio (SNR) and improve LIBS system limits of detection.

In this work, we present results comparing single and double pulse LIBS experiments. Nd:YAG and CO2 lasers operating at 1.064 μm and 10.6 μm, respectively, are used for single pulse experiments, while a combination of Nd:YAG prepulse and CO2 reheating pulse are used in double pulse experiments. The effects of long wavelength, long pulse heating by CO2 laser on LIBS spectra and analytical results are identified and compared with single pulse Nd:YAG LIBS systems. Spectral collection parameters such as gate delay and gate width are independently determined for each laser heating regime through time-resolved SNR calculations throughout the evolution of plasma emission. Subsequent time-integrated LIBS spectra and SNR are used to compare sensitivity of single and double pulse heating regimes with the goal of improving and significantly enhancing LIBS detection limits.

(576) **UV Resonance Raman (UVRR) Examines the Fibril Structure of a Model Polyglutamine Peptide, D2Q10K2**

Sanford Asher[1], David Punihaole[2], Liqi Feng[1], Jonathan Weisberg[1]; [1]Department of Chemistry, University of Pittsburgh; [2]Molecular Biophysics & Structural Biology Graduate Program, University of Pittsburgh

Huntingtons's disease is caused by expansions in polyglutamine (polyQ) rich DNA sequences. These polyQ repeats cause the proteins to aggregate into amyloid-like fibrils. Little is known about the structure of polyQ repeats of proteins and how they lead to aggregation. We use UVRR to investigate model polyQ peptides to elucidate fibril structure and the fibrillization mechanisms. We directly monitor the conformation and hydrogen bonding about the polyQ peptide bonds as well as the sidechain conformations and hydrogen bonding.

(577) **Advanced Instrumentation for Deep UV Raman Spectroscopy and Microscopy**

Vladislav Yakovlev[1], Georgi Petrov[1], Maria Troyanova-Wood[1]; [1]Texas A&M University

Vibrational Raman spectroscopy is one of the most powerful optical spectroscopic techniques, which plays a critical role in providing with a detailed structural information about molecules. The ability to collect Raman spectra using excitation of tunable visible and deep-ultraviolet radiation greatly improves our ability to interrogate molecular structure and undergoing transformations. However, most of the existing approaches are either too complex or too expensive to be used for the majority of those studies. As a part of the ongoing effort in our laboratory, we have developed and validated three alternative strategies for achieving reliable deep-UV (<250 nm) generation suitable for resonant Raman studies. The first one is based on the forth harmonic generation of a microchip Nd:YAG laser operating at 946 nm [1]. The second laser system is based on high-repetition rate picosecond laser, which is frequency converted using stimulated Raman scattering and is discretely tunable throughout the visible and the deep UV spectral region [2]. The last system is based on a nanosecond fiber laser which pumps an optical parametric amplifier seeded by a narrow-band tunable diode laser. Each of the above systems is based on the all-solid-state laser design utilizing diode-pumping and providing sufficiently long life-time (>20,000 hours) at a fraction of cost of intracavity-doubled Ar-ion laser. In the talk, we will discuss other aspects of the deep-UV Raman microspectrometer and outline several applications which are currently being developed in our laboratory.

References:
[1] M. Troyanova-Wood, G. I. Petrov, and V. V. Yakovlev, J. Raman Spectr. (2013) Accepteed.
[2] G. I. Petrov, and V. V. Yakovlev, Op. Lett. (2013) Submitted.

(578) **Resonance Raman Intensity Analysis of ClNO2 in Methanol**

Sophia Hayes[1], Marilena Trimithioti[1]; [1]University of Cyprus

Halogens such as chlorine are converted from halides, including $ClNO_2$, to reactive radicals by UV solar radiation. These radicals can affect ozone production and destruction in the stratosphere. Recently, it became clear that halogen radicals can also play a significant role in the chemistry of the troposphere. The photochemistry of $ClNO_2$ has been the subject of several studies in the gas and solid state that demonstrated a clear phase-dependent reactivity. Here, we report our initial studies of nitryl chloride in solution. Resonance Raman (RR) spectra of $ClNO_2$ dissolved in methanol after excitation within the 1^1A_1–2^1A_1 absorption band (D band) in the region 200-240 nm are presented. RR intensity along the NO symmetric stretch coordinate (ν_1) at 1291 cm^{-1} is observed at all excitation wavelengths, while limited intensity corresponding to the transition of the N-Cl symmetric stretch (ν_3) was only observed at 199.8 nm, while no intensity corresponding to the O-N-O symmetric bend (v2) was observed. Depolarization ratios and absolute Resonance Raman cross sections for ν_1 were obtained at several excitation wavelengths spanning the D band. Depolarization ratios were found to deviate significantly from 1/3, consistent with more than a single dipole-allowed electronic transition contributing to the scattering. RR intensity analysis (RRIA) reveals that two closely-spaced excited electronic states contribute to the scattering, which are dissociative along the Cl-N coordinate. In this study the role the solvent environment plays in $ClNO_2$ state energetics and excited structural evolution along fundamental coordinates will be discussed.

(579) **Exploring Membrane Protein Structure in the Context of Lipid Type, Protein Sequence and Protein-Protein Interactions by dUVRR**

Jason Cooley[1], Mia Brown[1], Michael Eagleburger[1], Iban Ubarrextena-Bilandia[2], Anna Klass[1], Jian Xiong[1], Renee JiJi[1]; [1]University of Missouri; [2]Icahn Mt. Sinai Medical School

Despite the fact that individual membrane proteins are found in and require membranes with specific lipid contents and fluidities, the bulk of membrane protein structure analyses have been carried out in detergent micelle environments. The dominant paradigm has been that membranes provide a cozy hydrophobic wrapping for a protein's greasy α-helical or β-sheet transmembrane spans. However, recent evidence indicates that significant differences in structure may arise from the manner in which the protein is solubilized. Does the bilayer and its physicochemical properties impart specific structural constraints to a protein? It is known that structural fluctuations are important for facilitating function in a membrane environment. A prime example of this need for fluctuations lays in the observation that the helicity of a transmembrane domain may facilitate its being recognized as a substrate for proteolysis within the membrane proper. Intramembrane proteolytic reactions of this ilk are best known for their roles in disease, e.g. by producing insoluble hydrophobic peptide fragments such as the Alzheimer's related Aβ peptides, but these reactions are also important in a myriad of regulatory roles in a given cell. Yet, it remains wholly unclear how, where and why helical content changes in these cleavable amphiphillic proteins, much less how this helical instability is related to eventual cleavage. This lack of knowledge can be traced back to the fact that structural analysis of membrane embedded proteins remains a challenging endeavor with our current spectroscopic toolkit. With this in mind, we have recently explored the use of deep-UV resonance Raman spectroscopy as an alternative methodology for membrane protein structural analysis in intact membranes. Initial studies have demonstrated that dUVRR is capable of simultaneously monitoring peptide backbone structural content and its relative hydration in a variety of lipid based sample preparations. We extend these findings here by addressing issues of the synergistic relationship between a proteins structure, the membrane environment it is found in and how these relate to the proteins amino acid sequence content. Strategies of isotope-assisted dUVRR analysis and spectral interpretation are outlined, with the aim of elucidating, localizing and predicting structural fluctuations in membrane embedded protein samples associated with intramembrane protein cleavage.

(580) **UV Raman Spectroscopy as a Probe of Structure and Dynamics of Amyloid Fibrils**

Igor Lednev[1], Dmitry Kurouski[1]; [1]University at Albany, SUNY

Amyloid fibrils are associated with many neurodegenerative diseases. All known amyloids including pathogenic and non-pathogenic forms display functional and structural heterogeneity (polymorphism) which determines the level of their toxicity. Despite a significant biological and biomedical importance, the nature of the amyloid fibril polymorphism remains elusive. We utilized deep UV resonance Raman spectroscopy (DUVRR) as well as other advanced vibrational techniques to probe the core, the surface and supramolecular chirality of fibril polymorphs. A new type of folding–aggregation phenomenon, spontaneous refolding from one polymorph to another was discovered [1].

Hydrogen-deuterium exchange DUVRR spectroscopy [2] combined with advanced statistical analysis [3] allowed for structural characterization of the highly ordered cross-β core of amyloid fibrils. We reported several examples showing significant variations in the core structure for fibril polymorphs including parallel and anti-parallel β-sheet in Amyloid β fibrils [4], (2) twisted β-strands in prion amyloid fibrils [5] and dissimilar resistance to the hydrogen-deuterium exchange of fibril polymorphs prepared from the same protein, but with a different state of disulfide bonds [6].

1) D. Kurouski, W. Lauro & I. K. Lednev. (2010). Amyloid fibrils are "alive": spontaneous refolding from one polymorph to another. Chem Comm 46, 4249-4251.
2) S. A. Oladepo, K. Xiong, Z. Hong; S.A. Asher, J. Handen & I. K. Lednev (2012). UV resonance Raman investigations of peptide and protein structure and dynamics." Chem Rev 112, 2604-2628.
3) V. A. Shashilov & I. K. Lednev (2010). Advanced statistical and numerical methods for spectroscopic characterization of protein structural evolution. Chem Rev 110, 5692-5713.
4) Popova, L.A.; Kodali, R.; Wetzel, R.; Lednev, I.K. (2010) Structural Variations in the Cross-β Core of Amyloid β Fibrils Revealed by Deep UV Resonance Raman Spectroscopy, J Am Chem Soc, 132, 6324-6328.
5) Shashilov, V.; Xu, M.; Makarava, N.; Savtchenko, R.; Baskakov, I. V.; Lednev, I. K. (2012) Dissecting Structure of Prion Amyloid Fibrils by Hydrogen-Deuterium Exchange Ultraviolet Raman Spectroscopy. J. Phys. Chem. B, 116, 7926–7930.
6) Kurouski, D.; Lednev, I.K. (2011) The impact of protein disulfide bonds on the amyloid fibril morphology. Int. J. Biomedical Nanoscience and Nanotechnology, 2, 167-176.

(581) **Terahertz Spectroscopy of Hydrogen-Bonded Glass-Forming Liquids**

Juraj Sibik, Axel Zeitler[1]; [1]University of Cambridge

We have measured the temperature dependent changes in the terahertz spectra of four different amorphous polyols: sorbitol, xylitol, threitol and glycerol. The absorption spectra of all studied polyols exhibit a clear change at the glass transition temperature Tg. This is expected as the relaxation time of the primary dielectric relaxation reaches timescales of 100s of seconds at temperatures below Tg, far too slow to contribute to absorption spectra at terahertz

frequencies. The results from the studied polyols are qualitatively different below Tg. Sorbitol, xylitol and threitol exhibit a change in the slope of temperature-dependent absorption at T = 0.6 Tg. This change has however different strength: it is most pronounced for the case sorbitol, less for xylitol while for threitol it is only barely detectable. In contrast, glycerol exhibits a continuous decrease of absorption with no obvious change in the slope. A straightforward explanation is that the change in the slope is related to the Johari-Goldstein relaxation process. The results thus show that the secondary relaxation vanishes from terahertz spectra at approximately 0.6 Tg in both sorbitol and xylitol but that there is no such secondary relaxation at terahertz frequencies in glycerol. This opens a number of questions on the origin of Johari-Goldstein relaxation. We discuss the obtained results in relation to the molecular mobility.

(582) **Observation of the Structural Evolution of Chemical Compounds using THz-TDS**

Edward Parrott[1], Axel Zeitler[2], Emma Pickwell-MacPherson[1]; [1]Department of Electronic Engineering, The Chinese University of Hong Kong, Hong Kong; [2]Department of Chemical Engineering and Biotechnology, University of Cambridge, UK

Terahertz time-domain-spectroscopy (THz-TDS) has been used to follow phase transitions of various materials, including metal oxides, pharmaceutical polymorphs and liquid crystals. We consider a number of recent studies that have used THz-TDS to follow the structural evolution of chemical compounds, including phase transformations and chemical reactions, to highlight the analytical capabilities of this technique. Furthermore, we demonstrate how complementary techniques, including x-ray diffraction studies and computational modeling can aid in the understanding of these spectra. Finally, we introduce recent results that demonstrate how THz-TDS is sensitive to subtle changes in the supramolecular arrangement, even in the absence of any recognized chemical or phase transformations.

(583) **Sweet Things are Made of This**

Philip Taday[1]; [1]TeraView

Sugar dominates the world's confectionary industry. In need most confectionary eaten in the western contains a significant percentage of sugar. To give a product a crunch when bitten, the sugar coating has to be crystalline. It is therefore important to understand the crystallization process. In this paper we will firstly use terahertz pulsed spectroscopy to follow the crystallization process of a solution of sucrose and then secondly terahertz pulsed imaging to monitor the build up of sugar coatings on the final product.

(584) **Detecting Early Onset of Crystallization in Pharmaceuticals using a Low Frequency High Throughput Raman Spectrometer**

Keith Gordon[1], Sara Fraser[1], Matthew Reish[1], May Mah[1], Clare Strachan[2]; [1]University of Otago; [2]University of Helsinki

The spectral region below 150 cm^{-1} is associated with solid lattice vibrations, or phonon modes. Terahertz spectroscopy is currently used to determine crystallinity of pharmaceuticals, however this utilizes relatively expensive apparatus. It is possible to obtain similar information available in this low cost, low frequency Raman setup. Pharmaceutical medicines of low solubility have poor uptake in the gastrointestinal tract, the amorphous forms of these drugs have increased solubility and hence biological uptake. The ability to rapidly monitor a series of samples for early stages of crystallization would be advantageous for the development and quality control of pharmaceuticals. A series of griseofulvin tablets were created with 0 - 10 % crystallinity at 2 % intervals for a calibration curve. Pure amorphous griseofulvin tablets were created to monitor crystallinity when stored at a range of temperatures (30, 35 and 40 degrees Celsius).

The experiments were carried out utilizing laser excitation of 784.9 nm from an Ondax Surelock™ LM Series diode laser. The Laser line rejection was accomplished with Optigrate BragGrate™ notch filters and Raman scattering detected using a Princeton Instruments LS 785 Spectrograph and 100 BR eXcelon CCD. The Raman spectra collected contained the spectral region -160 to 2150 cm^{-1}, hence containing both low and mid frequency spectral regions. The low (5-150 cm^{-1}) and mid frequency (200-1750 cm^{-1}) regions were modelled separately using partial least squares (PLS) to model % crystallinity. The resulting PLS models allowed a direct comparison of the two regions.

Low and mid frequency Raman spectroscopy gave similar prediction values for the percentage crystallization of griseofulvin. The rate of crystallization was dependent on the storage temperature with higher temperature conditions resulting in increased rate of crystallization.

(585) **Advances in MIcrobiological Identification Technologies**

Bradford Clay[1]; [1]bioMerieux, Inc.

Microbiological identification has been an application of high interest for spectroscopy/spectrometry. Methods used and currently in use will be reviewed; progress towards new faster and more cost-effective methods will also be covered.

(586) **Novel Platforms for SERS-Based Sensing of Infectious Disease**

Richard Dluhy[1]; [1]University of Georgia

Development of diagnostic methods for rapid and sensitive identification of biomedical pathogens is essential for the advancement of therapeutic and intervention strategies necessary to protect public health. Current diagnostic methods, e.g. culture, isolation, PCR, antigen detection, and serology, are often time-consuming, cumbersome, or lack sensitivity. We have investigated several different nanoparticle platforms for surface-enhanced Raman (SERS)-based identification and classification of pathogens. These platforms included metal colloids, nanosphere arrays, OAD nanorod arrays, and layer-by-layer nanoparticle assembly. The current talk will address the development of spectroscopic methods for pathogen detection based on these nanostructured SERS platforms. Examples will include the use of click chemistry for building carbohydrate microarrays as well as the detection of Mycoplasma pneumonia in simulated and true clinical specimens. We will present multivariate statistical analyses that indicate it is possible to identify, differentiate and classify pathogens based on their intrinsic SERS spectra, even down to the individual strain level.

(587) **Spectroscopy Characterization of Complex Particles: Applications to Biological Systems**

Luis H. Garcia-Rubio, Debra E. Huffman, Yulia M. Serebrennikova, Jennifer M. Smith; [1]Claro Scientific LLC.

It has been demonstrated that spectroscopic analysis can provide valuable quantitative insights into morphological and biochemical cellular transformations occurring during growth, disease, and/or genetic manipulations. Applications of spectrophotometric methods to biological systems, microorganisms and cells in particular, generally fall into three broad categories: methods aimed at resolving physical characteristics of the organisms (size, shape, etc.), methods aimed at their chemical composition, and cell-by-cell analysis techniques focused on counting and classifying in accordance to predefined parameters (size, shape, fluorescent tags, etc) accessible through spectrophotometric measurements. Techniques such as microscopy and flow cytometry are capable of high degree of sensitivity and can provide considerable amounts of descriptive information for cellular analysis, identification and classification. Although cell-by-cell analysis techniques have made dramatic improvements, they are still largely unsuitable for real-time continuous monitoring of many biological processes. Direct

spectrophotometric techniques such as FTIR, Raman Scattering, Uv-Vis-NIR, and Angular Light Scattering are suitable for real time process monitoring. The applications of the latter are generally in the context of monitoring limited sets of cellular parameters like cell counts, cell size, and the concentration of chemical species of interest such as chlorophyll, proteins, lipids, carbohydrates, etc. This presentation reviews the principles and the state of the art of a model-based analysis technique aimed at extracting the maximum amount of the information contained in spectrophotometric measurements of cell suspensions to characterize the state of biological processes. The approach reported herein has been used to quantitatively interpret the spectra of prokaryotic and eukaryotic organisms, for monitoring bioreactors, and for the design of innovative measurement configurations that enable simultaneous access to biological parameters of interest. Examples of successful applications of the model-based interpretation approach in the areas of cell characterization (algae and bacterial pathogens), medical diagnosis (malaria detection), real time continuous monitoring of bioreactors (blood cultures), and instrument design. The results from recent clinical studies further demonstrate the capabilities of spectrophotometric methods in the context of medical applications and point of care diagnosis.

(588) **Raman Spectroscopy as a Tool for Pathogen Identification in Clinical *in-vitro*-Diagnostics and Environmental Control: Discrimination Power and Robustness**

Denis Leroux[1], Isabelle Espagnon[2], Frédéric Mallard[1], Florian Michel[1], Denis Ostrovskii[1], Brad Clay[1], Charlene Gayrard[1], Pierre Joly[2], Armelle Novelli-Rousseau[1]; [1]bioMérieux S. A.; [2]CEA, LIST

Raman spectroscopy shows great potential for microbiological applications targeting clinical diagnostics and environmental control. Perceived assets are its high sensitivity (down to the single cell level), its moderately intrusive character (especially at the microbial colony level), the presumed possibility to acquire information with minimal or no sample preparation and its amenability to automation.

Our efforts have focused initially on pathogen identification of microbial colonies directly on growth media or on smears, of single cells; and more recently on Antibiotic Susceptibility Testing (AST) at the single cell level. Some key results in identification (classification rates up to 92 % for small databases containing 10 species, acquired directly on growth medium after 6 h of culture) and AST (determination of resistance on single cells after 2 hours of contact with antibiotics) will be presented and put in prospect with the scientific literature. Current identification systems will be mentioned to put our results in prospective with biochemical or mass mpectrometry identification techniques for which reference database sizes are approaching a thousand species. In an industrial perspective, perceived key attributes are (i) the ultimate discrimination power of Raman at the species level, (ii) its robustness towards sample preparation protocols and biological variability from non-microbial origin (complexity and compositional variability of clinical samples shall not be underestimated), (iii) the advantages associated with small biomass analysis and (iv) the possibility to get information about phenotypic microbial antibiotic susceptibility.

(589) **Approaching Big Data in Biological Research Imaging Spectroscopy with Novel Compression**

Jason Morrison[1], Yixuan Chen[1]; [1]University of Manitoba

As the size of spectroscopic data approaches limits of main computer memory, the need to have a compressed version that can be quickly searched becomes of greater importance. Fortunately the creation of "succinct" data structures for quick, compressed text search has been driven by search engines and genome mapping. This research focuses on providing a fast and space efficient data structure to answer information queries on spectroscopic data to enable exploratory data analysis. Our primary hypothesis was whether a conversion from decimal data to character/integer space could be done in a manner that enabled use of "succinct" structures and provide good compression. The preliminary research uses FTIR spectra of mouse tissues and a fungal sample and indicates that the hypothesis is true. The conversion from 32 bit floating point numbers to an integer mapped approximation scheme provides ~75% compression and the empirical entropy of the converted text promises a further reduction.

(590) **Scanning Angle Raman Spectroscopy: Measurements of Polymer Film Thickness, Composition and Structure**

Emily A. Smith[1,2], Vy H.T. Nguyen[1, 2], Jonathan Bobbitt[1, 2], Matthew Meyer[1, 2]; [1]U.S. D.O.E., The Ames Laboratory; [2]Iowa State University

Scanning angle (SA) Raman spectroscopy is applied to study polymer films to simultaneously measure polymer thickness, chemical composition and structure. A benefit of SA Raman spectroscopy over traditional (e.g., 180 degree backscatter) Raman spectroscopy for the measurement of 10 nm to 1 micron thick polymer films is a one to two order of magnitude signal enhancement. This enables the collection of nonresonant Raman spectra with second acquisition times and signal-to-noise ratios that exceed 100. The SA Raman technique uses a sapphire prism on which the polymer is coated. Raman spectra are collected as the incident angle of the 785-nm excitation laser is precisely varied from approximately 30- to 70-degrees. This range represents angles that span above and below the critical angle for total internal reflection. The SA Raman technique is applied to study polymer films used in organic photovoltaic devices, such as poly(3-hexylthiophene) (P3HT) and phenyl-C61-butyric acid methyl ester (PCBM) blend films, where the nanoscale morphology is critical for device function. The width of the ca. 1450 wavenumber C=C stretch is sensitive to P3HT order and is used to measure polymer film morphology on sapphire, gold, and ITO interfaces, including interfaces representing functional organic photovoltaic devices. The experimental measurements are modeled with calculations of the interfacial mean square electric field to determine the distance dependence of the SA Raman signal. SA Raman spectroscopy is also used to locate buried interfaces in stacked polymer layers of polystyrene and poly(methyl methacrylate) with tens of nanometer accuracy. The use of tailored substrates to reproducibly enhance the SA Raman signal and analyze weak Raman scattering polymers will also be discussed. Scanning angle Raman spectroscopy is a versatile method applicable whenever the chemical composition, structure and thickness of interfacial polymer layers needs to be measured. This work is supported by the Department of Energy, Office of Basic Energy Sciences.

(591) **Overcoming Sampling Limitations in Handheld Raman for Pharmaceutical and Bulk Samples**

Yvette D. Mattley[1], Michael W. Allen[1]; [1]Ocean Optics, Inc.

Miniaturization has driven Raman innovation in recent years. Once confined to the laboratory setting, Raman instruments have gone from benchtop instruments to compact, powerful integrated systems. While limited in resolution, these handheld instruments provide data for identification of a variety of different compounds. While homogeneous samples are the norm in a laboratory setting, non-uniform samples dominate real-world Raman applications. Accurate identification and quantification of non-uniform samples requires innovative sampling techniques to ensure the measurement is representative of the bulk sample. Other sampling challenges arise in applications where the Raman active component is sparse or the use of high average laser power causes sample damage or even violent explosions.

This paper discusses advances in optical sampling that overcome these limitations with the use of Raster Orbital Scanning (ROS). In

all conventional portable Raman spectrometers, a tightly focused beam is employed and the potential exists to inadequately sample the Raman-active compound. This leads to inaccurate identification. Here we present ground-breaking developments in design and strategies for optical interrogation of the samples, in both handheld and benchtop formats, that provides more accurate sample information and correct identification of non-uniform and irregularly shaped samples. Furthermore, these advances in sampling enable the use of lower laser power for sample measurement which is advantageous in sensitive or challenging samples. ROS delivers high instantaneous power for the collection of quality Raman spectra while the raster scanning reduces the average laser power therefore preventing sample damage.

In this paper, we will discuss the advances in optical sampling techniques and illustrate the advantages of this innovative sampling approach to overcome limitations associated with measuring the most difficult and challenging samples.

(592) **Novel Accurate Method for Orientation Quantification using Polarized Raman Spectroscopy**

Marie Richard-Lacroix[1], Christian Pellerin[1]; [1]University of Montreal

Molecular orientation has a significant impact on numerous physical properties of materials and is thus a critical parameter for their characterization. In recent years, confocal Raman spectroscopy, with its submicron resolution, has emerged as an indispensable tool for this purpose. However, strict quantification of the order parameters, (P2) and (P4), using this technique remains a challenging task. Indeed, the standard method used for orientation quantification is experimentally complex because it necessitates having access to an isotropic sample of the same chemical and phase composition as the sample of interest before any quantitative information can be extracted. This condition is often difficult, if not impossible, to meet, limiting greatly the applicability of Raman spectroscopy to characterize a wide variety of materials. We report here a new method for orientation quantification by Raman spectroscopy that is based on the most probable distribution and that eliminates this restrictive requirement. We demonstrate its wide experimental applicability using common polymer systems, such as high density polyethylene (PE), poly(ethylene terephthalate) (PET) and polystyrene (PS), that show vastly different levels of orientation. Our results unambiguously show that this new method is experimentally simpler and that it provides improved accuracy for quantifying the level of molecular orientation when compared to the standard method.

Richard-Lacroix, M.; Pellerin, C. Appl. Spectrosc. 2013, 67, 409.
Richard-Lacroix, M.; Pellerin, C. 2013 Submitted to Macromolecules

(593) **Low-frequency Raman and Terahertz Spectroscopies and Quantum Chemical Calculation Studies on Temperature-dependent Structural Changes in Nylon 6**

Yukihiro Ozaki[1], Erika Onishi[1], Harumi Sato[2], Shigeki Yamamoto[3], Kummetha Reddy[1], Daitaro Ishikawa[1], Shinya Ishii[4], Hal Suzuki[4], Hiromichi Hoshina[4], Yusuke Morisawa; [1]Kwansei Gakuin University; [2]Kobe University; [3]Osaka University; [4]RIKEN

Low-frequency Raman and Terahertz spectroscopies provide information about intermolecular vibrations such as hydrogen-bonds, which reflect the conformational changes in polymers. Nylon is one of the most widely used synthetic fibers, and its phase behavior and crystal structures have extensively been studied by various methods. The neighboring molecular chains of Nylon are connected by strong hydrogen bonds (N-H…O=C), which dominate the physical behaviors of Nylon. In this study, we have studied temperature-dependent structural changes of Nylon 6 by using low-frequency Raman, Terahertz spectroscopies and quantum chemical calculations of the spectra. To prepare α-form samples, several pellets of Nylon 6 were melted into HFIP(hexafluoro-2-propanol) solution, and then, its film was made by casting it. To prepare the stretched film for polarized Raman, several pellets were melted and pressed at 240° C and rapidly cooled with liquid nitrogen, and then the film was drawn up to approximately 400% at 160° C. We measured temperature-dependent Raman and Terahertz spectra of the cast film between 25 and 210° C in the heating process and also obtained Terahertz spectra in the temperature range from 25 to -259° C (14 K) in the heating process. Moreover, we measured polarized Raman spectra of stretched film at room temperature. The quantum chemical calculation was carried out for the dimer, trimer and tetramer of Nylon 6 by using the density functional theory(DFT) method (Gaussian09, CAM-B3LYP / 6-31+G**). As a result, a peak at 105 cm-1 showed a red shift in both of the Raman and Terahertz spectra with increasing temperature. Polarized Raman spectra indicated that the peak is polarized perpendicularly against the stretched direction of the film. Terahertz spectra at 14 K showed very clear separation of the peaks in the region of 90-130 cm-1. Moreover, the results of quantum chemical calculation yielded good agreements with the experimental spectra. Especially, the predicted Raman and Terahertz spectra became better and better by increasing the number of chains in the molecular model.

(594) **Detection of Chemical Nerve Agent Simulants using Flexible, Porous SERS-active Substrates**

Aaron D. Strickland[1], Robert Diaz-Morales[1], Michael J. Canfield[1]; [1]iFyber

Chemical nerve agents are a class of chemical weapons that share the common structural motif of a tetrahedral phosphorous bound to oxygen and a moderately good leaving group. Since their discovery just prior to World War II, phosphorous-based nerve agents have been used with horrifying effect as demonstrated by several recent attacks around the world; namely, use in Iraq in the late 1980s, the 1995 Tokyo subway attack using sarin, and the suspected use in Syria during 2012 and 2013. Nerve agents exhibit extraordinary toxicity in humans (e.g., as little as 10 μg/kg), which is largely a result of their resistance to hydrolysis, and thus, the ability of these compounds to persist long enough to bind and inhibit the enzyme acetylcholinesterase. This study describes a selective detection method for phosphorous-based nerve agents that utilizes of a new class of molecular sensor and surface-enhanced Raman scattering (SERS). The molecular sensor is designed around a chemical moiety comprised of an alpha effect nucleophile that undergoes specific substitution and rearrangement reactions in the presence of phosphorous-based new agents. Using nerve agent simulants, we show that this substitution/rearrangement mechanism produces a new chemical derivative, and the resulting spectral fingerprint can be monitored by Raman spectroscopy and SERS at less than parts-per-million levels. In addition to the nerve agent sensing technique, we will also describe the development of a flexible, porous SERS-active substrate used to provide trace detection of the simulants. These substrates exhibit enhancement factors of $>10^7$, and are produced in large volumes with a variability of <15% relative standard deviation in measured signal, substrate-to-substrate. The substrates are used to effectively measure analytes of interest in solid, liquid and vapor phases using several different form factors that are not possible using standard wafer processed SERS substrates.

(595) **Portable Ultra-High Resolution, Dynamic SERS Imaging System**

Eric Languirand, John Kiser[1], Brian Cullum[1]; [1]University of Maryland, Baltimore County

Ultra-high resolution chemical imaging using Raman spectroscopy can aid in the differentiation and identification of trace analytes for many applications, including, but not limited to forensics, environmental, biological and biomedical sciences. Unfortunately, spontaneous Raman spectroscopy is an intrinsically weak

phenomenon making trace detection inherently difficult. To circumvent this and provide the sensitivity necessary for sub-diffraction limited chemical imaging, we employ a specially designed surface enhanced Raman spectroscopic (SERS) nanoprobe. Unlike tip enhanced Raman spectroscopy (TERS), where a small tapered tip is raster scanned over a sample surface for ultra-high resolution image acquisition, our nanoprobes are fabricated from fiber optic imaging bundles that allow for entire image to be acquired in a single collection. This non-scanning tip thereby allows dynamic images to be taken. The SERS nanoprobes, which are central to this system, are fabricated using coherent fiber-optic imaging bundles consisting of 30,000 fiber elements. These probes are tapered via a micropipette puller to have individual fiber element tip diameters of 50 nm and still retain total internal transmission. Using a rapid 2-step dithering process, 20 µm diameter images can be obtained with 33-nm spatial resolution. This allows for dynamic, ultra-high resolution chemical imaging to be performed. Integration of these probes into a portable system makes this technology ideal for field applications as well as the laboratory.

(596) **Observation of Reaction Kinetics in Self-Assembled Monolayers using Surface- and Tip-Enhanced Raman Spectroscopy**

Evelien van Schrojenstein Lantman[1], Arjan Mank[4], Tanja Deckert-Gaudig[3], Onno Gijzeman[1], Volker Deckert[2, 3], Bert Weckhuysen[1]; [1]Utrecht University, Utrecht, The Netherlands; [2]Friedrich-Schiller University Jena, Jena, Germany; [3]Institute of Photonic Technology, Jena, Germany; [4]Philips Innovation Services, Eindhoven, The Netherlands

Self-assembled monolayers (SAMs) of molecules are widely studied systems that allow well-defined modification or functionalization of surfaces. Nanoscale patterning of such modified surfaces is possible by using masks and photochemistry. However, the analysis of these structures is thus far only possible using scanning probe microscopy techniques, such as atomic force microscopy or scanning tunnelling microscopy. Tip-enhanced Raman spectroscopy (TERS) has recently shown to be capable of following a nano-scale SAM modification in-situ. In addition, the nanometre-scale resolution inherent to this technique allows for qualitative analysis of the structure of the monolayer. [1] TERS has the promise to become a much more versatile technique, as it also provides nanoscale chemical information of the monolayer, and is thus not limited to characterization through physical properties like height differences. We show how reaction kinetics can be determined for a reaction in a monolayer using in-situ with surface-enhanced Raman spectroscopy (SERS) and tip-enhanced Raman spectroscopy (TERS). Through a dilution series of the concentration of reactant on the surface, the order of reaction and other characteristics can be determined. We show the applicability of this model by studying the photo-reduction of p-nitrothiophenol.

[1] E M van Schrojenstein Lantman, T Deckert-Gaudig, A J G Mank, V Deckert, B M Weckhuysen. Nat. Nanotech. 7, 583–6 (2012).

(597) **Effect of Ionization of Thiophenol on the Mechanism of Heterogeneous Adsorption on Gold Substrates by Surface-Enhanced Raman Spectroscopy**

Ashish Tripathi[1], Erik Emmons[1], Steven Christesen[2], Augustus Fountain[2], Jason Guicheteau[2]; [1]Science Applications International Corporation; [2]USA RDECOM Edgewood Chemical Biological Center

Thiophenol is a model system for adsorption studies of molecules on noble metal surfaces, due to the strong affinity of the –SH group for these metals. Time-, temperature- , and pH-dependent measurements of thiophenol adsorption on commercial nanostructured gold surface-enhanced Raman spectroscopy (SERS) substrates have been performed. Two distinct regimes were found depending on the ionization state (pH) of the thiophenol/analyte solution. At low pH the sulfhydryl proton remains attached in solution, and the kinetic adsorption profile obtained from the SERS intensity shows an s-shaped curve with an initially slow adsorption rate that deviates from a Langmuir profile. In addition, from temperature-dependent measurements, a small activation energy is obtained, indicating that physisorption is the rate limiting step. At high pH, where the sulfhydryl proton remains attached in solution, the kinetic adsorption profile follows a classical Langmuir profile and the activation energy is significantly higher than at low-pH, indicating that chemisorption is the rate-limiting step.

(598) **Tracing the Extent of Chemical Warfare Agent Decontamination Reactions Using Raman Spectroscopy**

Emmons Erik[1], Ashish Tripathi[1], Michael Ellzy[2], Jason Guicheteau[2], Ai Sohrabi[2], Steven Christesen[2]; [1]Science Applications International Corporation, Gunpowder Branch; [2]USA RDECOM Edgewood Chemical Biological Center

Since Raman spectroscopy provides highly-selective identification of molecular structures, it is a valuable tool for tracking the progress of chemical reactions. We have studied decontamination reactions of the toxic chemical paraoxon as well as the nerve agents soman (GD) and cyclosarin (GF) using time-resolved Raman spectroscopy. Changes in the spectra observed under basic conditions using aqueous NaOH as a decontamination solution allow the extent of decontamination to be tracked as a function of time, and are indicative of the identity of the final product. Due to the limited solubility of some of these chemicals in water, mixtures with additional ethanol to aid in dissolving the agents were also studied. The effect of ethanol on the rates of decontamination was assessed. Mass spectroscopy was also performed for confirmatory measurements of the decontamination process. Overall, Raman spectroscopy appears to be a valuable and fast way to track decontamination reactions.

(599) **Terahertz Raman of Nano Metal Oxides and Chalcogenides**

James Hamilton[1], Jorge Camacho[1], Neelanjan Bhattacharya[1], Ethan Becker[1]; [1]University of Wisconsin-Platteville

Ultra low frequency Raman peaks down to 5 cm-1 from the laser line were obtained for a variety of nano metal oxides, chalcogenides and perovskites.

(600) **Transmission Raman Spectroscopy and Low-Frequency Option: Development of Applications**

Renata Lewandowska[1], Vincent Larat[1], Ophelie Lancry[1], Catalina David[1]; [1]HORIBA Scientific

The Transmission Raman spectroscopy and low-frequency filters they are two options in the domain Raman Spectroscopy which appears recently on the market. The Transmission Raman Spectroscopy were developed for pharmaceutical field, but it can be successfully used in other domains like food, catalysis or cosmetics. Some examples will be presented here. The spectral region below 30cm-1 in Raman spectrum brings the information about the superstructures like the heterostructures or supramolecules, the conformation of the molecules, the intramolecular interactions or analysis of amorphous/nanostructured materials. Examples of the applications will be presented.

(601) **Chemical Imaging of Surface Chemistry in an Industrial Environment**

Michaeleen Pacholski[1]; [1]The Dow Chemical Company

In an industrial analytical facility, chemical imaging is a widely utilized tool which can be used to measure the spatial distribution of species on a surface. In some instances, surface imaging is used to confirm the heterogeneity of a sample. In others, surface imaging is used as an exploratory tool used to examine various materials for

information that can be linked to poor performance of a product (failure analysis).
In this presentation XPS, SIMS and SEM/EDS are discussed as robust surface analytical tools in industry. Various examples of expected and unexpected data from surfaces are discussed, emphasizing the role of these tools for failure analysis.

(602) **Selected Industrial Applications of X-Ray Photoelectron Spectroscopy**

Derrick Poirier[1]; [1]3M

Many of 3M's products are based on layers of materials that are bonded or adhered together. Depending on the application, it may be desired that the layers remain permanently bonded (e.g. outdoor signage), or that the layers be separable with a controlled, reproducible amount of force (e.g. roll of adhesive tape). Understanding and controlling the chemistries on surfaces to be adhered together, often at the level of the outer few nanometers, can be critical to achieving the desired performance. X-Ray Photoelectron Spectroscopy (XPS) provides elemental concentration and chemical bonding information from the outer ~3-10nm of a sample, and thus has many applications related to adhesion of materials. These include identification of contaminants that can prevent adhesion and assessing the presence or degree of surface chemical modification intended to promote adhesion. The talk will include examples of practical applications of XPS to industrial problems.

(603) **Secondary Ion Mass Spectrometry (SIMS) as a Practical, Applied Surface Analysis Method**

Paul Vlasak[1], Steven Pachuta[1]; [1]3M Company

Secondary Ion Mass Spectrometry (SIMS) has become a standard analytical method for surface characterization within many technology-based corporations. While still considered exotic in some circles, the SIMS technique is applicable to a wide range of sample types, provides information relevant to industrial process and product understanding, can be used effectively in defect and failure analysis, and has unique capabilities that justify its place in the analytical chemist's toolbox. A wealth of literature exists describing the SIMS method and its use in academic and industrial applications. While this collection of literature will orient the scientist to the fundamentals of the method and its range of applicability, the current presentation will stress the utility and practicality of the method in day-to-day problem solving. Adhesion, release, coating, wetting, optical properties, electrical properties, corrosion, catalysis, and bio-compatibility are all influenced by surface chemistry. At 3M, understanding surface chemistry is important for fundamental research, product and technology development, intellectual property substantiation and protection, investigation of manufacturing issues, and failure analysis. This presentation will demonstrate the utility of practical, applied SIMS using real-world examples that are investigated in hours or days rather than weeks or months.

(604) **Nanomechanical Testing: Tools, Techniques, and Real-World Applications**

Jeffrey Schirer[1]; [1]Hysitron, Inc.

Nanomechanical testing, often nanoindentation, has been well-established at a basic level for characterization of surfaces, small volumes of material, and low-dimensional structures, with the size scale of the applications or physical area of interest dictating the testing size scale required. The aspiration to understand nanoscale material behavior at smaller and smaller levels and in new capacities consequently drives continuous development of nanomechanical testing techniques. The use of nanomechanical testing, often in combination with complementary techniques, continues to be developed and refined for research pertaining to real-world, cutting-edge applications. Complementary and in-situ techniques used in combination with nanomechanical testing can include SPM, heating/cooling, electrical contact resistance, dynamic mechanical analysis, acoustic emission monitoring, SEM, and TEM. A considerably broad range of materials and applications can be characterized using a variety of nanomechanical testing techniques.

(605) **Closing the Loop on Catalyst Design – XPS as a Tool to Probe Catalyst Tuning in Ionic Liquids**

Peter Licence[1]; [1]University of Nottingham

It was not until 2005 that the rather obvious compatibility of ionic liquids with ultra high vacuum (UHV)-based spectroscopies was fully realised. Since that time, an ever-increasing portfolio of UHV based techniques including XPS, UPS, SIMS, TPD, SEM, TEM, and related synchrotron based experiments have been applied to the study of both pure ionic liquids and solutions thereof. UHV techniques give tremendous insight into many aspects of ionic liquid properties and the role that they play in chemical reactions and processes.

Since 2005 we have developed a series of robust spectroscopic protocols that allow the direct comparison of spectroscopic data, and more critically allows the investigation of subtle changes in binding energy that result from chemistry within the sample itself. The application of rigorous charge referencing protocols reveals subtle variations in the observed binding energies of photoemissions corresponding to elements located in charge carrier moieties. This data suggests partial charge transfer between the charged components of a given liquid, i.e. anion-cation interactions, particularly when the anion component is highly coordinating or strongly basic. XPS data will be used to illustrate the extremes of both coordinating (Cl-) and passive [Tf2N]- behavior in commonly used ionic liquids. The chemistry of ionic liquid mixtures is an emerging area of research that offers tremendous potential in applied fields, particularly those that are based upon the electrolytic properties of the liquid itself. The direct combination of different ions could provide a fine tuned balance between electrochemical stability, viscosity, conductivity and melting points. We explore the nature and local electronic environments within simple ionic liquid mixtures by direct XPS measurement. Common cation mixtures based upon both dialkyl imidazolium and dialkyl pyrollidinium based liquids are investigated and XPS data will be used to illustrate speciation and bulk structure in mixed anion-based systems as a function of molar fraction. The experiments illustrate opportunities to tune the electronic environment within ionic liquid mixtures and highlight a strategy that may be used to develop a palette of ionic liquids that may be blended to produce mixtures with tuneable chemical properties that could potentially impact upon catalytic performance.

(606) **Towards an Expert System for Inductively Coupled Plasma-Atomic Emission Spectrometry: An Automated Statistical Protocol for Flagging Matrix Interferences**

George Chan[1], Gary Hieftje[1]; [1]Department of Chemistry, Indiana University

Since the commercialization of the inductively coupled plasma (ICP) spectrometer about forty years ago, the ICP has become a popular tool for elemental analysis. All commercial ICP–AES spectrometers now available include some automated features (e.g., computer-controlled gas flows and solution pumps, programmed analysis, automatic calibration and line selection with multiline analysis, and statistical treatment of data). However, there is one essential component that is missing in these modern instruments — the ability to warn the operator when the analytical result is compromised by the presence of matrix interferences. Without dispute, the most important quality that an analyst expects is accuracy. The presence of matrix interferences, without the awareness and subsequent correction by an analyst, will lead to an analytical error that can be 30% or more. One possible reason for the lack of such alerting

capability in modern ICP–AES instruments is the complex nature of matrix interferences. There are three categories of matrix effects (sample-introduction-related, plasma-related, and spectral interferences), and their characteristics and behaviors are all different. Recently, we have developed a unified interference-flagging method that is effective for all three matrix-effect categories. Moreover, this developed indicator can be operated in an online fashion during an analysis and is applicable to both conventional lateral-viewing (i.e., side-on) and axial-viewing (i.e., end-on) observation modes. This simple all-in-one indicator is based on the fact that the relative magnitude and even the direction of the change in emission intensity caused by a matrix interference are not constant, but are functions of spatial locations in the plasma. Since the determined concentration of an analyte in a sample is proportional to the measured intensity, any uneven change in matrix effects along the spatial profile will cause the determined concentration to be spatially dependent, thus allowing the interference to be detected. A flat determined-concentration profile indicates absence of matrix interference whereas a dissimilar (i.e., curved) concentration profile offers a clear warning signal that the analytical results are compromised by interferences. A statistical protocol was developed to automatically classify a spatial profile as flat or curved. In this presentation, the theoretical basis of this statistical protocol will be discussed, and its effectiveness for automated signaling of matrix interferences will be evaluated.

(607) **The Liquid Sampling-Atmospheric Pressure Glow Dicharge-More Than Just a Toy**

R, Kenneth Marçus[1], Benjamin T. Manard[1], Richard E. Russo[2], Jhanis Gonzalez[2], David W. Koppenaal[3]; [1]Clemson University; [2]Lawrence Berekely National Laboratory; [3]Pacific Northwest National Laboratory

Of all the basic areas of chemical instrumentation, the field of atomic spectroscopy is the least evolved in terms of miniaturization. While the inductivley-coupled plasma (ICP) is the benchmark source, there has been no perceivable interest shown among instrument manufacturers to develop sources of greater power efficiency and lower consumable costs; not to mention any thoughts of transportability. This is in conflict to many efforts to minimize sample sizes and corresponding means of sample introduction. This laboratory began working 10 years ago on the use of alternative sources that may provide savings in size, power, and consumables. The liquid sampling-atmospheric pressure glow discharge (LS-APGD) operates at liquid flow rates of 10 – 100 μL min^{-1}, powers of less than 50 W (d.c.), and support gas flows of less than 100 mL min^{-1}. While early optical emission (OES) studies revealed very competitive figures of merit vs the ICP, it was only with the interfacing of the device to a mass spectrometer in 2011 that there was appreciable traction toward further developments. We describe here the basic analytical characteristics of the LS-APGD ionization source as it is applied in atomic mass spectrometry, including basic parametric dependencies of spectral structure and figures of merit. In addition to direct microvolume (10 μL) sample analysis, the device has proven to be very useful in vaporizing/ionizing particulates generated by femtosecond laser ablation. Most recently, a very comprehensive study was performed, studying the role of operational parameters on the fundamental plasma characteristics of electron number density, excitation temperature, and robustness. Basically, the plasma, which operates at power densities of 100x those of ICPs, is immune to significant changes in these figures of merit upon introduction of salt matrices or laser-ablated particles. The LS-APGD has many characteristics that bode well not just for transportable instruments, but also laboratory devices.

(608) **Spatially Resolved Fully Simultaneous Determination of Large Numbers of Isotope Concentrations and Isotope Ratios by LA-MH-ICP-MS**

Willi Barger, Dirk Ardelt[1], Maurice Reijnen[1], Oliver Primm[1]; [1]SPECTRO Analytical Instruments GmbH

Laser Ablation-ICP-MS has developed into a powerful tool for the determination of elements, element ratios and isotope ratios in solid samples. The analysis of more and more elements with high spatial resolution and from ever smaller sample sizes is a challenge for this technology. The development of a fully simultaneous ICP-MS brings several advantages for resolving this challenge: 'all' elements and isotopes can be determined in the same analytical run without sacrifying analysis time for any isotope. The simultaneous measurement also allows elimination of correlated noise, like flicker noise from the plasma or noise generated by the ablation process itself.

A double focussing sector field mass spectrometer in Mattauch-Herzog (MH) geometry was combined with a 4800-channel, large CMOS based semiconductor direct ion detector, placed in the focal plane of the magnet. Each of the channels operates fully simultaneously, using two different amplifications, covering the mass range from ~5 to 240 amu. The use of this new technology with laser ablation, for simultaneous chemical imaging of large numbers of isotopes, and analytical results for relevant samples, will be presented, with special emphasis on the expected advantages of the fully simultaneous detection.

(609) **Microwave Induced Plasma Source for Optical Emission and Mass Spectroscopy**

Jovan Jevtic[1], Ashok Menon[2], Velibor Pikelja[2]; [1]Milwaukee School of Engineering; [2]Radom Corporation

Radio-frequency (RF) inductively-coupled-plasma (ICP) is used in a great majority of commercial optical-emission-spectrometry (OES) and mass-spectrometry (MS) instruments for the production of optical emission and analyte ions. Despite a good match between the properties of ICP plasma and the requirements of many established analytical applications, the specific excitation and ionization mechanisms in RF plasma may be viewed as a limiting factor in achieving the full potential of OES and MS. A large body of research over a period of several decades has shown that microwave-induced-plasma (MIP) opens up analytical possibilities which complement and significantly extend the number of OES and MS applications. An increased interest in the last two years is illustrated by the publication of a comprehensive monograph on MIP analytical spectrometry and the commercial release of a new MIP-OES instrument. However, from a plethora of MIP solutions, such as plasmatrons, surfaguides, surfatrons, Beenakker, TEM, and Okamoto cavities, no single choice has emerged that can parallel the universal acceptance of an ICP coil. The lack of a well defined MIP hardware platform has delayed wider adoption and analytical development of the technique. We have taken a different approach by insisting on a microwave solution which parallels, as much as possible, the proven ICP coil design in terms of plasma shape, plasma zones, plasma-instrument interface, and compatibility with both OES and MS instruments. Based on an innovative design which exploits the remarkable electrical and thermal properties of advanced technical ceramics, we have used an advanced electromagnetic field simulation tool to perfect, build, and test a novel 1.2kW/2.45GHz atmospheric Nitrogen MIP plasma source. A nearly perfectly symmetric and purely inductive H-type field, an order of magnitude reduced losses, ability to operate on various gases, and a familiar ICP plasma shape, analytical zones, and interface lead us to believe that this source will provide chemists with a fertile instrument platform for producing exciting new analytical results in both OES and MS applications.

(610) **From Sample Dilution to Matrix Removal and Purification: Automating Sample Preparation for ICPOES, ICPMS and MC-ICPMS**

Paul Field[1], Patrick Sullivan[1]; [1]Elemental Scientific, Inc

To better understand bio, geo and biogeochemical processes, large quantities of high quality data are required. Over the past decade, advances in sample introduction techniques combined with analytical instrumentation have greatly improved productivity. Instrumentation for both trace metal concentration and isotopic ratio determination has improved analytical precision, accuracy and detection limits. However, many analyses still require significant sample preparation for which the laboratory bottleneck remains. The recent development of an automated sample preparation system provides a platform to address this bottleneck for a range of sample types and applications. The system uses specially designed valves, precise and accurate syringe control, and an autosampler all controlled by a flexible, yet simple, software package to automate tedious, time consuming sample preparation. The system allows sample loading, multiple acid washes, column conditioning and elution cycles necessary to isolate elements of interest and automatically collect up to 3 discrete eluent fractions at user-defined intervals (time, volume and flow rate). The platform can be custom designed to perform a range of functions from simple sample dilutions, automated matrix removal and preconcentration to purification of elements for isotopic analysis. Case studies from existing labs will be used to illustrate the systems wide range of capabilities. The seaFAST-picoTM is used to determine a variety of elements in seawater ranging from single digit ngL-1 concentrations of Mn, Fe, Co, Ni, Cu and Zn to ultra-trace levels (10s of pgL-1) of REEs. Newly developed protocols for the prepFAST-MC™ automate the purification of uranium isotopes from rocks, boron isotopes from carbonates and removal of Pu from radioactive samples for trace metal determination. On-going development that continues to explore new sample types and isotopic systems will also be presented.

(611) **Optimization and Application of Sensitivity-Enhanced Transmission Raman Spectroscopy**

Michael Pelletier; [1]Pfizer

Transmission Raman spectroscopy can provide improved accuracy for whole pharmaceutical tablet analysis by probing a larger volume of the tablet. The efficiencies for getting light into the tablet, and for collecting the Raman photons that are generated are usually poor, leading to greatly reduced sensitivity compared to traditional backscattering measurements. Many pharmaceutical tablets are excellent diffuse reflectors. For those tablets, transmission Raman sensitivity can be enhanced by re-directing lost photons back to the tablet surface. Some of those re-directed lost photons become Raman photons that reach the detector, thereby increasing sensitivity. Returning reflected laser photons to the tablet surface again and again effectively increases the laser power incident on the tablet. Returning uncollected Raman photons to the tablet surface effectively increases the tablet brightness, increasing the number of photons that can be collected from a given surface area and solid angle. Since the recycling of Raman photons occurs primarily via surface reflection, the sensitivity enhancement is largely unaffected by tablet self-absorption. Sensitivity enhancement factors of 40 to 60 were previously demonstrated using this approach. This talk will focus on the optimization and application of a sensitivity-enhanced transmission Raman cell for routine use in a commercial Raman instrument. The effect of reflective surface shape on sensitivity enhancement will be demonstrated using optical ray tracing and experimental measurements. The effect of tablet properties such as reflectivity and bulk absorbance on sensitivity enhancement will also be demonstrated. Practical considerations for routine operation will also be included in the optimization.

(612) **Vibrational Spectroscopy in the Field**

Luisa T.M. Profeta[1], Corrie L. Carnes[1], Jon D. Onstot[1]; [1]MRIGlobal

In an ideal world, portable spectroscopy equipment will operate and produce data that is equivalent to that of a high-end research grade spectrometer used by an expert spectroscopist. However, there are constraints on the technology to meet the demands of doing analysis in the field. The physical and operational constraints of fieldable equipment and limited formal training of the typical user drive nearly every aspect of product design (size & weight, ergonomics, display, interpretation of results, etc.). Since most end users are not trained spectroscopists, it is critical that the training they receive allows them to obtain data which has value. This presentation will cover teaching spectroscopy to non-spectroscopists, and critical considerations for analyzing unknown samples in the field as well as limitations seen using fieldable equipment for unknown analysis.

(613) **Handheld Spectrometers: The State of the Art**

Richard Crocombe[1]; [1]Thermo Fisher Scientific

"Small" spectrometers fall into three broad classes: small versions of laboratory instruments, providing data, subsequently processed on a PC; dedicated analyzers, providing actionable information to an individual operator; and process analyzers, providing quantitative or semi-quantitative information to a process controller. The emphasis of this paper is on handheld dedicated analyzers. Many spectrometers have historically been large, possible fragile, expensive and complicated to use. The challenge over the last dozen years, as instruments have moved into the field, has been to make spectrometers smaller, affordable, rugged, easy-to-use, but most of all capable of delivering actionable results. Actionable results can dramatically improve the efficiency of a testing process and transform the way business is done. There are several keys to this handheld spectrometer revolution. Consumer electronics has given us powerful mobile platforms, compact batteries, clearly visible displays, new user interfaces, etc., while telecomm has revolutionized miniature optics, sources and detectors. While these technologies enable miniature spectrometers themselves, actionable information has demanded the development of rugged algorithms for material confirmation, unknown identification, mixture analysis and detection of suspicious materials in unknown matrices. These algorithms are far more sophisticated than the 'correlation' or 'dot-product' methods commonly used in benchtop instruments. Finally, continuing consumer electronics advances now enable many more technologies to be incorporated into handheld spectrometers, including Bluetooth, wireless, WiFi, GPS, cameras and bar code readers, and the continued size shrinkage of spectrometer 'engines' leads to the prospect of dual technology or 'hyphenated' handheld instruments.

(614) ***In-vivo* Optical Spectroscopy in Skin and Cosmetic Research**

Tom Cambron[1], Joe Kaczvinsky[1]; [1]The Procter and Gamble Co.

Human skin has been extensively characterized by numerous noninvasive optical techniques including infrared (IR), near-infrared (NIR), and Raman spectroscopy. These non-invasive techniques enable in-vivo spectroscopic characterization of the molecular composition of skin and interactions between skin and topically applied products. These techniques provide complimentary information and provide key insight into skin condition when combined with other non-optical methods for characterizing skin. This presentation will highlight recent developments in the application of in-vivo optical spectroscopy for skin and cosmetic research.

(615) **Near Infrared Hyper-spectral Imaging for Controlling the Quality of Large Scale Transdermal Drug Manufacturing**

Benoit Igne[1], Carl Anderson[1], James Drennen[1]; [1]Duquesne University

The implementation of Process Analytical Technologies to transdermal manufacturing is often limited to weight measurements during dispensing and slow response at-line measurements. The development of Near Infrared Hyper-spectral Imaging has allowed the development of quality control and monitoring tools that provide, in real-time, relevant information about the laminate manufacturing (i.e. drug loading, coat weight, content of residual solvents). This presentation will discuss the deployment of an NIR imaging system for the real-time monitoring and control of a transdermal manufacturing line. Some of the features of the system will be described as well as the results that can be expected. Difficulties of scaling up of such PAT tools from laboratory to large scale manufacturing will be discussed.

(616) **Calcinated Gold Particle Nanofilms for Surface Enhanced Optical Sensing and MS Analysis**

Quan Cheng[1], Chih-yuan Chen[1], Sam Hinman[1]; [1]University of California Riverside

We present the fabrication of gold nanoparticle (AuNP) thin films that exhibit unique optical and electronic properties for allowing cross-platform measurement with surface plasmon resonance (SPR), mass spectrometry, and Raman spectroscopy. The fabrication is based on layer-by-layer deposition/calcination to generate a thin AuNP layer that is highly stable and reusable. SEM and AFM have been used to characterize the nano films. FDTD simulation has been carried out to understand the plasmonic resonance coupling and field enhancement property, and to search for conditions leading to better calcinated films. Sensing application with AuNP films will be discussed as well.

(617) **Plasmonic Nanorings for Biosensing and Materials Applications**

Kyunghee (Mike) Cho[1], Mana Toma[1], Gabriel Loget[1], Jennifer Wood[1], Aaron Halpern[1], Robert Corn[1]; [1]UC Irvine

A variety of surface plasmon-based detection methodologies including SPR, SPR imaging, SPR fluorescence and LSPR spectroscopy have been successfully applied for the multiplexed detection and identification of nucleic acids, proteins and carbohydrates via bioaffinity adsorption onto biopolymer microarrays. Plasmonic nanoring arrays are increasingly popular nanostructured interfaces that exhibit unique optical, electronic, and magnetic properties that can lead to novel biosensing applications. In this talk, we will describe our recent success at combining colloidal lithography and lithographically patterned nanoscale electrodeposition (LPNE) to create a novel low-cost method for the fabrication of silver, gold and nickel nanoring arrays over large areas. The nanoring arrays are fabricated in three steps: (i) first, a thin (70 nm) sacrificial Ni or Ag film was vapor-deposited onto a plasma-etched packed colloidal monolayer; (ii) the polymer colloids were then removed from the surface to create a nanohole array, a thin film of positive photoresist was applied, and a backside exposure of the photoresist was then used to create a nanohole electrode array; and (iii) this array of nanoscale cylindrical electrodes was then used for the electrodeposition of a gold, silver, or nickel nanorings. The photoresist and sacrificial metal film were subsequently removed to reveal a nanoring array in which all dimensions are set independently: the inter-ring spacing is fixed by the colloidal radius, the radius of the nanorings is controlled by the plasma etching process, and the width of the nanorings is controlled by the amount of charge passed during the electrodeposition process. A combination of SEM measurements and Fourier transform near-infrared (FT-NIR) absorption spectroscopy were used to characterize the nanoring arrays. These nanoring arrays exhibit very strong NIR plasmonic resonances that can be for refractive index biosensing applications. Further biosensing sensitivity can be obtained by coupling the adsorption of biofunctionalized nanoparticles to the nanoring arrays. Additional efforts on the fabrication of double nanoring arrays, split-ring arrays and other meta-material configurations that exhibit unique optical properties including polarization-dependent mid-IR plasmonic resonances will also be described.

(618) **Plasmonic Interaction with a Single Nanoparticle and a Nanohole Array**

Karl Booksh[1], Laurel Kegel[1]; [1]University of Delaware

The interaction of surface plasmons supported on a nanohole array and a single nanoparticle affixed to an atomic force microscopy probe (AFM) tip probe was studied for application in optimizing gap mode enhancement of the plasmonic field. Scanning probe microscopy controlled the AFM probe position and the location specific interaction of the single nanoparticle probe (SNP)-nanohole array surface plasmons was measured by darkfield surface plasmon resonance spectroscopy. Raster scanned darkfield imaging of the surface plasmons on the nanohole array is demonstrated, as well as image formation from measuring the SNP interaction at various (x.y) locations relative to the nanohole. Coupling of the nanoparticle to the nanohole array exhibited maximal coupling when the SNP resided within a nanohole, which resulted in a maximum SPR wavelength shift of 17 nm and an increase in scatter intensity of 31±4%. This technique may be expanded to mapping nanostructure coupling across three dimensions to determine optimal coupling conditions for use in biosensing and surface enhanced spectroscopy applications.

(619) **Metallic Nanoparticles and Surfaces for Surface Enhanced Raman Scattering**

Duncan Graham[1], David Thompson[1], Sam Mabbot[1], Sathkumara Mudalige[1]; [1]University of Strathclyde

Functionalized nanoparticles have been used in a number of different studies including detection of DNA at ultra low levels, immuno histochemistry and more recently as substrates for surface enhanced resonance Raman scattering (SERRS) based imaging approaches. The advantages of using metallic nanoparticles are that they are very bright in terms of their optical characteristics and also if functionalized in a particular manner to provide a SERRS response give a unique vibrational fingerprint. Here we present the functionalization of gold and silver nanoparticles in such a way that the enhancement effect can be greatly increased through biological recognition and as such effectively turns on the SERRS effect. This process can give rise to exquisite selectivity in terms of the interaction of the nanoparticles, especially when DNA hybridizations are used and single base mismatches can be analyzed at room temperature. Dye oligonucleotide silver nanoparticles (DOSN) have also been used to detect double stranded DNA through triplex formation to switch on the SERRS and a distance relationship between nanoparticles and SERRS response established for the first time. This approach has been extended to look at DNA-protein interactions, peptide-protein interactions and sugar-protein interactions. This presentation covers the full range of design, the optical properties and finally the biological properties of functionalized nanoparticles in relation to their assembly and how that relates to the provision of new biological knowledge.

(620) **Nanoparticle-based Competition Immunoassay for Methotrexate Detection in Serum Sample of Chemotherapy Patients**

Jean-Francois Masson[1], Sandy Shuo Zhao[1], Helene Yockell-Lelievre[1], Natalia Bukar[1], Joelle N. Pelletier[1]; [1]Universite de Montreal

A fully integrated, small surface plasmon resonance (SPR) sensor has been developed for the therapeutic drug monitoring (TDM) of methotrexate (MTX) levels in actual clinical samples. TDM of MTX therapy is essential in offering individualized patient treatment for optimized efficacy and minimized side effects. In this respect, we have implemented a novel method which provides direct readout of MTX concentrations in patient's serum on a SPR sensor. The developed method consists of employing folic acid functionalized gold nanoparticles (Fa-AuNP) in competition with MTX for a specific number of its targeted enzyme, human dihydrofolate reductase (hDHFR) immobilized on the sensor surface. First, the shape and size of AuNP has been optimized to maxime sensitivity, minimize nonspecific response and increase NP stability in storage solution. In addition, the SPR sensor has been tested for its selectivity to 7-OH MTX, a potential interfering metabolite. The sensor was calibrated with spiked MTX samples in a pool of serum from healthy patient, providing a model to mimick real clinical samples analysis. Non-specific adsorption from serum components has been minimized by an anti-fouling peptide monolayer. Preliminary data with actual clinical samples from a local hospital shows good agreement between the SPR method and LC-MS/MS and Fluorescence Polarization Immunoassay (FPIA). Ultimately, our work will focus on integrating our SPR based sensing platform for rapid and direct analysis of sera MTX levels in patients under chemotherapy in hospital laboratories.

(621) **Capillary Electrophoresis for High Throughput Proteomics**

Norman Dovichi[1], Liangliang Sun[1], Guijie Zhu, Xiaojing Yan[1]; [1]University of Notre Dame

Most proteomics studies employ LC-ESI-MS/MS analysis of peptides. We are investigating capillary electrophoresis (CE)-ESI-MS/MS as an alternative technology for bottom-up proteomics. We first developed a rugged and sensitive CE-ESI interface based on electrokinetically-pumped sheath-flow (1). This interface operates in the nanospray domain, produces low-attomole detection limits for capillary electrophoresis separation of peptides, and offers great flexibility in separation buffer conditions (1-2). We then analyzed the secreted protein fraction of M. marinum (3). We pre-fractionated the secretome to produce simpler samples that were better suited to the separation performance of capillary zone electrophoresis (CZE). The results of the analysis of 12 fractions were compared with conventional UPLC analysis of the unfractionated sample. CZE produced slightly more protein identifications in a slightly shorter time period than UPLC. 140 protein groups were identified by CZE-ESI-MS/MS in three hours from this sample. We have recently improved the system. In the single-shot analysis of the E coli proteome, we identified >1,300 peptides and >300 protein groups in a 50-min CZE separation (4). We have employed this separation system to analyze seven fractions from the E. coli proteome (5). This system produced 23,706 peptide spectra matches, 4,902 peptide IDs, and 871 protein group IDs in 350 min analysis time. In an alternative separations scheme, we employed capillary isoelectric focusing for the analysis of differential protein expression in PC12 cells undergoing differentiation following treatment with nerve growth factor (6); we identified 835 protein groups and produced 2,329 unique peptides IDs.

1. Wojcik et al. *Rapid Commun Mass Spectrom.* 2010; 24: 2554-60
2. Wojcik et al. *Talanta*. 2012; 88: 324-329
3. Li et al. *Anal Chem.* 2012; 84: 1617-22
4. Sun et al. *Anal. Chem.* 2013; 85; 4187-4194
5. Yan et al. *Proteomics* in press
6. Zhu et al. *Anal. Chem.* in press

(622) **Two Dimensional Liquid Chromatography: The Future of HPLC?**

Peter Carr; [1]University of Minnesota

Over the past half dozen years there has been a blossoming of interest in fast (sub multiple hour analysis time) comprehensive two-dimensional liquid chromatography (denoted LCxLC). Several instrument companies are now providing hardware to address this interest. Our laboratory has focused on improving the analysis time of LCxLC by looking at the time needed to do the second dimension separation (2t), which is really the key factor in controlling the overall analysis time. Keeping in mind that an entire 2D chromatogram is obtained by taking N "slices" out of the 1D (first dimension) chromatogram and subjecting each slice to a separation on a chemically independent ("orthogonal") second dimension phase the total analysis time will be N*(2t). Since the overall resolution is greatly compromised when N becomes smaller than the 1D peak capacity it is obvious that 2t needs to be kept small to keep N*(2t) reasonable. In the limit of very short overall analysis times 1D chromatography is always superior to 2D chromatography for various technical reasons which we will elucidate; however, as more time is allowed the 2D approach must become superior. The question naturally arises -- at how short of a total run time does the 2D approach become superior? If this time is sufficiently short (all else being equal) the 2D approach will "squeeze out" the 1D approach and become the dominant mode of liquid chromatography. We will explore the various factors involved and at least make explicit some of the issues in what is deviously sequestered in "all else being equal".

(623) **Improved Breast Cancer Detection from High-Resolution Fourier Transform Infrared (FT-IR) Spectroscopic Imaging**

Rohith Reddy[1], David Mayerich[1], Rohit Bhargava[1]; [1]University of Illinois at Urbana Champaign

Fourier transform infrared (FT-IR) spectroscopic imaging provides spatially resolved chemical information on a microscopic length scale. Chemical information from mid-IR features has been shown to be valuable in determining tissue cell types and in performing automated histopathology for breast cancer. Our goal is then to use both the spectral and spatial distribution of tissue cell types to perform improved diagnosis of cancer. However, the accuracy of cancer detection is limited by the spatial resolution provided by current imaging systems. Recent work has demonstrated "high-definition imaging", where data of significantly higher spatial detail than previously possible was obtained by making modifications to commercial, desktop FT-IR imaging instruments. These design improvements were based on an understanding of the optical system derived from rigorous modeling of light propagation through the imaging instrument. Here, we extend this work by demonstrating that it is possible to identify previously obscured tissue types by performing histological classification on breast cancer tissue. These features and based on bio-chemically derived spectral metrics (features) and can improve cancer detection accuracy. We present image classification results where classification of high-definition imaging results in a more accurate labeling of terminal ductal lobular units (TDLUs) which are obscured when using conventional FT-IR imaging. These results are compared to results from visible-light microscopic examination of chemically stained tissue. Results indicate that high-definition FT-IR imaging can provide information typically obtained from a variety of standard, clinically and diagnostically useful chemical stains all without the need for expensive and laborious chemical staining. Automated computer algorithms for breast cancer detection using high-definition FT-IR imaging data are also discussed.

(624) **CAP-LC and QQQ-ICPMS, for Detecting Phosphorus and Sulfur in DNA-protein Cross-links**

Jiawei Gong, Julio Figueroa[1], Morwena Solivio[1]; [1]University of Cincinnati

Along with the oxidation of guanidine, the ROS driven reactions between proteins and DNA (cross-links) generate the most common damages that nucleic acids can suffer. These are important reactions because if they remain unrepaired, permanent mutations or replication stops are formed leading to cytotoxicity. However, they are not well studied, mainly because of the lack of good analytical procedures with sufficient detection capabilities. Techniques, based on ultra-trace level detection of S and P, are good, but they are not without interferences. The state-of-the-art for interference removal is to use the newer QQQ-ICPMS approach by passing 31P+ in Q1, passing to Q2 operating in the reaction mode and adding O2, therefore generating 47PO+ with Q3 and leaving the usual NOH+, etc. interferences behind. Monitoring 47PO+ results a signal absent from polyatomic interferences. The lower detection levels, when compared with those from cells using the collision or energy discrimination modes, are a major plus for the QQQ-ICPMS. In conjunction with the high resolving power of capillary liquid chromatography, the new QQQ-ICPMS technology was applied to study a DNA-Protein cross-link, by following both 47PO+ and 48SO+ in the intact complex and in its enzymatic digestion products. A good assignment of S containing peptides was possible and the peptide link to the DNA oligonucleotide was identified. Complementary MS methods are used to identify the cross-link.

(625) **Mass Spectrometry Based Label-Free Multiplex Mutation Site Genotyping Method by Allele Specific Ligation and Probe Amplification**

Jung Hun Park[1], Ye Lim Jung[1]; [1]KAIST, Republic of Korea

A mass spectrometry based label-free multiplex mutation site genotyping method was developed by utilizing multiplex ligase reaction, universal polymerase chain reaction (PCR), and nicking reaction. In this new assay, multiplex ligase reaction was firstly performed by using mutant specific ligation probe sets. The primary probe is designed to have additional base sequences for a universal forward primer annealing site at the 3' end. The secondary probe is designed to perfectly match with the target mutation site at the 3' end and to have a universal reverse primer annealing site at the 5' end. Therefore, the ligation takes place only for a mutant case by ligase reaction. After that, universal PCR is performed with the ligated product as a PCR template. In the universal PCR step, the reverse primer which has nicking enzyme recognition site and mass marker sequences at the 5' end is utilized to produce PCR amplicon which contains nicking site and mass marker region. Finally, after nicking reaction with the PCR product, only mutant case can generate a mass marker. By analyzing the mass markers by the mass spectrometry, we can easily recognize mutations exist or not. We have successfully genotyped 12 mutation sites at once by using artificial template of breast cancer susceptibility gene (BRCA 1 gene) exon 11 region.

(626) **ToF-SIMS as a Tool for Probing Lipid Saturation in Acute Myeloid Leukaemia Cells Treated with a Novel Combination Therapy**

Joanna Denbigh[1], Andrew Southam[2], Farhat Khanim[2], Roy Goodacre[1], Nick Lockyer[1]; [1]Manchester Institute of Biotechnology, University of Manchester, UK; [2]School of Biosciences, University of Birmingham, UK

Time of flight secondary ion mass spectrometry (ToF-SIMS) is a powerful surface analysis technique which has seen much development in biological applications in recent years. The emergence of such applications has been largely driven by instrument developments in the last decade in which cluster primary ion beams (Aun+, Bin+, C60+) have been employed instead of atomic ions such as Ga+ and Cs+. These polyatomic cluster ion beams are capable of generating higher secondary yields from molecular materials, particularly higher mass species and thus increase the sensitivity of the technique making ToF-SIMS a novel tool for probing the surface of biological materials. Recently there have been a number of reports into the localisation of metabolite and lipid species in various mammalian tissues using ToF-SIMS and other mass spectrometry imaging (MSI) techniques. The unique advantage of SIMS amongst MSI techniques is its sub-cellular spatial resolution, potentially allowing single cell metabolite analysis. Acute myeloid leukaemia (AML) is an aggressive cancer made up of dysfunctional cells from the myeloid lineage. Current treatment includes high grade chemotherapy, which has the disadvantage of being very toxic and thus poorly tolerated in major cohort of elderly AML patients. Drug redeployment represents an alternative to chemotherapy and involves the use of existing drugs for situations they were not originally designed for. It has recently been shown that the combination of the cholesterol lowering drug, bezafibrate, and the female contraceptive, medroxyprogesterone acetate (combination denoted BaP) shows anti-leukaemic activity with no observable haematological toxicity in patients. Initial lipidomic analysis of BaP treatment in HL60 and K562 AML cell lines suggested the treatment down-regulates *de novo* phospholipid synthesis leading to an increase in the unsaturation of phospholipid acyl chains. Here we report data from an investigation into the lipidome of AML whole cells using ToF-SIMS. The aim is to assess the application of this technology to provide new insights into the chemical effects of drug treatment in cellular membranes, in particular the observation of changes in saturation state of phospholipids at the cellular level.

(627) **Using Attenuated Total Reflectance Fourier Transform Infrared Spectroscopy to Optimize Surfaces for the Immobilization of Nanolipoprotein Particles**

Jessica Moore[1], Elyse Towns[1], Craig Blanchette[2], Don Land[1]; [1]UC Davis; [2]Lawrence Livermore National Laboratory

Nanolipoprotein particles (NLPs), also known as reconstituted high density lipoproteins (rHDLs), are discoidal self-assembled particles. They are commonly used as model membranes for the purpose of studying membrane proteins and interactions with other biomolecules. NLPs can be formed with different apolipoproteins and lipids offering flexibility attractive for one of its more recent applications of serving as vaccine delivery platforms. Attenuated total reflectance Fourier transform infrared spectroscopy (ATR-FTIR) is a useful technique for lipid studies and is being applied here to find the optimal conditions for surface immobilization of NLPs. In this study, the NLPs used consist of the phospholipid, 1,2-dimyristoyl-sn-glycero-3-phosphocholine (DMPC) and the apolipoprotein, apoE422K . The integrated area under amide bands I and II indicates which surface conditions provide the greatest saturation of NLPs. This work will ultimately be extended to studying the secondary protein structure of the apoE422K incorporated in the NLPs.

(628) **The Automated FADU-Assay to Quantify Formation and Repair of DNA Strand Breaks -A Rapid and Meaningful Genotoxicity Quantification**

Miriam Unger[1], Marcel Pilartz[1], Maria Moreno-Villanueva[2]; [1]CETICS Healthcare Technologies GmbH, Esslingen am Neckar, Germany; [2]Department of Biology, University of Konstanz, Konstanz, Germany

At present, just a few of the available *in vitro* genotoxicity tests measure DNA strand breaks and their repair in live cells. The comet assay as the considered „gold standard“ is still not standardized and does not allow full automation so far. In this context, the present study is focused on the automation process of an alternative method, the “Fluorimetric Detection of Alkaline DNA Unwinding” (FADU)

assay. In this case, the detection of DNA strand breaks is based on the progressive DNA unwinding (denaturation) under highly controlled conditions. In a similar way, the repair of induced DNA strand breaks can be analyzed in live cell environment. It is shown that the most steps of the FADU method could be automated which allows precise dispensing of solutions and control of temperature and process time during the assay. Exemplary, the effects of DNA strand breaks in Jurkat-cells treated with different incubation time of X-ray radiation will be summarized, follow up by a discussion on the DNA repair of X-ray treated Jurkat-cells.

(629) **Nonlinear Optical (NLO) Imaging Approaches for Protein Crystal Detection and Crystal Quality Assessment**

Emma DeWalt[1], Victoria Begue[1], Judith Ronau[1], Shane Sullivan[1], Ryan Muir[1], Chittaranjan Das[1], Garth Simpson[1]; [1]Purdue University

X-ray crystallography has become the method of choice for high-resolution structure determination of proteins. Despite advances in X-ray crystallography techniques, much time and expense is still invested in screening for diffraction-quality crystals. In order to streamline crystal screening, a protein crystal detection method must be fast, non-destructive and specific for protein and crystallinity. During the last five years, second harmonic generation (SHG) and two-photon-excited UV fluorescence (TPE-UVF) imaging techniques have been developed for rapid, sensitive and selective protein crystal detection [1] [2]. SHG is the frequency doubling of light and arises only from ordered, non-centrosymmetric media (including chiral crystals). As a result, SHG provides excellent selectivity for crystallinity, as aggregated protein and protein solution will not have a coherent SHG response. Although SHG imaging produces high contrast images for the majority of protein crystals, SHG signals generally decrease with increasing crystal symmetry, producing relatively weak signals for crystals with high-symmetry space groups [3]. To increase confidence in crystal detection, TPE-UVF imaging was developed as an independent and complimentary method to SHG. TPE-UVF is based on intrinsic fluorescence of aromatic residues present in proteins. It is insensitive to salts, and overcomes the major limitations associated with conventional one-photon UV fluorescence methods [2]. However, TPE-UVF alone does not provide information on crystallinity, making the identification of small crystals in the presence of aggregated protein challenging.
Recently, polarization-resolved (PR) methods were developed to expand the applications and reduce limitations of NLO imaging of protein crystals. PR-SHG was shown to extend SHG imaging to provide a measure of not only crystallinity, but also crystal quality [4]. PR-TPE-UVF was developed to extend TPE-UVF to provide both protein and crystal specificity.

[1] Kissick, D. J.; Gualtieri, E. J.; Simpson, G. J.; Cherezov, V., Anal. Chem. 2010, 82(2), 491-497.
[2] Madden, J. T.; DeWalt, E. L.; Simpson, G. J. Acta Crystallographica D. 2011, 67, 839-846.
[3] Haupert, L. M.; DeWalt, E. L.; Simpson, G. J. Acta Crystallographica D. 2012, 68, 1513-21.
[4] DeWalt, E. L..; Begue, V. J.; Ronau, J. A.; Sullivan, S. Z.; Das, C. ; Simpson, G. J. Acta Crystallographica D. 2013, 69, 74-81.

(630) **Analysis of the Surface Aggregation of Phospholipids using Attenuated Total Reflectance Fourier Transform Infrared Spectroscopy**

Elyse Towns[1], Donald Land[1]; [1]University of California, Davis

Attenuated total reflectance Fourier transform infrared spectroscopy (ATR-FTIR) was used to monitor the structure of 100 nm small unilamellar vesicles of the phospholipid dipalmitoylphosphatidylcholine on zinc selenide (ZnSe) and germanium (Ge) surfaces. It was found that on ZnSe the vesicles remained intact and on Ge ruptured to form a planar lipid bilayer. ATR-FTIR is an ideal tool to monitor the surface aggregation because one can probe specific vibrational modes located within hundreds of nanometers of the solid-liquid interface. The absorbance, frequency and full width at half maximum (FWHM) of the symmetric methylene stretching band of the phospholipid tails was analyzed to confirm the different aggregate structures. The frequency of the peak maximum of the asymmetric phosphate stretching band was used to determine the hydration of the phospholipids. The intact vesicle structure on ZnSe has a lower phosphate band frequency than the bilayer on the Ge indicating the phospholipids are more hydrated in a vesicular structure. Phospholipid vesicles mimic a cellular membrane making the ability to form and monitor a surface of intact vesicles useful to study the interaction of membrane associated biomolecules in a native-like environment.

(631) **Material and Biological Properties Controlling the Interaction of Bacterial Cells with Nanomaterials**

Ian Gunsolus[1], William Chrisler[2], Dehong Hu[2], Cosmin Mihai[2], Galya Orr[2], Christy Haynes[1]; [1]University of Minnesota; [2]Pacific Northwest National Laboratory; [3]University of Wisconsin-Madison

Nanomaterials have highly reactive surfaces and unique physical and chemical properties relative to bulk material, which can lead to sometimes deleterious interactions with biological systems. Consequently, toxicological evaluation of nanomaterials is an area of increasing interest. Among two common model systems, isolated mammalian cells and whole microorganisms, nanomaterial interactions with the latter are more poorly understood. Due to a relative lack of endocytotic pathways, bacteria generally do not actively internalize nanomaterials. This combined with the small size of bacterial cells makes characterization of their interaction with nanomaterials difficult. Using a combination of flow cytometry and microscopy, this work demonstrates binding of CdSe quantum dots at the cell surface of Shewanella oneidensis MR-1. The cellular components responsible for nanomaterial binding, which have received limited attention previously, are considered, as well as the nanomaterial surface properties that influence interaction with these cells.

(632) **Novel on-Chip Capacitively Coupled Contactless Conductivity Detection using Injected Metal Electrodes**

Leigh D. Thredgold[1], Dmitriy Khodakov[1], Amanda V. Ellis[1], Claire E. Lenehan[2]; [1]Flinders Centre for NanoScale Science and Technology, Flinders University, Adelaide; [2]School of Chemical and Physical Sciences, Flinders University, Adelaide

Lab-on-a-Chip (LOC) production has been significantly propelled by the development of simple, low cost fabrication techniques. Nevertheless, there remains a considerable number of limiting factors in producing commercially viable LOC systems. These arise from the complex fabrication processes required to integrate commonly utilised detection systems with the microchip. Capacitively coupled contactless conductivity detection (C^4D) and its integration with microchip technologies has been well studied. However, most reported methods have practical limitations including multi-step electrode patterning/fabrication processes and difficulty in consistently aligning detection electrodes. This has the potential to either increase the time and cost of device production or adversely impact analytical performance. We demonstrate the use of injected gallium electrodes for capacitively coupled contactless conductivity detection (C^4D) within a microchip electrophoresis device. Evaluation of the electrodes for quantitative detection of electrophoretically separated lithium, sodium and potassium ions shows the system offers competitive detection limits of 3.0×10^{-5} M, 3.0×10^{-5} M and 2.6×10^{-5} M respectively. The fabrication process is fast, highly reproducible and eliminates difficulties with electrode alignment. Using this approach C^4D can be readily achieved in any microchip by simply adding extra 'electrode' channels to the microchip during design.

(633) **Screening Method for Oxytetracycline in Muscle and Skin Salmon by Derivative Spectroscopy and Its Comparison with Chromatographic Method**

M. Ines Toral[1], Tamara Sabay[1], Pablo Richter[1]; [1]University of Chile

Oxytetracycline (OTC) is an antibiotic widely used in the salmon industry. This paper proposes a screening method for OTC in muscle and skin salmon, which allows reducing the number of samples to be determined by confirmatory methods.

In this method, samples of 5.0 ± 0.1 g of salmon muscle and skin, were fortified with standard OTC and allowed to stand for 20 min, Was extracted with 20 mL of buffer pH 4.0 ± 0.1 Mc Ilvaine/EDTA, was stirred in vortex for 10 min and added 2 mL of trichloroacetic acid 0.1 mol/L. Then was vortexed for 5 min and centrifuged 15 min at 4000 rpm. The extraction process was repeated and then both supernatants were mixed and filtered. Then a clean up was realized, for which was used a peristaltic pump and a cartridge sep-Pak C-18, conditioned with methanol and distilled water (6/4). OTC was then percolated with 4 mL of oxalic acid in methanol $1x10^{-2}$ mol/L, and the extract was evaluated by UV-Vis spectroscopy, finding that the band between 325 and 420 nm is practically not affected by the matrix, for to eliminate this low effects, derivative spectra were used. The analytical signal was evaluated by second derivative, smoothing factor of 16000, amplification factor of 10000 and analytical λ 393 nm, obtaining a linear regression DU = $1.97x10^{5}$ C (mol/L) + 0.1922, the determination and quantification limits were 1.16 $x10^{-7}$ and 3.86 $x10^{-7}$ mol/L, respectively.

The proposed method was applied in enriched muscle and skin salmon and was obtained a recovery percentage of 83 ± 3%. This method is simple and allows the determination of OTC in muscle and skin salmon up to 150 µg / kg, which value is under maximum residuals limits permitted, regulated by USA and Japan.

The results were compared with those obtained by HPLC/FL being concordant and finding no false positives or negatives, therefore is possible use this method as screening against confirmatory methods.

The authors thank FONDECYT Project 1100103.

(634) **A Response Surface Experimental Design Approach for Optimizing the Analysis of Glyphosate in Aqueous Solutions using Fluorenylmethyloxycarbonyl Chloride (FMOC-Cl) derivatization and Liquid Chromatography Tandem Mass Spetcrometry (LC-MS/MS**

Misjudeen Raji[1]; [1]King Abdullah University of Science and Technology

In this report, response surface methodology, a versatile experimental design tool, is used to investigate the major experimental parameters that influence the derivatization yield of glyphosate in water using fluorenylmethyloxycarbonyl chloride (FMOC-Cl) and to determine an optimum level for those experimental parameters that showed most significant effects. In addition, the performance of another FMOC reagent, 9-Fluorenylmethyl N-succinimidyl carbonate (FMOC-OSu) for derivatizing glyphosate was investigated and compared to that of FMOC-Cl. All derivatized samples were analyzed by both LC-ESI-MS/MS and HPLC-UV. The chromatographic peak area corresponding to the derivative molecule was used as the design response. Preliminary study show that the molar ratio of FMOC-Cl to the analyte has a significant effect on the derivatization yield. A pH of between 8 and 9.5 was found to be optimum for the derivatization procedure. Interestingly, the derivatization yield of FMOC-OSu was consistently lower than that of FMOC-Cl by approximately an order of magnitude. Another interesting observation worthy of mentioning is the cloudiness that results each time the derivatization reagent is added to the buffered sample solution. It is suggested that this phenomenon can be attributed to the low solubility of the derivatization reagent in the aqueous buffer used for the derivatization. The extent of cloudiness was found (albeit by visual inspection) to be greater for FMOC-Cl compared to FMOC-OSu. in order to circumvent this problem, a 2:1 v:v ratio of methanol and borate buffer solution was used for the derivatization. The optimized condition will be applied to spiked water samples to validate the method.

(635) **Analysis of Wheatgrass Endophytes**

Kimberly Clapp[1], Christine MacTaylor[1]; [1]Salem State University

Endophytes are microorganisms found in the internal tissues of plants, and can be used to create bioactive compounds used by plants for defense against pathogens. Endophytes have been found to contain many useful products including antibiotics and anti-cancer agents. (1)

In this research, Wheatgrass endophytes were analyzed using a combination of GC-MS and microbiological inhibitory tests. Cultures were successfully grown on gel agarose plates and in sabouraud dextrose broth. GC-MS analysis showed the presence of a long chain methyl ester. In addition, an inhibitory effect was observed on the growth of E. coli and S. aureus after inoculating extracted samples in broth. At this time it is unknown whether the ester is responsible for any inhibitory effects or if it is another compound not seen on the GC-MS.

1. Guo B, Wang Y, Sun X, Tang K. Bioactive natural products from endophytes: A review. Applied Biochemistry & Microbiology [serial online]. March 2008;44(2):136-142.

(636) **Determination of Glyoxal, Methylglyoxal and Diacetyl at Physiological Concentrations in Urine by HPLC with Fluorimetric Detection, using 4-metoxi-phenylenediamine for Derivatization**

Armando Gomez[1], Katarzyna Wrobel[1], Alma Corrales[1], Ma. Eugenia Garay-Sevilla[1], Kazimierz Wrobel[1]; [1]University of Guanajuato

Glyoxal (GO) and methylglyoxal (MGO) are biomarkers of glycation processes and oxidative stress, therefore their determination in clinical samples has often been undertaken. The third □-ketoaldehyde considered in this work was diacetyl (DMGO), a by-product of microbial fermentation, present in different food products, alcoholic beverages and also detected in urine. The original idea of this work was to use 4- metoxi phenylenediamine (4MPD) as a derivatizing agent, diethylglyoxal (DEGO) as an internal standard and reversed phase liquid chromatography with fluorimetric detection. Quinoxalines were efficiently formed at neutral pH and at room temperature, thus avoiding undesirable analyte dimerization or their *de novo* formation. Specifically, urine samples (200 µL) were spiked with 0.2 µg DEGO, mixed with 200 µL acetonitrile and centrifuged. The supernatant was diluted with 400 µL of phosphate buffer 50 mM, pH 7.3:acetonitrile (1:1); 10 µL 4MPD 1 µg/mL (containing 2-mercaptoethanol as antioxidant) were added and the mixture was left overnight. Finally, the sample was acidified (20 µL HCl 1 M) and saturated with NaCl for phase separation; 100 µL of acetonitrile phase was diluted with water (1:3) and 25 µL were injected to HPLC-FLD system (Agilent 1200 series). The separation of GO, MGO, DMGO and DEGO quinoxalines was accomplished within 12 min, using C18 Kinetex column (150 x 3 mm, 2.6 µm) from Phenomenex and gradient elution with three mobile phases (A - 0.8% acetic acid, 0.6% triethylamine, pH 4.3; B – methanol; C – acetonitrile). Calibration range was 5 - 250 µg/L, r2 >0.999, detection limits evaluated as 6□ for GO, MGO, DMGO were 0.5 µg/L, 0.2 µg/L and 0.1 µg/L, respectively. Within-day precision for real world samples did not exceed 6%. Several urine samples from healthy volunteers and diabetic patients were analyzed. No statistically significant differences were detected between the results obtained by external calibration versus standard addition method (ANOVA). The sensitivity of proposed here procedure enabled for detection of differences between analyte concentrations in urines from patients at different clinical conditions.

(637) **An Integrated Microfluidic Device for Trapping**

Alaknanda Amin[1], Christine Carlson[1], Jörg Woehl[1]; [1]University of Wisconsin-Milwaukee

Optical traps or "laser tweezers", which are capable of trapping microscopic dielectric particles through the production of steep electromagnetic field gradients, have been significant in the development of the field of biophysics and the manipulation of microscopic objects. We have developed a new tool for the trapping and manipulation of nanoscale objects including single molecules, the corral trap, which has distinct characteristics that set it apart from other trapping techniques. In order to increase the versatility of this new trapping tool, steps have been taken to integrate corral traps in a microfluidic cell. The production of such integrated devices based on focused ion beam milling and optical lithography techniques will be presented in detail. Corral trapping in microfluidic devices is expected to have important future applications in areas such as biomedical assays, ultra-sensitive biochemical analysis, and DNA manipulation and screening

(638) **Room-temperature Ionic Liquids: Tunable Solvents for the Removal of Dyestuffs from Aqueous Waste Streams**

Sarah Oplawski[1], Mark Dietz[1]; [1]University of Wisconsin-Milwaukee

Among the major classes of water pollutants, dyestuffs have proven to be particularly problematic, both in terms of the quantities released to the environment and the difficulties involved in their recovery from aqueous solution. Each year, textile mills worldwide discharge millions of gallons of dye-laden effluents, leading to significant adverse environmental impact as a consequence of the high chemical oxygen demand and toxicity of these effluent streams. For this reason, there has been considerable interest in the development of a means by which to remove dyes from aqueous waste streams. Textile mills generally employ a combination of physical, biological, and chemical methods, many of which are inefficient and expensive. Liquid-liquid extraction employing ionic liquids (ILs), a novel class of organic solvents typically comprising a bulky asymmetric organic cation in combination with any of a wide variety of anions, has the potential to overcome these problems. In this work, a variety of imidazolium-based ionic liquids were evaluated for their ability to extract representative cationic and anionic dyes from aqueous solution. UV-visible spectrometry was employed to determine the extent to which each dye is extracted from aqueous solution as a function of pH. Ionic liquids comprising small cations were found to extract cationic dyes more efficiently than ILs incorporating larger cations. Conversely, ILs comprising large cations extracted anionic dyes more efficiently than those based on small cations. Although these results suggest that ionic liquids show promise in treating textile wastewater, further progress requires that the mechanism of dye extraction in these systems be elucidated.

(639) **Chemical Analysis of Major and Minor Components in Fuel and Hydrocarbon Liquids**

Josef Simeonsson[1], Vamshi Inumula[1], Eric Kennehan[1], Ashley Frazzini[1]; [1]Youngstown State University

The commercial scale-up of a renewable energy technology that efficiently converts waste polymer materials to hydrocarbon fuels and liquids is the focus of a project being led by RESPolyflow Corp. of Akron, Ohio. Youngstown State University is working with RESPolyflow on this project by performing chemical characterizations and analyses of sample materials that are generated by the waste-to-fuels pyrolysis process. This presentation will provide a description of the analytical methods used to perform analyses of the waste-to-fuels product liquids including gas chromatography-mass spectrometry (GC-MS) for characterizing major and minor hydrocarbon components, inductively coupled plasma-mass spectrometry (ICP-MS) for measurements of trace elements, and element specific methods for nitrogen, sulfur and halide content in the sample liquids that utilize sample combustion combined with chemiluminescence spectrometry, molecular fluorescence spectrometry and ion chromatography detection approaches. Results will be presented for each of these analytical methods to demonstrate how they are used to characterize the product liquids and also how the results allow comparisons of the product liquids to standard gasoline and diesel fuels.

(640) **ATR Spectra of Polyethylene Films - Orientation and Crystallinity**

Chris Lynch[1,2], Richard Spragg[1], Ben Perston[1]; [1]PerkinElmer ASLS, Seer Green, UK; [2]PerkinElmer Inc., Shelton, CT

The crystallinity of polyethylene is sometimes estimated from the relative intensities of the CH2 rocking bands at 730 and 720cm-1. Crystalline regions contribute to both bands while the amorphous component appears near 720cm-1. ATR spectra of LDPE films show an increase in the relative intensity at 720cm-1 with increased pressure. This is not simply a surface effect as it can also be seen in transmission spectra of films after pressing, but it does not correspond to an increase in amorphous content. Rather it results from a change in orientation of the polymer chains perpendicular to the plane of the film. Both the bands at 730 and 720cm-1 have dipole moment changes that are perpendicular to the chain direction. However the dipole moment change for the 730cm-1 band typically has a preferential direction in the plane of the film while for the 720cm-1 band the direction is primarily normal to the plane of the film. The transmission spectra of films tilted with respect to the beam direction before and after pressing show that the average chain orientation is forced more into the plane of the film by pressure. Polarized ATR measurements are sensitive to 3-dimensional orientation and have been used to measure surface orientation in polymer films. In the case of LDPE films such measurements are complicated by the pressure dependence of the orientation. A further issue is that the spectral contributions of long-chain additives with a high degree of orientation also change significantly with pressure. We show that attempts to measure either crystallinity or orientation in LDPE films must be regarded with caution.

(641) **AFM-based Chemical and Mechanical Property Characterization of Interconnects in Semiconductors**

Michael Lo[1], Sean King[2], Eoghan Dillon[1], Qichi Hu[1], Roshan Shetty[1], Craig Prater[1]; [1]Anasys Instruments; [2]Intel Corporation

Spectroscopic characterization of interconnects and circuitries in semiconductors has particularly gained significant traction as dimensions for breakthroughs and failure analysis are continuously shrinking. Often, analyses may only be in tens of micrometers or smaller in most cases. This poses a significant challenge to infrared microspectroscopy as its spatial resolution is diffraction limited to approximately 3 - 10 μm or larger. To achieve better spatial resolution, a broadly tunable infrared laser is coupled to an atomic force microscope (AFM-IR). Here, pulses of the IR laser impinge onto the sample at its absorption band and cause rapid thermal expansion inducing vibrations in the AFM tip that is directly in contact with the sample. Amplitudes of the ringing motion of the AFM tip are then recorded as the same tip scans over an area of interest. By detecting only the perturbations directly underneath the AFM tip, spatial resolution below the diffraction limits of IR radiation could be achieved. In this manner, the IR absorption spectra for a *ca.* 1.5 μm wide interlayer dielectric (ILD) in a microelectronic Cu interconnect could be detected locally and selectively highlighted in between metallic features. To complement the AFM-IR technique, AFM-based contact resonance (CR-AFM) measurements were additionally performed to probe the relative mechanical property of the different materials in the said microelectronic sample. The resonant frequency of the AFM tip is controlled by modulating the alternating current going through a

specialized ThermLever™, which interacts with the magnetic field with a magnet nearby. As this tip scans from ILD to other metallic layers, the frequency of the AFM tip vibration would change. This is mostly due to the variations in the mechanical stiffness from one material to another. By combining the AFM-IR and CR-AFM techniques, both chemical and mechanical characterization of microelectronics can be achieved using an AFM at high spatial resolution.

(642) **Temperature and Consentration Dependence of Far Ultraviolet Spectra in Alcohol-Hexane Solution ~ Alternation of Hydrogen Bonding~**

Yusuke Morisawa[1], Yukihiro Teramoto[1], Yukihiro Ozaki[2]; [1]Kinki University; [2]Kwansei Gakuin University

In a liquid phase, alcohols form aggregates with hydrogen bonding. Macroscopic properties such as density and viscosity will be influenced by structures of these aggregates. Because of this importance, there are many experimental and theoretical researches about the aggregates of alcohols. Most of researches employed vibrational spectroscopy focused on O-H. As a result of complex splits in the spectra of aggregates, the observed spectra appear as a large broad band for many kinds of aggregates. In the region of Far Ultraviolet (FUV), water and alcohol have transitions due to lone pair on the oxygen atom. These transitions are apparently affected by hydrogen bonding because electrons of lone pair take an important role in the hydrogen bonding. FUV Spectrum of methanol in the pure-liquid states have already reported by using attenuated total reflection (ATR) - FUV spectroscopy. Concentration dependence of tail structure in the region of 190-210 nm has been observed. The molar absorption coefficient of the tail structure was decreasing with the increase of the concentration of methanol. In the present study, temperature dependence of the tail structure for the alcohol-hexane solution of the different concentration. Temperature dependence of the molar absorption coefficients were increasing with the increasing of temperature for the conc-solution, on the other hand, that for the diluted solution were decreasing. We will discuss about this alternation of the temperature dependence.

(643) **A Simple Method to Obtain Absorption Spectra at Sub-Micrometer Spatial Resolution using a Transmission Grating Spectrograph**

Dharmendar Kumar Sharma[1], Arindam Chowdhury[1]; [1]Indian Institute of Technology Bombay, Mumbai, India

Spectral imaging by using a combination of a transmission grating (TG) and an array detector allows for simultaneous detection of the non-dispersed image and the dispersed spectra. This high-throughput method has the advantage over conventional techniques in terms of data- collection efficiency, cost, and spatiotemporal resolution, and has therefore been used to perform spatially-resolved fluorescence spectroscopy. Yet, the applicability of this method for spatially-resolved absorption measurements has not been explored. We have developed a methodology to efficiently obtain spatially-resolved absorption spectra of solid samples using white light sources and a TG-CCD based microscope. We provide examples of various fluorescent and non-fluorescent samples to validate the applicability of this method in obtaining reliable absorption spectra with nominal requirement of the material (few drops of ~μM solution). Further, using an adjustable slit, we demonstrate the importance of spatial selection in determining the spectral (or energetic) resolution of the acquired spectra in terms of spectral features such as peak positions and line-widths. The use of narrow slits becomes even more crucial when concentration gradients exist, or in presence of several absorbing species separated by a few micrometers, which results in spectral broadening as well peak-shifts. Finally, we show that the developed method can also be used to determine concentration gradients of absorbing species within cellular environments at high spatial resolution.

(644) **Use of Raman and Infrared Spectroscopy to Study the "Fuzzy Chemistry" of the Formation of Iron(III) Hydroxide Polymorphs**

Dale L Perry[1], Nicolaza Pariona[2], Karla I Camacho[2], Arturo I Martinez[2]; [1]Lawrence Berkeley National Laboratory, University of California, Berkeley, CA; [2]Center for Research and Advanced Studies of the National Polytechnic Institute, Cinvestav - Saltillo, Coahuila, Mexico

The synthetic reaction mechanisms of many materials are dependent on trace amounts of elements to effect the formation of a unique , structural polymorph, the process exhibiting the concept of "fuzzy chemistry," many of them being oxides or hydrated oxides. One such oxide system is that of the forms of lead(II) oxide, PbO, which gives different colored materials relative to which phase is formed [Applied Physics A: Materials Science and Processing, 89, 77 (2007)]. By choosing the dopants in the syntheses, one can tailor a desired end-product. The present work describes the use of Raman and infrared spectroscopy to both follow the reaction of formation and identify the final product in the FeOOH series of compounds, with the primary focus being on the formation of β – FeOOH (akaganeite) and the spectral differences with its other structural polymorphs. Experimental factors involved in the syntheses are discussed, along with the spectral details of each phase. Raman and infrared differences for the structural phases are compared. DLP wishes to acknowledge support of the U. S. Department of Energy under Contract Number DE-AC02-05CH11231. This work was supported by the Initiative of Multidisciplinary Projects of Cinvestav.

(645) **Evaluating a Modified NDIR Approach for Measuring Silica on Filter Samples of Coal Dust**

Art Miller[1], Thomas Grant[2], Grant King[1], Tim Nicholes[2], Brett Bollier[2]; [1]CDC/NIOSH; [2]Gonzaga University

Miners are exposed to various respiratory hazards, including inhalation of dust containing microscopic particles of crystalline silica. Exposure to silica dust is associated with the development of silicosis, pulmonary tuberculosis, and other airway diseases. Despite extensive knowledge of both causes of silicosis and effective preventative actions, silica exposures in many occupational settings continue, and risks are particularly high in both coal and non-coal mines. To address this, NIOSH is conducting studies and developing methods for the in-mine measurement of airborne silica in order to reduce silica exposure in the mining industry. Research is aimed at evaluating a variety of field-portable spectrometers for end-of-shift (EOS) silica measurement on filter samples of mine dust. Such EOS data would give miners timely feedback regarding potentially prolonged periods of overexposure prior to receiving analytical results. The success of a recent study comprising the on-filter analysis of silica by FTIR has led NIOSH to investigate a novel approach to infrared spectrometry based on the non-dispersive Infrared (NDIR) method. NDIR utilizes a bandpass filter that only allows a small range of wavelengths to strike the detector, allowing for a simpler design that may be amenable for field portable silica measurement. This poster describes a preliminary proof-of-concept study that demonstrates the feasbility of using such an approach for measuring silica directly on filter samples of mine dust.

(646) **Variable-Pathlength Cavity Spectroscopy: Development of a Real-Time Monitoring System**

Ryan A. Schmeling[1], Peter Geissinger[1], Joseph H. Aldstadt[1]; [1]Dept. of Chemistry & Biochemistry, University of Wisconsin-Milwaukee

We are developing a novel approach to ultra-trace analysis by molecular absorption spectroscopy. In Variable-Pathlength Cavity Spectroscopy (VPCS), a high-finesse optical cavity is formed by

introducing light from a pulsed dye laser (488 nm) in the same manner as used in Cavity Ring-Down Spectroscopy (CRDS). However, unlike CRDS, the cavity exit mirror contains a slit (1.0-mm width) that is rotated at high frequency on an axle, thereby transmitting a fraction of the trapped light to a photomultiplier tube detector. In this approach, absorbance data can therefore be recorded directly. Because the frequency of mirror rotation can be varied, the pathlength can be adjusted as a means to encompass a broad concentration range. In earlier prototypes, the VPCS instrument was manually aligned and the data were manually reduced. In the current prototype instrument, FPGA (Field-Programmable Gate Array) hardware and LabVIEW software are used to automate the process of data collection and reduction. With the implementation of the FPGA hardware and LabVIEW code, more precise data collection and reduction can thus be realized. In this presentation, we will describe the hardware modifications and software program structure. We will also present results in which we characterized the relationships of the key instrumental factors as measured by the effect on pathlength enhancement – particularly the relationships of the beam's angular offset (which describes the position of the exit slit with respect to the point on the mirror where the pulse enters the cavity) and the rotational speed. Characterization of the beam profile to observe the effect that the exit slit has on the light as it exits the cavity will be described as well.

(647) **A Spectroscopy Study of the Transformation of Ferrihydrite to Hematite**

Dale L Perry[3], N. Pariona[1], J. Quispe-Marcatoma[2], U.D. Chacón Hernández[2], W. T. Herrera[2], E. Baggio-Saitovitch[2], Dale L Perry[3], Arturo I. Martinez[1]; [1]Center for Research and Advanced Studies of the National Polytechnic Institute, Cinvestav-Saltillo, Carr. Saltillo-Mty. Km 13, 25900 Ramos Arizpe, Coahuila, MEXICO; [2]Centro Brasileiro de Pesquisas Físicas, Rio de Janeiro, 22290-180, BRAZIL; [3]Lawrence Berkeley National Laboratory, University of California, Berkeley, California 94720 USA

The transformation of ferrihydrite depends on many different factors such as trace amounts of cations, pH, temperature, the source of ferrihydrite, and the reaction atmosphere. These conditions affect the formation of a single or mixture of iron oxide phases. By choosing the trace cations in the syntheses and optimizing other experimental parameters, one can tailor a desired end-product. This paper describes the use of X-ray diffraction and Mossbauer spectroscopy to both follow the reaction and identify the final product in the transformation of ferrihydrite. Here it is demonstrated that pure hematite can be synthesized under optimal conditions, and mixtures of hematite/goethite/magnetite can be obtained, if trace cations exceed the optimal limit. Using the experimental results, a possible transformation mechanism is discussed. DLP wishes to acknowledge support of the U. S. Department of Energy under Contract Number DE-AC02-05CH11231. This work was supported by the Initiative of Multidisciplinary Projects of Cinvestav.

(648) **Recent Advances in Broadly Tunable & Narrow Linewidth Mid-IR Lasers - Addressing the Varied Needs of Molecular Spectroscopy**

Robert Shine Jr[1], David Arnone[1], Leigh Bromley[1], David Caffey[1], William Chapman[1], Vince Cook[1], Timothy Day[1], Allen Priest[1], Michael Pushkarsky[1]; [1]Daylight Solutions, Inc

The wide range of applications based on molecular spectroscopy is driving a diverse range of mid-infrared source requirements. We present recent developments in both broadly tunable and narrow linewidth quantum-cascade-laser-based sources addressing these requirements.

(649) **Recent Advances in Glow Discharge Optical Spectrometry for the Characterization of Materials**

Patrick Chapon[1], Christophe Morin[1], Philippe Hunault[1]; [1]HORIBA Scientific

RF GD OES provides direct measurement of the chemical composition of thin and thick layers – conductive or non-conductive, as a function of depth with excellent depth resolution. The technique relies on the sputtering of a large area of the material of interest (conductive or not) by a high density (10^{14}) and low energy RF plasma. The RF GD plasma allows very fast erosion (typically 2-10nm/s on metals, several microns per minute) with minimum surface damage (as the incident particles have an average energy of about 50eV).

Presentation will show that these characteristics can be very beneficial in preparing samples for SEM to access and reveal such things as embedded inclusions in stainless steels, or to enhance surface preparation prior to EBSD measurements of W carbides.

Features and benefits of a recent patented development permitting the ultra fast erosion of polymer layers with excellent depth resolution will be shown. Finally, cross measurements between XPS and RF GD are also of great interest. Results on Photo Voltaic CIGS absorbers will be presented and XPS measurements performed within the GD craters will allow us to discuss the GD etching mechanisms.

(650) **Fabrication of Silver-Mesoporous Silica Core-Shell Nanomaterials and Evaluation of Silver Dissolution: Effects of Different Core Morphologies**

Ashish Datt[1], Ian Gunsolus[1], Maral Mousavi[1], Carlos Perez De Jesus[1], Philippe Buhlmann[1], Christy Haynes[1]; [1]University of Minnesota

Over the past decade, nanotechnology has grown rapidly with scientific advancements in the fields of drug delivery, imaging and other biomedical applications. As a consequence, there is a need to understand the toxicological behavior of the nanoparticles towards human health and the environment. Silver nanoparticles, in particular, are used in various cosmetics, toys, wound dressings and clothing due to the antimicrobial properties that result from the dissolution of Ag to Ag+. As this dissolution process can cause bacterial cell death, there is a need to study the effect of silver nanoparticle dissolution behavior with different morphologies of silver nanoparticles. In this research, novel core-shell mesoporous silica nanomaterials were fabricated to encapsulate different morphologies of silver nanoparticles, including nanospheres, nanoprisms and nanocubes. The core-shell nanomaterials were extensively characterized using several microscopic and spectroscopic techniques, including dynamic light scattering, transmission electron microscopy, scanning electron microscopy, and UV-Vis spectroscopy. The silver dissolution measurements were performed using a selective and dynamic technique, Ag+-selective electrodes (ISEs) with ionophore-doped fluorous membranes. The silver dissolution profiles of the core-shell nanomaterials were compared with that of bare silver nanoparticles, demonstrating that core size and morphology as well as shell thickness and porosity significantly influence Ag+ release.

(651) **Evaluating the Kinetics of Nanoparticle-Molecular Interactions for Spectroscopy**

Binaya Shrestha[1], Thomas Heiderscheit[1], Amanda Haes[1]; [1]University of Iowa

Gold nanoparticles exhibit novel optical properties (i.e. localized surface plasmon resonance (LSPR)) which depend on their shape, size, and local environment. A consequence of the LSPR is improved S/N for molecular detection via surface-enhanced spectroscopies including surface-enhanced Raman scattering (SERS). Herein, both LSPR and SERS signals will be monitored simultaneously as a function of 2-naphthalenethiol and gold nanoparticle concentrations. Nanoparticle surface modification, agglomeration, aggregation, and

sedimentation will be modeled as a function of time. MATLAB programs will be used to batch process spectroscopic data, and reaction velocities will be determined using DynaFit. Five different aggregation kinetic models will be evaluated and statistically compared to correlate nanoparticle-molecule interactions as a function of time. As a result, these kinetic models should facilitate experimental design using solution-phase nanoparticles for various biological and chemical sensing applications.

(652) **Measurement of Particulate Carbon Using Laser-induced and Spark Plasma Emission Spectroscopy: Application to Measurement of Airborne Carbon Nanomaterials**

Pramod Kulkarni[1], Lina Zheng[1], M. Eileen Birch[1], Gregory Deye[1], Dionysios Dionysiou[1]; [1]Centers for Disease Control and Prevention

We extend the application of our aerosol spark emission spectroscopy system (J. Anal. At. Spectrom., 2012, 27, 1101) to measurement of engineered carbon nanomaterials. The system incorporates coaxial electrodes that preconcentrate the incoming aerosol particles for subsequent near-real-time analysis using two separate plasma sources: laser-induced and pulsed high-voltage spark plasma. Preconcentration is accomplished through focused electrostatic deposition of charged aerosol particles onto the tip of a cathode or a ground electrode. Following deposition, laser-induced plasma is introduced on the cathode tip using a pulsed laser (50-100 mJ/pulse). In case of high-voltage spark plasma, a high voltage pulse is applied between the electrodes, leading to formation of pulsed spark discharge with energy ranging from 50-300 mJ/pulse. The particulate matter collected on the cathode tip is ablated, atomized and electronically excited by the laser and spark plasmas, resulting in atomic emissions that are subsequently recorded using a broadband optical spectrometer for element identification and quantification. The total particulate carbon determined is a good surrogate measure of carbon nanomaterials when particulate organic carbon (OC) and elemental carbon (EC) from other sources are absent or minimal, or correction for the bias can be made. The system was calibrated and detection limit were determined for total carbon using carbon emission at 247.85 nm (C I) and carbonaceous test aerosols. To improve the selectivity for carbon nanomaterials, the cathode was heated to 300-500 ^{o}C to minimize the contribution of condensed OC. The detection limit for total carbon, measurement selectivity as a function of cathode temperature, results compared with EC obtained by NIOSH Method 5040, and application to near real-time measurement of single- and multi-walled carbon nanotubes will be presented and discussed.

(653) **Modeling Heat Transfer through Multiple Interfaces of Differing Phase for Predictive Temperature Cycling Regulation**

Bradley M. Moran[1], Peter Geissinger[1], Jorg C. Woehl[1]; [1]University of Wisconsin-Milwaukee

Conducting spectral experiments in the cryogenic regime offers two important benefits. Due to the significant minimization of phonon coupling, electronic transitions are able to approach their lifetime limited values, leading to less broadened spectral features. Furthermore, the conformational degrees of freedom existing in low lying energy states can be probed if the ability to systematically control and cycle the temperature of a sample is a possibility[1]. Possessing precise thermal control thus requires the classification and regulation of the heating and cooling behavior of a sample's environment. Therefore, the establishment of a model that systematically predicts heat flows throughout the system becomes a necessity. This investigation looks to accurately and predictively model the thermal characteristics of a 9VSRD-SVT-22 Janis Research Dewar; however, modeling methods are broadly applicable. The ability to cycle between various temperature values during temperature cycling experiments and dependably modulate the heater such that desired temperature set-points are quickly achieved without overshoot is essential. The temperature within the cryostat is controlled by an internal heater and is monitored at both the heater and at the sample stage. Heat transfer occurs through multiple interfaces and phase boundaries between the sample, heater, and cryogen reservoir. Conductive and convective processes are explored, taking into account specific geometrical and material constraints, thermal conductivities, temperature varying heat transfer coefficients and thermal resistance at boundary layers. Both transient and steady-state models are investigated and are compared for predictive ability and consistency to experimental data.

1.) D. Leeson et al., J. Phys. Chem. B 101, 6331 (1997).
2.) Barron, Randall F. Cryogenic Heat Transfer. Ann Arbor: Taylor & Francis, 1999. 41-76.
3.) Bell, Kenneth J.. "Heat Transfer." Albright's Chemical Engineering Handbook. Boca Raton: CRC Press, 2009. 479-566.

(654) **Immobilizing a DNA Molecule within an Electrostatic Corral**

Xavier Udad[1], Alaknanda Amin-Patel[1], Christine Carlson[1], Jorg Woehl[1]; [1]University of Wisconsin-Milwaukee

Nanotechnology is the manipulation of matter on a very small scale, down to the level of individual molecules. The idea of controlling single molecules is crucial to the advent of nanotechnology. Modern industrial manufacturing predominantly employs an assembly line process in order to produce goods. Many scientists have tried to envision an assembly line on the molecular level. There are many specific problems that must be overcome in order for nanotechnology to come to fruition. In order to control and manipulate a single molecule, the first step is to isolate or trap it. Isolating a single molecule has wide application in numerous fields, not just nanotechnology. Biologists could immobilize individual cells or proteins; chemists could observe fundamental reactions. Often times, immobilizing a single molecule requires that it be altered, modified, or have its functionality changed in order to facilitate the trapping. Altering a molecule's behavior can be a shortcoming especially in the case of studying biophysical processes such as protein folding. The "corral trap" represents one possible method for isolating single molecules without altering its functionality. The corral trap is essentially a thin layer of metal that has small microscopic holes embedded in its surface. When a wire is attached to the surface of the metal and a voltage is applied, a potential well is formed where the holes are. The potential well can be described as a build-up of electrons, which are negatively charged. The shape of the potential well is circular. Because of its shape, the potential well can uniformly surround a negatively charged DNA molecule and keep it immobilized in an aqueous solution environment.

(655) **Silver Speciation in Commercially Marketed Products Containing Silver Nanoparticles**

Traci Hanley[1], Ryan Saadawi[1], Julio Julio Landero-Figueroa[1], Peng Zhang[1], Joseph Caruso[1]; [1]University of Cincinnati, Department of Chemistry, Cincinnati, OH

The broad spectrum antibacterial effects of silver have been known since antiquity. This has led to commercially marketed consumer products, labeled to contain silver nanoparticles (CMAgNP, commercially marketed silver nano products). Such CMAgNPs have been shown to release silver, but the chemical species remains largely unknown1. Methods to identify and quantitate the chemical form of silver released from or associated with CMAgNPs are in demand to evaluate the health risks associated with these products. Elemental speciation is commonly employed to identify/quantitate various chemical forms of an element; then inferences can be made relating the quantity of a particular chemical species to the toxicity risk for a given individual. Toxicity differences between silver species exists as studies indicate silver cations (Ag+) upon entering the cell exhibit greater primary toxicity compared to other silver forms such as

nanoparticle (AgNP), Ag0, AgCl-, and silver complexes which are considered to have negligible toxicity [2, 3]. Much of the toxicity associated with nanoparticles can be attributed to more effective delivery of Ag+ inside the cell, which is otherwise significantly less mobile and less toxic without such nanofacilitated delivery. The presented study demonstrates the speciation of Ag+ and AgNPs in starch stabilized colloidal silver solutions using cation exchange chromatography in combination with ICPMS for Ag+ quantitation and UV-Vis for AgNP detection. This method is applicable to AgNPs/Ag+ colloidal solutions with the goal of being able to detect, quantify, and speciate Ag+ versus AgNPs present in or released from CMAgNP.

1 J. Farkas, H. Peter, P. Christian, J. A. Gallego Urrea, M. Hassellov, J. Tuoriniemi, S. Gustafsson, E. Olsson, K. Hylland, K. V. Thomas, Environ Int 2011, 37, 1057-62 S0160-4120(11)00057-2 [pii] 10.1016/j.envint.2011.03.006.
2 H. T. Ratte, Environmental Toxicology and Chemistry 1999, 18, 89-108 10.1002/etc.5620180112.
3 Z. M. Xiu, Q. B. Zhang, H. L. Puppala, V. L. Colvin, P. J. Alvarez, Nano Lett 2012, 12, 4271-5 10.1021/nl301934w.

(656) Single Molecule Confocal Fluorescence Lifetime Correlation Spectroscopy for Accurate Nanoparticle Size Determination

Bonghwan Chon[1], Kimberly Briggman[1], Jeeseong Hwang[1]; [1]National Institute of Standards and Technology

Unlike ensemble averaged measurements of many particles, the characterization of physico-chemical properties of single nanoparticles (NPs) provides information on the detailed distribution of individual properties in the entire population. This information is essential in understanding and controlling the interaction of nanoparticles among themselves in engineering self-assembled structures, developing nanoparticle-based biological and chemical assays, and assessing and controlling their influence on the environment, health, and safety.

We report on an experimental procedure in confocal single molecule fluorescence lifetime correlation spectroscopy (FLCS) to determine the range of excitation power and molecule concentration in solution under which the application of an unmodified model autocorrelation function is justified. This procedure enables fitting of the autocorrelation to an accurate model to measure diffusion length (r) and diffusion time (τ_D) of single molecules in solution. We also report on the pinhole size dependency of r and τ_D in a confocal FLCS platform. This procedure determines a set of experimental parameters with which the Stoke-Einstein (S-E) equation accurately measures the hydrodynamic radii of spherical nanoparticles, enabling the determination of the particle size range for which the hydrodynamic radius by the S-E equation measures the real particle radius.

(657) Standoff Material Characterization by Mid-Infrared Quantum Cascade Laser Reflection Spectroscopy

Mark Norman[1], John Coates[2]; [1]Block Engineering; [2]Coates Consulting

Non-contact analysis of materials is often attempted with optical techniques like near-infrared diffuse reflection and Raman scattering. But ultimately these techniques are limited by the amount of spectral information they produce or by the standoff distances they provide. A mid-infrared quantum cascade laser (QCL) offers an extremely bright excitation source that is highly collimated and eye-safe. This enables reflection measurements at distances of 15 cm or greater with excellent spectral quality in the information-rich "fingerprint" region. Furthermore, the QCL does not pose any concerns of fluorescence or sample degradation. This presentation will show reflection data for a variety of bulk materials including solvents, polymers, pharmaceuticals, and coatings obtained with a commercial QCL spectrometer. The effects of specular and diffuse reflection under various measurement conditions will be discussed. Implications for using this technique for rapid, non-contact analysis in a variety of applications will also be examined.

(658) Effects of Particle Size on Infrared Reflectance Spectra

Tanya Myers[1], Yin-Fong Su[1], Carolyn Brauer[1], Thomas Blake[1], Timothy Johnson[1]; [1]Pacific Northwest National Laboratory

This paper examines the effects of particle size on reflectance spectra in the 1.3 – 16.67 micron range for various inorganic salts. The bulk inorganic materials were ground with a mortar and pestle and then sieved to obtain the following particle size ranges: 0-45, 45-90, 90-180, 180-250, 250-500, and >500 microns. The spectra were recorded using a Fourier transform infrared spectrometer equipped with an integrating sphere to measure either the diffuse or total reflectance of the bulk samples. The spectra were rich with structure and strongly dependent on the mean particle size of the sample. Volume scattering played a key role in which the reflectance increased with decreasing particle size. As the wavelength increases, interesting effects were observed where volume scattering no longer dominated the spectral features. For example, Reststrahlen bands, which are dominated by surface scattering, exhibited a relatively minor change with particle size. These studies clearly show that particle size has an enormous influence on the measured reflectance spectra for bulk material; successful identification requires sufficient and representative reflectance data to bracket the scenario.

(659) Flexible Probes for Process-Spectroscopy

Viacheslav Artyushenko[1], Alexey Bocharnikov[1], Joachim Mannhardt[1], Tatiana Sakharova[2]; [1]art photonics GmbH; [2]General Physics Institute of RAN

Within the last 2 decades the synergy of fiber optics with UV-Vis-NIR-spectroscopy enables fast growth of fiber spectroscopy applications in lab and industry because of several reasons:

a) eliminated need to take samples for lab analysis from a running process - replaced by remote reaction monitoring in-citu & in real time;

b) high transmission of silica fibers in 0,2-2µm range for remote process-control at hundreds meters from spectrometer;

c) robust design of various spectral probes to monitor reactions at high pressure, high or low temperature, vibrations, in toxic or aggressive media, etc.

While silica fiber spectroscopy is limited by silica glass transmission till 2µm, the new types of Mid IR-fibers enable analysis in 2-17µm finger-print range - the most informative for molecular vibration analysis. Flexible bridge between chemical reactor and IR-spectral systems of various type (FTIR, LED, QCL, IR-filter, etc.) can be based on Polycrystalline IR-fibers from Silver Halides, chalcogenide glass IR-fibers or hollow waveguides. Parameters of the most advanced probes based on these fibers and waveguides are compared in review presentation to guide for their best selection in different spectroscopy methods: ATR-absorption, Transmission and Reflection. Special focus is made on industrial probes compatible with process-interfaces - designed to clean probe optics and to provide full automated process control in industry.

(660) Rapid, Nondestructive Estimation of Surface Polymer Layer Thickness using ATR FTIR Spectroscopy and Synthetic Spectra Derived from Optical Principles

B. Andre Weinstock[1], Christopher Loose[1]; [1]Semprus BioSciences Inc.

We have developed a rapid, nondestructive analytical method that estimates the thickness of a surface polymer layer with high precision but unknown accuracy using a single attenuated total reflection Fourier transform infrared (ATR FTIR) measurement. Because the method is rapid, nondestructive, and requires no sample preparation, it is ideal as a process analytical technique. Prior to implementation,

the ATR FTIR spectrum of the substrate layer pure component and the ATR FTIR and real refractive index spectra of the surface layer pure component must be known. From these three input spectra a synthetic mid-infrared spectral matrix of 0nm to 10000nm-thick surface layers on substrate is created *de novo*. A minimum statistical distance match between a process sample's ATR FTIR spectrum and the synthetic spectral matrix provides the thickness of that sample. We show that this method can be used to successfully estimate the thickness of polysulfobetaine surface modification, a hydrated polymeric surface layer covalently bonded onto a polyetherurethane substrate. A database of 1850 sample spectra was examined. Spectrochemical matrix-effects unknowns, such as the non-uniform and molecularly novel polysulfobetaine-polyetherurethane interface, were found to be minimal. A partial least squares regression analysis of the database spectra versus their thicknesses as calculated by the method described yielded an estimate of precision of ±52nm.

(661) **Electron Solvation Process Examined with Multi-Channel Femtosecond Time-Resolved Near-IR Spectroscopy at 1.0 to 1.5 Micrometer**

Koichi Iwata[1], Setsuka Arii[1], Tomohisa Takaya[1]; [1]Gakushuin University

Solvated electrons show a characteristic absorption band in the visible to near-infrared region. The absorption maximum is first observed in the near-infrared region at 1 micrometer or longer. The maximum then shows a blue-shift as the solvation process proceeds. We examine the initial process of the electron solvation with multi-channel femtosecond time-resolved near-IR spectroscopy. We irradiate sample liquids with a femtosecond ultraviolet pulse of 40 fs duration and create electrons by multi-photon excitation. The near-infrared portion of the white light continuum generated by the 800 nm light pulse from a Ti:sapphire regenerative amplifier is used as the probe pulse. The probe pulse after the sample is dispersed by a spectrograph and is detected by an InGaAs array detector. Reliable determination of the absorption maximum is possible with the use of the array detector. We fit a single exponential function to the peak shift observed for dehydrated methanol and ethanol. The obtained time constants are 10 ps in methanol and 30 ps in ethanol.

(662) **Deep Ocean LIBS: Calibration Issues**

Stanley Angel[1], Joseph Bonvallet[1]; [1]Department of Chemistry and Biochemistry, The University of South Carolina

The development of *in situ* chemical sensors that can provide real time, multi-elemental sensing capability would be a significant advance over current oceanographic technology. To this end, laser induced breakdown spectroscopy (LIBS) has been used to carry out a wide range of laboratory measurements to validate the use of LIBS in aqueous solutions under realistic oceanic pressures, with a long-range goal of deploying a LIBS system on Alvin or other deep-ocean submersibles to measure the elemental composition of deep-ocean hydrothermal vent fluids. The results of our studies indicate an ability to measure the alkali and alkaline metals at ppm levels at pressures up to 3 × 10E7 Pa (~2800 m water depth equivalent), and that matrix effects produced by interactions between elements in mixtures (such as seawater) are minimal. Science studies using a LIBS instrument would include tracing the extent of hydrothermal vent fluids by mapping relative changes in Li concentrations and measuring changes in concentrations of key elements (e.g., Mn, Ca, Na, Li, and K) around vents that show phase separation. An ongoing issue using single-pulse LIBS in bulk aqueous solution is variability in the intensity of the LIBS emission. A current study to improve precision in LIBS measurements is to use an element of known or fixed concentration in water as an internal standard. The use of O and H as internal standards for high pressure LIBS measurements in water looks promising. In this talk, the results of our latest studies using O, H, and other elements as internal standards to improve the precision of LIBS measurements will be presented.

(663) **Planetary Geochemical Investigations by Raman-LIBS Spectroscopy (RLS)**

Samuel Clegg[1], Roger Wiens[1], Anupam Misra[2], Shiv Sharma[2], Steven Bender[1], Raymond Newell[1], James Lambert[3], Sue Smrekar[3], M. Darby Dyar[1], Sylvestre Maurice[4]; [1]Los Alamos National Laboratory; [2]University of Hawaii; [3]Jet Propulsion Laboratory; [4]Institut de Recherche en Astrophysique et Planétologie

Raman and Laser-Induced Breakdown Spectroscopy (LIBS) are highly synergistic analytical techniques that are sensitive to the molecular and elemental composition, respectively. They are also eminently integratable into a single remote or *in situ* Raman-LIBS spectrometer (RLS) capable of planetary geochemical investigation on Mars, Venus and elsewhere. Our approach to RLS is to produce the LIBS spark with a focused 1064 nm Nd:YAG laser and use the frequency doubled 532 nm output from the same laser to excite the Raman active modes. For remote applications the same telescope can be used to direct the lasers onto the sample as well as collect the RLS emissions and direct the signals into an integrated suite of spectrometers. In this paper, I will describe some of the preliminary geochemical experiments completed with several breadboard instruments under Mars and Venus planetary conditions. Just like the ChemCam instrument operating on the NASA Mars Rover Curiosity, RLS is especially well suited for investigations under the reduced Martian surface conditions, 933 Pa (7 Torr) of mostly CO2 at ~-100C to +25C. However, the surface of Venus is a harsh ~9300 kPa (~92 atm) supercritical CO2 atmosphere at ~467C and the spacecraft that land on Venus have a typical lifetime of many hours. Whether operating on Mars or Venus, remote mineralogical (molecular) and geochemical (elemental) analysis with a remote RLS instrument can collect far more data than any contact technique. Preliminary results from the analysis of many geochemical standards under Martian and Venus surface conditions will be presented.

(664) **Incorporating Laser-Induced Breakdown Spectroscopy (LIBS) into Undergraduate Education**

Daniel Kwasniewski[1,2], Rosemarie Chinni[1]; [1]Alvernia University; [2]University of Southern California

Details on how LIBS is incorporated into undergraduate education at Alvernia University will be discussed. The primary focus will be two laboratory experiments that were designed and published in the Journal of Chemical Education and an undergraduate research project that was published in the Journal of Visualized Experiments. The first experiment is designed for an Analytical/ Instrumental course. Here, the students used LIBS to analyze pressed synthetic silicate samples containing a wide variety of elements at varying concentrations. Calibration curves were created and used to determine detection limits and sensitivity for the specific elements of interest. The next experiment is applicable for a Physical Chemistry lab. The students analyzed various metal electrodes using LIBS. Emission data from specific elemental lines in the collected spectra were used to create Boltzmann plots which allowed for calculation of plasma temperature. The Stark broadening conditions were used to determine the plasma's electron density. This experiment is designed for students to develop an understanding of how the LIBS spectrum can be used to determine plasma diagnostics. In the undergraduate research project, LIBS was used to analyze pressed synthetic silicate samples using various energies and different timing parameters (gated vs. non-gated detection). Calibration curves were plotted and used to determine detection capabilities. Generally, the results showed that there was not a significant loss in detection capabilities using low energies and non-gated detection. These experiments were designed for students at the undergraduate level and introduced them to the LIBS technique. The students gained valuable experiences

using LIBS and are able to see its usefulness for atomic analyses throughout these various labs. The introduction of LIBS at the undergraduate level can help to enhance its reputation as a viable analytical technique.

(665) **Modeling of Trace Elements (Li, Ba, Sr, and Rb) using Curiosity's ChemCam and Early Results for Gale Crater, Mars**

Ann Ollila[1], Horton Newsom[1], Agnes Cousin[2], Roger Wiens[2], Sylvestre Maurice[3], Olivier Gasnault[2], Olivier Forni[3], Jeremie Lasue[3], Anya Rosengooding[4]; [1]University of New Mexico; [2]Los Alamos National Laboratory; [3]Institut de Recherches en Astrophysique et Planétologie; [4]Albuquerque Public High School

The Mars Science Laboratory rover, Curiosity, has successfully begun to explore Gale crater, Mars, seeking evidence of past or present habitable environments. Its ChemCam instrument package includes a Laser-Induced Breakdown Spectroscopy (LIBS) instrument to provide chemical data on geologic targets and a remote micro-imager for context imagery. ChemCam can detect many important trace elements that provide useful clues to understanding the local geology. Chemcam can detect all elements independent of the mass and has very good detection limits for the alkali and alkali Earth metals. In this study we focus on the detection and quantification of Li, Ba, Sr, and Rb in relevant geological materials. Both univariate peak area models and multivariate Partial Least Squares (PLS) models are presented. Trace elements are difficult to model due to the small number of peaks present, their small size and the possible presence of geochemical correlations that may bias predictions based on the presence of a major element that tends to be correlated with the trace element. Several PLS models were attempted, including 1) a standard PLS technique using ChemCam's full wavelength range, 2) the full wavelength range with each wavelength bin variance standardized and mean centered, 3) and a reduced wavelength range to focus on the trace element peaks in question that have a high correlation to that element. Results are compared to univariate modeling and all models are validated using data taken under a variety of ChemCam operating conditions at different distances and energies. Early results from Gale crater reveal the first detections of Li on Mars, up to ~60 ppm, the highest observed Sr and Rb, > 1000 ppm and > 100 ppm respectively, and Ba > 500 ppm. These results provide clues to mineralogy and geological processes that have occurred on Mars, which resulted in enrichments in these elements.

(666) **Analysis of Calcium in CO2-laden Brine (NaCl-CaCl2) by Laser-induced Breakdown Spectroscopy (LIBS)**

Christian Goueguel, Dustin McIntyre[2], Jinesh Jain[2], Jagdish Singh[3], Athanasis Karamalidis[1]; [1]Carngie Mellon University; [2]USDOE National Energy Technology Laboratory; [3]Mississippi State University

Carbon capture and storage (CCS) has been proposed as a viable means for reducing anthropogenic carbon dioxide (CO_2) emissions. This entails the injection of supercritical CO_2 in deep underground brine-filled reservoirs, which requires the CO_2 to remain either supercritical, or in solution in the saline formations. However, risks of leakage of the injected CO_2 or resident fluids such as brine, is a major concern associated with the injection of large volumes of CO_2 in storage formations. For instance, migration of CO_2-laden brine could contaminate drinking water resources, or endanger vegetation and animal life as well as human health. In this study, we propose the use of laser-induced breakdown spectroscopy (LIBS) technique for evaluating potential leaks of CO_2-laden brine from the injection sites. Brine samples of NaCl and $CaCl_2$ salts were prepared at various Ca concentrations. A Q-switched Nd:YAG laser providing pulses of 9 ns and operating at 1064 nm has been used to create the plasma in bulk aqueous solution. Measurements were performed in CO_2-filled high pressure cell. We report on the investigation of the influence of CO_2 on LIBS signal; especially, we examined the effect of CO_2 pressure on the 422.67 nm Ca line intensity. In addition, the effect of laser pulse energy and temporal gating on calcium detection in NaCl-$CaCl_2$ brine solution at various CO_2 pressures was evaluated.

(667) **Localized Surface Plasmon Resonance Biosensing: Multiplexed Arrays and Single Nanoparticle Tracking**

Richard Van Duyne[1], Julia Ruemmele[1], W. Paige Hall[1], Laura Ruvuna[1], Laura Sagle[1], Julia Bingham[1], Chunming Liu[2], Paul Cremer[2]; [1]Northwestern University; [2]Texas A&M University

In recent years, Localized Surface Plasmon Resonance Imaging (LSPRi) has emerged as a flexible technique for label-free biological sensing using both arrays and single particles. At the ensemble level, we constructed an instrument capable of high-throughput, multiplexed LSPRi by passing collimated white light through a liquid crystal tunable filter. [1] This allowed us to scan across a range of wavelengths on a large area nanopatterend substrate simultaneously. Using this setup, we have demonstrated the homogeneity and high sensitivity to changes in refractive index across the surface. More importantly, we have proven the multiplexing capability and high selectivity of the instrument in a single-chip binding curve of anti-biotin and hybridization of complementary DNA strands. Using a super resolution plasmonic imaging microscope, we obtained the position and LSPR scattering spectrum of individual gold nanoparticles moving in water. [2] The particles diffused across a cell membrane mimetic, supported lipid bilayers, which also contain a ganglioside lipid (GM1). Most of the particles freely diffuse across the bilayer, but some of the particles became confined between the GM1 cluster domains. In monitoring the number of confined diffusion particles, we directly measured a percolation threshold of ~22%, which is important in cell signaling and compartmentalization. Our new setup accomplished this with a spatial resolution of 6.7 nm, 33 millisecond time resolution, and 1 nm spectral resolution.

References

(1) Ruemmele, J.A.; Hall, W.P.; Ruvuna, L.K.; Van Duyne, R.P. Anal. Chem., 85, 4560-4566 2013

(2) Sagle, L.B.; Ruvuna, L.K.; Bingham, J.M.; Liu, C.; Cremer, P.S.; Van Duyne, R.P. J. Am. Chem. Soc., 134, 15832–15839 2012

(668) **Bacterial Detection through Combined Siderophore-Based Molecular Recognition and Second-Generation Plasmonics**

Paul W. Bohn[1,2], Yang Yang[1], Sean P. Branagan[1], Cheng Ji[2], Marvin J. Miller[2]; [1]Department of Chemical & Biomolecular Engineering, University of Notre Dame, Notre Dame, IN; [2]Department of Chemistry & Biochemistry, University of Notre Dame, Notre Dame, IN

Bacterial iron acquisition is essential for pathogenicity and, thus, provides an attractive and heretofore little-used target for the development of microbe-selective biomarkers for selective detection. Work described here targets a fundamental metabolic activity of specific bacteria, the siderophore-mediated metabolic uptake of iron, to mediate the capture and confinement of targeted pathogens. The resulting disruption of the near-surface dielectric response function then serves to signal the presence of the bacterium in the sample. We anchor the bacteria-spe¬cific siderophore so that the targeted bacteria, while ingesting the siderophore, also become anchored to the surface - a process that is sensitively detected second-generation SPR, specifically phase-sensitive SPR. Several different capture motif/bacterial combinations have been investigated, and SPR detection is envisioned in both a laboratory (card-and-reader) and field (self-developing) format.

(669) **Location Dependent Localized Surface Plasmon Resonance and Surface Enhanced Raman Spectropy of Gold Nanoplates at the Single Particle Level**

Francis Zamborini[1], Aiqin Fang[1], Lanlan Bao[1], Srinivas Beeram[1]; [1]University of Louisville

In this presentation we will describe recent studies exploring the localized surface plasmon resonance (LSPR) and surface enhanced Raman spectroscopy (SERS) properties of gold metallic nanoplates at the single nanoparticle level by the combination of dark-field light scattering and Raman microscopy. We have been able to selectively localize antibodies and spherical gold nanoparticles onto the edge and vertex sites of gold nanoplates for enhanced LSPR and SERS detection of proteins and small molecules. There is clearly a general trend that the LSPR shift and Raman enhancement are significantly larger for analyte located at vertex and edge sites compared to terrace sites, but the detection occurred from many nanoparticles with dispersity in the size, shape, analyte coverage, and location. Here we describe LSPR shifts and Raman enhancement measured at individual nanoplates with and without spherical gold nanoparticles coupled to their surface, where dispersity is no longer an issue and we can study the characteristics one nanoplate at a time. This dramatically reduces the line width in the LSPR spectrum and provides more confidence in where the Raman spectrum is obtained. The location of protein analyte and spherical nanoparticles on the gold nanoplates is determined by atomic force microscopy and scanning electron microscopy of the same gold nanoplates and correlated to the LSPR and SERS results. The results provide valuable information needed to optimize the sensitivity of nanoparticle enhancement in LSPR and Raman detection strategies.

(670) **Plasmonic Metal@Silica Fluorescent Nanoprobes for Biosensing Applications**

Denis Boudreau[1]; [1]Université Laval

The development of nanomaterials displaying enhanced luminescence properties is an active field of research. In particular, it has recently been shown that the brightness and photostability of molecular dyes can be improved by placing them near noble metal nanoparticles, and that plasmonic coupling with the metal increases the range and efficiency of Förster resonant energy transfer (FRET) between donor and acceptor shell-encapsulated fluorophores. During this seminar, I will present our recent progress with the design of such hybrid core-shell luminescent nanoparticles for molecular typing procedures such as blood genotyping.

(671) **Detecting Plasmon Resonance Energy Transfer with Differential Interference Contrast (DIC) Microscopy**

Ashley Augspurger[1], Anthony Stender[1], Rui Han[1], Ning Fang[1]; [1]Iowa State University

Gold nanoparticles are ideal probes for studying intracellular environments as well as energy transfer mechanisms due to their plasmonic properties. Plasmon resonance energy transfer (PRET) relies on a plasmonic nanoparticle to donate energy to a nearby resonant acceptor molecule, a process which can be observed due to the plasmonic quenching of the donor nanoparticle. In this study a gold nanosphere was used as the plasmonic donor, while the metalloprotein cytochrome c was used as the acceptor molecule. Differential Interference Contrast (DIC) microscopy allows for simultaneous monitoring of complex environments and noble metal nanoparticles in real time. Using DIC, we were able to perform single particle analysis of PRET over time and observe the reversibility of PRET in microfluidic devices that are designed specifically to fulfill the requirements of nanoparticle imaging in transmitted DIC microscopy. Single particle studies of PRET were also performed in a cellular environment while undergoing ethanol induced apoptosis.

(672) **Why are Women Underrepresented in Science? Evidence For and Against 5 Common Hypotheses**

Karla S. McCain[1]; [1]Austin College

This talk will explore the evidence for and against five common explanations for women's underrepresentation in science. The issues raised in these hypotheses range from the epistemology of the scientific method to possible differences in mathematical abilities between the genders to the difficulty in combining careers in science with family. Evidence from a variety of disciplinary perspectives will be presented to explain facts that seem contradictory on the surface. For example, women publish fewer papers in scientific journals, but are cited by other authors more. Women scientists report consistently that they have observed sexism and discrimination during their career, but never been the target of it themselves. One study has shown that a woman's resume needs to show twice the productivity as that of a man to be rated as having equal competence. Maria Goeppert Mayer did not receive tenure until after she won the Nobel Prize in physics. This material is taken from a class I developed and have taught in a variety of formats.

(673) **A Spectroscopist's Perspective on Working in Government Laboratories**

Nicole Crane[1,2]; [1]Naval Medical Research Center; [2]Uniformed Services University of Health Sciences

Graduate school only confirmed that I had made the right choice to enter into a career of science. I enjoyed the constant need to learn more, often about medicine and biology, the development of thinking "outside of the box", and the endeavor of overcoming the challenges that research presented. Over the years, I learned to interact with an interdisciplinary team of varying educational levels including undergraduate students, graduate students, postdoctoral fellows, professors, and clinicians. I believe that this experience has been crucial for me to form the adaptive research philosophy that I utilize today. Since graduate school, I have been afforded some unique opportunities working in government research facilities, including the FBI Academy, the National Institutes of Health (NIH), the Naval Medical Research Center (NMRC), and the Uniformed Services University of the Health Sciences (USUHS). I will present my perspective on working within a DoD environment, on the challenges (and advantages) of DoD funding, and why it has been a rewarding experience.

(674) **Building a Successful Spectroscopy Career via a Non-Traditional Path**

Gloria Story[1]; [1]The Procter & Gamble Company

Professional spectroscopists traditionally start their careers after completing a graduate degree, or some post-doctoral research. This presentation describes one non-traditional path; learning at the bench, partnering with others that are more than willing to share their expertise and encourage opportunities to share with others. Taking advantage of opportunities for exposure and utilizing a network of experts, in-house and externally through professional society contacts, a challenging yet rewarding career as a highly-valued member of the scientific community is possible. A summary of milestones of one such journey will be shared and will hopefully spark discussion on the future development of spectroscopy careers.

(675) **How Taking a Risk Changed my Future**

Anna Tisinger; [1]Agilent Technologies

Chemistry has always been a passion for me. However, I also enjoyed being around people. I eventually decided to study chemistry as a high school student in Warsaw, Poland, which seemed like a good choice at the time because there were many distinguished women chemists in Poland. During my studies at University of Warsaw, I developed a very good professional relationship with an electrochemical professor, who offered me an opportunity to travel to

the US to begin Ph.D. studies with a distinguished electrochemist at Miami University. At this time - I was completing my MS work in physical Organic chemistry - I did not see many job opportunities in Poland, and I felt that I needed a change, so I accepted the offer and relocated to the US to begin my Ph.D. work. The decision to leave was difficult, due to physical distance from home and to the language barrier. I later recognized that my English skills were extremely limited, even after taking many English language lessons, prior to relocation. Early on, I used a dictionary to help translate the textbook chapters, and I took English lessons, sponsored by the university. After 4.5 years, I received my Ph.D. and began work in US for a major analytical instrument supplier. Not only did I get my degree, I started my professional career in US, obtained citizenship, got married and started a family. Without taking the initial risk, which seemed daunting at the time, I would not have changed my future in such a positive way, both professionally and personally.

(676) **Computational Microscopy, Sensing and Diagnostics for Telemedicine and Global Health Applications**

Aydogan Ozcan[1]; [1]University of California, Los Angeles

Today there are more than 6.5 billion cell-phone users in the world, and the majority of these cellphones are being used in the developing parts of the world. This massive volume of wireless phone communication brings an enormous cost-reduction to cellphones despite their sophisticated hardware and software capabilities. Utilizing this advanced state of the art of the cell phone technology towards point-of-care diagnostics and/or microscopic imaging applications can offer numerous opportunities to improve health care especially in the developing world where medical facilities and infrastructure are extremely limited or even do not exist.

Centered on this vision, in this talk I will introduce new imaging and detection architectures that can compensate in the digital domain for the lack of complexity of optical components by use of novel theories and numerical algorithms to address the immediate needs and requirements of Telemedicine for Global Health Problems. Specifically, I will present an on-chip cytometry and microscopy platform that utilizes cost-effective and compact components to enable digital recognition and 3D microscopic imaging of cells with sub-cellular resolution over a large field of view without the need for any lenses, bulky optical components or coherent sources such as lasers. This incoherent holographic imaging and diagnostic modality has orders of magnitude improved light collection efficiency and is robust to misalignments which eliminates potential imaging artifacts or the need for realignment, making it highly suitable for field use. Applications of this lensfree on-chip microscopy platform to high-throughput imaging and automated counting of whole blood cells, monitoring of HIV+ patients (through CD4 and CD8 T cell counting) and detection of waterborne parasites towards rapid screening of water quality will also be demonstrated. Further, I will discuss lensfree implementations of various other computational imaging modalities on the same platform such as pixel super-resolution imaging, lensfree on-chip tomography, holographic opto-fluidic microscopy/tomography. Finally, I will demonstrate lensfree on-chip imaging of fluorescently labeled cells over an ultra wide field of view of >8 cm^2, which could be especially important for rare cell analysis (e.g., detection of circulating tumor cells), as well as for high-throughput screening of DNA/protein micro-arrays

(677) **Novel On-Chip Biophotonics for Trapping and Imaging**

Kishan Dholakia[1]; [1]University of St Andrews

This talk will explore a number of themes related to the field of Biophotonics with an emphasis for microfluidic applications. In particular we will look at innovative use of optical beam shaping and laser use for the optical trapping, rotation of particles and Raman analysis

Raman spectroscopy provides intrinsic biochemical markers for noninvasive analysis of biological samples but is often hindered by the presence of fluorescence background. We present an innovative modulated Raman spectroscopy technique to filter out the Raman spectra from the fluorescence background. The method is based on the principle that the fluorescence background does not change whereas the Raman scattering is shifted by the periodical modulation of the laser wavelength. Exploiting this physical property and importantly the multichannel lock-in detection of the Raman signal, the modulation technique fulfills the requirements of an effective fluorescence subtraction method [1]. We have applied this method on chip and using fibre probes [2] and even applicability to surface enhanced Raman studies for background free detection [3]. If we now turn to trapping, we can use light in combination with plasmonics for optical sorting of nanoparticles based on size [4]. By using circularly polarised trapping light we can spin microscopic particles. These reach a terminal rotation speed dictated by a number of factors including the local viscosity of the medium. In this way we have not only performed studies in liquid but in picoliter volumes of gas [5].

[1] A DeLuca et al. Anal. Chem 82, 738 (2010)
[2] P. Ashok et al., J Biophotonics 4, 514 (2011); Lab Chip 11, 1262 - 1270 (2011); S. Dochow et al., Biomedical Imaging 1, 383 (2013)
[3] B. Praveen et al. Analyst, in press (2013)
[4] M. Ploschner, T. Cizmar, M. Mazilu, A. Di Falco, and K. Dholakia, Nano Lett 12, 1923 (2012).
[5] Y Arita et al., Anal Chem. 83, 8855 (2011)

(678) **Digital Microfluidic Magnetic Separation for Particle-based Immunoassays**

Alphonsus Ng[1], Kihwan Choi[2], Ryan Fobel[1], Aaron Wheeler[1, 2]; [1]Institute of Biomaterials and Biomedical Engineering, University of Toronto, Canada; [2]Department of Chemistry, University of Toronto, Canada

There is great interest in miniaturizing robotic immunoanalyzers using microfluidics to speed up analysis, lower reagent consumption, and reduce the cost and size of instruments. A promising microfluidic format for immunoassay is Digital microfluidics (DMF), a technique in which fluids are manipulated as discrete droplets on devices bearing an array of electrodes buried under an insulating dielectric. Recent work has seen DMF applied to magnetic particle-based immunoassays for the quantification of various analytes at clinically relevant concentrations. Here, we report a significant advance over the state-of-the-art for DMF immunoassays, featuring three new characteristics: complete sample-to-analysis automation, parallel sample processing, and full factorial design of experiments (DOE) optimization. The use of DOE is becoming increasingly important for maximizing information output from minimum experimental effort. To date, however, there have been no reports of DOE optimization of microfluidic immunoassays (of any format), likely because of a lack of automation, parallelization, and control. We developed a new integrated platform (approximately the size of a shoebox) capable of performing complete immunoassays (i.e., sample in, analysis out) with minimal manual intervention. This platform comprises three core components: a Pogo pin interface for digital microfluidic control, an integrated photo multiplier tube for chemiluminescent detection, and an adjustable magnet for magnetic particle separation. To test this platform, we implemented a three-level full factorial DOE optimization for thyroid-stimulating hormone (TSH) immunoassays, varying three factors: 1) analyte concentration, 2) incubation time, and 3) sample volume. This resulted in an optimized protocol that reduced detection limit and analysis time by up to 5-fold and 2-fold, respectively, relative to previous work.

In summary, this represents the first DOE-optimized microfluidic immunoanalyzer (of any format). We propose that this platform has great potential for the quantitative analysis of disease biomarkers at

near-patient settings around the world, including community hospitals, physicians' offices, and small clinical laboratories.

(679) **Ultrasensitive Detection of Dyes and Proteins by Surface-Enhanced Raman Spectroscopy (SERS) in Capillary Electrophoresis (CE)**

Pierre Negri[1], Zachary Schultz[1]; [1]University of Notre Dame

We are incorporating capillary electrophoresis (CE) with surface-enhanced Raman spectroscopy (SERS) for highly sensitive detection of analytes in fluidic environment using a sheath liquid flow cell. The system consists of a fused silica capillary pinned to the bottom of a flow channel that delivers the sample in the detection region. Hydrodynamic focusing generated by a sheath flow inside the flow channel is used to direct the analyte molecules onto a planar SERS substrate and utilizes the intensive electric field near the substrate surface for Raman enhancement. The potential of implementing CE and SERS is demonstrated for the separation and subsequent spectroscopic identification of dyes and proteins. Sequential and high throughput flow detection of separated analyte molecules is achieved at nanomolar concentrations using a 50 ms acquisition without significant memory effect or fouling of the SERS substrate. Given the robustness, simplicity, sensitivity, and reproducibility of the current CE-SERS detection strategy, we envision the potential and applicability of this optofluidic device to provide highly detailed structural information to solve diverse problems in biochemical analysis.

(680) **SPRi: A Flexible Platform for Diagnostic Signatures in Blood**

Stephen Vance[1], Marinella Sandros[1]; [1]University of North Carolina at Greensboro

Measuring proteomic biomarkers which are shed into the bloodstream during disease progression serve as non-invasive mode for clinical diagnostic. However, the greatest challenge in their detection is their rarity in the blood. Several techniques have been developed to detect these diagnostic signatures with each one having unique advantages and limitations. The work presented here highlights the flexibility and sensitivity of the Surface Plasmon Resonance imaging (SPRi) platform to detect multiple protein biomarkers simultaneously.

Detection of multiple biomarkers simultaneously holds the potential for determining patient status in the acute phases of the disease and predicting recovery. Some pertinent biomarkers are present at low levels (< 1nM) in blood and often below the capabilities of ELISA or mass spectrometry. Our laboratory is developing a detection platform by integrating SPRi with nanomaterials to detect multiple biomarkers simultaneously at real time with high sensitivity and specificity. Preliminary data with C-reactive protein (CRP), an inflammatory biomarker, was detected with high specificity and after the introduction of nanoparticles resulted in a 16 fold enhancement of SPRi signal.

(681) **Advancement in Low Pressure LIBS Detection of Laser-Induced Confined Plasma**

Soo-Jin Choi[1], Kang-jae Lee[1], Jack Yoh[1]; [1]Seoul National University

The LIBS plasma characteristics are strongly dependent on the conditions of the ambient surrounding including its pressure. In general, lower pressure causes a rapid expansion of the plasma volume, leading to a faster decay of the excited species' number density and shorter plasma lifetime. In this study, we devised novel confinement method for laser-induced plasma using a CCD detector with a long gate width.

In a LIBS system (RT250-Ec, Applied Spectra Inc.), Q-switched Nd:YAG laser operating at 1064 nm with 5-7 ns pulse duration at pulse energy of 50 mJ at 10 Hz is focused onto the surface of a sample placed inside of a vacuum chamber. The laser beam is perpendicular to a surface of Aluminum plate sample. The gate delay is varied from 0.1 to 0.5 μs while gate width is set to 1.05 ms. Sample is mounted on a XYZ stage inside a chamber de-pressurized from 760 to 0.34 torr to provide the pressure dependent test conditions for the laser-induced plasma. A carefully selected confining material for plasma was acrylic window of 7 mm thickness. The confining window was placed and spaced about 2 mm on top of aluminum plate for allowing free expansion of the plasma upon laser irradiation. We confirmed critical signal decrease with lowering the pressure if no confinement is applied. Furthermore, plasma was undetectable at pressure below 1 torr. When the plasma is confined using the acrylic window, a noticeably high signal to noise ratio was obtained and lasted until 0.34 torr, which is the minimum pressure attainable via the vacuum chamber. The signal intensity of Al-396.152 nm peak was enhanced by 4 times at 1 torr with the present plasma confinement scheme. Our findings suggest that low pressure LIBS detection can be significantly enhanced when CCD detector at longer gate width is used together with acrylic window that effectively confines the laser-induced plasma for significant extension of the plasma lifetime. Minor element detection at increased sensitivity can be expected.

(682) **LIBS: Carbon Swan Plasma Emission Spectroscopy**

Michael Witte[1], Christian Parigger[1]; [1]University of Tennessee Space Institute

In this work, we report measurements and analysis of time-resolved carbon Swan spectra following laser ablation. Accurate line-strengths are utilized in computation of the C_2 spectra for fitting of the measured data. Measurements of plasma that contains carbon have a variety of interests. Carbon Swan spectra, for example, are reported in combustion and/or explosion of hydrocarbon fuels, or are of interest in exploring the physical characteristics of low-temperature stars and interstellar medium. The C_2 molecule has an advantage in that its lowest rotational levels are sensitive to temperature variation, and higher rotational levels are sensitive to the surrounding gas density and radiation field. Carbon is a crucial element for life and is the 4th most abundant element; therefore, it is important to ascertain accurately the origin and processes in which it forms. In this respect, it will be essential to have precise knowledge of C_2 interactions. Studies include formation of C_2 due to recombination in an effort to understand the formation of C_2 and C_n following laser ablation of graphene. For laser ablation of graphene with 190 milliJoule 13 nanosecond Nd:YAG pulses at a wavelength of 1.064 micrometer, our results show temperatures in the range of 4500 to 6500 K for delays in the range of 45 to 20 microseconds after optical breakdown.

(683) **Direct Analysis of Biodiesel Fuel to Simultaneously Determine Na and K by Tungsten Coil Atomic Emission Spectrometry**

George L. Donati[1], Stacia E. Dancsak[1], Sidnei Silva[2], Joaquim A. Nobrega[2], Bradley T. Jones[1]; [1]Wake Forest University; [2]Federal University of Sao Carlos

Biodiesel is a promising renewable alternative to fossil fuels. High levels of Na and K are present in this fuel because NaOH and/or KOH are used as catalysts in its production. These metals can contribute to ash build-up in the engine, which results in corrosion, reduced performance and shorter engine lifetime. Sample viscosity, immiscibility with aqueous solutions and high carbon content can affect sensitivity, accuracy and precision in biodiesel analyzes. Most methods require total decomposition of the organic matrix, which can be time consuming and significantly impact sensitivity. In this work, tungsten filaments extracted from commercially available 150 W, 15 V light bulbs are used to successively decompose biodiesel's organic matrix, and atomize and excite the analytes to simultaneously determine Na and K by tungsten coil atomic emission spectrometry

(WCAES). A small solid state power supply and a handheld CCD-based spectrograph are used in the instrumental setup. A 140 s heating program with pyrolysis temperatures of approximately 1000 K in a 10 % H2, 90 % Ar atmosphere is used. No sample preparation other than simple dilution in methanol is required. Direct analysis of 10 μL sample aliquots, with atomization gas temperatures of approximately 1350 K, results in limits of detection (LOD) as low as 19 and 66 μg/kg of biodiesel for Na and K. The dynamic linear ranges and repeatabilities were calculated as 1.5 and 1.6 decades, and 5.7 and 2.7 % (RSD, 0.5 mg/L, n = 12) for Na and K, respectively. The procedure was applied to a biodiesel reference sample and no statistical differences were observed between reference (20 mg/kg) and determined values at a 95 % confidence level, for both analytes, by applying the standard additions method. Three different biodiesel samples were analyzed and concentrations between 6.08-41.30 and 10.75-95.60 mg/kg were determined for Na and K, respectively. The procedure is simple, fast, potentially portable and environment friendly. Only small volumes of methanol are used and no residues are generated. Powers of detection are compared to other traditional methods, with the typical advantages of a simple dilute-and-shoot procedure.

Acknowledgements
CEES, WFU, USA
FAPESP, UFSCar, Brazil

(684) **Simultaneous Atomic Absorption and Atomic Fluorescence Spectrophotometery for Mercury Determination in Water Samples**

Sumedh Phatak[1,2], David Gunn[1]; [1]Milestone Inc.

There are more than 1300 commercial testing labs in the US with one out of three samples tested related to water. With EPA regulated methods such as 1631, 245.7 and 245.1, emphasis on mercury levels and analysis has never been stronger. These methods suggest mercury analysis on two different instruments, Cold Vapor Atomic Absorption Spectrophotometer (CVAAS) and Cold Vapor Atomic Fluorescence Spectrophotometer (CVAFS). Most labs in compliance with these regulations analyze their samples on the two separate systems mentioned, consequently reducing their productivity, increasing waste and reagent costs and maintenance of two systems. This presentation will illustrate a novel way of analyzing mercury in water samples, simultaneously incorporating both CVAAS and CVAFS in a single system. The presentation will also provide insight into:

*Several challenges analyzing mercury in water samples
*Technical discussion around simultaneous CVAAS and CVAFS measurement
*Principle of operation and key features in FMA-80/AAS system
*Experimental Hg data analysis
*Increasing productivity and ROI for water testing labs

(685) **LIBS: Aluminum Monoxide Emission Measurements**

David Surmick[1], Christian Parigger[1]; [1]University of Tennessee Space Institute

Current studies of laser-induced optical breakdown include measurement and analysis of aluminum monoxide spectra following laser ablation accomplished with nanosecond pulsed Nd:YAG laser radiation. Aluminum monoxide (AlO) measurements are of interest in a wide range of applications, for example, use as a thermometer for aluminum containing combustion or study of the interactions in the atmospheres of super-giant stars. Applications in combustion research focus on accurately determining the temperature of an aluminized solid rocket propellant using multiple temperature analysis techniques. Thermal background emissions from the propellant are analyzed using constant and non-constant thermal emission models. Thermal emissions are modeled using Planck's radiation law and Wien's displacement law for constant and non-constant emissivity, taken to be a function of their wavelength. The AlO emission temperatures are determined by fitting collected spectra with non-linear fitting algorithms. Analysis of AlO spectra is also investigated for the purpose of modeling the atmospheres of super-giant stars. Though aluminum monoxide is rarely observed in the spectra from astrophysical sources it has been observed in the circumstellar envelopes of asymptotic giant branch stars. Temperature analysis of the rotational structure of AlO spectra is applied in studies of the interactions between the outer layers of the giant star and its circumstellar envelope.

(686) ***In vivo* Validation for Transcutaneous Raman Spectroscopy of Bone in Humans**

Francis Esmonde-White[1], Karen Esmonde-White[2], Michael Morris[1]; [1]Dept. of Chemistry, University of Michigan; [2]Dept. of Internal Medecine, University of Michigan Medical School

Raman spectroscopy enables the non-destructive measurement bone properties. Over the past several years, Raman spectroscopy has been demonstrated for measuring the properties of bone in animal tissues, animal cadavers, human tissues, human cadavers, and even living animals. We have developed a methodology for validating non-invasive Raman measurements of bone in humans. These validation measurements involve measuring a transcutaneous Raman spectrum of the proximal tibia, followed by measurements of a nearby region of the proximal tibia bone exposed *in vivo* during a surgical procedure, and further follow up with comparison to Raman microscopy measurements of bone fragments recovered from a nearby region of the tibia. The transcutaneous and exposed-bone *in vivo* measurements use a low power density to minimize patient risk. Results from this ongoing clinical study will be presented.

(687) **Devising and Comparing the Assessment of Raman Spectroscopic Classification Models for Lesion Discrimination in Freshly Excised Stereotactic Breast Biopsies with Microcalcifications**

Narahara Chari Dingari[1], Ishan Barman[1], Jaqueline Soares[1], Anushree Saha[2], Sasha McGee[2, 4], Wendy Liu[2, 3], Donna Plecha[2, 3], Nina Klein[2,3], Ramachandra Rao Dasari[1], Maryann Fitzmaurice[2]; [1]Massachusetts Institute of Technology, Cambridge, MA; [2]Case Western Reserve University, Cleveland, OH; [3]University Hospitals Case Medical Center, Cleveland, OH; [4]University of North Carolina at Chapel Hill, Chapel Hill, NC

The primary mammographic signs of breast cancer are microcalcifications and are target for stereotactic breast needle biopsy. We established and compared different approaches for developing Raman classification algorithms to diagnose invasive and *in situ* breast cancer, fibrocystic change and fibroadenoma that can be associated with microcalcifications. In our study, Raman spectra were acquired from tissue cores obtained from fresh breast biopsies and analyzed using a constituent-based breast model. Diagnostic algorithms based on the breast model fit coefficients were devised using logistic regression, C4.5 decision tree classification, k-nearest neighbor (k -NN) and support vector machine (SVM) analysis, and subjected to leave-one-out cross validation. The best performing algorithm was based on SVM analysis (with radial basis function), which yielded a positive predictive value of 100% and negative predictive value of 96% for cancer diagnosis. Importantly, these results demonstrate that Raman spectroscopy provides adequate diagnostic information for lesion discrimination even in the presence of microcalcifications, which to the best of our knowledge has not been previously reported.

(688) **Label-free Time-course Study of Human Embryonic Stem Cells Differentiation by Raman Micro-Spectroscopy**

Flavius C. Pascut[1], Adrian Ghita[1], Spandan Karla[1], Virginie Sottile[1], Chris Denning[1], Ioan Notingher[1]; [1]The University of Nottingham

Raman micro-spectroscopy (RMS) was used for online label-free monitoring of in-vitro differentiation of stem cells inside micro-bioreactors while maintaining the cells in growth medium under physiological conditions. Detection and imaging of biochemical markers produced time- and spatially-resolved images of biomolecular changes taking place inside intact embryoid bodies (EBs) during cardiogenic differentiation. The Raman spectra showed that the onset of spontaneous beating of EBs, at day 7 in the differentiation process, coincided with an increase in intensity of the Raman bands at 1340 cm^{-1}, 1083 cm^{-1}, 937 cm^{-1}, 858 cm^{-1}, 577 cm^{-1} and 482 cm^{-1}, attributed to the formation of myofibrils and accumulation of glycogen in the CMs. Spectral maps corresponding to these bands had a high positive correlation with the expression of cardiac-specific α-actinin obtained by immuno-fluorescence imaging of the same EBs. These biochemical changes are hallmarks for the formation of cardiac tissue and reflect the development of contractile machinery within the cardiomyocytes. This technique therefore can be used for discrimination of individual live CMs within highly heterogeneous cell populations. The discrimination accuracy of CMs from other phenotypes yielded >97% specificity and >96% sensitivity. In addition RMS was used to identify, image, and quantify potential molecular markers for label-free monitoring of the differentiation status of live neural stem cells (NSCs) *in vitro*. Principal component analysis (PCA) and linear discriminant analysis (LDA) models based on Raman spectra of undifferentiated NSCs and NSC-derived glial cells enabled discrimination of NSCs with 89.4% sensitivity and 96.4% specificity. The differences between Raman spectra of NSCs and glial cells indicated that the discrimination of the NSCs was based on higher concentrations of nucleic acids in NSCs. Spectral images corresponding to Raman bands assigned to nucleic acids for individual NSCs and glial cells were compared with fluorescence staining of cell nuclei and cytoplasm to show that the origin of the spectral differences were correlated to cytoplasmic RNA. The spectral maps revealed cytoplasmic regions with concentrations of RNA as high as 4 mg/mL for NSCs, while the RNA concentration in the cytoplasm of the glial cells was below 1 mg/mL

(689) **Differentiating Healthy and Cancer Cells Using Surface-Enhanced Raman Scattering**

Mustafa Culha[1,2,3,4], Sevda Mert[1, 2, 3, 4]; [1]Yeditepe University; [2]Genetics and Bioengineering Dept.; [3]Atasehir, Istanbul; [4]Turkey

Surface-enhanced Raman scattering is used for the differentiation of human kidney adenocarcinoma (ACHN), human kidney carcinoma (A 498) and non-cancerous human kidney embryonic cell (HEK 293) lines. Silver nanoparticles (AgNPs) are used as substrates in the study. A small volume of AgNP colloidal suspension is placed onto the cells grown on CaF2 slide and the slide is dried at the overturned position. This sampling method allows concentrating the AgNPs onto the fixated cells. A number of SERS spectra acquired from each of three types of cell are statistically analyzed to differentiate the cells. Multivariate statistical methods, PCA and LDA, are performed to produce diagnostic algorithms for differentiation of the three-kidney cell types. This study suggests that SERS can be combined with PCA-LDA based algorithms for the diagnosis and prognosis of cancer. The assignments of the observed bands on the SERS spectra are attempted in relation to the biochemical and metabolic changes during cancer formation in a cell.

(690) **Intermolecular Interaction in Transparent Surfactant Gels Examined Using a Low-wavenumber Raman Microspectrometer**

Ashok Zachariah Samuel[1], Koichi Iwata[1]; [1]Gakushuin University

Lipid bilayers host multiple functional entities in biological membranes. Despite decades of research, analogous artificial functional membranes are far from perfect. Limitation has been the lack of knowledge of many intermolecular interactions existing in such self-assembled systems. Surfactant molecules are structural equivalents of biological lipids. In dilute surfactant solutions, hydrophobic interactions between long alkyl chains and hydrophilic interaction between the ionic head groups lead to their molecular assembly into micelles, vesicles etc. Micellar solution of cationic surfactants is known to form a gel on addition of gelators like sodium salicylate. However, the interactions leading to gelation remains a matter of speculation. It is widely believed that the head group ionic interaction plays a major role. We have investigated the interaction between the gelator and surfactant in detail to resolve this mysterious behavior. Raman spectroscopy is well suited for such investigations, especially the lower wavenumber region that are enriched in weak intermolecular vibrational signatures. A Raman microspectrometer has been modified to suit the investigations in this lower wavenumber region. To our great surprise, we find that the ionic interaction between the charged head groups of gelator and surfactant plays a negligible role in gelation. Interaction between the hydrocarbon methylene units and the aromatic pi electrons has become evident in our study. This interaction is characterized by an unusually strong Raman signature in the low wavenumber region (below 200 cm^{-1}). Disproving the conventional belief, we demonstrate that simple benzene molecules can induce gelation in surfactant bilayers and micelles. Our finding will be a unique contribution to the on-going efforts towards directed self-assembly.

(691) **Peering Into the Digital Crystal Ball with Hyperspectral Imaging**

Robert Lodder[1]; [1]University of Kentucky

"Big Data" are becoming an increasingly important topic in industrial and academic research. Big Data refers to a collection of data sets so large and complex that it becomes difficult to process using on-hand database management tools or traditional data processing applications. The challenges include capture, curation, storage, search, sharing, transfer, analysis, and visualization. Like hyperspectral imaging, Big Data are capable of providing very specific information from within a vast amount of more general data, but only if the right questions can be asked. One of the big problems regarding Big Data is that a large amount of information an organization has is not structured and cannot be used to make intelligent decisions. Being able to utilize Big Data requires sophisticated computational tools, especially when the data are constantly changing and growing (for example, gathering information on transactions for a business). When inquiries about the data generalizations need to be made, Bid Data can be further dissected. Cloud computing has offered a way of working through massive amounts of Big Data by spreading the work out over multiple systems and providing deep resources. The cloud computing approach tends to be very useful for businesses that can just pay per use, eliminating costs associated with owning and maintaining expensive software. Real time analysis of Big Data, when information is constantly added or changed, is also an area where computing has proven to be very useful.

(692) **An ApoE Model in Mathematica for BSN272 Metabolism**

Jarrod Williams[1,2]; [1]Biospherics.net; [2]University of Kentucky

BSN272 has been shown to reduce atherosclerosis and excess weight gain in ApoE -/- mice. BSN272 competes for absorption in the gastro intestinal tract with molecules that can exacerbate the metabolic syndrome. It has been used in clinical trials for diabetes and shown to

significantly reduce HbA1c levels. This promising medication for patients with diabetes may also have a beneficial effect in cardiovascular disease. The hypothesis that BSN272 might have a beneficial effect in atherosclerosis was test in ApoE -/- mice were a western diet. The drug demonstrated ability to steadily and significantly lower triglycerides over a sixteen week period. The triglyceride levels were reduced even below the levels in mice on a control diet. The declining triglyceride levels were modeled for ApoE -/- mice using Mathematica. The computational model and the actual results can be used in conjunction to closely modulate the dose by way of a Dynamic Data-Driven Application System (DDDAS).

(693) **Some Processes R BEST Modeled in Higher DImensions**

Andrew Brooks[1]; [1]0trak; [2]University of Kentucky

In an age where we are able to make measurements and observations in unprecedented number, we have created for ourselves a new challenge: how do we interpret this information? Because high-dimensional data presents difficulties to existing statistical methods, new ones must be exploited to uncover meaning. As hyperspectral imaging approaches become widespread in numerous fields in research and industry, the problem of analysis will only continue to increase in importance. We present implementations and explorations in the use of recently-developed statistical approaches to finding meaning in high-dimensional data. SIRS (sure independent ranking and screening), a method developed by Zhu et al., presents a new way to screen data for active predictors in circumstances where the number of variables measured greatly outnumbers the quantity of samples taken. SIRS is able to provide exceptional accuracy in screening and identifying inactive predictors for certain outcomes from active predictors. BCBCSF, a method developed by Li et al. for use in similar situations, is designed to correct the “feature selection bias” of approaches used to identify active predictors, which occurs as a result of an increase of the amount of noise relative to the useful data caused by the procedures of screening the data. Finally, we present the method of bootstrapping multidimensional clusters described by Maitra for determining the number of clusters in a high-dimensional dataset.

(694) **When DOes a Nanotechnology Device Become a Drug?**

Jarrod Williams[1]; [1]Biospherics.net; [2]University of Kentucky

The boundaries of the FDA’s current definition of drugs and devices is being challenged by the emerging capabilities of nanotechnology in the field of medicine. While a device can be designated as something that does not depend on chemical means of action, and a drug is labeled as something that does rely on a chemical means of action, nanotechnology can have both physical and chemical actions. Size is usually considered a factor in the decision to classify nanotechnologies, but some can be as small as molecules and have little chemical effect. Where should the line separating drugs and devices be drawn as the FDA continues to regulate this new technology? In the current method, a primary mode of action is determined when nanotechnology products have a combination of effects from physical to biological to chemical. This mode then categorizes the new product. Programmable nanotechnology can initially act as a device or a drug or a combination at user command. How will FDA regulate this new nanotechnology?

(695) **What Would Turing Say?**

Robert Lodder[1]; [1]University of Kentucky

A Turing test is a test of a machine's ability to exhibit intelligent behavior equivalent to, or indistinguishable from, that of an actual human. In the test, a judge engages in a natural language conversation with a human and a machine designed to generate performance indistinguishable from that of a human being. All participants are separated from one another. If the judge cannot reliably tell the machine from the human, the machine is said to have passed the test. What would Turing ask a simulation? A dynamic data-driven application simulation is programmable, but not really intelligent. What kind of analysis applies to intelligence? There is a biological equivalent to the Turing Test in SETI (the Search for Extraterrestrial Intelligence). There are basically two methods available to prove the existence of an intelligent life form - capture or communication. One example of the capture method is the "discovery" of the platypus near the Hawkesbury River in 1797 by white settlers in Australia. Unfortunately, the first one died before actually reaching Europe. The finding caused an uproar in the scientific circles of Western countries where such a creature had never been seen before. Scientists had trouble believing that the odd-looking animal actually existed, and it was believed that the platypus was actually a fabrication (an "imposter"). Five years passed before scientists were certain that the platypus actually existed and was not a fake. Use of the capture method poses many problems when applied to an intelligent life form, including the requirement of achieving close proximity to the life form. In the past, capture has often led to the death of the organism whose existence was the object of debate. Humans have exhibited the tendency to dissect new life forms with which they are unfamiliar. Proponents of modern SETI rely on the communication method, in which signals from space and received and analyzed, and signals are transmitted in the hope of reaching other intelligent life forms. In a SETI test, how would Turing have conversed with a clearly intelligent alien that did not speak anything close to human language? As drugs and nanodevices converge and programmability becomes a criterion for classification, a sort of Turing test may be used to assist.

(696) **Two-Dimensional Liquid Chromatography: The Future of HPLC?**

Peter Carr[1]; [1]University of Minnesota

Over the past half dozen years there has been a blossoming of interest in fast (sub multiple hour analysis time) comprehensive two-dimensional liquid chromatography (denoted LCxLC). Several major instrument companies are now providing hardware to address this interest. Our laboratory has focused on improving the analysis time of LCxLC by looking at the time needed to do the second dimension separation (2t), which is really the key factor in controlling the overall analysis time. Keeping in mind that an entire 2D chromatogram is obtained by taking N “slices” out of a 1D chromatogram and subjecting each slice to chromatography on a chemically independent (“orthogonal”) second dimension (denoted 2D) phase the total analysis time is N*(2t). Since the overall resolution is greatly compromised when N becomes much smaller than the 1D peak capacity it is obvious that 2t needs to be kept small. In the limit of very short overall analysis times 1D chromatography is always superior to 2D chromatography for various technical reasons which we will elucidate; however, as more time is allowed the 2D approach becomes superior. The question naturally arises -- at how short of a time does the 2D approach become superior? If this time is sufficiently short (all else being equal) the 2D approach will squeeze out the 1D approach. We will explore the various factors involved and at least make explicit some of the issues in “*all else being equal*”.

(697) **Characterization of Carbon Nanomaterial Modified Silicas for Use in Two-Dimensional High Performance Liquid Chromatography**

Dwight Stoll[1], Tuan Tran[1], Ian Gibbs-Hall[1], Paul Young[1], John Danforth[1], Jonathan Thompson[2]; [1]Gustavus Adolphus College; [2]United Science, LLC

Over the past few years we have prepared a number of stationary phases based on high purity silica by deposition and/or bonding of a variety of carbon nanomaterials. Our interest in the properties of these materials is driven both the attractive positive characteristics of similar, existing materials (e.g., Porous Graphitic Carbon), and the

deficiencies of these same materials. Specifically, the unique selectivities of existing materials that enable isomer separations and enhanced retention of polar and polarizable compounds are particularly useful in two-dimensional liquid chromatography (2DLC) where stationary phase chemistries that are complementary to existing bonded phases are needed for successful 2D separations. However, the existing materials have several weaknesses for separations of some compound classes that seem to be insurmountable in spite of decades of research, including: prohibitively high retention, poor peak shape, poor efficiency, and high substrate chemical activity (e.g., as in the case of carbon deposited on zirconia substrates. In this presentation we will review the physical and chemical characteristics of the materials we have prepared, and demonstrate how they complement existing materials. We will present selectivity and efficiency data using simple probe molecules, and demonstrate the application of the recently prepared materials in 2DLC separations that cannot be analyzed using existing carbon-based stationary phases. Finding suitable pairs of highly complementary stationary phases for use in 2DLC remains one of the major challenges in the field. We believe that the continued development of carbon-based phases will help alleviate this problem.

(698) **Development and Application of Two Dimensional HPLC for Small Molecule Pharmaceutical Analysis**

Todd Maloney[1], Mark Argentine[1], Brian Scherer[1]; [1]Eli Lilly and Company

Two dimensional HPLC (2D HPLC) is a relatively new tool for pharmaceutical analysis. While the instrument components to build 2D HPLC systems have been available for many years, software enabling integration of multiple data streams with concomitant peak tracking/reconciliation has only recently been developed. These advancements combined with the fundamental gain in peak capacity and higher sample throughput make 2D HPLC an ideal tool for complex samples (e.g., monoclonal antibodies, biomarkers, tryptic digests, etc.) that are commonly found in pharmaceutical labs. Although powerful for the analysis of complex samples, the speed and resolving power of the 2D separation can present new challenges in method performance, sample solubility and injection solvent mismatch. For many small molecule applications the orthogonal selectivity offered by the second dimension column is as critical as the speed/resolving power of the 2D method. In our presentation we will share our experiences optimizing 2D HPLC methods for applications evaluating concurrent achiral/chiral analysis, genotoxic impurity identification, and leachables/extractables. Instrument attributes and performance for different applications will also be presented.

(699) **Use of Two-Dimensional HPLC in a Contract Lab Environment for MS Analysis of Unknown Analytes in Mobile Phases Containing Non-Volatile Modifiers**

David Sherlock[1]; [1]PPD

Preferred for their robustness and flexibility, phosphate and other non-volatile buffers still make up the majority of HPLC mobile phases encountered in the analysis pharmaceutical products. Chromatographic impurities encountered during development and routine testing must be carefully monitored and then identified if they continue to be of concern. The first line of analysis requested in the identification process is usually LCMS and this can be challenging when the mobile phase is non-volatile and therefore incompatible with MS analysis. Traditionally two approaches are used to work around this problem; fraction collection of the peak of interest and/or redevelopment of the LC method to utilize volatile buffers. Both of these approaches have potentially large drawbacks. At PPD we use a two dimensional LC approach to isolate peaks of interest into a mobile phase compatible with MS. This system was built in-house and is now used for upwards of 80% of the impurity ID requests that come to us. It is fast and precise and has the added advantage of the secondary separation often being able to separate impurities co-eluting in the original chromatography. This presentation shows an overview of the equipment used at PPD and summarizes the process of taking in a new client method, setting up the secondary chromatography, and generating suitable data. Examples of primary and secondary chromatography will be shown.

(700) **New Tools for Metallomics**

Gary Hieftje[1], Steven Ray[1], Alexander Graham[1], Elise Dennis[1], Christie Enke[2], David Koppenaal[3], Charles Barinaga[3]; [1]Indiana University; [2]University of New Mexico; [3]Pacific Northwest National Laboratory

In the field of Metallomics, as in many others, advances are driven as much by new tools as by novel applications. In turn, new tools are often developed by discovery-driven work rather than by hypothesis-driven studies. In this lecture, two new tools developed on this basis will be discussed, and their potential impact assessed. Both are derived from investigations into "distance-of-flight mass spectrometry" (DOFMS), a new sort of mass spectrometry that is similar in architecture to time-of-flight mass spectrometry (TOFMS), one of the most common types of mass spectrometry used in metallomics investigations. Both TOFMS and DOFMS have no upper mass range, so are attractive for biomolecule analysis, and both feature very high repetition rates, so can be employed for detection of species that have been separated by high-speed chromatography or electrophoresis. In DOFMS as in TOFMS, ions are accelerated to a mass-dependent velocity. In TOFMS, the mass-to-charge ratio (m/z) of those ions is then determined from the time they reach a fast detector positioned at the end of a field-free region. In contrast, in DOFMS, ions are not allowed to emerge from the field-free region but are pushed sideways onto an array of detectors stationed part way down the region. A single detector is therefore not required to do all the work, and high-speed electronics are not needed. The result is a broader dynamic range and simpler instrumentation. In one new implementation of DOFMS, collection surfaces are substituted for the detector array, so mass-separated biomolecular ions can be accumulated and studied by other methods. In a second extension, DOFMS principles are applied to TOFMS, so higher resolution can be obtained.

(701) **Our Metallomics Picture Correct? Consequences of Solvent Composition and Analytical Sample Preparation Methods**

R. Kenneth Marcus[1], Derrick Quarles[1], Benjamin Manard[1], Carolyn Burdette[1]; [1]Clemson University

The act performing a metal speciation determination, i.e., identification of the chemical form of a metal-containing molecule, is inherently limited by the ability to preserve said species through the course of sample acquisition, storage, and any sorts of chemical clean-up or separation steps to which the analyte is exposed. Depending on the nature of the metal-ligand (used generically), adverse solvent conditions can either lead to complete dissociation or at minimum changes in the ligand identity (e.g., oxidation might occur). Therefore, one must examine each step in the processing of biological samples and what the ramifications they may have on the speciation profile. For example, changes in ionic strength experienced in a electrolyte-rich separation (e.g., ion exchange chromatography or capillary electrophoresis) can alter equilibrium binding constants, or in fact lead to competitive binding situations and ion displacement. The potential pitfalls encountered in such situations will be treated by example for the seemingly simple case of the metal-transport protein, transferrin.

As an extension of this example, one must also be cognizant of the potential matrix effects imposed on analytical methods such as MALDI and ESI-MS. This laboratory has capillary-channeled polymer (C-CP) fibers as stationary phases for HPLC separations and

solid phase extraction (SPE) pre-concentration steps prior to MALDI and ESI-MS. In both of these cases, the presence of salts at concentrations of >50 mM can be problematic. Thus C-CP fibers in either a micropipette tip or microcolumn format can be used to first immobilize the proteins (allowing the salt matrix to pass) and then be eluted from the surface in solvents that are amenable to the method at hand. The utility of these materials in the area of protein mass spectrometry will be discussed.

(702) **Study of Protein/DNA binding via Phosphorus and Sulfur Detection via triple quadrupole ICP-MS A Study of Protein/DNA binding via Phosphorus and Sulfur Detection**

Julio Landero-Figueroa[1], Morwena Solvio[1], Jiawei Gong[1], Edward Merino[1], Joseph Caruso[1]; [1]University of Cincinnati

The covalent bond between nucleic acids and proteins (DPC) is a permanent modification that can lead to mutation or DNA replication stops, causing cytotoxicity. The traditional methods to study DPC involve molecular mass spectrometric techniques that can identify the molecules involved, but the quantification and stoichiometry of the DNA-Protein are difficult tasks to perform with these approaches. The phosphorous and sulfur contained in DNA and protein respectively, can be used as native elemental tags for analysis, and this allows identification and quantification to be assessed in the same experiment. The low LOD for both S and P in the triple quad, QQQ, will be used to analyze intact DPC complexes as well as enzymatic digests (protein and DNA digestion) to elucidate binding site(s) and stoichiometry of a model system formed by a 27mer DNA oligonucleotide with a RNAse protein. Along with complementary molecular mass spectrometry, this will lead to a new qualitative/quantitative methodology to analyze these important bio molecular interactions.

(703) **Metallomics in MIcrobiology**

David W. Koppenaal[1]; [1]Pacific Northwest National Laboratory

The use of metals as probes in understanding the biology of microbes is a rapidly growing field. The probe metals may be adventitious (natural) or added as tags for specific biological moieties or complexes. This paper will describe recent investigations into microbial metallomics using mass spectrometry techniques, including liquid chromatography ESI-ICP mass spectrometry and combined cytometry-mass spectrometry (CyTOF MS) techniques.

(704) **Metallomics Studies for Fungal Disease Remission via Zn Deprivation – An Emphasis on Free Metal Imaging**

Joseph Caruso[1], Julio A. Landero-Figueroa[1], Kavitha Subramanian-Vignesh[1], George Deepe[1]; [1]University of Cincinnati

In recent studies, we have developed a model for zinc metalloprotein regulation to damage or destroy a pathogenic fungus, *Histoplasma capsulatum*. Part of these studies used 'metal imaging dyes' (fluorescing metal chelating agents when metal bound). However, the question arose regarding the specificity and selectivity of these 'dyes.' We address this question in this presentation. Fluorescent dyes are widely used in the detection of free Zn^{2+} and Ca^{2+} in living cells. However, the metal-binding specificity over other cations and selectivity for detection of free vs. protein-bound metal in cells remains unclear. We have characterized the metal binding properties of commonly used dyes for Zn and Ca in cells. By tracing the fluorescence emission signal along with UV-Vis detection and SEC-ICPMS in tandem, we demonstrate that while Zinpyr-1 fluoresces weakly in the low-molecular weight (LMW) region containing free (labile or exchangeable) Zn^{2+}, FluoZin-3 AM, Newport Green DCF and Zinquin ethyl ester display weak fluorescence, lack of metal specificity and respond strongly in the HMW region. In an unperturbed cellular environment, the Ca^{2+} binding dyes tested, Ca Green-1 AM, Oregon Green BAPTA-1, Fura red and Fluo-4 lacked detection of labile Ca as shown by SEC-ICPMS, but displayed fluorescence in regions containing Zn, Fe and Cu binding species. Our studies indicate that Zn^{2+} and Ca^{2+} binding dyes exhibit degeneracy in metal recognition and generally lack selectivity for free/labile metals. Thus, in live cell imaging studies for Zn^{2+} and Ca, $^{2+}$ the fluorescence contribution by these dyes may collectively result from binding to free and protein-bound metals as well as membrane bound metals and from affinity for other divalent cations.

(705) **The Business of Commercializing Analytical Technologies**

Mark Druy[1]; [1]Physical Sciences inc.

So you think you created a new measurement technique, what next? How do I commercialize it? During the course of this presentation, we will discuss different routes to commercialization and key factors of success for the various routes. Topics discussed include sizing the market and competition, intellectual property protection, fund raising, licensing, and strategic partnerships.

(706) **Stories from the Front Lines - Technology Transfer Terrors and Triumphs**

Jeremy Shaver[1], Barry Wise[1]; [1]Eigenvector Research

More and more academic research programs are feeling the pressure to transfer their technology inventions to industrial start-ups. The universities see this as a way to improve prestige and possibly bring in money from licensing. But the route from laboratory benchtop to hospital bedside can be exceptionally rough. The research needed to assure continued funding from a grant may not be consistent with fully characterizing the biological / chemical system or the analytical instrumentation. On the other hand, start up companies who lack the deep experience with hardware or laboratory methods can completely misinterpret data or hardware performance. Add a lack of understanding of design of experiments and characterization of interferences or system noise, and a start-up company can be set up for failure.

The result can be millions of wasted dollars, and, more importantly, the lost opportunity for good science to turn into viable solutions as beneficial household and medical devices. We will discuss our observations on how some successful, and some unsuccessful, researchers and start-ups have handled the technology transfer process; And, from the point of view of collecting and analyzing good data, what their biggest mistakes frequently are.

(707) **Steps for Commercializing Spectroscopic Devices in a Regulated Industry**

Bradford Clay[1]; [1]bioMerieux, Inc.

Many research groups world-wide are exploring diagnostic applications using spectroscopic and spectrometric methods. Promising results are presented yearly at conferences like SciX, but there does not appear to be new medical devices and diagnostics commercially available. One reason is a lack of familiarly with the necessary requirements and activities to design and seek approvals to market devices. While this presentation will not replace guidance documents and standards, it will explain steps to create documentation for regulatory submission.

(708) **From an Academic Invention to a Commercial Product: Steps Taken to Translate a New Analytical Took into a Marketable Device**

Martin Zanni; [1]University of Wisconsin-Madison

I am a chemistry professor at the University of Wisconsin-Madison and co-founder of the company PhaseTech Spectroscopy, Inc. In my talk, I will describe the path that I took to commercialize a new analytical infrared instrument that my university research group developed. That path included patenting the technology with the University, building a prototype and founding a company. As an academic, I found that most steps were straightforward, but learned

that experience is a big help. I will present some of the technological and business hurdles that we faced and what I learned from the process.

(709) **Utilising the IRENI Beamline to Provide an Enhanced Understanding of Human Breast Calcifications and Their Association with Diseased Tissue**

Nick Stone[1,2], Marleen Kerssens[2,3], Catherine Kendall[1,2,3]; [1]University of Exeter; [2]Gloucestershire Hospitals NHS Foundation Trust; [3]Cranfield University

The accurate and safe detection and diagnosis of breast cancer is a significant issue in the UK, with annual incidence of around 46,000 women and 300 men [CRUK 2011]. Early diagnosis of the disease allows more conservative treatments and better patient outcomes. Mammographic screening has demonstrated itself to be effective at identifying lesions within older women. However, the identification of a suspect lesion does not provide the clinician with its benign or (pre-)malignant status. Therefore the removal of tissue for histopathological staining is necessary to make this diagnosis. In 2008/9, 2.1 million women were screened in the UK. Approximately 4.4% of women screened were referred for further assessment and only 0.8% of those women screened were found to have malignancies. [www.cancerscreening.nhs.uk] This demonstrates that 74,860 women in 2008/9 had further investigations including excisional biopsy, posing risks and anxiety to the patient, and significant costs to the NHS. Breast calcifications although used as an indicator for disease in mammography (even though the vast majority of women have calcifications when they get older) have largely been ignored as diagnostic markers. Here using FTIR spectral imaging we demonstrate that breast calcifications have a composition directly related to the surrounding breast pathology. Furthermore we explore the heterogeneity of calcification compositions and the interface between the calcifications and the tissue in exquisite detail by utilising twelve mid-IR synchrotron beams, high NA optics and an FPA-FTIR imaging. This work has been performed at the IRENI beamline – Aladdin synchrotron, Wisconsin. A Selection of multivariate techniques have been employed to provide a measure of compositional variation across the hyperspectral images. Results show that there is a progression seen in the calcification composition, with decreasing carbonate concentration in the outer zones of the calcifications. This leads to a hypothesis that the carbonate substitution of the calcium hydroxyapatite is more readily dissolved in malignant tissues due to the surrounding tissue exhibiting a lower pH. This is believed to increase the carbonate solubility.

(710) **FT-Infrared (FT-IR) Spectroscopic Tomography: Development of a 3D mid-IR Spectral Imaging Technique**

Miriam Unger[1,2], Julia Sedlmair[3], Michael Martin[4], Carol Hirschmugl[1]; [1]Department of Physics, University of Wisconsin-Milwaukee, Milwaukee, WI.; [2]CETICS Healthcare Technologies GmbH, Esslingen am Neckar, Germany.; [3]Synchrotron Radiation Center, University of Wisconsin-Madison, Stoughton, WI.; [4]Advanced Light Source Division, Lawrence Berkeley National Laboratory, Berkeley, CA.

The IRENI beamline at the SRC in Stoughton, Wisconsin has developed a way to rapidly acquire 2D images with full mid-IR spectral information at high spatial resolution by filling a focal plane array detector. Recently, we have extended this to a full spectral-tomography technique which provides not only the rich spectral information, but also this in a full three dimensional field of view. The presented technique greatly enhances the capabilities of FT-IR microscopy, providing a wealth of information for advanced spectral analyses and could spark a new generation of spectral-tomography synchrotron technologies. The presentation is focused on the introduction of the technical and experimental setup. Furthermore, the results of a variety of samples from biology, plant sciences, natural minerals, polymers and other scientific disciplines will be presented.

(711) **FTIR Spectrochemical Imaging at the Diffraction Limit**

Kathleen Gough[1], Catherine Liao[1], Alexandra Ciapala[1], Peter Trokajlo[1], Benedict Albensi[1], CJ Mundy[1], Julia Sedlmair[3,4], Carol Hirschmugl[2]; [1]University of Manitoba; [2]University of Wisconsin-Milwaukee; [3]US Forest Service, Forest Products Laboratory, Madison WI; [4]Synchrotron Radiation Center, University of Wisconsin-Madison, Stoughton, WI

Our research focus is spectroscopic characterization of tissues and small organisms at biologically relevant length and time scales, to achieve a better understanding of the molecular basis of differences in health and disease. This talk will present recent results from our on-going FTIR spectrochemical image analyses of post-mortem brain tissue sections from Alzheimer's Diseased brain and from two transgenic mouse models for AD. Large area surveys are obtained with an Agilent Cary 670/620 FTIR microscope with Focal Plane Array (FPA) detector (U. Manitoba), and high resolution images with the mid-infrared beamline IRENI (InfraRed ENvironmental Imaging, Synchrotron Radiation Center, U Wisconsin-Madison). At IRENI, twelve synchrotron beams are imaged onto an FPA to create spectrochemical images with a pixel resolution of $0.54 \times 0.54\ \mu m^2$, an increase of two orders of magnitude over standard thermal source systems, permitting analysis at sub-cellular dimensions. The enhanced speed of data acquisition facilitated by the brilliance at IRENI, plus FPA multiplexing, has enabled the first ever IR tomography experiments. We are using FTIR TOMO, pioneered by Hirschmugl and Martin in 2012, to do 3D FTIR tomography of sea ice diatoms from arctic waters. Algal diatoms are a primary nutrient source for the marine ecosystem, particularly in the early spring, and are likely being affected by the recent rapid changes in the arctic environment. Here our long term goals are to understand the effects of nutrient and light stress in biomass composition and to evaluate the sea ice–derived biomarker IP25 (Ice Proxy with 25 carbon atoms).

(712) **Using Synchrotron Light for Integrated Spectroscopic Studies of Disturbed Energy Metabolism and Oxidative Stress within the Brain**

Mark Hackett[1], Ferenc Borondics[2], Carol Hirschmugl[3], Phyllis Paterson[1], Helen Nichol[1], Ingrid Pickering[1], Graham George[1]; [1]University of Saskatchewan; [2]Canadian Light Source; [3]University of Wisconsin

Stoke is the second largest cause of death in North America, and those who survive often experience delayed neurodegeneration. Although a tragic outcome of stroke, the delay in neurodegeneration provides hope of a "therapeutic window in time" for administration of preventative therapy. Despite significant research into the cause of neurodegeneration, the exact mechanisms remain unknown, however, it is widely accepted that cerebral ischemia, defined as insufficient oxygen and energy supply, is the initiating mechanism. A wide array of techniques are available to the neuroscientist to study biochemical mechanisms of neurodegeneration, however, few methods provide high spatial resolution imaging and detailed biochemical information. For example, traditional imaging methods such as fluorescence microscopy (in combination with immuno-histochemistry) provide high resolution images (i.e., sub-cellular), but typically reveal alterations of cellular morphology and/or the distribution of one or two specific molecules. In contrast, conventional biochemical methods, such as tissue homogenisation followed by enzymatic assay or mass spectroscopic analysis provide a wealth of detailed chemical information, but at poor spatial resolution (typically at the whole tissue level). Therefore, a technique or suite of techniques which provides both high spatial resolution imaging and a wealth of biochemical information would greatly aid research of the overall biochemical picture during neurodegeneration after brain ischemia.

Our studies combine three methods available with synchrotron light, X-ray fluorescence (XRF) mapping of ions and metals, X-ray absorption spectroscopy (XAS) at the sulfur K-edge to study sulfur speciation in-situ, and Fourier transform infrared (FTIR) spectroscopic imaging to study metabolic alterations and protein oxidation. Each of these methods is capable of imaging at cellular or sub-cellular resolution when coupled with synchrotron light. Specifically, we optimised sample preparation methods for application of all three analyses to the same sample, or serial sections of the same sample. This approach has been used to investigate early alterations in ion channel dysfunction and altered intracellular ion homeostasis following ischemia, which promotes excessive free radical generation and oxidative stress. Specifically, this presentation will highlight the contribution made to this research program through the use of FTIR spectroscopic imaging with multi-beam wide-field illumination of focal plane array detectors.

(713) **Probing Bonding and Dynamics at Adsorbate/Graphene Interfaces**

Eric Mattson[1], Kanupriya Pande[1], Miriam Unger[1, 3], Shumao Cui[2], Marija Gajdardziska-Josifovska[1], Michael Weinert[1], Junhong Chen[2], Carol Hirschmugl[1]; [1]University of Wisconsin-Milwaukee, Physics Dept.; [2]University of Wisconsin-Milwaukee, Mechanical Engineering Dept.; [3]Synchrotron Radiation Center

The adsorption of atoms and small molecules on graphene-based materials is of high significance to the materials science community, particularly in the fields of gas sensing and heterogeneous catalysis. Despite the relevance of such systems in many scientific and industrial applications, fundamental studies of adsorption on graphene-based materials are lacking. This is largely due to the difficulty in performing spectroscopic studies on the adsorbate/graphene interface. Low dimensionality and small lateral dimensions of realistic samples require the use of microscopic techniques with high throughput; in particular, single-domain samples derived from solution phase materials are typically less than or equal to 10-20 micrometers in any lateral dimension. Here we present synchrotron-based infrared (IR) microspectroscopy studies of several systems of interest, including the adsorption of NH3, NO2, and CO on graphene and reduced graphene oxide (RGO). The graphene samples are grown by chemical vapor deposition, and the RGO samples are prepared from hydrazine-reduction of graphene oxide (GO) suspensions. IR studies are performed at the synchrotron radiation center (SRC, Stoughton, WI) using the IRENI beamline. The high optical throughput at this beamline enables studies of gas-solid interfaces on the micrometer-scale. The substrate materials are characterized using normal incidence transmission and grazing incidence reflection to identify native functional groups in the substrate materials. Adsorption studies are carried out in a custom flow cell equipped with IR-transparent diamond windows using a normal incidence transmission geometry. Using this approach, we are able to identify the adsorbed fragments and characterize their interaction with the substrate. In particular, we find that residual oxygen atoms in RGO play are reactive towards many target molecules and play an important role in the final adsorption products.

(714) **Ultrafast Laser Induced Breakdown Spectroscopy for 3-Dimensional Chemical Imaging**

Vassilia Zorba[1]; [1]Lawrence Berkeley National Laboratory

Ultrafast lasers offer significant advantages in laser ablation, including suppressed thermal effects and non-linear phenomena resulting in spatially and axially confined laser-material interaction. In this work we demonstrate the use of Ultrafast Laser induced Breakdown Spectroscopy (LIBS) for spatially resolved 3-Dimensional chemical imaging of energy related materials including electrochemical energy storage and interfacial layers. Single and double-laser pulse geometries in the optical far-filed as well as near-field optics schemes are also explored to assist towards improving resolution and further minimizing the requirements for ablated mass in laser-ablation based chemical analysis as they relate to nanoscale applications.

(715) **The Application of LIBS in the Failure Prediction of Hear Transfer Surface in Boilers**

Jidong Lu[1], Shunchun Yao[1], Jun Li[1], Meirong Yao[1], Bo Zhang[1]; [1]School of Electric Power, South China University of Technology

The microstructure changes of heat transfer surfaces will lead to dramatically degrade in material properties until it has insufficient mechanical strength to stand for internal pressure and then to be failure. In this work, the matrixes effects of LIBS were used to detect the microstructures changes in order to predict the trend of failure. The steel samples from boiler tube with different microstructures and different grade of pearlite spheroidization were prepared for analysis with LIBS. The plasma parameters and intensity ratio of ionic to atomic spectral lines had been studied and compared with each other. The results reveal that the difference of ionic Fe lines is more obvious than atomic Fe lines between pearlite/ferrite and martensite. The ablated volume of pearlite/ferrite is distinctly larger than that of martensite, whereas there is no significant difference between the plasma temperature of pearlite/ferrite and that of martensite. Additionally, the line intensities of Fe, Mn, V, Cr and Mo of raw steel sample are stronger than that of pearlite spheroidization samples, whereas there is no significant difference of plasma temperature among these samples. It is also found that a positive relationship exists between the ionic to atomic line intensity ratio, electron density and the hardness of different grade of pearlite spheroidization samples individually.

At last, the principal component analysis method was proved to classify the plasma spectrometry obtained near broken point and far from broken point of boiler tubes respectively. It is considered that LIBS could be used to determine the microstructure and material properties changes of heat transfer surfaces in boilers.

(716) **Use of Laser Induced Breakdown Spectroscopy for the Analysis of Poultry Products**

Gary Gamble[1]; [1]USDA-ARS

Laser Induced Breakdown Spectroscopy is evaluated as a potential method to characterize a wide range of poultry product quality and safety characteristics. In one part of this study, breast meat quality indices, including pH and water holding capacity, were treated as dependent variables for correlation against LIBS spectra. Chemometric analysis of the acquired data demonstrates that pH may be predicted from LIBS spectra with a correlation coefficient of > 0.95. In a second part of this work, eggshell depth profiles acquired using LIBS are demonstrated to provide information regarding chemical variations occurring at different eggshell depths. This information is further utilized to build a chemometric model for the prediction of eggshell breaking strength based upon chemical variability between different eggshell samples.

(717) **Challenges and Advantages of Extraterrestrial LIBS**

Ryan Anderson[1], Jeremie Lasue[2], Sam Clegg[3], Roger Wiens[3], Ann Ollila[4], Olivier Forni[2], Sylvestre Maurice[2], Steve Bender[3], Alissa Mezzacappa, Nourredine Melikechi; [1]U.S. Geological Survey; [2]Institut de Recherche en Astrophysique et Planétologie; [3]Los Alamos National Laboratory; [4]University of New Mexico

ChemCam is the first Laser-Induced Breakdown Spectroscopy (LIBS) instrument used on the surface of another planet, and it has proved to be a valuable addition to the Curiosity rover payload. The ability to rapidly analyze geologic materials up to 7 meters from the rover greatly increases the number of targets for which compositional information can be obtained and identifies targets of interest for further study with other instruments. The small spot size (250-550

microns) provides information about the individual grains in coarse-grained geologic targets. The number of laser shots and the number and arrangement of analysis points on the target can be customized for specific purposes (e.g., depth profiles, transects of linear features, etc.). ChemCam is sensitive to light elements that cannot be directly detected by other instruments on the rover, and the measurement of hydrogen in particular is of interest on Mars. ChemCam also includes a remote micro imager, which has proven essential for the interpretation of spectra in geologic context, and provides high resolution images independent of the LIBS analysis. ChemCam is also capable of passive spectroscopy. Operating a LIBS instrument on Mars also presents many challenges. Background subtraction, distance corrections, and temperature-dependent wavelength calibration are necessary to properly interpret the data; and analyzing small targets pushes the rover's pointing capability to its limits. The rover carries 10 calibration targets of known composition to aid in correcting for differences between Earth and Mars. All other ChemCam targets are naturally occurring martian rocks and soils, which are often not homogeneous at the scale of the LIBS spot, making bulk compositions challenging to obtain. We use multivariate and univariate methods to determine target compositions, but the efficacy of these methods is limited by the number and diversity of the reference materials analyzed in LIBS laboratories on Earth under similar conditions. Despite the challenges, ChemCam has demonstrated the power of LIBS as an analytical technique, particularly in energy, mass, and data-limited conditions, and it is likely that LIBS instruments will continue to play an important role on future missions to Mars and other planetary bodies such as Venus and the Moon.

(718) **Laser Induced Breakdown Spectroscopy (LIBS) for Monitoring of Carbon Sequestration**

Jinesh Jain[1,2], Dustin McIntyre[1], Christian Goueguel[1], Barbara Kutchko[1], Brian Strazisar[1]; [1]USDOE-National Energy Technology Laboratory; [2]URS Corporation

The ability of reservoirs to retain stored CO2 is an important issue in carbon capture and sequestration (CCS) program. The risk of CO2 leakage could be due to degradation/alteration of seal and/or reservoir integrity. Technologies concomitant to physical storage of CO2 such as reliable measurement, monitoring, and verification (MMV) techniques are needed to ensure that the integrity of the storage site is maintained. We propose the use of laser induced breakdown spectroscopy (LIBS) to detect carbon dioxide leaks and follow degradation of seal/reservoir material to aid in successful application of CCS. LIBS has a real time monitoring capability and can be reliably used for the elemental and isotopic analysis of solid, liquid, and gas samples. The flexibility of probe design and use of fiber optics make it a suitable technique for real time measurements in harsh conditions and at hard to reach places. We have successfully applied the technique to determine carbon and other elements in soil, brine, and air samples. Our recent experiments are utilizing LIBS measurements in high pressure vessels to mimic the pressure and temperature conditions of injection formations. The results from these experiments will be presented and the discussion will include the development of a field deployable LIBS unit for real-time and long-term monitoring of CO2 at storage sites.

(719) **Past Present and Future Applications of Supercritical Fluid Chromatography (SFC)**

Terry Berger[1]; [1]SFC Solutions, Inc.

In a supercritical fluid chromatography (SFC) applications compendium published in 1989, fully 80% of 341 chromatograms used capillary or micro-packed columns, pure CO_2 and pressure or density programming. Only 16% used flow and composition control with binary pumping, packed columns, and UV or MS detection. Only 30 chromatograms dealt with pharmaceuticals, 6 were chiral separations. In contrast, 91 dealt with polymers, 18 with polymer additives, 44 with fuels. More chromatograms (36) dealt with food and fatty acid analysis (18) than pharmaceuticals. In 1992 a second generation of SFC equipment was introduced that allowed both capillary and packed column operation. Over the next decade, packed column SFC became firmly entrenched in the pharmaceutical industry, particularly for chiral analysis, and then purification. Today, >90% of all users are in the pharmaceutical industry usually in discovery but increasingly into development. By 2000 capillary SFC equipment had largely disappeared, and most of the older applications became unsupported.

A new generation of equipment has been introduced over the last 5 years, but this equipment primarily addresses improvements in speed and sensitivity. None of this new equipment performs pressure programming or has an FID. While some of the older applications can be performed using composition programming, there is definitely something missing. Never the less a number of the application areas popular 20-30 years ago have become neglected. Many of those applications can now be performed on sub-2µm particles.

(720) **Efficiency of SFC Columns in Different Thermal Conditions**

Donald Poe[1], Krzysztof Kaczmarski[2], Abhijit Tarafder[3], Georges Guiochon[3]; [1]University of Minnesota Duluth; [2]Rzeszow University of Technology Poland; [3]University of Tennessee Knoxville

Since the early papers on SFC by Sie and Rijnders almost 50 years ago, a satisfactory explanation for the effects of flow rate and pressure drop on efficiency when columns are operated near the critical point of the mobile phase has been lacking. Recent research has shown that radial temperature gradients associated with enthalpic expansion and cooling of the mobile phase are the principal cause of efficiency losses under these conditions. We conducted a systematic investigation on the efficiency of a packed column eluted with supercritical carbon dioxide at 323 K and outlet pressures from 90 to 150 bar with the column in two different thermal environments. We used a 150 x 2.0 mm ID stainless steel column packed with 5-micron Spherisorb-C8 particles and normal alkanes as test solutes. When operated in a convective air bath the column exhibited severe efficiency losses when the outlet pressure was below 120 bar. The efficiency of the same column enclosed in a shell made of foam insulation was mostly restored at outlet pressures down to 100 bar. The van Deemter plots for both thermal conditions showed an abnormal dependence of the plate height (HETP) on the flow rate at low outlet pressures, exhibiting a maximum in the HETP at flow rates around 1 mL/min and a 20-bar pressure drop. At higher flow rates the efficiency improved and the van Deemter plots then showed the normal dependence of increasing plate height with increasing flow rate. The unusual van Deemter plots will be explained using results of a numerical model and examination of the thermophysical properties of the CO2 mobile phase flowing through the packed bed. These results indicate that it should be possible to conduct fast, efficient separations with supercritical CO2 at low outlet pressures by operating columns under near-adiabatic conditions.

(721) **Determination of Equilibrium Isotherms in Supercritical Fluid Chromatography**

Georges Guiochon[1], Fabrice Gritti[1], Abhijit Tarafder[2], Fahimeh Kamarei[1], Peter Vajda[1]; [1]University of Tennessee, Knoxville, TN; [2]Waters Corporation, Milford, MA

Compared to traditional mobile phases used in liquid chromatography, those used in supercritical fluid chromatography (SFC) are much more compressible and less viscous, which has a profound effect on the experimental conditions that are used in preparative applications of SFC. A low viscosity is associated with high diffusion coefficients. Thus, optimum reduced velocities in SFC are larger than in HPLC and separations have to be run at higher

velocities. Accordingly, there is a significant pressure drop along SFC columns, the mobile phase density decreases continuously and the volumetric flow rate increases along the column. As a consequence of the density decrease, the retention factors of all compounds vary in a large proportion from the inlet to the outlet of the column, so the values that are measured from the chromatograms are mere "averages". The design of SFC instruments into which the carbon dioxide and the organic modifier must be pumped separately and mixed affects markedly the experimental conditions. Slight modifications in our instrument that eliminate the significant band spreading caused by the large dwell and mixer volumes allowed the elution of fronts as sharp as or even sharper than those recorded in HPLC. The influence of the mobile phase compressibility on the various possible methods of measurements of equilibrium data is discussed. The methods of frontal analysis, perturbation, frontal analysis and elution by characteristic points, and RTM were studied and used. The issue of the interpretation of these "average" data for the determination of equilibrium isotherms in solid/supercritical fluid adsorption system is raised. The results obtained with different compounds, e.g., caffeine on a C18 bonded HPLC column, carbamazepine, and the enantiomers of naproxen on Whelk-O1, using methanol or ethanol as modifier are discussed. The values obtained for the performance of preparative separations in SFC and HPLC are compared.

(722) **The Marriage of SFC and Mass Spectrometry: An Old Romance Rekindled**

John Van Antwerp[1]; [1]Waters

SFC has historically been interfaced to MS using APcI due to the nature of the compounds that were amenable to SFC and the physical challenges of handling supercritical fluids. Over the last few years, we have seen a resurgence in Analytical SFC, and the range of compounds being analyzed by the technique has expanded to include more polar compounds. The increased robustness and reliability of these systems has seen more of these systems being interfaced to mass spectrometers using different ionization techniques . This talk will focus on the challenges of interfacing SFC to MS and will explore the various approaches that have been taken to overcome those challenges. It will also highlight examples of SFC/MS applied to different compound classes.

(723) **Application of SFC in Process Analytical Chemistry**

Yanqun Zhao, Wayne Pritts[1]; [1]AbbVie, Inc

Process analytical chemistry serves as a critical function in the drug development process. A variety of analytical techniques are needed to support the analytical research and development activities. Supercritical Fluid Chromatography (SFC) has been used in process analytical chemistry to meet the increasing demand for better efficiency. In this presentation, the typical applications of Supercritical Fluid Chromatograph (SFC) in process analytical chemistry will be discussed with highlighted examples, especially in the area of chiral separations.

(724) **Hyperspectral Chemical Sensing and Imaging using Optimized Binary Compressive Detection**

Owen Rehrauer[1], David Wilcox[1], Bharat Mankani[1], Dor Ben-Amotz[1]; [1]Purdue University

A key bottleneck of current hyperspectral imaging strategies is the time required to collect and process the collected data. The recently developed optimized binary compressive detection (OB-CD) strategy provides a means of addressing this issue. Here we describe a Raman spectrometer based on this strategy, and demonstrate its ability to classify, quantify, and image pure components and mixtures. The results obtained using the OB-CD strategy are also compared with those obtained using other hyperspectral imaging methods.

(725) **Confocal Raman Microscopy for *in-situ* Measurement of Octanol Water Partition Coefficients in Single Femtoliter-Volume Particles**

Jay Kitt[1], Joel Harris[1]; [1]University of Utah

Current methods for measuring water octanol partition coefficients require large quantities of analyte and long times for partitioning and *ex-situ* quantification. In the current work, these challenges are addressed using confocal Raman microscopy in combination with liquid-liquid extraction *in-situ* within single, femtoliter chromatographic-silica particles allowing fast measurement of water octanol partition coefficients from picoliter volumes of source-phase solution. Specifically, the internal pore volumes of C_{18} chromatographic particles are filled with octanol. A single particle is then captured and allowed to equilibrate with an aqueous solution of analyte. Raman scattering is collected from a small confocal volume within the particle. In an example application, an octanol-filled particle was equilibrated with naphthoic acid solutions of varying pH to investigate the pH dependence of partitioning. By comparing the Raman scattering intensity of the ring breathing mode of within particle naphthoic acid to the scattering of the CH_2 twisting modes from the surface C_{18} chains and within particle octanol, quantitative determination of the equilibrium concentration of naphthoic acid in the octanol, C_{18} receiver phase was possible. The resulting titration curve spanned a range surrounding the pKa of naphthoic acid and resulted in a determination of logP values ranging from 2.3±0.2 at pH 5.0 to 3.60±0.04 at pH 2.5, which correspond to the varying protonation states of the acid.

(726) **Resolution in 3D Confocal Raman Imaging: The Contribution of Physics, Instrumentation, and Sample**

Jianyong Yang[2], Wei Liu[2], Thomas Dieing[1], Klaus Weishaupt[1], Ute Schmidt[1]; [1]WITec GmbH, Ulm Germany; [2]WITec Intruments Corp. Knoxville, Tennessee

Raman spectroscopy has for decades been used in materials research to identify the unique molecular composition of a material. The combination of Raman spectroscopy with microscopy (in particular with confocal microscopy) reduced the volume from which the Raman information is collected. The parallel optimization of the optical and electronic detection components required for a confocal Raman microscope reduced the integration time necessary for the acquisition of a complete Raman spectrum. Tens of thousands of complete Raman spectra can be acquired within a short timeframe, enabling Raman imaging. Intelligent software algorithms (e.g. cluster analysis) further optimized the Raman imaging capabilities even for spectra with relatively low signal to noise ratio. Three-dimensional confocal Raman imaging using hundreds of thousands of spectra allows the reconstruction of pseudo 3D structures reflecting the chemical variations within the samples in all three spatial directions. All of these measurements underlie to various limiting factors and the measured result is mostly a convolution of such factors. Basic physics puts the first limitation to the results and can be explained by the diffraction theory. There are however different criteria which are currently used to define these limits, such as the full width at half maximum (FWHM) of the airy function to the Sparrow- or the Rayleigh criterion. In combination with the instrument function, the physical limit is the ultimate resolution a system can achieve. It is desirable to minimize the impact of the instrument function and thus to be as close as possible to the physical limit. Apart from this physical and instrumentation limitation, the sample of course also plays a crucial role for what is measured, since the image in the end is a convolution between the sample and the instrument resolving power. The impact of the sample nature becomes increasingly important when moving from 2D to 3D confocal Raman imaging: Jumps in refractive index, small scattering centers as well as focus distortion then also start to play an important role. This contribution is intended to shed light on the different limitations and influencing

factors in 3D Confocal Raman Imaging. Ideal testing structures as well as real-world examples will be presented to illustrate the various effects and possibilities.

(727) **HTVS Enhanced Hyperspectral Imagers for Process Analytics and Security Threat Detection**

Jeffrey Meade[1], Andrew Cenko[1], Bradford Behr[1], Arsen Hajian[1]; [1]Tornado Spectral Systems

Tornado Spectral Systems' High Throughput Virtual Slit (HTVS) technology greatly reduces the classic trade-off between spectral resolution and instrument sensitivity in dispersive spectrometers—we commonly see 5 to 10 times better sensitivity compared to slit-based systems with equivalent spectral resolution and system volume. The HTVS anamorphically reformats the input aperture in the pupil plane to reduce the width of the PSF along the dispersive axis while leaving the cross-dispersive axis and the f/# unchanged. Based on the conservation of étendue and the law of optical invariance it is possible to define the optical invariants along orthogonal axes differently as long as the total étendue remains constant. Because HTVS performs the reformatting in the pupil plane, the spatial information of the input aperture is preserved, thus allowing HTVS to be easily incorporated in imaging spectrometer systems. Line scanning spectral imaging systems (pushbroom) enhanced with HTVS technology decouple the spatial and spectral resolution from one another so each can be independently optimized for a particular system design. Because of the enhancement in the spectral resolution from HTVS, the imaging slit can be widened by huge factors (e.g. 10x) with no cost to spectral resolution, thus allowing the collection of more light. This is particularly useful in low-light imaging scenarios or where spatial discrimination is not a high priority. Tornado's HTVS-enabled pushbroom hyperspectral imaging system, the S4, has been used in a variety of Raman chemical imaging and stand-off Raman experiments, particularly focused on assembly line imaging scenarios for pharmaceutical analyses and security scanning. For example, the S4 has been used to differentiate birth control pills from placebos in pre-packaged containers based on their Raman spectral signatures; this capability addresses the recent accidental packaging of 100% placebo in a batch. The S4 has also been used to identify different liquids in plastic bottles and detect trace amounts of dangerous substances in an airport security scanner scenario. We expect that HTVS-equipped systems like the S4 will open up new low-cost high-quality sensing and testing solutions for problems requiring multiple sample positions or hyperspectral imaging in general.

(728) **Evaluation of Crystalline Content in Poly-L-lactide Using Raman Hyperspectral Imaging**

Venkata N K Rao Bobba[1], John F. Turner II[1]; [1]Cleveland State University

The degree of molecular ordering strongly influences the physical and chemical properties of polymers and can affect the rate of degradation in the body as well as in the environment. In anisotropic polymers, the formation of crystalline domains alters the electro-mechanical, elastic, thermal, and optical properties along different directions within the crystalline regions. The development of polymers with tailored properties is important for many applications in bioscience, pharmaceutical science, materials science, and environmental science - among others. The relationship between the physical/chemical properties of a polymer and its crystalline morphology is important for predicting performance. Conventional methods such as thermal analysis and dynamic mechanical analysis provide insights about the characteristics of the bulk polymer. There is a considerable need, however, for nondestructive methods that can provide spatially resolved information about the structural details of crystalline domains. In the work presented here, we have developed a non-destructive method based on wide-field Raman imaging to investigate crystalline domains in cold-drawn poly-L-lactide (PLLA). By combining Raman hyperspectral imaging with novel correlative pattern recognition algorithms, a map of PLLA crystallinity is generated. The degree of crystalline order and the spatial extents of the crystalline domains are revealed. The orientation of functional groups within the domains is investigated using Raman polarization spectroscopy and the results are in good agreement with earlier studies of PLLA crystalline structure. The design of the Raman imaging system and a theoretical description of the multivariate image analysis approach are presented.

(729) **FDA's New Authority to Regulate Tobacco Products**

Christina Young[1]; [1]U.S. Food and Drug Administration (FDA), Center for Tobacco Products, Office of Science

The Family Smoking Prevention and Tobacco Control Act amended the Federal Food Drug and Cosmetic Act (the Act) to grant FDA the authority to regulate the manufacture, marketing, and distribution of tobacco products to protect public health and to reduce tobacco use by minors. Relevant sections of the Act related to chemistry include authorities regarding tobacco product evaluation and the development of tobacco product standards. The Office of Science develops, evaluates and applies a multi-disciplinary science approach to inform and support FDA's Center for Tobacco Product's (CTP) regulatory goals and objectives. FDA has an interest in supporting research that provides additional scientific data to inform tobacco regulatory activities. Analytical chemistry plays a significant role in FDA's ongoing research effort. For example, a major focus of FDA research is on developing methodology for extracting, separating, and detecting the quantities of harmful and potentially harmful constituents (HPHCs) in tobacco and tobacco smoke. To date, FDA has identified 93 HPHCs in tobacco and tobacco smoke. While well-established, validated methods exist for determining the quantities of some of these 93 analytes, such methods do not exist for most of the identified HPHCs. Advances in analytical chemistry research are still needed, not only to assist stakeholders in fulfilling statutory obligations, but also so that FDA can base its regulatory actions on a sound scientific basis, fulfilling its mission of protecting and promoting public health.

(730) **Quantitative Analysis of Volatile Organic Constituents in Mainstream Cigarette Smoke**

Clifford Watson[1]; [1]Centers for Diease Control and Pevention

We have developed a new method that provides accurate quantification of 25 volatile organic compounds (VOCs) in mainstream smoke. We used this approach to characterize the VOC levels in 50 U.S. cigarette brands using the standard ISO smoking regimen and an "intense" smoking regimen. We generated results based on automated analysis of mainstream cigarettes smoke vapor phase and particulate constituents collected in Tedlar bag and on glass fiber filter pads and analyzed using gas chromatography with isotope dilution mass spectrometry for quantification. Of the compounds analyzed with this method, a number of them have been identified by the Food and Drug Administration as harmful or potentially harmful constituents in tobacco smoke. One of our objectives was to examine the influence of cigarette design parameters on mainstream VOC deliveries and the change in delivery when using different smoking regimens. We observed strong correlations between the select cigarettes design parameters (e.g., rod length, tobacco weight, filter length, paper porosity, and pressure drop and VOC levels). This method has good throughput, excellent specificity, and abundant sensitivity and is well suited for measuring and monitoring mainstream cigarette smoke VOC levels.

(731) **Selected Aromatic Amines by Gas Chromatography Mass Spectrometry: Challenges of Mainstream Cigarette Smoke**

Alexandra Martin[1]; [1]Arista Laboratories, Inc.

Six of the 93 compounds currently included on the FDA's established list of harmful and potentially harmful constituents in tobacco products and tobacco smoke (HPHCs) are primary aromatic amines (PAAs): 4-aminobiphenyl, 1- and 2-aminonaphthalene, o-anisidine, 2,6-dimethylaniline, and o-toluidine. These compounds are routinely found in mainstream tobacco smoke and are typically analyzed by gas chromatography mass spectrometry (GC-MS). Mainstream smoke is a challenging matrix to work with due to the large number of potentially interfering compounds, the generation and stability of the matrix and the low detection levels required. A successful analysis cannot be done using the resolving power of the instrument alone; it can only be accomplished in conjunction with extensive sample clean-up.

The method described here is used routinely in a high-sample throughput CRO and demonstrates the successful GC-MS analysis of PAAs in tobacco smoke using a combination of ion-exchange and non-retentive solid phase extraction (SPE) clean-up steps.

Primary aromatic amines are found in the particulate fraction of mainstream tobacco smoke and can be collected using a 44 mm Cambridge filter pad (CFP). Once smoking is complete the CFP is extracted with 1.6 N HCl for 30 minutes using mechanical shaking. The sample extract is passed through a MCX ion exchange SPE cartridge where the aromatic amines are retained. The cartridge is washed with further acid, the pH is adjusted and then the aromatic amines are eluted using dichloromethane. The dichloromethane eluate is cleaned further using non-retentive silica SPE prior to derivatization with pentafluoropropionic acid anhydride and analysis by GC-MS using negative chemical ionization. Results obtained by this method compare well to published methods. It is also superior to similar methods performed by LC-MS/MS, which struggle with the resolution of 4 aminobiphenyl from 3-aminobiphenyl, which is also present in samples.

The detection limits for this method range from 0.09 – 2.5 ng/cigarette & 0.15 – 4.2 ng/cigarette when following the ISO and Canadian Intense regimes, respectively.

(732) **Some Real-Time and Batch Sample Analysis Mass Spectrometry-Based Techniques to Inform Tobacco Product Regulation**

Marielle Brinkman[1], Sydney Gordon[1], Stephanie Buehler[1], Kandice Cross[1], Robyn Kroeger[1], Hyoshin Kim[1], Ian MacGregor[1], Douglas Turner[1], Theodore Klupinski[1], Erich Strozier[1]; [1]Battelle Memorial Institute Tobacco Exposure Research Laboratory, Columbus, OH

As part of its mandate under the Tobacco Control Act, the FDA Center for Tobacco Products (CTP) has identified ten research priority areas, including understanding the toxicity of cigar, smokeless, electronic nicotine delivery, hookah and dissolvable tobacco products. Identifying metrics by which to evaluate the public health impact of tobacco use, the CTP has established a list of harmful and potentially harmful constituents (HPHCs). Although tobacco product emissions and content are important components of a product's overall toxicity, user behavior and resulting human exposures are critical to understanding the difference in harm among the many tobacco product types and brands available. We have applied real-time and batch sample mass spectrometry-based techniques to characterize HPHC content of tobacco products themselves, and, through crossover acute laboratory trials, HPHC exposures associated with smoked and smokeless tobacco-product use by humans. The real-time techniques used in our laboratory for the analysis of mainstream smoke and exhaled breath are proton transfer reaction-mass spectrometry (PTR-MS) for puff-by-puff characterization of selected volatile HPHCs, and an electrical low pressure impactor for the characterization and collection of fine/ultrafine particles. The collected particulate allows us to use batch sample mass spectrometry techniques to characterize the semi-volatile HPHCs that are attached to the particles as a function of particle size. Real-time techniques offer the advantage of immediate analysis of a dynamically changing smoke matrix in order to more closely approximate user's real-world HPHC exposures, and the ability to make measurements in exhaled breath over time to determine rates of HPHC metabolism in the body and puff-by-puff changes in HPHC delivery. Batch sample mass spectrometry-based techniques, including two-dimensional gas chromatography–time-of-flight mass spectrometry (GC×GC-TOFMS), allow us to conduct new and emerging tobacco product biomarker discovery in addition to sensitive part-per-trillion detection of volatile and particle-bound organic HPHCs to characterize tobacco product content and estimate deposition of HPHCs in the body. Taken as a whole, these techniques can be used to generate the evidence needed to determine where a given tobacco product lies on the continuum of harm and the impact a variation in a product's physical or chemical design has on human exposures.

(733) **Determination of Carbonyl Compounds in Tobacco Products by Gas Chromatography Mass Spectrometry**

Peter Joza[1], Mingliang Bao[1], Andrew Masters[1]; [1]Labstat International ULC

A reliable method using pentafluorobenzylhydroxylamine derivatization for the routine analysis of trace carbonyl compounds, including formaldehyde, acetaldehyde, acetone, propionaldehyde, acrolein, methyl-ethyl ketone (MEK), butyraldehyde, and crotonaldehyde, in tobacco products has been developed. One gram of tobacco product, using a mixture of three isotope-labelled carbonyls as internal standards, was initially extracted with water. An aliquot of the aqueous extract was derivatizated with o-(2,3,4,5,6-pentafluorobenzyl)-hydroxylamine hydrochloride (PFBHA). The PFBHA derivatives of the carbonyls were extracted with hexane and analysed by gas chromatography-mass spectrometry (GC-MS). The method was applied to the analysis of the Kentucky reference 3R4F cigarette filler and the four CORESTA smokeless reference products. Formaldehyde (0.300 - 6.45µg/g) and acetaldehyde (0.849 - 18.4µg/g) were detected in all tested products. Acetone (0.197 - 3.31µg/g) and propionaldehyde (0.156 - 1.07µg/g) were found in the 3R4F, CRP1, CRP2, and CRP3. Levels of MEK, butyraldehyde, and crotonaldehyde were found to be below the method detection limit for all tested reference products. The accuracy and precision of the method were evaluated using spiked matrix samples of each of the products analyzed. All investigated carbonyl compounds, with the exception of acrolein, demonstrated excellent recoveries (87 - 114%) and precision (0.2 - 7.6%) for each of the different spiked tobacco products. These recoveries were far more consistent than observed using a more common 2,4-dinitrophenylhydrazine derivitization and HPLC-UV analysis. Acrolein, when spiked directly on the product, was found to be unstable. The linear range of the method was from 0.08 to 27µg/g with detection limits ranged from 0.03 to 0.08µg/g, dependent on the compound.

Using this method, storage conditions (storage time, container, and temperature) were found to directly impact the yields of carbonyls detected in reference tobacco product samples (3R4F, CRP2, CRP3), being both compound and sample matrix dependent; concentrations of formaldehyde in all tested products gradually increased as the storage time increased, while the concentrations of acetone in 3R4F samples dramatically decreased as the storage time increased.

(734) **Process Optimization for Shake Flask Bio-treatment of Disperse Yellow 9 Textile Dye with White-rot Fungi and their Enzymes**

Muhammad Ramzan[1], Muhammad Asgher[1], Raymond Legge[2]; [1]University of Agriculture Faisalabad; [2]University of Waterloo

Industries that release highly colored effluents are textiles, paper and pulp mills, dye-making industries, alcohol distilleries and leather industries. Effluents from these industries contain chromophoric compounds and can be mutagenic and inhibitory to aquatic biosystems. Bioremediation utilizes metabolic potential of microorganisms in order to clean up the environmental pollutants to less hazardous or non-hazardous forms. White-rot fungi and their lignin degrading enzymes; laccase, manganese peroxidase and lignin peroxidases are useful in the treatment of colored industrial effluents and other xenobiotics. This study was designed to investigate the oxidation (decolorization/degradation) of three selected synthetic dyes; Bromophenol Blue (BB), Acid Violet 7 (AV7) and DisperseYellow 9 (DY9), by white-rot fungus Trametes versicolor. The best decolorized dye DY9 was selected for subsequent optimization studies. After the step by step applications, the highest color removal yield was 93% in DY9 sample after 120 h of incubation at 35°C, pH 4.5 in krik medium with added 1% starch and 0.01% ammonium sulphate as carbon and nitrogen source respectively. Ligninolytic enzyme activities were correlated to dye decolorization and maximum manganese peroxidase activity 416.33 U/ml was also noted in the maximally decolorized medium. The result indicated that T. versicolor was obviously able to breakdown synthetic dyes and manganese peroxidase was considered as a major lignin-degradation enzyme in this reaction. Manganese peroxidase enzyme play an important role in the bioremediation of these dyes and its activity is induced by dyes. The effects of dye concentration, fungal inoculum size as well as pH were studied. Samples were periodically collected for the measurement of color unit, laccase, manganese peroxidase and lignin peroxidase activity.

(735) **Imaging Mass Spectrometry of Three-Dimensional Cell Culture Systems**

Eric Weaver[1], Amanda Hummon[1]; [1]University of Notre Dame

Three dimensional (3D) cell culture offers a level of intermediate complexity between traditional monolayer cell culture and animal models. Applying 3D culture methods to the colorectal carcinoma cell lines HCT116 and HT29 we have grown tumor mimics, also called spheroids, as large as 1mm in circumference that share the same pathophysiological characteristics of tumors *in vivo*. This includes the development of nutrient, oxygen and metabolite gradients that develop across different regions of the spheroids, leading to distinct microenvironments within these models. In order to take full advantage of what these models have to offer, we have developed imaging mass spectrometry (IMS) methods to examine protein distribution across sections of these spheroids. We have been working to develop and apply a variety of chemometric techniques that will help us determine statistically relevant changes in protein expression in the different microenvironments, as well as highlight subtle relationships between differentially expressed proteins in various regions of the spheroids. We have applied Principal Component Analysis and Hierarchical Clustering to our datasets. These analyses have enhanced our ability to discern relationships between protein species that would otherwise go unnoticed during manual analysis. The combination of IMS and various chemometric techniques, with standard proteomic mass spectrometric sequencing by tandem mass spectrometry, will allow us to target specific proteins that are implicated in the progression of cancer. Our specific focus will be on identifying proteins that show changes in expression over time in the outer regions of the spheroids upon the induction of a migratory phenotype in these cells. With this novel combination of techniques, we can gain a unique view of important changes that lead cancer cells to escape the primary tumor mass and metastasize to other regions of the body.

(736) **Targeted Imaging of biomolecules by Tip Enhanced Raman Spectroscopy**

Hao Wang[1], Zachary Schultz[1]; [1]University of Notre Dame

As an emerging spectroscopic tool for surface analysis, Tip-enhanced Raman spectroscopy (TERS) has been applied to investigate molecules with large Raman cross-section, such as carbon nanotubes, dye molecules, and semiconductors. Technical difficulties in extending TERS to biological samples include generating sufficient Raman signals with a single scanning probe and locating the region of interest (ROI). Targeted TERS imaging combines atomic force microscopy (AFM) and surface enhanced Raman spectroscopy (SERS), and provides not only the topography of the desired ROI, but also the molecular fingerprint of the chemical species around it. By employing a ligand conjugated Au nanoparticle (GNP) probe, we create an aggregated nanostructure of GNPs when the Au TERS tip scans over a desired probe. The paper presented here explores this targeted TERS approach with different conjugated Au probes and demonstrates the detection and imaging of the biomolecules beneath the GNP probe. This imaging approach provides both high spatial resolution in nanometer scale and sufficient enhancement for biomolecule detection.

(737) **Raman Spectroscopy Paired with Dynamic Light Scattering: Probing Higher-order Structure of Pprotein Biotherapeutics**

Linda H Kidder[1], Wei Qi[1], Kevin Dahl[1], Kenneth S. Haber[1], E. Neil Lewis[1]; [1]Malvern Instruments

The integration of Raman spectroscopy with Dynamic Light Scattering enables the non-invasive and non-destructive determination of numerous chemical, structural and physical properties of protein therapeutics. Raman spectroscopy derives information about protein structure (secondary and tertiary) by monitoring molecular vibrations via spectral peak positions, shapes, and intensities. Dynamic light scattering (DLS), on the other hand, is a workhorse technique for determining the hydrodynamic diameter of proteins in solution, and more importantly provides information about the relative stability of formulations. The complementary nature of these results provides novel and potentially useful insights that may help develop stable biotherapeutics. We will present DLS and Raman data collected on protein and biopharmaceutical samples. Specifically, the evolution of protein secondary and tertiary structure as related to aggregation events will be presented.

(738) **Proteins Dielectrophoresis: A Promising Purification Method**

Fernanda Camacho-Alanis[1], Asuka Nakano[1], Alexandra Ros[1]; [1]Arizona State University

Dielectrophoresis (DEP) is a non-destructive transport mechanism where motion of particles occurs toward or away from regions of high electric-field gradients in a microfluidic channel. When applied to biomolecules, DEP has great potential as a bioanalytical tool for pre-concentration, fractionation, and separation using microfluidic platforms. However, in contrast to well-characterized biological cells, the mechanism of protein DEP is not well understood limiting its potential for bioanalytical applications. In addition, the nano-meter size of proteins forces to achieve nano-structured constrictions in microfluidic devices in order to enhance the DEP force acting on proteins, and allow the characterization of their DEP behavior. We study the DEP of proteins using two different approaches to build nano-structured microfluidic devices: the first combines optical lithography with focused ion beam milling to create nano-posts in a microfluidic channel; the second method is based on creating nanometer constrictions using only optical lithography by controlling

the thickness of the photo resist in a multilayer process. These devices have allowed us to study the parameters under which proteins can be manipulated and concentrated. Applied potential and frequency conditions were investigated under which DEP concentration was maximized. In the future, these conditions will allow choosing optimized parameters and design geometries for analytical devices employing DEP of proteins, such as in fractionation, purification or separation.

(739) Raman Spectroscopy and Translational Research: Application in Diagnosis and Characterization of Heterotopic Ossification

Katherine E. Cilwa[1], Jonathan R. Peterson[2], Benjamin Levi[2], Stewart C. Wang[2], Michael D. Morris[1]; [1]Department of Chemistry, University of Michigan; [2]Department of Surgery, University of Michigan Medical School

Heterotopic ossification (HO) is the formation of bone in regions of soft tissue following trauma, burns, amputations, and orthopaedic surgery. HO is a debilitating condition with particularly high incidence in young adults, despite a higher rate of musculoskeletal injury in the elderly population, and is highly associated with combat related injuries (62-65%) and severe burns (60%). Early diagnosis is rare, prophylaxis is limited, and treatment is complicated by impaired rehabilitation and functional deficits. Identifying demographics and markers for patients at high risk for developing HO will aid in earlier diagnosis and improved outcome. Understanding the pathogenesis of HO is an important step toward identifying high risk populations and developing therapeutic treatments and prophylaxis. The application of Raman spectroscopy for detection and characterization of HO is presented here for both mouse models and human specimens. Effects of age on Raman metrics were studied. In a mouse model, effects of inflammation suppression, type of trauma, and gene regulation were examined. Raman measurements differentiated between areas of varied HO maturity, cortical bone, and soft tissue. Early HO showed low crystallinity and mineral-to-matrix ratios compared with more advanced stages and with normal bone tissue. Burn injury resulted in increased HO development and increased mineral-to-matrix ratios. Raman metrics of specimens with greater HO volume development exhibited greater spatial heterogeneity of mineral-to-matrix ratios. Burn injury in young specimens accentuated this effect. Apyrase, an ATP hydrolyzing enzyme administered post injury at the burn site, reduced HO formation at remote locations. Transgenic mice with knockout of type 1a receptor for bone morphogenetic protein demonstrated reduced HO formation even following burn injury. Low crystallinity and mineral-to-matrix ratios are also found in measurements of HO specimens from humans who sustained injuries in motor vehicle accidents and are markers for HO. Raman spectroscopy aids in the detection and characterization of HO. Inflammatory responses to burn injury increase the formation of HO, particularly in young, healthy organisms.

(740) Non-invasive *in vivo* Collection of Biochemical Information from Human Bone using Spatially Offset Raman Spectroscopy; Developing Methodology for Clinical Investigation

Jemma Kerns[1], Kevin Buckley[2], Helen Birch[1], Anthony Parker[2], Pavel Matousek[2], Richard Keen[3], Allen Goodship[1]; [1]Institute of Orthopaedics and Musculoskeletal Science, University College London, U.K.; [2]Laser Facility, STFC Rutherford Appleton Laboratory, Oxfordshire, U.K.; [3]Royal National Orthopaedic Hospital, Stanmore, U.K.

Spatially offset Raman spectroscopy (SORS) allows chemical identification of a substance through a covering translucent material e.g., bone through skin [1]. Raman spectroscopy has been applied to measure differences between bone with different levels of mineralisation, and disease states [2]. Unlike current clinical technologies (e.g., DXA) SORS facilitates the examination of both the mineral and collagen phases of the bone and inverse SORS (iSORS) been developed into an instrument for a clinical study to acquire transcutaneous measurements, non-invasively [3-5]. The aim of this study is to test the hypothesis: a biochemical signature may be acquired transcutaneously *in vivo* of human bone, allowing the hydroxyapatite and collagen differences in degenerative bone conditions to be assessed.

Human participants(n=65) were recruited into a clinical study (REC approval 08/H0724/34). In addition, the tibia bone of a cadaveric leg was measured transcutaneously, then directly (Vesalius Clinical Training Centre, University of Bristol). The iSORS instrument (Cobalt Light Systems, Oxfordshire, UK) uses an 830nm laser, capped at 30mW per 3.5mm diameter aperture for use *in vivo*; for optimum acquisition conditions the laser power is adjusted with the spatial offset to stay within the safety limits. A band target entropy minimisation (BTEM) method was used to decompose the iSORS spectra into pure components [6]. Spectra acquired directly from the cadaveric tibia bone were comparable to the spectra acquired from the decomposed spectrum of bone acquired transcutaneously. Optimised for a high signal to noise ratio, bone spectra were acquired from participants from depths of ~4mm. The next step is to extract the pure bone spectrum reproducibly and compare spectra from different disease cohorts to see if the differences seen ex vivo are detectable. We demonstrate iSORS has the capability of detecting biochemical changes to bone, transcutaneously *in vivo*, providing important new information about bone disorders.

1. Matousek (2005) Appl Spectrosc,59,393-400
2. Buckley (2012) J Raman spectrosc,43,1237-1243
3. Matousek (2006) Appl Spectrosc,60,758-63
4. Schulmerich (2008) J Biomed Opt,13,020506
5. Okagbare (2012) J Biomed Opt,17,90502-1
6. Widijada (2003) Appl Spectrosc,57,1353-62

We wish to thank the Royal National Orthopaedic Hospital and patients for supporting this study, and the EPSRC (EP/H002693/1) for funding.

(741) Tip-enhanced Raman Spectroscopic Study of Epitaxial Graphene on SiC Silicon Face and SiC Carbon Face

Toshiaki Suzuki[1], Satoshi Minami[1], Yasunori Kutsuma[1], Koji Ashida[1], Tadaaki Kaneko[1], Yusuke Morisawa[2], Tamitake Itoh[3], Takeshi Miura[4], Yukihiro Ozaki[1]; [1]Kansei Gakuin University; [2]Kinki University; [3]National Institute of Advanced Industrial Science and Technology (AIST); [4]Unisoku

Graphene has been the focus of a wide variety of research regarding its unique material properties, for example elasticity, charge carrier mobility, optical transparency, and chemical stability. The character of graphene is changed by an interaction with a substrate and the distortion of local graphene structure. Raman spectroscopy can explore the graphene property, for example the number of layers, structure, and defects of graphene. However, spatial resolution of Raman scattering is restricted by the diffraction limit of light. The spatial resolution of tip-enhanced Raman scattering (TERS) is determined by the radius of a tip and can exceed the diffraction limit of light. In the present study, we measured TERS spectra of epitaxial graphene on the silicon carbide (SiC) substrate prepared by SiC thermal decomposition method, and compared the obtained TERS spectra with the corresponding Raman spectra. In raman spectra of the graphene on SiC Si-face, graphene signal and SiC signal are observed. However, in TERS spectra, SiC signals were enhanced stronger than graphene signals. On the other hand, the graphene signals were enhanced stronger than the SiC signal in TERS result of the graphene on SiC C-face. The mechanism of growth of the graphene on Si face is different from that on C-face. It is expected that difference of the TERS enhancement should occur by the difference of interface layer.

(742) **Toward Surface Enhanced Raman Correlation Spectroscopy (SERCoS)**

Steven M. Asiala[1], Zachary D. Schultz[1]; [1]University of Notre Dame

Analytical tools with high temporal sensitivity and chemical specificity are required to further the understanding of chemical dynamics at biologically relevant interfaces. The signal enhancement associated with surface enhanced Raman spectroscopy (SERS) makes SERS a strong candidate for the interrogation of biomembranes in a label-free fashion. Toward this end, we demonstrate detection and correlation analysis for macromolecular assemblies interacting with a highly enhancing SERS substrate. Spectral acquisition on the millisecond timescale allows for monitoring of particle diffusion dynamics through auto- and cross-correlation analysis. Surface enhanced Raman correlation spectroscopy (SERCoS) shows promise for the analysis of multiple targets simultaneously and label-free study of chemical organization and dynamics in biomembrane systems.

(743) **Label-Free Electrochemical SERS-based Assay for DNA Analysis Based on the Use of DNA Intercalators**

Evanthia Papadopoulou[1], Nittaya Gale[1], Sarah, A Goodchild[2], Simon Weller[2], David W Cleary[2], Tom Brown[1], Philip N Bartlett[1]; [1]School of Chemistry, University of Southampton, Highfield, Southampton; [2]DSTL, Porton Down, Salisbury, Wiltshire

Detection of specific DNA sequences and identification of single-nucleotide polymorphisms (SNPs) are crucial for bacterial strain differentiation and ultimately could be used in disease diagnosis. The most common surface-enhanced Raman spectroscopy (SERS) -DNA discrimination assays employ a synthetically attached label group to the DNA molecules to be detected. A disadvantage of this approach is that it increases the cost and complexity of the assay. Lower cost, label free assays have begun to emerge in recent years.

We have recently demonstrated a unique, label free, SERS-based assay for detecting DNA hybridization at an electrode surface. [1] In a typical assay the ssDNA probe is chemically modified at one end by a series of three di-thiol linkers. The probe is attached to a Raman-active gold sigmoidal segment void (SSV) surface adopting a perpendicular orientation followed by hybridization with complementary DNA to form dsDNA. The surface-immobilized dsDNA is exposed to a binding agent that is selective for dsDNA (methylene blue) and acts as a reporter molecule. Upon application of a negative potential, the dsDNA denatures and the Raman intensity of the reported molecule decreases sharply. The melting potentials of dsDNA can be used in discriminating mutations. In the current study, dsDNA is immobilized in a horizontal orientation by using DNA probes that are chemically modified at both ends by a series of three di-thiol linkers. The advantage of this flat configuration is that the intercalator is situated closer to the interactive surface and provides a larger signal enhancement of its Raman modes. Electrochemical melting of the immobilised dsDNA allows the discrimination of longer DNA sequences. This approach is more suitable for the analysis of large genetic fragments. In addition, being able to control the DNA orientation gives the advantage of controlling the orientation of intercalators with respect to the surface. Utilizing surface selection rules, the binding mechanism of the intercalators with the dsDNA is examined.

(1) Johnson, R. P.; Richardson, J. A.; Brown, T.; Bartlett, P. N. J. Am. Chem. Soc. 2012, 134, 14099.

(744) **Gold Nanorods - Surface Modification for SERS**

Amanda Haes[1]; [1]University of Iowa

Gold nanorods are optically interesting for SERS applications because (1) their plasmonic properties can be tuned from visible to near-IR wavelengths and (2) the resulting characteristic electric fields that extend from the metal surface generate a sensing volume for sensitive local dielectric sensing. In this presentation, silica surface modification strategies on gold nanorods will be employed to reduce unwanted dielectric changes without suppressing SERS detection of small molecules. The influence of CTAB during silica modification as well silica shell thickness will be evaluated. The resulting materials will converted into SERS-active materials using an internal etching procedure whereby the inner silica layers are selectively etched. The SERS activity of small molecules will be evaluated as a function of time and nanomaterial structure and homogeneity. Material design strategies which promote electromagnetic stability and SERS activity using gold nanorods will be shown to be important for the quantitative detection of small molecules.

(745) **Role of Plasmonic Interactions and Other Factors in Nanoparticle-based Immunoassays**

Marc Porter[1], China Lim[1], Nicholas Owens[1], Jennifer Granger[1]; [1]University of Utah

Immunoassays using surface-enhanced Raman scattering (SERS) as the detection methodology are capable of ultralow-level detection of antigens. An in-depth analysis of the plasmonic coupling essential to reproducible SERS intensity for immunoassays is described. It is found that coupling between extrinsic Raman labels (ERLs) and a planar gold surface is significant; coupling between neighboring ERLs also plays a role in immunoassay performance. Additionally the extent of ERL-ERL plasmonic coupling and planar surface-ERL coupling are influenced by the nature of adsorbed antibodies on the planar surface. Lower concentrations of antibodies lead to a slight increase in antigen binding capacity and result in ERLs residing more closely to the planar gold surface, thus yielding an increase in SERS enhancement. Clustering of antibodies on the surface leads to the formation of two-dimensional ERL aggregates. Small aggregates of ERLs are advantageous to increasing the per ERL SERS intensity, while large aggregates have a net negative impact.

(746) **Probing the Optical Near Field Behavior of Asymmetric Plasmonic Nanoantennas**

Jennifer S. Shumaker-Parry[1]; [1]University of Utah

Localized fields produced by plasmonic antennas lead to enhancements in spectroscopy, provide a tunable probe depth for plasmon-based sensing, and are the basis for control of light-matter interactions in nanoscale volumes. The localized fields may be manipulated through control of structural features of plasmonic architectures and interparticle plasmon coupling. In nanocrescent plasmonic antennas, simulations predict enhanced fields to be localized around the tips and backbone of the structure in a manner that depends on the polarization of the incident light. In order to probe the near field behavior, we have used localized multi-photon photopolymerization. Due to its nonlinear nature, multi-photon absorption is an inherently weak process that requires high light intensity. The locally enhanced optical near field leads to local multi-photon absorption under conditions of low intensity due to the antenna effect of the nanocrescents. Using scanning electron microscopy (SEM) and atomic force microscopy (AFM), we have mapped out localized regions of photopolymer. Through the photopolymer mapping, we have observed different near-field distributions dependent on polarization of incident light. For dispersed nanocrescents, when the incident light is polarized along the short axis, photopolymer is observed on the outer edges of the nanocrescent tips, and for incident light polarized along the long axis, photopolymer is observed to be spanning the nanocrescent tips and extending into the inner edge of the crescent. The near field behavior for coupled nanocrescent arrays is much different, with regions of enhanced fields localized between nanocrescents. Mapping of the optical near field behavior provides a basis for tuning the near-field distribution in these asymmetric plasmonic antennas.

(747) **Hydration Effects on Plasmonic Coupling in a Gold Nanoparticle Enabled SERS Immunoassay**

Jeremy Driskell[1]; [1]Illinois State University

Gold nanoparticle (AuNP) enabled surface enhanced Raman scattering (SERS) immunoassays offer a number of advantages relative to conventional assay platforms, including higher sensitivity and greater multiplexing capacity. AuNP-based SERS assays employ a SERS tag that consists of a AuNP modified with a Raman reporter molecule and an antibody that is used to indirectly detect antigen captured on a smooth metallic substrate. Recent theoretical and experimental investigations have established that plamonic coupling between the AuNP and the underlying smooth gold film leads to a hot spot in the gap, which is responsible for the large signal enhancement. Furthermore, enhancement of the Raman signal dependents significantly on the separation distance between the AuNP and gold film. In this presentation, a series of AuNP-Au film constructs are prepared using small organic crosslinkers and antibody-antigen interactions to systematically control the gap between the AuNP and Au film. Raman spectroscopy and scanning electron micrsocopy (SEM) are used to characterize each construct and elucidate structure-activity relationships. Interestingly, results indicate that the hydration state of the constructs affects the plasmonic coupling and SERS signal. Further insight into fundamental limitations of AuNP-enabled SERS assays will facilitate rational design of novel bio-specific ligands which maximize SERS sensitivity.

(748) **High Fidelity Polydopamine Surface Attachment Chemistries for SPR Imaging Applications of Biopolymer Microarrays, Nanostructured Surfaces and Biofunctionalized Nanoparticles**

Jennifer Wood[1], Gabriel Loget[1], Kyunghee Cho[1], Mana Toma[1], Aaron Halpern[1], Robert Corn[1]; [1]University of California, Irvine

The multiplexed detection of nucleic acids and proteins via bioaffinity adsorption onto biopolymer microarrays has become a primary tool for biological researchers throughout the world. Ultrasensitive biosensing methods for detecting DNA, RNA and proteins at extremely low (e.g., femtomolar) concentrations hold the promise of facilitating the identification of better biomarkers for early disease detection and strategies for post-treatment patient monitoring. This transformational research has been achieved in great part due to the success of an ever-increasing range of novel surface plasmon-based detection methodologies including SPR, SPR imaging, SPR fluorescence and localized SPR (LSPR) spectroscopy. All of these ultrasensitive multiplexed SPR biosensing methods require surface attachment chemistries on both planar and nanostructured surfaces that are reliable, reproducible and of very high fidelity. Additionally, surface enzyme chemistries can also be used to greatly increase the sensitivity and selectivity of these surface bioaffinity sensing methods; these advanced biosensing techniques also require reliable surface attachment methods that do not interfere with the surface enzymatic processes. In this talk we will describe the use surface attachment chemistries for the fabrication of single-stranded DNA monolayers on microarrays, nanoparticles and nanorings based on chemically or electrochemically deposited polydopamine (PDA) multilayers. The PDA film deposition is characterized with a combination of SPR, SEM, AFM and electrochemical measurements. The PDA films are then used to fabricate DNA microarrays for near infrared nanoparticle-enhanced SPR imaging and FT-NIR LSPR biosensors. The electrochemically deposited PDA films can be used in conjunction with nanoscale electrodeposition techniques to create DNA-modified PDA nanowires and PDA nanoring arrays that can be used to control the self assembly of biofunctionalized magnetic nanoparticles and the nanoscale placement of fluorescent probes (e.g., molecular beacons).

(749) **Multi-segment Injection-Capillary Electrophoresis-Mass Spectrometry for Biomarker Discovery in Metabolomics**

Philip Britz-McKibbin[1], Naomi Kuehnbaum[1], Aleisha Kormendi[1], Jenna Gillen[2], Martin Gibala[2]; [1]Department of Chemistry and Chemical Biology, McMaster University; [2]Department of Kinesiology, McMaster University

Separation science plays a key role for enhancing the performance of mass spectrometry (MS)-based metabolomic studies. However, sample thoughput is limited when using conventional separation platforms with gradient elution involving a "single" sample injection. In this case, major efforts are devoted to quality assurance and data pre-processing to correct for long-term instrumental drift that are time-consuming and/or subject to bias. To address this challenge, we have introduced a new approach for multiplexed analysis based on multi-segment injection (MSI)-CE-MS that enhances sample throughput while improving data quality. A unique advantage of CE is that separations use a homogeneous aqueous buffer system, thus allowing for multiple sample plugs to migrate under similar electrophoretic conditions. We demonstrate that up to seven distinct sample plugs can be analyzed simultaneously within a "single capillary" while maintaining isomeric resolution without deleterious ion suppression. In effect, MSI-CE-MS offers the sample throughout analogous to direct injection-ESI-MS while retaining the benefits of a high resolution separation, including greater selectivity and better quantiative reliability for complex biological samples. MSI-CE-MS was used as a high throughput platform for untargeted profiling of polar metabolites and their isomers derived from plasma filtrates without complicated sample handling. Time-resolved metabolomic studies were also performed to examine the putative health benefits of high intensity interval training (HIT) among a group of obese/overweight female subjects as a therapeutic tool for type 2 diabetes prevention. Plasma markers of differential treatment responses to HIT intervention were identified among sub-groups of non-diabetic yet high risk subjects. MSI-CE-MS offers a unprecedented approach for enhancing sample throughput up to an order of magnitude while simplfying data pre-processing requirements that is urgently needed for biomarker discovery and personalized medicine.

(750) **New Ways of Using Capillary Electrophoresis to Study Proteins**

Robert Kennedy[1]; [1]University of Michigan

We have explored several new ways to use capillary electrophoresis (CE) or microchip electrophoresis (MCE) for assaying proteins, measuring protein-protein interactions, or measuring protein function. These methods include: 1) a microchip Western blot; 2) screening for modulators of protein-protein interactions; and 3) high throughput screens of enzyme function. Western blotting is arguably the most widely used affinity separation method and on of the most common ways to assay proteins; however, it is a slow and manually intensive procedure. We have developed way to interface chip separations to membrane capture for an automated and high throughput Western blot. Protein-protein interactions have emerged as an interesting drug target; however, screening for potential drugs is hampered by current methods. We have shown that CE is a potentially powerful and relatively artifact free way of screening for such drugs. We are investigating improved throughput by using droplets, e.g. segmented flow, to introduce samples to a chip allowing assays at 0.5 to 1 Hz per channel.

(751) **Bioanalysis for Biocatalysis: Multiplexed Capillary Electrophoresis–Mass Spectrometry Assay for Aminotransferase Substrate Discovery and Specificity Profiling**

Maxim V. Berezovski[1], Gleb G. Mironov[1], Antony D. St.-Jacques[1], Alexander Mungham[1], Matthew G. Eason[1], Roberto A. Chica[1]; [1]University of Ottawa

In this work, we introduce an entirely automated enzyme assay based on capillary electrophoresis coupled to electrospray ionization mass spectrometry termed MINISEP-MS for Multiple Interfluent Nanoinjections-Incubation-Separation-Enzyme Profiling using Mass Spectrometry. MINISEP-MS requires only nanoliters of reagent solutions and uses the separation capillary as a microreactor, allowing multiple substrates to be assayed simultaneously. The method can be used to rapidly profile the substrate specificity of any enzyme and to measure steady-state kinetics in an automated fashion. We used the MINISEP-MS assay to profile the substrate specificity of three aminotransferases (E. coli aspartate aminotransferase, E. coli branched-chain amino acid aminotransferase, and Bacillus sp. D-amino acid aminotransferase) for 33 potential amino acid substrates, and to measure steady-state kinetics. Using MINISEP-MS, we were able to recapitulate the known substrate specificities and to discover new amino acid substrates for these industrially-relevant enzymes. Finally, we were able to reproduce the apparent KM and kcat parameters for the branched-chain amino acid aminotransferase reaction with its substrate L-valine. Because of its many advantages, the MINISEP-MS assay has the potential of becoming a useful tool for researchers aiming to identify or create novel enzymes for specific biocatalytic applications.

(752) **Punctuated Microgradients in Bioanalysis**

Mark A. Hayes[1]; [1]Arizona State University

Early demonstrations of capillary- and microchip- based electrophoresis have shown extraordinary resolution using high fields, showing deuterated vs. hydrogenated and sub-millisecond separations fully based on interactions of the analyte with the solvent/buffer and the applied field. These results were generally obtained in systems operating in a linear mode—spreading and diluting a mixture out along a single axis.

This presentation focuses on a new approach enabled by the short length-scale of microdevices and strong local field gradients. Electrophoretic exclusion (EpE) and gradient dielectrophoresis (gDEP), which use electric field gradients, are presented in detail here. Electrophoretic exclusion uses a constant flow field with an induced electric field gradient, differentiating species based on electrophoretic mobility. Gradient dielectrophoresis sets electrophoresis against dielectrophoresis. We have developed an underlying theoretical framework for both projects. It turns out that they were largely equivalent in a non-obvious way: the core feature that generated some unexpected results is the creation of punctuated microgradients separated by flat field zones. This uniquely minimizes the effects of diffusion by dramatically increasing the local restoring forces. The most important outcome and the unifying feature of this approach is that the models extend to any force which can be induced into dispersed microgradients in the presence of a static counter field. This concept has been shown for two applications and points to improved metrics of time, dynamic ranges (number of species and concentration), resolution, physical footprint, power, cost, portability, range of targets, and system integration.

(753) **Mechanistic Insight into the Improvements in Proteome Coverage and Low Abundance Protein Quantitation through Digestion and Depletion**

Bryan Fonslow[1], Mark Hixon[2], John Yates III[1]; [1]The Scripps Research Institute; [2]Takeda San Diego, Inc.

In the human cell there are estimated to be greater than 30,000 translatable genes with a protein abundance dynamic range of greater than six orders of magnitude. These cellular characteristics place an overwhelming demand on the quantitative analysis of whole proteomes. This analytical challenge has been adeptly addressed by the analysis of proteins at the peptide level using shotgun proteomics, but many challenges still remain. For instance, highly-sampled peptides from abundant proteins present a large proteomic background that inhibit the identification and quantification of peptides from low abundance proteins. We recently demonstrated improvements in proteome coverage and quantitation metrics of low abundance proteins within whole proteomes through a novel digestion and depletion strategy prior to a standard shotgun proteomics experiment. [1] Briefly, ten-fold more protein mass than regularly analyzed was subjected to a limited digestion. Using a molecular weight cutoff spin filter, ~ 90% of the protein mass was depleted as peptides. The remaining polypeptides were digested to completion and compared to a complete digestion of the same protein mass without the depletion step in triplicate shotgun proteomics runs. We identified ~25% more proteins overall in depletion runs, with 3-fold higher sequence coverage and quantitation metrics of low abundance proteins. Conceptually, we rationalized the gains from selective digestion and removal of abundant proteins, as peptides.

Through derivations using the classical Michaelis-Menten competitive substrate model and further quantitative analysis of our data we provide a refined depletion mechanism that better describes the complex mixtures we previously depleted and analyzed. Our derivations describe depletion of early-generated peptides from proximal fast tryptic cleavage sites with high specificity constants (V/K). Relative peptide abundance metrics exhibit a trend expected by the theoretical considerations and definitively re-illustrate quantitative gains from the depletion method. In our reanalysis, we do find that depletion and enrichment of single peptides on average account for ~ 30% of observed depletion or enrichment of proteins, respectively. These results indicate that consideration of tryptic sites and peptides in the digestion and depletion mechanism is essential and that depletion of highly-sampled, abundant, "proteotypic" peptides has the same effect as depleting an abundant protein to improve identification and quantification of low abundance proteins.

1. Fonslow, B.R. et al. Digestion and depletion of abundant proteins improves proteomic coverage. Nat. Methods 10, 54–56 (2013).

(754) **Optical Sensors via Infrared Absorption Spectroscopy for the Detection of Homemade Explosives**

Kevin Major[1], Kenneth Ewing[2], Rajendra Joshi[1], Menelaos Poutous[1], Catalin Florea[3], Jasbinder Sanghera[2], Ishwar Aggarwal[1]; [1]UNC Charlotte; [2]Naval Research Laboratory; [3]Sotera Defense Solutions

Homemade explosive devices are a major concern for the international community. A key defense against their use is the development of highly sensitive and selective chemical sensors. Additionally, these sensors must be able to selectively operate in natural, often quite complex environmental backgrounds. Traditionally, explosive devices are detected by measuring specific characteristic signals which are directly related to the target. This approach often suffers from low selectivity and sensitivity and faces inherent challenges when operating in complex backgrounds. We have chosen to develop a system that utilizes a different approach to study the "optical bouquet" of the full mixture of volatile chemicals associated with the explosive devices. To accomplish this, we plan to develop a set of overlapping filters which allow for the resolution of these optical bouquets. Because chemical analysis and chemical sensing are inherently linked fields of research we have chosen to utilize infrared (IR) absorption spectroscopy to measure these optical bouquets, as IR absorption is one of the most ubiquitous methods for chemical analysis. We demonstrate that a fuel oil/acetone/hexanes chemical system allows for an interesting case study for the separation of IR chemical bouquets using a three filter system with

Gaussian profiles. This system provides a necessary complex overlap of infrared absorption signals to determine the selectivity of such an approach. We show the calculated optical response of each component of this chemical system with respect to the three filter set. This work shows the potential for such detection of optical bouquets from a variety of homemade explosives and other devices.

(755) **Comparison of Vibrational Spectroscopic Techniques with Powder X-ray Diffraction for the Quantitative Measurement of Crystalline/Amorphous Content in Pharmaceutical Solids**

Mark Sullivan[1], David Heaps[1], Richard McKay[1], Xiao Hua Zhou[1], Edward King[1], Ajit Narang[2], Benjamin Wong[2]; [1]Advantest America, Inc.; [2]Bristol Myers Squibb

The formulation of active pharmaceutical ingredients in an amorphous form, usually as a solid dispersion in a polymer matrix, is an important strategy for increasing the solubility and bioavailability of poorly soluble drugs. The development of amorphous dispersions requires a sensitive analytical technique to test for the occurrence of crystallization in products on stability and for QC testing in commercialization. Vibrational spectroscopy is often cited as an alternative approach to widely used x-ray powder diffraction for the detection of crystallinity. In this paper we present the results of a comparative study using NIR, Raman and Terahertz Pulsed Spectroscopy for the quantitative measurement of low levels of crystallinity in a pharmaceutically relevant system. The results are reported following the typical method validation criteria, specificity, limit of detection, and robustness along with total analysis time.

(756) **Node Attenuation to Enhance Apparent Spectral Fine Features**

Isao Noda[1]; [1]University of Delaware

Node attenuation is a recently developed mathematical technique to enhance the apparent resolution and fine feature of spectra, especially those with highly overlapped bands. Unlike the previously known techniques, like the second derivatives and Fourier self deconvolution (FSD), node attenuation does not produce side lobes with opposite signs near the peak center. Therefore it can be safely applied even to enhance difference spectra containing both positive and negative peaks. Furthermore, the degree of feature enhancement is essentially independent of the intrinsic width of individual peaks. The second derivative and FSD spectra both tend to selectively emphasize narrow peaks in enhancement at the expense of broad peaks, which often becomes weak and obscure after the treatment. Such band-width dependent enhancement also tends to amplify certain spike-like noise and unwanted contributions from minor interfering species with sharp spectral features, such as water vapor. Node attenuation seems to effectively circumvent such problems associated with the band-width sensitivity of previous techniques. The technique is still in an early stage of development. Current state of the node attenuation technique will be reported, and how it can be used to identify hidden fine features of complex and overlapped spectra of natural or mixture products will be discussed.

(757) **Distribution Analysis for Quality Evaluation of Pharmaceutical Tablet by using a Newly Portable NIR Imaging Device (D-NIRs)**

Daitaro Ishikawa[1], Kodai Murayama[2], Takuma Genkawa[3], Mkoto Komiyama[2], Yukihiro Ozaki[1]; [1]Kwansei Gakuin University; [2]Yokogawa Electric Co.; [3]University of Tsukuba

In the situation of Manufacturing of medical supplies, introduction of Process Analysis Technology (PAT) has been advanced. Especially, at a coating process, understanding distribution of contents in the pharmaceutical tablet with a high speed is important. NIR technology was efficiency as PAT tool so that it has several features that are non-contact and non-destructive. Moreover NIR chemical imaging was noticed due to recognize to distribution of tablet on line. Therefore, in present study, the contents distribution analysis of tablets was carried out by using a newly NIR developed device, DNIRS (Yokogawa Electronic Co.). D-NIRS has 3 main parts, that is, spectrometer (P-NIRS), imaging unit and source unit. PNIRS is typical policrometer but due to achieve high speed and high spectral resolution measurement , it uses high density(640 element and 20μm pitch) InGaAs Photo diode array sensor(made by Yokogawa Electronic Co). Measurement range is 950nm～1700nm, and S/N is around 10-4 ABS on all of wave region. Source is halogen, it connects by fiber to imaging unit. As main feature for high speed imaging, it accepted line scanning method by 2 galbano millers. As coating reagents, Mg-stearate was added 0 to 50 % on the tablet after first pressing, and as the others, added to several contents to became sum of tablet weight to 100g. Thickness of each tablet was 2.5mm ±0.1mm, diameter of those was Φ8mm and 5 tablets were made for one contents. Diffuse reflected NIR spectra of tablets was obtained by DNIRS, spectral acquisition area was 10×10mm per each tablets. The NIR spectra were measured in the wavelength region of 950nm to 1700nm with 1nm intervals. From second derivative of the NIR spectra, change of the contents of coating reagents was assignment of 1217nm for Mg-stearate. The accuracy of quantitative of contents became more than R2=0.9, RMSE was less than 2.00. The distribution result obtained by skewness of second derivative in a tablet clearly identified the low quality tablet. This result suggested that DNIRS was efficiency to evaluate of coating quality.

(758) **Near Infrared Imaging Enables Chemical Analysis of Milled Wheat Fractions Physically Separated by Particle Size**

Mark Boatwright[1,2], David Wetzel[2], Jeffrey Gwirtz[3], Elieser Posner[4]; [1]Department of Biochemistry and Molecular Biophysics, Kansas State University, Manhattan, KS; [2]Microbeam Molecular Spectroscopy Laboratory, Kansas State University, Manhattan, KS; [3]JAG Services, Inc., Manhattan, KS; [4]ESP International, Savyon, Israel

Previously, our laboratory described and reported wheat endosperm determination for intermediate products of flour milling unit processes from quantitative near infrared imaging. Data derived enabled endosperm mass balance calculation from the product of endosperm concentration and flow rates of intermediate product streams. In flour milling, preprocessing of grain prior to conventional milling, or particle size reduction followed by physical fractionation based on particle size may result in select botanical part concentration. Traditionally, optimization for purity of each intermediate produced is a trial and error process gauged by the weight of inorganic residue after ignition or classical laboratory procedures reporting the botanical part composition as a function of particle size. The practical purpose of this report is to demonstrate optimization of physical segregation processes by objective measurement of the chemical composition of individual intermediate products. The utility of this optical, analytical chemical approach is shown for the products of select unit processes.

(759) **Application of Process Analytical Technology (PAT) in Pharmaceutical Manufacturing - FDA perspective**

Bogdan Kurtyka[1]; [1]FDA

FDA's guidance (PAT - A Framework for Innovative Pharmaceutical Development, Manufacturing, and Quality Assurance, September 2004) defines PAT as a system for designing, analyzing, and controlling manufacturing through timely measurements of critical quality and performance attributes of raw and in-process materials and processes, with the goal of ensuring final product quality. The guidance extends the term "analytical" in PAT beyond its traditional meaning to include chemical, physical, microbiological, mathematical, and risk analysis methods applied in an integrated manner. From this perspective, modern approaches to pharmaceutical manufacturing, such as Quality by Design, Real Time Release

Testing, and Multivariate Statistical Process Control, although formally not identified as PAT, fit very well into overall PAT definition. PAT systems become especially important for continuous manufacturing, where working real time in-process controls, early fault detection, and feed-back/feed-forward mechanisms are critical to assuring final product quality. The presentation will discuss application of Process Analytical Technology for monitoring and control of pharmaceutical processes from a regulatory point of view.

(760) **The Development and Application of PAT Tools to Achieve Process Understanding**

Brian Marquardt[1], Mel Koch[1]; [1]University of Washington

Process Analytical Technology (PAT) has provided value to the chemical related industries (pharmaceuticals, oil and gas, consumer products and foods) for years to optimize productivity and quality by gathering data to develop and monitor processes. Continued advancement in the capability of measurement tools supports efforts in improving process monitoring and control. These advances have been driven by Quality by Design (QbD) and QA (Quality Assurance) approaches to achieve process understanding as a way to develop and improve process control. A few primary advances in this field have been the development and focus on process specific analytics and in the miniaturization of historical analytical technology. When these news tools are combined with advances in process sampling and new sensor application platforms they are proving to be valuable approaches for implementing Process Analytical Technology (PAT) in many applications. The development and application of these new tools for high throughput experimentation, process optimization, advanced data handling, and subsequent process monitoring will have a large impact on quality manufacturing and quality control in a variety of industrial applications. This presentation will describe the current state of the art in NeSSI systems as the sampling backbone for new process sensor/instrumentation packages for PAT. Examples of new PAT sensors and miniaturized instruments will also be presented and discussed with emphasis on process understanding and control.

(761) **PAT – Past, Present & Future – A personal perspective**

John Richmond[1]; [1]Bruker Optics Inc.

There is a view that PAT was invented by the FDA back in 2002 when Ajaz Hussein announced the FDA guidance on the need for process monitoring, control & understanding in pharmaceutical manufacturing. This is a misconception – PAT or Process Analytical Technology – has been around for a long time. Back in the 1980's and 1990's online NIR was implemented in routine use in the chemical and petrochemical industries for applications such as hydroxyl value of polyols or octane number of gasoline. I personally installed and developed models for these applications using scanning monochromator NIR technology which was considered state of the art 30 years ago. What the FDA did was to adopt current industry best practice into an industry whose philosophy was that quality could be "tested in" by extensive testing of final products and impurities. The FDA approach focused on a risk based scientific approach whereby rapid methods (inline/online/at-line) would be implemented to control processes and release products at each stage of manufacturing. Processes from raw material testing to content uniformity of solid dosage forms and stages in between such as drying and granulation where envisaged with real time sensors at every conceivable point feeding back real time information to control systems whereby assuring the quality of the product. Early adopters from Pfizer, GSK and others set to work and manufacturers expected a huge boost in our product sales. The reality is that over the past 10 years , this implementation has been really slow on the uptake and whilst the top 20 pharmaceutical companies invested in RMID systems, the broader visions of PAT have not yet become a reality. However, all is not lost and the future looks bright. Future trends in continuous processing will require many online/inline sensors as it will not be possible to wait for a lab release test and the advent of hand held, portable and faster new technology applicable in many areas look as though they will remove many of the barriers to implementation and that the FDA vision from more than 10 years ago may in fact now become a reality

(762) **Imaging Quantum Effects in Biological Systems**

Gregory S. Engel[1]; [1]The University of Chicago

Photosynthetic antenna complexes operate with near perfect quantum efficiency and steer excitonic motion with exquisite precision. Optimized by evolution, these complexes exploit both incoherent (Förster) energy transfer along with coherent (wavelike) motion of energy. We seek to isolate and copy the microscopic details of this mechanism to enable coherent energy transfer in synthetic systems. To this end, we have created a new femtosecond optical spectroscopy by exploiting gradients in analogy to MRI. This approach permits us to image the underlying excited state dynamics within photosynthetic antenna complexes. We find a strong and unprecedented mixing between states of the chromophores and some bath modes within the system. The implications of this mixing for excitonic transport will be discussed along with new results showing long-lived coherence engineered into a family of novel synthetic small molecules demonstrating the same underlying design principles.

(763) **Ultra-compact LIBS Systems: Utilizing Microchip Laser Engines to Enable New Applications and Markets for LIBS**

Jason Eichenholz[1], Scott Buchter[2]; [1]Open Photonics Inc.; [2]Lasersec

Today, most Laser Induced Breakdown Spectroscopy (LIBS) systems are large and bulky. This is typically due to the fact that the laser exciting the plasma is a nanosecond q-switched flashlamp pumped system illuminating the target with tens of millijoules of energy. This is a very inefficient laser and process. In addition the spectrometer system and electronics are complicated and expensive due the precise timing requirements to time gate out the continua from the elemental spectra. We have developed an extremely small diode pumped solid-state laser system that produces a small spot size and has just enough energy to create a small microplasma. The laser runs at a high rep rate (~4-5 kHz) and the spectrometer integrates the signal from multiple plasmas from the laser, significantly reducing the complexity of the electronics.

The laser engine incorporates a focusing lens and the collecting optics to direct the plasma emission to a fiber coupled spectrometer via an SMA905 connector. We will also discuss a new handheld based system ideal for several new applications.

(764) **Biometrics from the Stable Isotope Analysis of Amino Acids in Human Hair**

Glen Jackson[1,2], Yan An[3], Kateryna Konstantynova[2]; [1]Forensic & Investigatice Science, WVU; [2]C. Eugene Bennett Department of Chemistry, WVU; [3]Department of Chemistry and Biochemistry, Ohio University

Instrumental methods of analysis can provide elemental, proteomic and isotopic information about human hair samples, which, because of their objectivity, scientific foundation, and statistical nature, offer many advantages over forensic hair microscopy. However, there are no known methods that provide investigative leads about a suspect from a questioned hair sample, such as a suspect's age, sex, race, region-of-origin, genetic disorders, disease state(s) or body mass index, among other traits. We herein provide preliminary evidence that isotope ratio mass spectrometry (IRMS)—which is already in use in many government forensic laboratories and has passed Daubert standards for admissibility in court on many occasions—has the potential to offer this solution. We performed compound-specific isotope IRMS on 14 amino acids from the hair of twenty female subjects. More subjects will be analyzed by the presentation date.

Analysis was performed on the underivatized amino acids using a mixed-phase LC-IRMS system. Statistical analyses were used to evaluate and classify the first 20 female participants into selected groups based on the information from detailed questionnaires that each subject completed. Statistical techniques such as canonical discriminant analysis (CDA) have the ability to overlook the covariance of amino acid isotope ratios between individuals caused by different dietary habits and instead highlight the selective differences caused by the grouping factor(s).

For the cohort of 20 female subjects, we are able to predict a subject's body mass index group and age group from their hair with accuracies exceeding 93% (based on original discriminant rules). We can use the discriminant rules to identify amino acids in hair that are specific markers for certain group classifications and thus point directly to physiological and biochemical reasons for the classifications. Unlike bulk isotope ratio approaches, our compound-specific approach appears to have the potential to go beyond region-of-origin or geospatial movements of individuals to the provision of physical and characteristic traits about the individuals.

(765) **Portable Spectrometry: Making Good Use of CMOS Detectors**

Alexander Scheeline[1], Thu Anh Bui[1, 2]; [1]SpectroClick Inc.; [2]Vietnam National University Hanoi

The world is awash in megapixel CMOS cameras, many if not most of which are not yet used for spectrometry. While there are crowd-sourced cell phone spectrometers for sale, the owner of the patent on cell phone spectrometry has apparently not (as of April, 2013) mass-marketed a cell-based analytical device. Why not? Making a portable spectrometer is rife with challenges in alignment, calibration, dynamic range, and data reduction. This talk reports a means to use any CMOS camera with sufficient pixels to do absorption spectrophotometry, reflectance spectrophotometry, or fluorescence spectrometry. The clever use of areal detectors is central to overcoming the limitations of inexpensive, noisy, low dynamic range detection, and to give nearly instantaneous results. Use of live, interfaced cameras and of JPEG images for data acquisition is demonstrated. The potential for kinetics measurements is explored. Opportunities for disruptive spectrometric technology are identified.

(766) **2D FT Electronic Spectroscopy of Quantum Dots in the Short-Wave Infrared**

David Jonas[1], Samuel Park[1], Dmitry Baranov[1], Byungmoon Cho[1]; [1]University of Colorado at Boulder

High efficiency next generation photovoltaics must have bandgaps in the short-wave infrared region (1000-2000 nm). We have developed the first femtosecond two-dimensional Fourier transform spectrometer in this wavelength region and used it to record the 2D FT spectra of oleate capped colloidal lead selenide quantum dots. The quantum dots were prepared in our laboratory by a hot injection synthesis and kept under air-free and moisture-free conditions throughout experiments. The synthesis is reported to produce lead rich surfaces, suitable for testing predictions about the intervalley splitting in spherical lead chalcogenide quantum dots. TEM indicates the quantum dots are ellipsoidal, with a 3.1±0.3 nm short axis and a 4.4±0.4 nm long axis; the short axis is consistent with the diameter deduced from a literature sizing curve and the first exciton absorption peak at 1.09 eV. As a function of waiting time, the real 2DFT correlation spectra exhibit a rapid evolution over the first picosecond. The relationship between the physical structure of the quantum dots, features in their 2D spectra, and their quantum confined electronic structure will be discussed.

(767) **FACSS and Its Annual Conference – 40 and Fabulous. The Good, the Bad, and the Innovative or Origin, Analysis, and Future Directions**

Ian Lewis[1]; [1]FACSS

The Federation of Analytical Chemistry and Spectroscopy Societies (FACSS) was formed in 1972 and organized its first annual meeting in 1974. The SciX meeting in Milwaukee in 2013 represents the 40th annual meeting. In this presentation, the author will give his perspective on the organization, the history of the organization, the many individuals who have contributed much, and the conference that for many years bore the federation's name. The presentation will conclude with an insight from the Governing Board's perspective on where it is hoped SciX and FACSS are heading.

(768) **A Year is a Long Time in Publishing**

May Copsey; [1]Royal Society of Chemistry

Scientific publishing – dinosaur or brave new world? This presentation will look at the changing face of academic scientific publishing, and how issues facing authors such as open access, ethics, dissemination, recognition and metrics are all playing a role in how publishing is evolving. We will also examine the way that publishers including the Royal Society of Chemistry are responding, in an effort to support researchers with the dissemination of their research and to ensure the impact of this is maximised, whilst fulfilling their funder's mandates.

(769) **What does a Seventeenth Century Academy Have to Offer to Science Today?**

Martyn Poliakoff[1]; [1]University of Nottingham

The Royal Society is the UK's academy of sciences. It claims to be the world's oldest continuously operating academy of sciences. Founded in 1660, it currently has ca 1450 Fellows across world, including 150 foreign Members. I am the so-called Foreign Secretary and one of the Vice-presidents of the Society. In this lecture, I try to answer the question in the title by explaining some of the current functions of the Society in the modern world. These functions including promoting the role of science to national and international policy makers, championing young scientists and fostering their research careers, shaping the future of science education and bringing science to the general public.

(770) **The Lawyer Ate My Paper: Can Industry Do Science in the Age of Litigation?**

Fred LaPlant[1]; [1]3M

The system of patents and legal protection afforded inventors has been an enabling factor in the innovation and creativity of the past two centuries. The system of freely shared information in a community of scientists has been an enabling factor in the explosion of scientific advances over the past two centuries. Profit and knowledge are not mutually exclusive, but the interests of business and the interests of academia must be balanced to maintain healthy scientific growth. With universities ever more focussed on patenting research, and industry sensitized to releasing the slightest competetive advantage, has this balance tilted too far in the wrong direction? This talk will explore the issues surrounding disclosure of scientific information, and the challenges scientists face in making good money and doing good science.

INDEX OF AUTHORS

INDEX OF AUTHORS

INDEX OF AUTHORS

INDEX OF AUTHORS

INDEX OF AUTHORS

INDEX OF AUTHORS

INDEX OF AUTHORS

INDEX OF AUTHORS

INDEX OF AUTHORS

INDEX OF AUTHORS

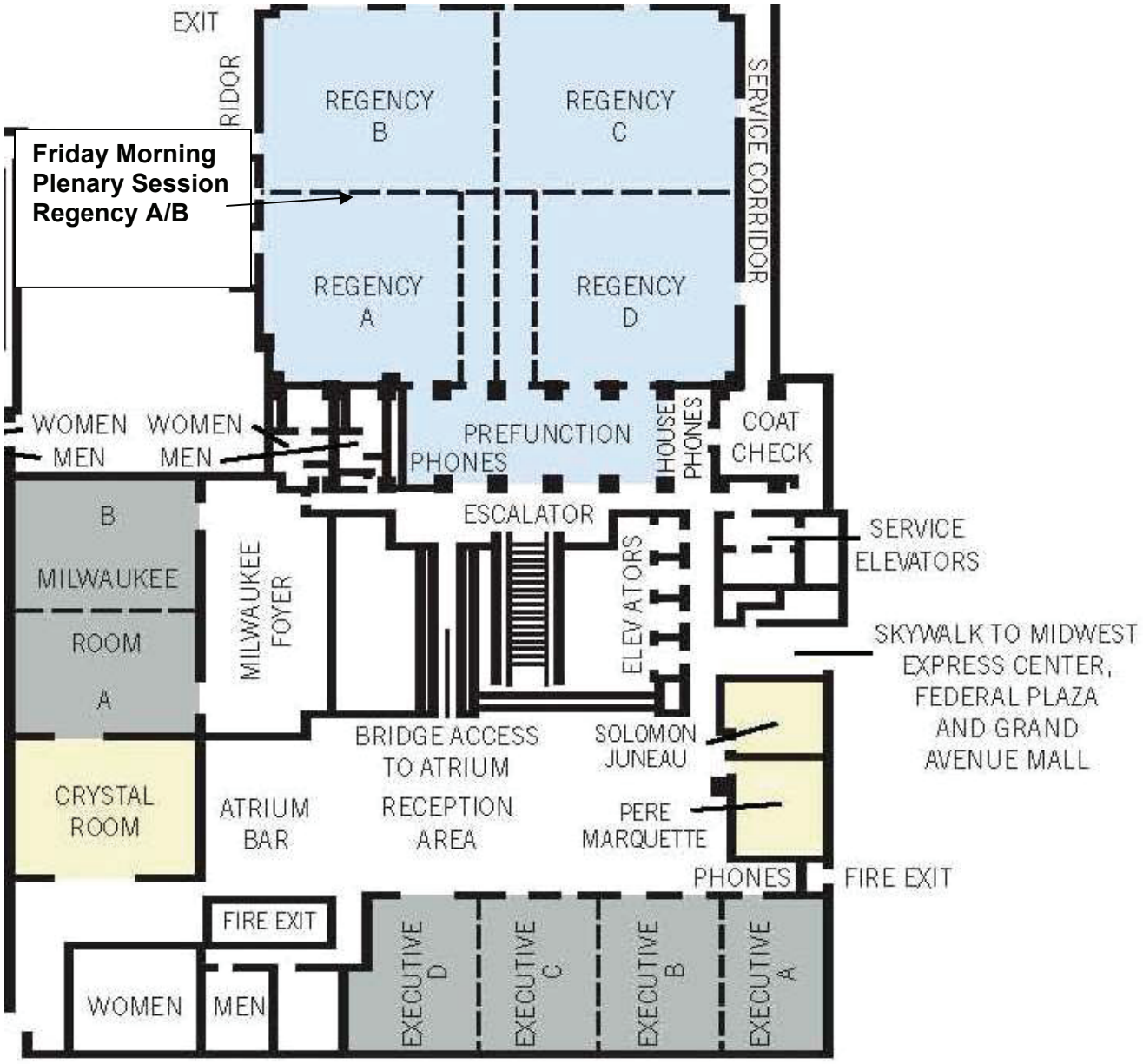
INDEX OF AUTHORS

INDEX OF AUTHORS

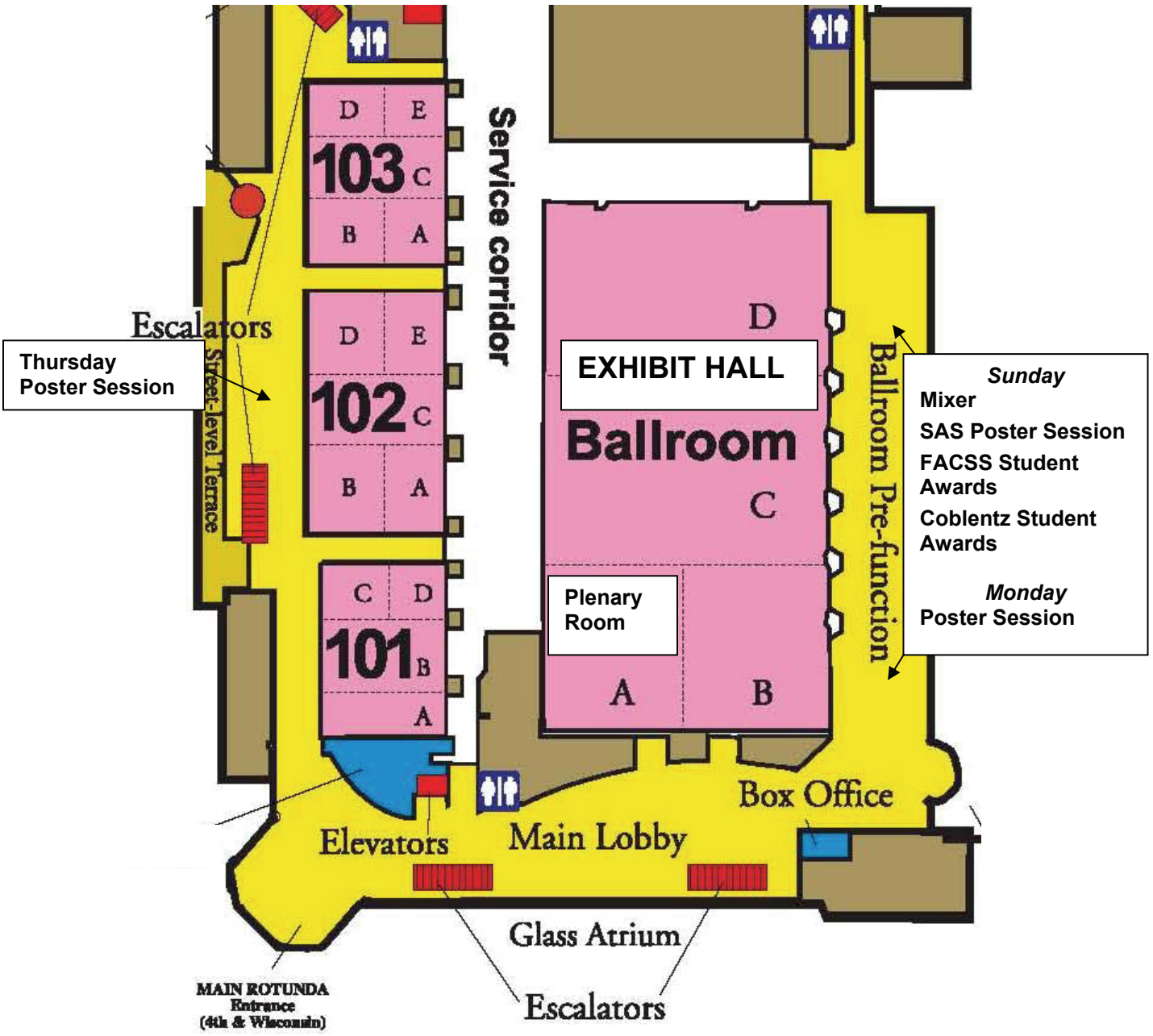
INDEX OF AUTHORS

INDEX OF AUTHORS

HYATT HOTEL FLOOR PLAN

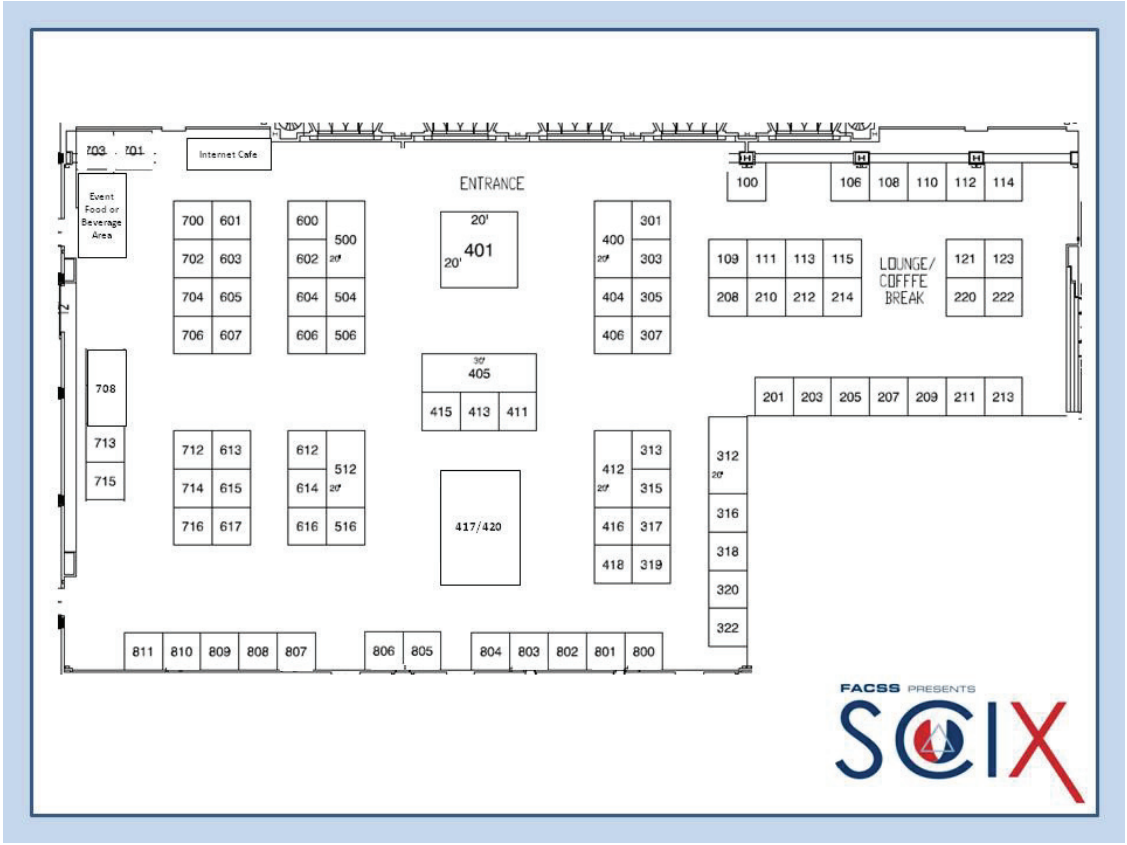


WISCONSIN CENTER FLOOR PLAN



SciX EXHIBITORS

ACS Division of Analytical Chemistry	807
Advantest America, Inc.	708
AES Electrophoresis Society	702
Agilent Technologies, Inc.	111
AIST-NT Inc.	504
Anasys Instruments Corp.	406
Andor Technology	803
Applied Spectra, Inc.	606
Avantes	319
B&W Tek, Inc.	506
BaySpec, Inc.	208
Block Engineering	115
Bruker Corporation	512
Catalina Scientific Instruments, LLC	301
CeramOptec Industries Inc.	205
Coates Consulting	516
Coblentz Society	808
Eigenvector Research, Inc.	415
Elemental Scientific, Inc	113
Energetiq Technology, Inc.	612
Enwave Optronics, Inc.	601
FACSS/SciX	
FiberTech Optica, Inc.	313
Fiveash Data Management, Inc.	715
GBC Scientific Equipment	607
Harrick Scientific	110
HORIBA Scientific	401 Island
Ibsen Photonics	617
ICP Information Newsletter, Inc.	604
INDATECH	802
Innovative Photonic Solutions	405
Iridian Spectral Technologies	615
Kaiser Optical Systems, Inc.	500
Light Age, Inc.	413
Milestone, Inc.	212
Neaspec GmbH	106
New Folder Consulting	613
Ocean Optics, Inc.	417/420
Ondax, Inc.	600/602
OPOTEK, Inc.	805
Optigrate Corp	404
Oriel Instrument, Inc.	214
P&P Optica Inc.	800
PD-LD, Inc.	418
Photonic Cleaning Technologies	416
PIKE Technologies	700
Pittcon	713
Princeton Instruments, Inc.	100
Quantel USA	303
Renishaw, Inc.	603/605
Retsch Inc.	108
Rigaku Raman Technolgies	411
Royal Society of Chemistry	614
RPMC Lasers, Inc.	203
SciAps, Inc.	201
Scinco	317
Shimadzu Scientific Instruments, Inc.	210
Snowy Range Instruments	806
Society for Applied Spectroscopy	809-811
Spectral Systems LLC	716
Spectroscopy Magazine / Advanstar	318
Technology Networks.com	316
Thermo Scientific	312
Thorlabs	704
Tornado Spectral Systems	412/414
TSI Incorporated	109
Wasatch Photonics	305/307
Waters	207
Wiley-Blackwell	315
WITec Instruments Corp.	400



MEMBER ORGANIZATIONS:

American Chemical Society's Analytical Division

AES Electrophoresis Society

American Society for Mass Spectrometry

ANACHEM

The Coblentz Society

Council for Near Infrared Spectroscopy

The Infrared and Raman Discussion Group

International Society of Automation-Analysis Division

The North American Society for Laser-Induced Breakdown Spectroscopy

Royal Society of Chemistry Analytical Division

Society for Applied Spectroscopy

The Spectroscopical Society of Japan

NATIONAL MEETING OF:

Society for Applied Spectroscopy (SAS)

The North American Society for Laser-Induced Breakdown Spectroscopy (NASLIBS)

FACSS
2019 Galisteo St. Bldg. I-1
Santa Fe, NM 87505 (USA)
(505) 820-1648

THE GREAT SCIENTIFIC EXCHANGE

SCIX2014

THE PREMIER MEETING FOR ANALYTICAL CHEMISTRY AND ALLIED SCIENCES

SEPTEMBER 28 - OCTOBER 3

GRAND SIERRA RESORT • RENO-TAHOE

2014 FOCUS: ADVANCES IN ANALYTICAL CHEMISTRY THROUGH DATA FUSION

Presented By The Federation of Analytical Chemistry and Spectroscopy Societies