FACSS 2008

Tomorrow's Analytical Sciences Today!

Reno, NV Sept. 28 – Oct. 2

Final Program
Book of Abstracts

Federation of Analytical Chemistry and Spectroscopy Societies

Society for Applied Spectroscopy National Meeting

www.facss.org

Sept. 28 - Oct. 2
RENO, NV
Grand Sierra Resort

50th Anniversary
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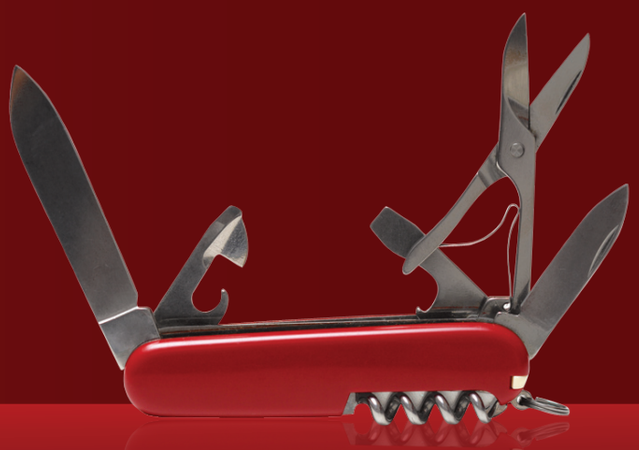

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Attention Presenters: Check this final program to verify the schedule of your talk or poster. Changes may have occurred since the preliminary program.

FACSS International Office
2019 Galisteo Street, Building I-1, Santa Fe, NM 87505
(505) 820-1648 ❍ Fax: (505) 989-1073 ❍ facss@facss.org ❍ www.facss.org

WELCOME TO FACSS 2008

WELCOME TO FACSS 2008: "TOMORROW'S ANALYTICAL SCIENCES TODAY"

We are excited you are here at the 35th annual Federation of Analytical Chemistry and Spectroscopy Societies (FACSS). The Reno organizing team wants to say welcome and we hope that you find this week to be both professionally stimulating and enjoyable. An excellent technical program that involves both poster sessions and oral symposia has been put together that we hope you will find are both timely, interesting, and cutting edge. We also have an exciting group of plenary speakers and award winners. The successful Hands-On workshops are continuing again this year.

HAPPY BIRTHDAY SAS!! This year marks the 50th Anniversary of **The Society for Applied Spectroscopy (SAS)**. This is an exciting achievement for SAS and during the week there will be some special celebrations and recognition to honor this achievement that we are sure you will want to be a part of. FACSS wants to congratulate SAS on their anniversary and to express our hope that the next fifty are as exciting and productive as the first fifty years have been.

The well received web based employment bureau is back for a second year! Wednesday evening is different this year in that we have a networking event that is open to everyone and starts early and goes into the night. This service is free for all registrants.

On Monday there are two plenary speakers this year. In the morning James Heath will be giving a lecture titled **New Bioanalytical Technologies for Probing the Paradoxical Relationship of the Immune System and Cancer** and in the afternoon Gary Hieftje will be discussing **His 40 Years of Contributions to Atomic Spectroscopy and Analytical Chemistry.** Each morning the sessions will start with Plenary Speakers comprised of award this years award winners. We hope that you will come and give them your support land congratulations on their honors.

The exhibits this year are exciting and represent a lot of new technology that must be seen to be appreciated. We will again have Monday Night Exhibit Opening Ceremony and reception which is a great time to interact with fellow attendees and exhibitors.

FACSS 2008 "*Tomorrow's Analytical Sciences Today!*" will continue the tradition of providing workshops presented by leading experts to attendees and students on timely subjects. Topics include vibration and imaging spectroscopy, bioanalytical and pharmaceutical techniques, process analytics and basic chemometrics.

To enhance everyone's ability to interact and network more, the Wednesday Evening Event this year is open to all registrants. It will start in the Exhibits with food and beverages for all and will include entertainment. The evening event will continue with "FACSS after Dark" with more food, beverage, entertainment and networking opportunities for all. We hope everyone will make time in the schedules for what we think will be an enjoyable evening.

FACSS 2008 "*Tomorrow's Analytical Sciences Today!*" is a unique conference in the analytical community that brings together researchers and scientists from a variety of scientific disciplines in academia, government and industry into one location. We hope that you enjoy this conference which is built to maximize your opportunity to communicate, share ideas and network with other analytical scientists in both you and different disciplines. If you enjoy what FACSS offers please be sure to let your colleagues that are not here know what they missed.

Gary Brewer, Governing Board Chair 2008
Greg Klunder, Program Chair 2008
Brandye Smith-Goettler – Workshops Chai
John Hellgeth, General Chair 2008
Mike Carrabba, Exhibits Chair 2006-2011
Drew Manica and Erica Kyllo – Employment Bureau

GENERAL INFORMATION

LOCATION: All conference symposia, exhibit and workshops will be held at the Grand Sierra Resort.

PROGRAM. This printed program contains titles and abstracts as submitted by the authors. It is not possible to edit these submissions.

SPEAKERS. There will be a LCD projector for each symposium. Speakers must supply their own computer with their presentation. Each speaker should adhere to the time allotted for the talk.

SPEAKER READY ROOM. A room is equipped with an LCD projector. The speaker ready room is in Nevada 12.

POSTER SESSIONS.

Sunday SAS Sponsored Student Poster Session – *Silver State Pavilion S1 extension*

- SAS Poster Session and Welcome Mixer 5:00 – 7:00 PM

Monday Poster Session – *Exhibit Hall S1 extension*

- 12:30 – 2:00 PM poster session. Set up poster by noon and remove by 5:00 PM. Odd numbered posters present 12:30 - 1:15 PM; even numbered present 1:15 - 2:00 PM

Tuesday Poster Session – *Exhibit Hall – S1.*
Posters remain up all day. Set up posters between 7:30 – 8:00 AM and remove by 5:00 PM

- Morning Session 9:00 – 10:15 AM. Odd numbered posters present
- Afternoon Session 1:30 – 3:00 PM. Even numbered posters present

Wednesday Poster Session – *Exhibit Hall – S1.*
Posters remain up all day. Set up posters between 7:30 – 8:00 AM and remove immediately at 3:00 PM

- Morning Session 9:00 – 10:15 AM. Odd numbered posters present
- Afternoon Session 1:30 – 3:00 PM. Even numbered posters present

Thursday Poster Session – *Nevada Room.*
Posters remain up all day. Set up posters between 7:30 – 8:00 AM and remove by 5:00 PM

- Morning Session 9:00 – 10:15 AM. Odd numbered posters present
- Afternoon Session 1:30 – 3:00 PM. Even numbered posters present

FACSS WORKSHOPS. A list of workshops, descriptions, and the locations begin on page 34. You must register for a FACSS workshop at the conference registration desk.

EMPLOYMENT BUREAU. The bureau is located in Nevada 1. The center will be open Monday through Wednesday, 9:00 AM to 5:00 PM and 9:00 AM – 3:00 PM on Thursday. See page 37 for additional information.

EXHIBITS The exhibition is located in Silver State Pavilion S1 and will be open as follows**:** See page 25 for details.

Monday (Opening Reception)	**5:00 PM – 7:00 PM**
Tuesday	**9:00 AM – 5:00 PM**
Wednesday	**9:00 AM – 3:30 PM and 5:00 – 7:00 PM**

BREAKS. Monday morning break will be held in the Silver State Foyer and the afternoon break will be during the poster session in S1 extension. Tuesday and Wednesday breaks will be held in the Exhibit Hall (S1). Thursday breaks will be in the Nevada Room.

INTERNET ACCESS. Complimentary wireless internet access is available in the Exhibit Hall, SS Foyer, and Employment Bureau. The access ID is FACSS 2008.

REGULATIONS.

1. There is no smoking in any conference area.
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.

SPECIAL EVENTS.

SUNDAY

3:40 – 5:00 PM	**"What's Hot" Exhibitor Presentations**, *S1 Extension*
5:00 – 7:00 PM	**Welcome Mixer and SAS Sponsored Student Poster Session**, SAS, FACSS, and Coblentz Student Award Presentations, *S1 Extension*

MONDAY

8:00 AM	**Plenary Lecture.** New Bioanalytical Technologies for Probing the Paradoxical Relationship of the Immune System and Cancer, **James Heath,** Professor of Chemistry at Caltech, Professor Molecular & Medical Pharmacology at UCLA, Director of the National Cancer Inst NSB Cancer Ctr**,** *S2/S3*
4:00 PM	**Plenary Lecture**. His 40 Years of Contributions to Atomic Spectroscopy and Analytical Chemistry**, Gary Hieftje,** Indiana University, *S2/3*
5:00 – 7:00 PM	**Reception for Exhibit Opening** (wine, beer, light hors d'ouvres) *Exhibit Hall S1*
6:45 PM	**Chemistry of Wines – A Tasting Event.** Wine Tasting lead by Dr. J. Ernest Simpson, California State University – Pomona. Ticket required*, Sierra 1/2 on Mezzanine*

TUESDAY

8:00 AM	**Charles Mann Award for Applied Spectroscopy**. Shift Happens: Developments in Raman Sampling, **Ian R. Lewis**, Kaiser Optical Systems, *S2/3*
8:30 AM	**ANACHEM Award.** Gas-Phase Bio-Ion Reactions and Bioanalysis**, Scott McLuckey**, Purdue University, *S2/3*
12:20 PM	**"What's Hot" Exhibitor Presentations**, *S1 Extension*
12:30 PM	**SABIC Innovative Plastics sponsored Roundtable discussion and lunch for students.** *Sierra 1/2 on Mezzanine*
6:00 PM	**Raman Reception**, *S2/3*
7:00 PM	**SAS Reception (members only),** *Nevada 56/7*

WEDNESDAY

8:00 AM	**SAS Applied Spectroscopy William F. Meggers Award**. Development of a Multiplex Spectrometer for Doubly-Resonant SFG Spectroscopy**, Taka-aki Ishibashi** and **Toshibi Maeda**, Hiroshima University, *S2/3*
8:30 AM	**SAS Applied Spectroscopy Lester W. Strock Award.** Modeling of Plasmas, Plasma-Solid and Laser-Solid Interaction, **Annemie Bogaerts**, University of Antwerp*, S2/3*
12:20 PM	**"What's Hot" Exhibitor Presentations**, *S1 extension*
5:00 PM	**Wednesday Evening All Inclusive Event,** complimentary for all conferees**.** *Exhibit Hall*
7:30 PM	**FACSS After Dark,** complimentary for all conferees, *Exhibit Hall extension*

THURSDAY

8:00 AM	**Ellis R. Lippincott Award:** Molecular Plasmonics: Single Molecule SERS, Exploring the Plasmonic Periodic Table, and Plasmon Microscopy, **Richard P. Van Duyne,** Northwestern University, *S2/3*
8:30 AM	**Coblentz Clara Craver Award:** Nonlinear Vibrational Spectroscopy for the Analysis of Biological Membranes. **John C. Conboy**, University of Utah, *S2/3*

EVENTS OF SPECIAL INTEREST TO STUDENTS

Sunday Evening, *S1 extension*

- Welcome Mixer – 5:00- 7:00 PM
- SAS Sponsored Student Poster Session – 5:00 – 7:00 PM
    - SAS, FACSS and Coblentz Student Award presentations

Monday through Thursday

- FACSS Student Poster Awards will be presented daily.

Monday

- Employment Bureau, *Nevada 1*
  Monday – Wednesday 9:00 AM – 5:00 PM; Thursday 9:00 AM – 3:00 PM
- SAS Student Reception, 7:30 – 9:30, *Whitney Room, Mezzanine Level*

Tuesday

- 12:30 PM, **SABIC Innovative Plastics** Sponsored Employment Roundtable Discussion and complimentary lunch in Sierra 1/2, Mezzanine Level. *Sign up at conference registration desk.*

COMPANION REGISTRATION

Companion registrations do not include access to symposia or exhibit hall other than for special events. Cost is $55 and includes the following:

Sunday: Evening Welcome Mixer*;* **Monday***:* coffee/pastries 9:00 AM *and* Exhibit Hall Opening Reception*;*
Wednesday: Evening Events beginning at 5 PM in Exhibit Hall

5:00 PM
WEDNESDAY EVENING EVENT and FACSS AFTER DARK
Exhibit Hall

This year at FACSS, there will be an all-inclusive Wednesday Evening Event. Aftr the oral session, meet you colleagues in the exhibit hall and enjoy food and beverage as well as magic and comedy provided by Becky Blaney. Once the events in the exhibit hall close walk into the adjoining room for FACSS After Dark. This event will provide an opportunity for more mingling, food and beverage, as well as dancing and Karaoke. ***There is no additional charge for the Wednesday Evening Events.***

FACSS ORGANIZATION

Member Organizations of FACSS
American Chemical Society, Analytical Division
American Society for Mass Spectrometry
ANACHEM
Analysis Division of Instrument Society of America
Coblentz Society
Royal Society of Chemistry
Society for Applied Spectroscopy

FACSS is the National Meeting for the Society for Applied Spectroscopy and the Coblentz Society

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Program Chair	**Greg Klunder,** *Lawrence Livermore National Laboratory* E-mail: klunder1@llnl.gov
Workshop Chair	**Brandye Smith-Goettler,** *Merck*
Employment Chair	**Drew Manica and Erica Kyllo,** *SABIC Innovative Plastics*

2008 Program Section Chairs

Awards	**Curt Marcott,** *Light Light Solutions, Inc. LLC*
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Bioanalytical	**Ken Christiansen**, *Clemson University*
Chemometrics	**Barry Lavine**, *Oklahoma State University*
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Forensics	**Mary Carrabba**, *Southern Oregon University*
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Process	**Brian J. Marquardt**, *University of Washington*
Raman	**Ian R. Lewis,** *Kaiser Optical Systems, Inc.*
Surface Plasmon Resonance	**Karl S. Booksh**, *University of Delaware* **Roger Terrill,** *San Jose State University*
TeraHertz	**Mike Claybourn,** *AstraZeneca, Ltd*
SAS Student Poster Session	**Bonnie Saylor** and **Victor Hutcherson**, *Society for Applied Spectroscopy*

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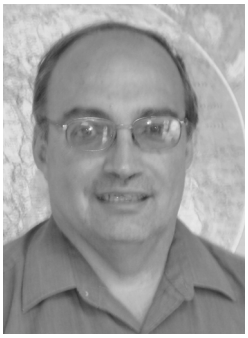

Gary Brewer
ABB

Gary Brewer is a Product Manager – Photometers for ABB Process Analytics in Lewisburg, WV where he has worked for the past 20 years. He started for ABB as an Applications Chemist before moving into product management several years ago. Prior to joining ABB, he worked for Menardi-Southern in Los Angeles, CA for 6 years as a coatings chemist and manufacturing manager after spending 2 years working as an Environmental Chemist for General Electric in Lebanon, PA. Gary got started in process analytics immediately after college by working for the Department of Energy in Morgantown, WV on the demonstration project of the first fluidized bed boiler in a Power Utility Industry. Gary got his B.S. in Chemistry from Fairmont State College in Fairmont, WV in 1978. Gary has been active in the Analysis Division of ISA for the past 20 years and has been an ISA delegate to FACSS since 2000. He enjoys camping, hiking and other outdoor activities as well as an avid fan of the WVU Mountaineers! He is married to a wonderful wife and has two children – a son in graduate school at Miami University in Oxford, OH and a daughter at Radford University in Radford, VA.

GENERAL CHAIR

John Hellgeth
Hewlett-Packard Company

Presently, John Hellgeth serves as a Senior Member of the Technical Staff at Hewlett-Packard in San Diego where he specializes in materials characterization using thermomechanical methods coupled with spectroscopic and optical imaging techniques. He received his B.S. in Biochemistry from Virginia Tech and his Ph.D. in Analytical Chemistry, also from Virginia Tech, in 1986. John's graduate work was with Prof. Larry Taylor in the development of hyphenated chromatographic separations coupled with spectroscopic detectors. His post-doctoral activities included teaching undergraduate and graduate chemistry courses as a Visiting Professor and conducting research efforts with Dr. Thomas Ward in the creation of high performance materials within NSF Science and Technology Center on High Performance Polymeric Adhesives and Composites. During this time, he developed novel hyphenated themomechanical/vibrational spectroscopic methods to assess structure/property correlations of materials and use of embedded fiber optic sensors to gauge cure state in real-time for 'smart' processing of high performance composites. In 1992 with Nicolet Instruments Corporation, he provided applications development and training for clients in infrared and Raman spectroscopic techniques. In 1996, he joined Spectra-Tech, Inc. as product manager for vibrational microspectroscopy and began the development of the Continuum IR microscope. As an Associate Research Fellow at Kimberly-Clark Corporation in 1998, he established an advanced vibrational spectroscopy facility specializing in chemical imaging and multiple modulation spectroscopic methods for materials characterization. John served as a consultant with The SRN Company, LLC, providing training in vibrational spectroscopic methods, chemical analysis and research support for clients prior to joining HP. John has served the FACSS organization in several capacities in its programs, workshops and governing board over the past decade. He is actively involved with the Society for Applied Spectroscopy and the Coblentz Society, where he served as a board member and its president (2001-2003). Outside of HP and spectroscopy, John is often found running forest trails training for ultra-marathons, searching for elusive thermals while hang gliding, and tricking out the performance of an old Mazda Miata he hopes to bring to a track someday.

FACSS CHAIRS

PROGRAM CHAIR

Greg Klunder

Lawrence Livermore National Laboratory

Greg is a staff scientist at Lawrence Livermore National Laboratory (LLNL) where he is a member of the Functional Materials and Molecular Structures group and the Forensic Science Center. He received a B.S. in Chemistry from Virginia Tech and a Ph.D. from North Carolina State University studying flame spectroscopy under the direction of Dr. Charles Boss. In 1990, he took a post doctoral position at Lawrence Berkeley Laboratory with Dr, Richard Russo and then moved to LLNL where he has been since.

Greg has been involved in a several different of areas of research including photothermal spectroscopy, fiber optic chemical sensors, capillary electrophoresis, laser ablation mass spectrometry, near infrared and terahertz spectroscopies, and SPME GC-MS. His current projects involve remote detection of explosives based on vapor phase chemical detection and near-infrared spectroscopy, determination of stability of gun propellants, and separation of uranyl species with capillary electrophoresis using time-resolved laser-induced fluorescence and NMR detection. He is a regular attendee at FACSS which has been helpful in providing him with a broad background and understanding of many different analytical techniques. He has always enjoyed the quality and diversity of the science and the camaraderie with other scientists at FACSS

Outside the lab, Greg enjoys a many outdoor activities including, cycling, running, Ultimate Frisbee, hiking, camping, skiing and snowshoeing. He also enjoys playing guitar and listening to blues music and exploring its history. Greg has 2 very active sons (Will, 5, and David, 4) who keep him busy and young at heart.

EXHIBITS CHAIR

Michael Carrabba

The Hach Company

Dr. Mike Carrabba is currently the Director of The Hach Company's Homeland Security Technologies Air Systems Division where he is working on using spectroscopy for the detection of biological hazards. He received his B.S. in Chemistry from Salem State College in 1981 and his Ph.D. from Tufts University in 1985. Mike'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, Mike 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 Raman instrumentation and techniques, several of which resulted in U.S. patents. After leaving EIC, Mike joined Chromex, Inc, a manufacturer of Raman spectroscopy systems, as Marketing Manager and most recently was the OEM Division Manager at Jobin Yvon, Inc. Mike has been very active in FACSS over the years serving as Governing Board Chair (2002), Program Chair (2000), Program Section Chair for Raman (1992-1999, 2001), Chairperson of the Long Range Planning Committee and as a member of the Governing Board. In 2003 he received the ASTM Award of Merit 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 the Williams Wright Award for Applied Spectroscopy. He is also a member of the Society for Applied Spectroscopy (SAS) and Coblentz Society. On the home front, his wife, Professor Mary Widmark Carrabba of Southern Oregon University, a highly skilled Infrared microscopist and the former treasurer for SAS, complements Mike's Raman background

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October 18 – 22, 2009

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Louisville, KY

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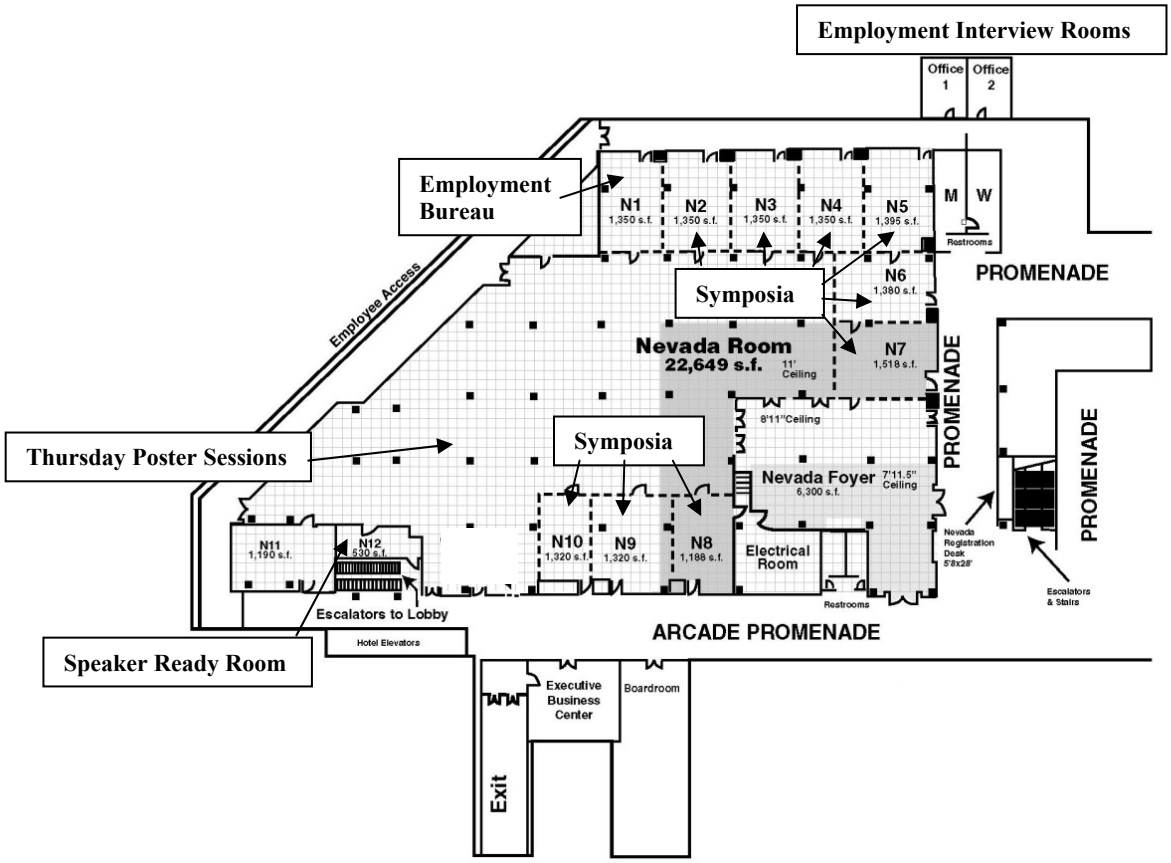
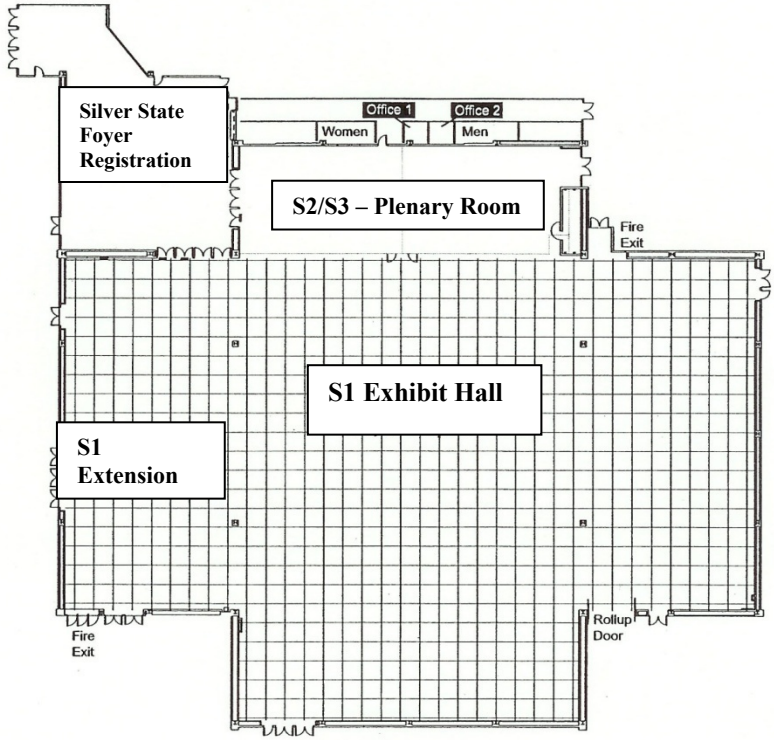
Program Chair: Curt Marcott – marcott.ca@pg.com

Exhibit Chair: Mike Carrabba – mcarrabba@hach.com

FLOOR PLANS


Employment Interview Rooms
Office 1
Office 2
Employment Bureau
N1 1,350 s.f.
N2 1,350 s.f.
N3 1,350 s.f.
N4 1,350 s.f.
N5 1,395 s.f.
M
W
Restrooms
PROMENADE
Symposia
N6 1,380 s.f.
Employee Access
Nevada Room 22,649 s.f. 11' Ceiling
N7 1,518 s.f.
8'11"Ceiling
PROMENADE
Thursday Poster Sessions
Symposia
Nevada Foyer 6,300 s.f. 7'11.5" Ceiling
PROMENADE
N11 1,190 s.f.
N12 530 s.f.
N10 1,320 s.f.
N9 1,320 s.f.
N8 1,188 s.f.
Electrical Room
Nevada Registration Desk 5'8x28'
Escalators & Stairs
Restrooms
Escalators to Lobby
ARCADE PROMENADE
Hotel Elevators
Speaker Ready Room
Executive Business Center
Boardroom
Exit


Silver State Foyer Registration
Office 1
Office 2
Women
Men
S2/S3 – Plenary Room
Fire Exit
S1 Exhibit Hall
S1 Extension
Fire Exit
Rollup Door

FACSS AWARDS

The Tomas Hirschfeld Scholars and the FACSS Student Award recognize outstanding contributions by individuals who are Ph.D. and M.Sc. candidates.

TOMAS HIRSCHFELD SCHOLAR

Christopher R. Field
University of Illinois

Presentation, Wednesday, 3:00 PM, Room N7

Christopher R. Field is a graduate student in the Department of Chemistry at the University of Illinois at Urbana-Champaign where he works for Professor Alexander Scheeline and Professor Richard Masel. Prior to his graduate work, Christopher earned a B.S. in Chemistry and Computer Science from Drake University in Des Moines, IA. His research interests include a wide range of topics from acoustically levitated drop reactors to carbon nanotube-based gas phase sensors for miniature GC systems, with a primary focus on development of new instrumentation. Using his knowledge of instruments and computer programming, Christopher has designed, implemented, and automated a variety of instruments to help researchers achieve ground-breaking results. For creatively overcoming problems in research, Christopher was selected as a finalist for the Lemelson-Illinois Prize for Innovation and Inventiveness in 2007-2008 and participated in the Roundtable on Entrepreneurship Education (REE) Fellows Program hosted by Stanford University.

TOMAS HIRSCHFELD SCHOLAR

Matthew Keller
Vanderbilt University

Presentation, Tuesday, 11:35 AM, Room N3

Matthew Keller is a Ph.D. student working with Anita Mahadevan-Jansen in the biomedical optics lab at Vanderbilt University. He received his B.E. in biomedical engineering from Vanderbilt in 2003, and his M.S. in biomedical engineering from Vanderbilt in 2006. Matt has been involved with several research projects at Vanderbilt, including the use of organotypic raft cultures as a model of skin to show that Raman spectroscopy can detect malignancy associated changes in the epithelium for stromal disease. His current focus is improving margin analysis during breast conserving surgery, which is a key factor in preventing breast cancer recurrence and costly second operations, through a variety of optical techniques, including reflectance, fluorescence, and Raman spectroscopy. Matt has shown that Raman spectroscopy can classify breast tissues into four pathological categories with 99% accuracy. He has also shown that spatially offset Raman spectroscopy (SORS) can be used to overcome limitations in terms of interrogation depth of standard Raman techniques, so that breast tumor signatures can be detected under 1-2mm of normal tissue, as needed to be clinically useful for margin analysis. Matt's work has been presented at several international meetings, both in the United States and Europe, and has been published in a variety of leading journals. He has received several awards, including the Founder's Medal as the top undergraduate in his class, a Howard Hughes Medical Institute Pre-doctoral Fellowship, and a recently awarded Department of Defense Breast Cancer Research Program Pre-doctoral Fellowship.

FACSS AWARDS

FACSS STUDENT AWARD

David Strasfeld

University of Wisconsin, Madison

Presentation, Tuesday, 11:55 AM, Room N10

David Strasfeld is a graduate student working with Dr. Martin T. Zanni in the Chemistry Department at the University of Wisconsin, Madison. Prior to matriculation at UW, David completed his undergraduate work with Dr. Richard Loomis at Washington University in St. Louis. David's research thus far has centered on using shaped, ultrafast, mid-infrared laser pulses to gain insight into condensed phase structure and dynamics. David began his graduate work by developing a mid-infrared pulse shaper and subsequently utilizing it in coherent control and 2D-IR experiments. David is currently employing shaper-based, automated 2D-IR spectroscopy towards better understanding the structural kinetics of human amylin aggregation in hopes of elucidating the type II diabetes disease mechanism. For his research efforts, David has been awarded the John Sowden Prize, the Hypercube award and a UW Distinguished Graduate Student fellowship, and has served as a delegate to the 56th Lindau Meeting of Nobel Laureates. David's research has been published in numerous journals and presented at a variety of international conferences. Additionally, David is an avid Frisbee player and founding member of the bicycle advocacy group, MadFBC.

TOMAS HIRSCHFELD AND FACSS STUDENT AWARDS
Call for Applications for 2009

The Tomas Hirschfeld Scholar(s) 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 2009 FACSS meeting in Louisville, KY (October 18 - 22). In 2008 two Tomas Hirschfeld Scholars and one FACSS Student Award 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 FACSS web site 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 web site submission form, and submitting three sets of the following:

a) the form, available on the FACSS web site
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 a session highlighting young scientists and their work.

The FACSS Web site will begin accepting abstracts and applications for FACSS student awards in January 2009**.** Go to www.facss.org to submit an application.

CHARLES MANN AWARD

For Achievements in the Field of Applied Raman Spectroscopy

Ian R. Lewis

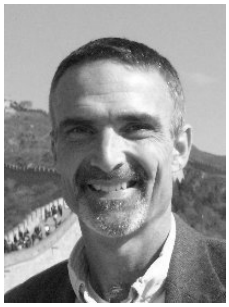
Kaiser Optical Systems

Presentation, Tuesday 8:00 AM, S2/3

Ian R. Lewis was born in 1968 in Weston-Super-Mare, 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 Interdisciplinary Research Center 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 in 1992 he went to the University of Idaho to work as a postdoctoral research associate in the laboratories of Professor Peter Griffiths. 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. During his time at Kaiser he has also served as a senior scientist, the Research Products manager, and is currently global Marketing Manager. At Kaiser, Ian splits his time between business development, market development, product market positioning, collaborations, and Raman education activities including short-courses. He has been an active participant in past-FACSS conferences, was the Program Chair for the 2007 meeting in Memphis, and has been the Raman section chair in 2000, and from 2002 to the present. He has organized scientific sessions at several additional conferences including EAS. Ian served as a board member of the Coblentz Society from 2004-2008. He serves as 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 is the co-liaison from committees E13 to E55. During his career Ian has published approximately 45 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 serves on the editorial advisory board of Spectroscopy Magazine, and American Pharmaceutical Review. Ian is an active reviewer for a number of international journals and a member of several scientific societies.

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.



Scott A. McLuckey

Purdue University

Presentation, Tuesday 8:30 AM, S2/3

Scott A. McLuckey received his B.S. in Chemistry at Westminster College (New Wilmington, PA) in 1978 and doctorate in Analytical Chemistry at Purdue University (West Lafayette, IN) in 1982, where Professor Graham Cooks served as his thesis advisor. He then served as a Postdoctoral Fellow at the FOM Institute for Atomic and Molecular Physics (Amsterdam, The Netherlands) until late 1983. He was then awarded a Wigner Fellowship at Oak Ridge National Laboratory in the Analytical Chemistry Division. While at Oak Ridge, he served in such capacities as Group Leader, Organic and Biological Mass Spectrometry, and Section Head of Analytical Spectroscopy within the Chemical Sciences Division. In 2000, he moved to Purdue University where he is Professor of Chemistry. Dr. McLuckey's research emphases have been placed in the areas of gas-phase ion chemistry and instrumentation for organic and biological mass spectrometry. Fundamental aspects of ionization, unimolecular reactions, and bi-molecular reactions have been studied with the goal of improving the capabilities of analytical mass spectrometry. Ion activation, ion/molecule reactions, and ion/ion reactions have been major focal areas within the context of the mass spectrometry/mass spectrometry experiment. Instrumentation for tandem mass spectrometry has also been highlighted with emphasis on electrodynamic ion traps and ion trap/hybrid instruments. This research has been described in over 230 papers appearing in the peer-reviewed literature. He has been awarded five U.S. Patents on various technologies associated with mass spectrometry. The major current areas of emphasis are the identification and characterization of macro-molecules, primarily via whole molecule tandem mass spectrometry, and ion/ion reaction chemistry. Recognition for the work has included the Biemann Medal from the American Society for Mass Spectrometry in 1997, Oak Ridge National Laboratory Scientist of the Year in 1999, The Lockheed Martin Nova Award in 1999, The Curt Brunneé Prize from the International Mass Spectrometry Society in 2000, and the American Chemical Society Division of Analytical Chemistry Chemical Instrumentation Award in 2007. Dr. McLuckey has served as an editor of the International Journal of Mass Spectrometry since 1977 and either serves or has served on the editorial boards of Analytical Chemistry, the Journal of Mass Spectrometry, Rapid Communications in Mass Spectrometry, the Journal of the American Society for Mass Spectrometry, Mass Spectrometry Reviews, and the Chinese Journal of Mass Spectrometry. He has co-taught short courses at the annual American Society for Mass Spectrometry on Fundamental Aspects of Mass Spectrometry (3 years) and Quadrupole Ion Traps (6 years). He was recently elected Vice President for Programs and President-Elect of the American Society for Mass Spectrometry.

SOCIETY FOR APPLIED SPECTROSCOPY AWARDS

DISTINGUISHED SERVICE AWARDS

Recognizing members for their long-time service to the society

Deborah K. Bradshaw

AS Training

Debbie Bradshaw is consultant in the field of atomic spectroscopy. For over 25 years, since obtaining degrees in Biology and Chemistry from the University of Central Florida in Orlando, she has worked in this field as both a user and as a source of technical support and training in atomic spectroscopy instrumentation and analysis.

Debbie has been a member of SAS since 1981, when she attended her first FACSS meeting In Philadelphia, PA. She has been a regular FACSS attendee and SAS member ever since that time. In her years as an SAS member, she has become active in various aspects of the Society. She has been a short course instructor, has served on the Membership Committee and been Membership Chair, was Treasurer in 2002 through 2004, was Publicity Chair (2005) and currently serves as the Spectroscopy News Editor for *Applied Spectroscopy*. She organized and served as chair for the 2008 SAS Technical Symposia at PittCon.

Peter Griffiths

Peter Griffiths has worked in the field of vibrational spectroscopy for over 40 years. After receiving his doctorate from Oxford University, he did postdoctoral research at the University of Maryland with Professor Ellis Lippincott. He then worked as Product Specialist for Digilab, Inc. in Cambridge, MA and Manager of Analytical Services with Sadtler Research Labs in Philadelphia before accepting his first academic position at Ohio University in 1972. He moved to the University of California, Riverside in 1982 and was appointed as Chair of the Chemistry Department of the University of Idaho in 1989. He plans to retire from full-time employment in June, 2008.

Griffiths has published 280 papers and over 40 chapters on various aspects of vibrational spectroscopy. The book on FT-IR spectrometry that he wrote with James de Haseth in 1986 sold over 9,000 copies; the second edition of this book was published last year. With John Chalmers, he edited the five-volume Handbook of Vibrational Spectroscopy in 2002 and three volumes on polymer spectroscopy, pharmaceutical R&D and medical diagnosis have been published in the last two years. He is perhaps best known for his development of diffuse reflection spectrometry and hyphenated techniques. His research group has recently finished the development of a completely automated open-path FT-IR spectrometer for continuous atmospheric monitoring. Working with Manning Applied Technology, Griffiths' group has constructed an ultra-rapid-scanning interferometer that allows full infrared spectra to be measured in 5 ms; plans are underway to reduce this time down to 1 ms. They have applied this instrument to the study time-resolved adsorption and are currently using it (in collaboration with his colleague Tom Bitterwolf) to very fast stopped-flow measurements of inorganic reactions. His research group is now investigating several aspects of surface-enhanced infrared and Raman spectroscopy.

Griffiths has won a number of national and international awards including the Coblentz Award, the Spectroscopy Society of Pittsburgh Award, the Bomem-Michelson Award, the Prëgl medal of the Austrian Society of Analytical Chemistry, the New York SAS Gold Medal, the Birth Award, and Honorary Membership of the Society for Applied Spectroscopy. He was awarded an Alexander von Humboldt senior research fellowship in 2006, which he spent at the Technical University of Dresden. After his official retirement from the University of Idaho, he will be an Erskine Fellow at the University of Canterbury, Christchurch, New Zealand in the fall of 2008. Griffiths is the director of the courses on infrared and Raman spectroscopy that are help annually at Bowdoin College each July. He was President of the Society for Applied Spectroscopy in 1994 and is Associate Editor of *Applied Spectroscopy*.

HONORARY MEMBERSHIP AWARD

Recognizing those individuals who have made exceptional contributions to spectroscopy

Jeanette Grasselli Brown

Jeanette Grasselli Brown is the former vice president of research for Standard Oil and a 1950 graduate of Ohio University. Dr. Grasslli Brown served 38 years in industrial research , retiring in 1989 as Director of Corporate Research for BP America (formerly The Standard Oil Company) where she was responsible for 250 people and a $40 million budget. She served as a Distinguished Visiting Professor and Director , Research Enhancement at Ohio University, Athens, Ohio. Appointed by Governor Voinovich to the Ohio Board of Regents a coordinating body for all higher education and reappointed by Governor Taft as Chair. She holds 1 patent , 80 publications and 9 books in the field of infrared and Raman spectroscopy. She received her B.S. in Chemistry from Ohio University and M.S. from Case Western Reserve University.

LESTER W. STROCK AWARD

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

Presentation, Wednesday 8:30 AM, S2/3

Annemie Bogaerts

University of Antwerp

Annemie Bogaerts was born in Antwerp (Belgium) in 1971. She received her M.Sc. and Ph.D. degrees in chemistry, in 1993 and 1996, respectively, from the University of Antwerp in Belgium. She became a Professor in Physical Chemistry in 2003, at the University of Antwerp. Her current research activities include the numerical modeling of glow discharges, used in analytical chemistry and for technological applications, as well as the modeling of laser-solid interaction (for laser ablation and laser plasma spectroscopy) and plasma-solid interaction (for surface modifications and thin film deposition).

WILLIAM F. MEGGERS AWARD

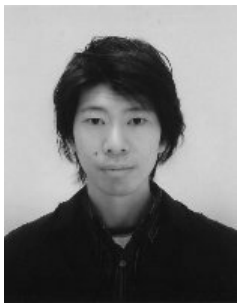
Recognizing the author(s) of an outstanding paper appearing in Applied Spectroscopy

Presented to Taka-Aki Ishibashi and Toshiki Maeda for "Infrared-Ultraviolet Sum-Frequency Generation Spectrometer with a Wide Tunability of the Ultraviolet Probe" May 2007, pp. 459-464.

Presentation, Wednesday 8:00 AM, S2/3

Taka-aki Ishibashi

Taka-aki Ishibashi received his BSc and MSc Degrees from the University of Tokyo under the supervision by Professor Mitsuo Tasumi, in 1986 and 1988. In 1989, he joined "Ultimate Molecular Spectroscopy" project headed by Professor Hiro-o Hamaguchi at the Kanagawa Academy of Science and Technology (KAST). He earned his PhD Degree in 1997 from the University of Tokyo for his studies on nonlinear Raman scattering under the direction of Professor Hamaguchi. From 1997 to 1999, he worked with Professor Hamaguchi, as a Research Associate at the University of Tokyo. In 1999, he went back to KAST to become a vice-project leader of "Ultimate Surface Reaction" project, where he was responsible for the spectroscopy group of the project. In 2004, he moved to Hiroshima University, when he became an Associate Professor. His current research focuses on development and applications of nonlinear vibrational spectroscopy for surfaces and interfaces.



Toshiki Maeda

Toshiki Maeda was born in 1980 in Fukuoka, Japan. He received his M.Sc. degree in Physical Chemistry from Hiroshima University in 2007. He is continuing research for his Ph.D. degree under the direction of Professor Taka-aki Ishibashi. He is currently working on the fields of vibrational sum-frequency generation spectroscopy.

GRADUATE STUDENT AWARD

Recognizing a graduate student for outstanding research in spectroscopy

Sean Burrows

Texas Tech Univeristy

Presentation, Wednesday 3:20 PM, N7

Sean M. Burrows received his B. S. in Chemistry with a minor in Mathematics from the University of Central Florida in 2004. Currently he is a doctoral candidate in analytical chemistry under the guidance of Dr. Dimitri Pappas at Texas Tech University.

Sean is interested in qualitative and quantitative observation of biomolecular complexes using single molecule fluorescence anisotropy. He has developed methods to determine the fraction of free and bound species in a system by classifying probe molecules based on their anisotropy. This approach could find application in drug design to determine which drugs exhibit optimal binding. Sean is also studying the photophysical properties of phycobiliproteins. These proteins are sensitive over the visible spectrum and exhibit sophisticated energy transfer for light harvesting. He uses molecular recrossing events and anisotropy to investigate triplet states and photobleaching of phycobiliproteins and their conjugates. Sean co-authored three publications, is supported by the Robert A. Welch Foundation, and has presented at his alma mater and two conferences.

Sean has received the American Institute of Chemists Award for Demonstration of Excellence by a Graduate of Bachelor of Science in the Chemistry Program in 2004-2005, the Orlando Section of the American Chemical Society Outstanding Undergraduate Student Award in 2001 and Outstanding Achievement in Analytical Chemistry Award from the University of Central Florida in 2001-2002. He is a member of the Society for Applied Spectroscopy

Christina Young

Georgia Institute of Technology

Presentation, Wednesday 3:40 PM, N7

Christina Young received a Bachelor of Science in chemistry with ACS certification from the University of South Carolina in Columbia, South Carolina in 2005. Her undergraduate research, under the advisement of Dr. S. Michael Angel, focused primarily on the study of laser induced breakdown spectroscopy (LIBS) of aqueous solutions at high pressures. In the summer of 2005, she left USC to pursue a doctorate in chemistry at the Georgia Institute of Technology.

Christina is currently a Ph.D. candidate under the direction of Dr. Boris Mizaikoff at the Georgia Institute of Technology, School of Chemistry and Biochemistry working on a collaborative project with ExxonMobil Research and Engineering Company at Annandale, New Jersey. Christina's primary research interests include the development of sensitive and selective FT-IR and quantum cascade laser (QCL) based gas sensors for a variety of applications including but not limited to biomedical diagnostics, process monitoring, quality control/assurance, environmental analysis, and security surveillance. She is also interested in the fabrication, characterization, and optimization of photonic materials and devices for the integration of optical sensing systems. Her work has led to first and second place poster awards at FACSS 2006, and an invited oral presentation at FACSS 2007.

SOCIETY FOR APPLIED SPECTROSCOPY

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José A.C. Broekaert

Dr. Jose Broekart studied chemistry at the University of Gent (Belgium), Ph.D. in 1976. Alexander-von-Humboldt Research Fellow in Germany in 1977 and from 1978 to 1991 researcher at the Institut für Spektrochemie und Angewandte Spektroskopie (now: ISAS-Institute for Analytical Sciences), Dortmund (Germany). Lecturing graduate research courses in atomic spectrometry at the University of Antwerp (Belgium) since 1983. "Geaggregeerde voor het hoger onderwijs" (Doctor of Science) degree at the University of Antwerp in 1985. From 1991 to 1998 Associate Professor of Inorganic/Analytical Chemistry at the University of Dortmund. From 1998 to 2002 Full Professor of Analytical Chemistry at the University of Leipzig (Germany) and sincel 2002 at the University of Hamburg (Germany). In 1998 Visiting Fulbright Research Scholar at Indiana University (Bloomington, IN). Since 2004 Adjunct Professor of Chemistry at Indiana University (Bloomington, IN).

Research interests include analytical chemistry with special reference to atomic spectrometry with plasma discharges (ICP, MIP, GD) and interests in sample introduction as well as in environmental and material analytical chemistry.

President of German Working Party on Applied Spectroscopy (DASp) from 1995-1998 and since 2002. Member of the Extended Executive Committee of the International Association for Environmental Analytical chemistry (IAEAC) since 2002. Organizer of "1991 European Winter Conference on Plasma Spectrochemistry, Dortmund, 3rd International Colloquium on Process Related Environmental Analytical Chemistry (PREACH), Leipzig (2000), GDCh Training course: "Atomspektrometrie" (annually from 2000 to 2005) and 34th International Symposium on Environmantal analytical Chemistry (ISEAC34), Hamburg (2006). Co-organizer of biannual "Anwendertreffen Plasmaspektrometrie" (since 1980) and the annual "Anwendertreffen: Röntgenfluoreszenz- und Funkenemissionsspektrometrie" (since 1994).

Member of Editorial Boards of Applied Spectroscopy and ICP Information Newsletters and of Editorial Advisory Boards of Analytical and Bioanalytical Chemistry, International Journal of Environmental Analytical Chemistry, Mikrochimica Acta as well as of Spectrochimica Acta, Part B. (Co)author of 209 refereed and ca. 100 unrefereed papers/chapters/books including a textbook "Analytical Atomic Spectrometry with Flames and Plasmas" (Wiley-VCH, 2002 – 2nd edition appeared 2005).

Cecil Dybowski

Cecil Dybowski was born September 23, 1946, in Yorktown, Texas, the son of Hermin Romana and Ruth Joyce (Geffert) Dybowski. He spent his childhood on a dairy farm near Kenedy, Texas. After graduating (as valedictorian) from Kenedy High School in 1965, he attended the University of Texas at Austin, where in 1969 he obtained the Bachelor of Science of Chemistry with honors. Continuing his studies at the University of Texas at Austin, he worked with Charles Gordon Wade on NMR analysis of liquid crystalline materials, and in 1973 he received the degree of Doctor of Philosophy (in Chemical Physics). Subsequently, he was a Research Fellow in Chemical Engineering at the California Institute of Technology, where he worked with the late Robert Walton Vaughan on the application of NMR spectroscopy to catalytic systems. In 1976, he joined the faculty of the University of Delaware as Assistant Professor of Chemistry, where he currently holds the rank of Professor. He is a member of the American Chemical Society, the American Physical Society, the Society for Applied Spectroscopy, the Materials Research Society, the American Association for the Advancement of Science, and the Delaware Academy of Sciences, among others.

Aside from over one hundred seventy research papers, he is the co-author of two books: *Transient Techniques in the NMR of Solids* (Academic Press, 1985) with B. C. Gerstein, and *NMR Spectroscopy Techniques* (Dekker, 1987) with R. L. Lichter. He is a member of the editorial boards of *Solid State Nuclear Magnetic Resonance*, *Magnetic Resonance Reviews*, *Applied Spectroscopy*, and the *Open Chemical Physics Journal.* He is currently Associate Editor of *Applied Spectroscopy* and Associate Editor of the *Encyclopedia of Analytical Chemistry*. He has been a member of the Executive Committee of the Experimental Nuclear Magnetic Resonance Conference, the Governing Board of the Eastern Analytical Symposium, and International Advisory Committees of various International Symposia on Magnetic Resonance in Colloid and Interface Science. Among his outside interactions, he was a Visiting Scientist at E. I. du Pont de Nemours and Company, Inc. in 1982, as well as a Visiting Professor of Chemical Engineering at the University of California at Berkeley in 1998. He has been Professeur Associé in the Laboratoire de Chimie des Surfaces at the University of Paris VI (Université Pierre et Marie Curie) and distinguished visiting professor at the Jagiellonian University in Krakow, Poland. Among his honors are the S. P. McElvain Lectureship at the University of Wisconsin at Madison, and the Delaware Valley Section of the Society for Applied Spectroscopy's Spectroscopist of the Year. In 2007 he was honored with the Delaware Section Award of the American Chemical Society. He was elected a Fellow of the American Association for the Advancement of Science in 2004 and a Fellow of the Society for Applied Spectroscopy in 2008.

Professor Dybowski's research group (which has included 19 Ph.D.s, 3 M.S. students, nine postdoctoral associates and visitors, and approximately 30 undergraduate research students over the years) has addressed analytical and physical problems in a variety of areas, but the most notable contributions have been in the use of NMR spectroscopy to analyze materials in situ. His research interests include the technology of NMR spectroscopy, analysis of heterogeneous catalysts, investigation of polymer response to external forces, dynamics of molecules in restricted spaces, and analysis of minerals and materials. Recent studies have focused on understanding the NMR spectroscopy of heavy spin ½ nuclei such as lead-207, mercury-199, tin-119, etc. in solid materials.

He is married to Dr. Mary Agnes Kaiser, and they have a daughter, Marta Marie, born Januray 28, 1987.

Richard Mathies

Prof. Richard Mathies, Ph.D., is Professor of Chemistry at the University of California-Berkeley. In collaboration with Prof. Evan Williams, he co-founded the Center for Analytical Biotechnology. Prof. Mathies' recent work in the area of biotechnology and the Human Genome Project has led to the development of new high-speed, high-throughput DNA analysis technologies such as capillary array electrophoresis and energy transfer fluorescent dye labels for DNA sequencing and analysis. He also pioneered the development of microfabricated capillary

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

electrophoresis devices, capillary array electrophoresis microplates, and microfabricated integrated sample preparation and detection methods. His early work at Berkeley focused on the use of resonance Raman and time resolved optical spectroscopy to elucidate the structure and reaction dynamics of energy and information transducing photoactive proteins.

Professor Mathies received his B. S. Degree in Chemistry in 1968 at the University of Washington, an M. S. Degree in 1970 and a Ph. D. in 1973 in Physical Chemistry at Cornell University. After two years at Yale (1974-76) as a Helen Hay Whitney Postdoctoral Fellow, he joined the Chemistry Department at the University of California at Berkeley in 1976, where he was an Alfred P. Sloan Fellow (1979-81). He is a Member of the Biophysical Society, American Optical Society, American Society for Photobiology, and AAAS. He has received the Harold Lamport Award from the New York Academy of Sciences (1983); American Society for Photobiology Research Award (1989); Frederick Conference on Capillary Electrophoresis Award (1998); A.D. Little Lecturer, M.I.T. (1998); and Association for Laboratory Automation 2001 Research Award. He is author of over 250 publications and 20 patents on photochemistry, photobiology, bioanalytical chemistry and genome analysis technology.

Leopold May

Leopold May was born in Brooklyn, NY, on November 26, 1923. While in high school, he gave lectures on Flame Testing at the Westinghouse Science Hall at the New York World's Fair in 1940. He received a BChE from City College of New York in 1944. After service in the U. S. Navy as an electronic technician, he received a M.S. in 1949 and a PhD In 1951 from the Polytechnic Institute of Brooklyn. His doctoral research was on the electrolytic separation of hydrogen and deuterium using a mass spectrometer to measure the isotopes.

His first job was doing cancer research at the Francis Delafield Hospital associated with the Columbia University's Medical School, NYC. The work involved infrared and mass spectroscopy as well as physical biochemical measurements. In 1954, he moved to the Psychiatric Institute of the University of Maryland Medical School in Baltimore, MD, as Research Associate in Psychiatry. He advanced to Instructor in Psychiatry, probably the only chemist in the world to hold this position. Here, he studied the infrared spectra of brain tissues and brain proteins and neurochemistry. While at the Psychiatric Institute, he taught chemistry in the evening school of Johns Hopkins University.

In September 1959, he joined the faculty of the Chemistry Department of The Catholic University of America, Washington, DC, as Assistant Professor teaching analytical chemistry and spectroscopy. His initial research was in infrared spectroscopy of brain lipids and lipoproteins. In the period, 1963-1968, he lectured at the Infrared Institute, Canisius College, Buffalo, NY. In 1965, he was a Guest Worker at the National Bureau of Standards involved in Mössbauer spectroscopy. Then, he used Mössbauer spectroscopy to study biochemicals and other materials. In 1967 and 1968 he organized and directed workshops in Mössbauer spectroscopy at The Catholic University of America. During his sabbatical year (1972-1973), he did research at the Department of Biochemistry, Tel-Aviv University, and Soreq Nuclear Physics Center, Israel. In the summers of 1974 and 1975, he was a NASA/ASEE Summer Faculty Fellow, at the Goddard Space Flight Center, Beltsville, MD, doing research on batteries. As an Exchange Scientist, he did research in Mössbauer spectroscopy at the Institute of Chemical Physics of the Academy of Sciences of the U.S.S.R. in Moscow, U.S.S.R. in 1976-1977 and June 1978. In the early eighties, he studied on the effect of radiation on biochemicals at the Armed Forces Radiobiology Research Institute in Bethesda, MD, using electron spin resonance as he continued his teaching and research at Catholic University. In 1980, he was appointed a Senior Lecturer in the Fulbright Program where he gave a course to graduate students and faculties of the Universities of Lima, Peru, on coordination chemistry. He also undertook research with some students and faculty. In the summer of 1983, he was awarded a Navy/ASEE Summer Faculty Research Associate at the Naval Medical Research Institute, Bethesda, MD, where he did research on the effect of electric fields on lipids using electron spin resonance. The sabbatical year of 1984-1985 was spent at the Racah Institute of Physics, Hebrew University of Jerusalem, Jerusalem, Israel, doing Mössbauer spectroscopy research. In the summer of 1987, he did research at the Lawrence Livermore National Laboratory, Livermore, Cal., on the Mössbauer spectroscopy of iron alloys. On December 31, 1996, he retired from the university, and the university appointed him Professor Emeritus. He was Research Mentor and Research Scientist in the Department of Physics, Morgan State University, Baltimore, MD, during from 2000 to 2003.

He is a founding member of the Baltimore-Washington Section of the Society of Applied Spectroscopy and served as Treasurer and Chairman of (1957-1960) of the Section. From 1959 to 1960, he was Contributing Editor of *Applied Spectroscopy* for the section, Spectroscopic Tricks, and served as Managing Editor and Editor-in-Chief (1960-1964). From 1968 to 1975, he was on the Editorial Board of *Applied Spectroscopy*. In 1971, he served as president of the Society for Applied Spectroscopy. Since 2006, he has contributed "Monthly Historical Events In Spectroscopy" to the Spectrum Newsletter. He is Emeritus Member of the Society for Applied Spectroscopy and the American Chemical Society.

The Baltimore-Washington Section of the Society for Applied Spectroscopy honored him by making him an Outstanding Member in 1972. For service to the university, the Vatican awarded him the Benemerenti Medal in 1988. He was given a Special Recognition Award by the American Chemical Society in 1994 for his contributions to the Milestones in Chemistry Calendar. He has received Certificates of Appreciation from the Chemical Society of Washington for his "Monthly Historical Events in Chemistry" (2005) and from the Society for Applied Spectroscopy "For Organization and Authorship of the SAS 50th Anniversary History Poster" (2008). He was inducted in Phi Lambda Upsilon and Sigma Pi Sigma honorary fraternities.

His research activities led to presenting invited lectures on his work in many parts of the globe: Hunfeld-bei-Fulda, Germany; Chandigargh and Varanazi, India; Tel Aviv, Israel; Osaka, Japan; Lima and Huaraz, Peru; Moscow, Russia; Singapore; Taschkent, Uzbekistan, and in the United States (universities, government laboratories, local section meetings, and national meetings (American Chemical Society and Society for Applied Spectroscopy)). He has 146 publications including four books in spectroscopy. His monthly events in chemistry and spectroscopy appear in the SAS Spectrum Newsletter, MIX (for Mössbauer Spectroscopists), and six American Chemical Society local section newsletters. His current research interests include chemical applications of infrared and Mössbauer spectroscopies and the history of chemistry and spectroscopy.

He is married and has two sons and one grandson.

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Laurence A. Nafie

Laurence A. Nafie received his Ph.D. from the University of Oregon in 1973, studying resonance Raman scattering, and from 1973 to 1975 he was a postdoctoral associate at the University of Southern California, working on the discovery and confirmation of infrared vibrational circular dichroism (VCD). In 1975 he joined the Chemistry faculty at Syracuse University to establish a research program in VCD and Raman optical activity (ROA). In 1978, he was named an Alfred P. Sloan Foundation Fellow and was promoted to Professor in 1982. In 1979 he proposed and carried out the first measurements of Fourier transform VCD, now the basis of all commercial VCD instrumentation. He was appointed Chairman of the Chemistry Department in 1984 and served until 2000. In 1988 he measured the scattered circular polarization (SCP) form of ROA for the first time that is now used in the only commercially available ROA spectrometer. In 1989 he predicted theoretically a new form of ROA called dual circular polarization (DCP) ROA that was confirmed experimentally in his laboratory in 1991. In 1995 he became founding Editor of the journal *Biospectroscopy*, published by John Wiley & Sons, and from 2001 to 2004 appearing as *Biopolymers: Biospectroscopy*. In 1996, he co-founded with Dr. Rina Dukor the company, BioTools, Inc., to market advanced vibrational spectroscopy instrumentation, including the Chiral*IR* VCD and Chiral*RAMAN* ROA spectrometers. In 2000, he was named Distinguished Professor of Chemistry at Syracuse University. He was awarded the Coblentz Award (1981), the Bomem Michelson Award (2001), and the William F. Meggers Award (2001). In 2003, he served as President of the Society of Applied Spectroscopy. He has over 250 publications and several patents awarded or pending.

Geraldine Richmond

Geraldine Richmond is the Richard M. and Patricia H. Noyes Professor in the Department of Chemistry and Materials Science Institute at the University of Oregon. Richmond received her bachelor's degree in chemistry from Kansas State University and her Ph.D. in chemical physics at the University of California, Berkeley where she worked under the direction of Prof. George Pimentel. Her research using laser spectroscopy and computational methods has focused on understanding the chemistry and physics that occurs at complex surfaces and interfaces that have relevance to important problems in energy production, environmental remediation, atmospheric chemistry and biomolecular surfaces. Over 160 publications have resulted from this research. Recent awards for her scientific accomplishments include the American Chemical Society Garvan Medal (1996), the Oregon Scientist of the Year by the Oregon Academy of Science (2001), the Spectrochemical Analysis Award of the American Chemical Society (2002), the Spiers Medal of the Royal Society of Chemistry (2004), a Guggenheim Fellow (2007) and the Bomem-Michaelson Award (2008). She is a fellow of the American Physical Society and the American Association of the Advancement of Science and an elected Fellow of the American Academy of Arts and Sciences (2006).

Richmond has served and continues to serve on many science boards and advisory panels. Most recent appoinments include Associate Editor of Annual Reviews of Physical Chemistry (2006-2008), Chair of the Science Advisory Committee of the Stanford Synchrotron Radiation Laboratory (2006-2008), Chair of the Basic Energy Sciences Advisory Board of the Department of Energy (1998-2003) and as a governor appointee to the State of Oregon Board of Higher Education where she served as a member, Vice President and imterim President over her seven year term (1999-2006). She has testified on science issues before committees in the U.S. Senate, the U.S. House and the Oregon House of Representatives.

She is the founder and chair of COACh (Committee on the Advancement of Women Chemists), an organization assisting in the advancement of women faculty in the sciences. Over 3000 science faculty, students, postdocs and administrators have benefitted from professional training and networking workshops developed by COACh. She has been honored for these efforts by the Presidential Award for Excellence in Science and Engineering Mentoring (1997), the American Chemical Society Award for Encouraging Women in the Chemical Sciences (2005) and the Council on Chemical Research Diversity Award (2006).

Alfred Sanz-Medel

Alfredo Sanz-Medel is Professor in the Department of Physical and Analytical Chemistry of Oviedo´s University (Spain) since 1982. He is author or coauthor of around 500 scientific publications in international journals, several patents and books. Dr. Sanz-Medel´s present research interests include the following main lines:

1. New atomic detectors and ion sources for ultratrace analysis using plasmas with MS detection.
2. New molecular optical sensors particularly those based on the use of quantum dots.
3. Hybrid Techniques, coupling a separation unit and an atomic detector, for ultratrace and trace metal speciation to solve biological and environmental problems.
4. Speciation for proteomics, integrating MS "molecular" [MALDI- and Electrospray-$(MS)^n$] and "atomic" (ICP-MS) techniques and introducing the extensive use of ICP-MS to carry out "heteroatom-tagged proteomics", both for qualitative and quantitative purposes.

Dr. Sanz-Medel is Editor of Analytical and Bioanalytical Chemistry (Springer Verlag, Heidelberg, Germany) since January, 2002. He has received, in the recent Euroanalysis in Antwerp, the 2007 Robert Kellner Award.

Alexander Scheeline

Alexander Scheeline is Professor of Chemistry at the University of Illinois at Urbana-Champaign. He received a B. S. in chemistry from Michigan State University in 1974, working with S. R. Crouch on kinetics methods of analysis. He received a Ph.D. in chemistry from the University of Wisconsin-Madison in 1978, working with J. P. Walters on spark emission spectroscopy. Following a post-doctoral year at the National Institute for Standards and Technology and two years at the University of Iowa, he moved to the University of Illinois at Urbana-Champaign. He has been a Program Officer at the National Science Foundation (1990-1991), and has served as an officer in the Federation of Analytical Chemistry and Spectroscopy Societies (program chair 1986, governing board chair 1989) and the Society for Applied Spectroscopy (secretary 1998-2000). In addition, he has served on the Society's publication committee, nominating committee, and education/tour speaker committee. He was an SAS local section tour speaker in 1987. In 2008, he completed six years as Book Review Editor for *Applied Spectroscopy*. He (with co-workers) is a two-time winner of the W. F. Meggers Award. Currently he is Online Articles editor for the Analytical Sciences Digital Library. His research interests have included atomic spectroscopy, instrument design,

sensors, kinetics, flame and plasma diagnostics, and the dynamics of nonlinear systems. Spectroscopic research has included development of theta pinch discharges for emission spectrochemical analysis, development of echelle spectrometry for pulsed discharges, flow-mapping in thermal reactors, multi-channel measurements of oscillatory reactions, and kinetics measurements on microliter levitated droplets.

ELLIS R. 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.

Richard P. Van Duyne

Northwestern University

Presentation, Thursday, 8:00 AM, S2/3

Richard P. Van Duyne is Charles E. and Emma H. Morrison Professor of Chemistry at Northwestern University. He is known for the discovery of surface-enhanced Raman spectroscopy (SERS), the invention of nanosphere lithography (NSL), and development of ultrasensitive nanosensors based on localized surface plasmon resonance (LSPR) spectroscopy. His research interests include all forms of surface-enhanced spectroscopy, nanofabrication, molecular plasmonics, tip-enhanced Raman spectroscopy (TERS), ultrahigh vacuum scanning tunneling microscopy combined with surface-enhanced spectroscopy, Raman spectroscopy of mass-selected clusters, ultrahigh vacuum surface science, structure and function of biomolecules on surfaces, surface-enhanced spectroscopic methods for chemical and biological sensing, and application of SERS to the study of works of art. Professor Van Duyne has been recognized for his accomplishments with the Ellis R. Lippincott Award, Optical Society of America (2008), Professeur invite classe exceptionnelle – University Pierre et Marie Curie, Paris, (2008), the National Science Foundation Creativity Extension Award (2007), L'Oreal Art and Science of Color Prize (2006), American Chemical Society Nobel Laureate Signature Award for Graduate Education (2005), election to American Academy of Arts and Sciences (2004), the American Physical Society Earle K. Plyler Prize for Molecular Spectroscopy, the Surfaces in Biomaterials Foundation Excellence in Surface Science Award (1996), the Pittsburgh Spectroscopy Award (1991), the Phi Lambda Upsilon Fresenius Award (1981), the Coblentz Society Memorial Prize in Molecular Spectroscopy (1980), and the Alfred P. Sloan Fellowship (1974). He is also a fellow of both the American Physical Society and the American Association for the Advancement of Science. 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).

The Society for Applied Spectroscopy
Cordially Invites You to Celebrate Our
50 Years of Service to the Spectroscopy
Community During Our Annual
Wine and Cheese Awards Reception
Tuesday, September 30, 2008
7:00 p.m. in Ballroom N6/N7

This is a member's only event.

To join the Society, call 301-694-8122 or see the meeting registration form in this program.

COBLENTZ SOCIETY CLARA 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

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

John C. Conboy

University of Utah

Presentation, Thursday, 8:30 AM, S2/3

Professor John C. Conboy is an Associate Professor of Chemistry and Henry Eyring Scholar at the University of Utah. His research encompasses the development and application of novel bioanalytical and analytical techniques for the exploration of interfacial phenomena in biology and separation science; including the investigation of lipid structure and dynamics in cellular membranes by sum-frequency vibrational spectroscopy (SFVS), the measurement of protein and small molecule adsorption to biological surfaces using chiral second harmonic generation (C-SHG) and the study of ion transport between immiscible liquids by electrochemical and spectroscopic methods. His research group has pioneered the use of SFVS for the investigation of lipid asymmetry and movement across the cellular membrane. In particular, they have discovered that the translocation of lipid species (also known as lipid flip-flop) across a lipid bilayer is a facile process. These findings have brought into question some of the long held beliefs regarding the dynamic movement of lipids in biological membranes. The Conboy group has also used C-SHG as a label-free detection method for protein and small molecule adsorption to biological membranes based on their chiral structure. These studies have also lead to the development of the first chiral nonlinear microscope for direct spatial visualization of such molecular interactions. Professor Conboy earned his Ph.D. at the University of Oregon with Professor Geraldine Richmond. He has held post doctoral appointments at the University of Minnesota (Professor Paul Barbara), and at the University of Arizona (Professor Scott Saavedra) as a National Institutes of Health (NIH) Postdoctoral Fellow. John joined the University of Utah in 2000 and from 2003 – 2006 was the Henry Eyring Assistant Professor, and in 2006 became the Henry Eyring Scholar and Associate Professor. Professor Conboy has over 40 publications to his credit and has presented his research findings at over 30 conferences including the American Chemical Society National Meeting, the Federation of Analytical Chemistry and Spectroscopy Societies National Meeting (FACSS), and the Pittsburgh Conference. In addition, he has organized several symposia on the biophysics of membranes, analytical chemistry at the biology interface, and spectroscopy at interfaces. John is member of, the Coblentz Society, the Society for Applied Spectroscopy, the American Chemical Society, and the Biophysical Society.

COBLENTZ STUDENT AWARDS

For many years, the Coblentz Society has encouraged young scientists to pursue studies in 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, and a brief description of their research appear in the Society's *Newsletter* in the August issue of *Applied Spectroscopy*.

Awardees	**Professors and Affiliations**
Mohamed Zuhair Mohamed Rishard	Former student of Professor Jaan Laane, Dept of Chemistry, Texas A&M University
Adil Shash	Former student of Professor Nordulf W. G. Debye, Dept. of Chemistry, Towson University

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 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

PREVIOUS FACSS BOARD AND MEETING CHAIRS

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

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	Exhibits

2003 – Fort Lauderdale

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

2004 – Portland

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

2005- Quebec City, Canada

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

2006 – Orlando

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

2007 – Memphis

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

SOCIETY AND COMMITTEE MEETINGS AND EVENTS

FACSS

All meetings are located on the Mezzanine Level.

Saturday, September 27, *McKinley*
1:00 PM Long Range Planning committee

Sunday, September 28, *McKinley*
7:00 PM Program Committee

Wednesday, October 1
9:00 AM 2008 Planning/Budget Committee, *McKinley*
10:00 AM Planning/Budget Committee for Louisville (2009), *McKinley*
11:00 AM Planning/Budget Committee for Raleigh (2010), *McKinley*
1:00 PM Budget and Finance Committee, *McKinley*
1:00 PM Web Site Meeting, *Shasta 1*

Thursday, October 2, *McKinley*
1:00 PM Executive Committee
6:30 PM Governing Board Meeting

ASTM

Monday, September 29, *Shasta 1, Mezzanine Level*
Noon – 1:00 PM E13.10 Molecular Spectroscopic Optical Imaging
1:00 – 2:30 PM E13.08 Raman Spectroscopy

Tuesday, September 30, S 2/3
6:00 PM Raman Reception

COBLENTZ

Monday, September 29, *McKinley, Mezzanine Level*
8:00 PM Board Meeting

SOCIETY FOR APPLIED SPECTROSCOPY

All committee meetings will take place on the Mezzanine Level

Sunday, September 28
8:00 AM – 5:00 PM SAS Executive Committee Meeting and Lunch, *McKinley*

Monday, September 29
12:00 – 1:30 PM Publication Committee Meeting/Lunch, *McKinley*
7:30 – 9:30 PM Student Event for SAS student members, *Whitney Room*

Tuesday, September 30
12:00 – 1:30 PM Membership Committee Meeting/Lunch, *McKinley*
4:30 – 6:30 PM SAS Governing Board Meeting, *McKinley*
7:00 –11:00 PM SAS Wine and Cheese Reception, *Nevada 6/7 (members only)*

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.

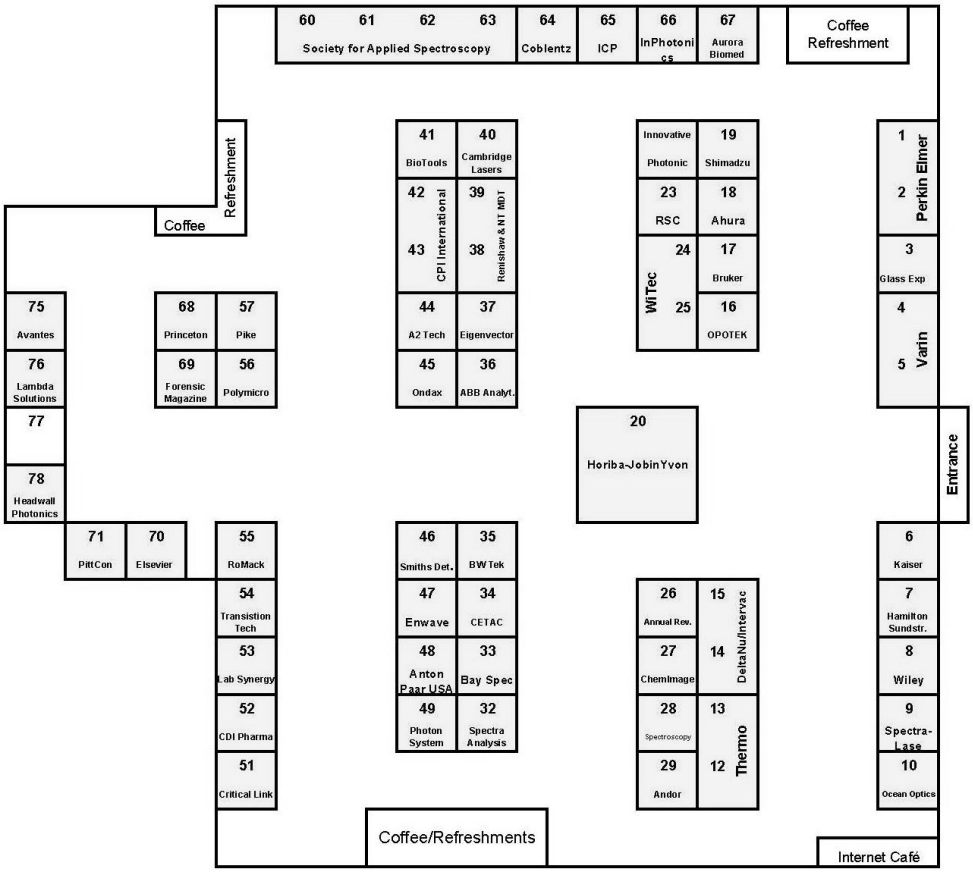
Sunday, September 28, 2008 5-7 p.m. *(during the FACSS mixer)*

Sponsored by
The Society for Applied Spectroscopy and FA CSS

FACSS EXHIBITORS

A2 Technologies	Booth 44	InPhotonics, Inc.	Booth 66
ABB Analytical	Booth 36	Kaiser Optical Systems, Inc.	Booth 6
Ahura Scientific, Inc.	Booth 18	Lab Manager Magazine	Table Top
Andor Technology	Booth 29	Lab Synergy	Booth 53
Annual Reviews	Booth 26	Lambda Solutions, Inc	Booth 76
Anton Paar USA	Booth 48	NT-MDT	Booth 38
Aurora Biomed	Booth 67	Ocean Optics, Inc.	Booth 10
Avantes	Booth 75	Ondax, Inc.	Booth 45
B&W Tek, Inc.	Booth 35	OPOTEK, Inc.	Booth 16
BaySpec, Inc.	Booth 33	PerkinElmer Life & Analytical Sciences	Booth 1,2
BioTools, Inc.	Booth 41	Photon Systems	Booth 49
Bruker Optics, Inc.	Booth 17	Pike Technologies	Booth 57
Cambridge Laser Laboratories, Inc.	Booth 40	Polymicro Technologies, LLC	Booth 56
CDI Pharma	Booth 52	Princeton Instruments, Inc.	Booth 68
CETAC Technologies	Booth 34	Renishaw, Inc.	Booth 39
ChemImage Corporation	Booth 27	RoMack, Inc.	Booth 55
Coblentz Society	Booth 64	Royal Society of Chemistry	Booth 23
CPI International	Booth 42	Russell Publishing	Table Top
Critical link, LLC	Booth 51	Shimadzu Scientific Instruments, Inc.	Booth 19
Delta Nu / Intevac, Inc.	Booth 14/15	Smiths Detection	Booth 46
Eigenvector Research, Inc.	Booth 37	Society for Applied Spectroscopy	Booth 60/61/62/63
Elsevier - Materials Today	Table Top	Spectra Analysis	Booth 32
Enwave Optronics, Inc.	Booth 47	Spectra-LAse, Inc.	Booth 9
Glass Expansion	Booth 3	Spectroscopy Magazine	Booth 28
Hamilton Sundstrand Corporation	Booth 7	Thermo Fisher Scientific	Booth 12/13
Headwall Photonics	Booth 78	Transition Technologies, Inc.	Booth 54
HORIBA Jobin Yvon	Island 20	Varian, Inc.	Booth 4,5
ICP Information Newsletter, Inc.	Booth 65	Wiley Blackwell	Booth 8
Innovative Photonic Solutions	Booth 22	WITec Instruments	Booth 24/25

EXHIBIT HALL LAYOUT



EXHIBITOR DESCRIPTIONS

A2 Technologies **Booth 44**
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Phone: 203 312 1106
www.a2technologies.com
A2 Technologies, is the innovator and manufacturer of portable Fourier Transform Infrared (FTIR) spectrometers that have been designed to take analysis out of the lab and put it into to the hands of users in the field. A2 Technologies has just launched one of the smallest, most compact FTIR spectrometers available on the market, Exoscan. Weighing less than seven pounds, the Exoscan was designed for non-destructive on-site surface and bulk analysis applications such as, composite production and degradation, coatings analysis, surface preparation, incoming quality control, quality assurance and first article inspection.

ABB Analytical **Booth 36**
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Ahura Scientific, Inc. **Booth 18**
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Annual Reviews publications operate as a high quality filter, prioritizing and synthesizing the primary research literature in 37 different disciplines for the Biomedical, Life, Physical, and Social Sciences. Our comprehensive review articles help scientists, students and researchers prioritize and navigate the vast amount of primary research literature and data that is available to them. The Annual Review of Analytical Chemistry®, aims to provide a perspective on the field of analytical chemistry. It addresses measurement science in general, with a focus on concepts, materials, chemicals, and/or processes. The series draws from disciplines as diverse as biology, physics, and engineering, with analytical chemistry as the unifying theme. Some topics reviewed in the current volume include atmospheric analysis, atomic force microscopy, CARS imaging, electrochemistry on the nanoscale, nanoparticle sensors, on-chip multiplexing analysis, planetary and interstellar chemistry, nuclear magnetic resonance, mass spectrometry, biosensors, and chromatography. Subscriptions are available for institutions, consortia and individuals. http://anchem.annualreviews.org

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Broomfield, CO 80021-2560
Phone: 303 410 8668
www.avantes.com
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B&W Tek, Inc. **Booth 35**
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Newark, DE 19713
Phone: 302 368 7824
www.bwtek.com
B&W Tek, Inc. is leading the way in the development of photonic components and instrumentation. With emphasis on low cost, high performance lasers and spectrometers, we strive for versatility - innovating solutions to analytical, industrial, medical, biophotonic, and diagnostic applications. As a result, we lead worldwide sales of Raman spectrometers. In order to maintain this trend we value all feedback as an opportunity to further expand our capabilities. Challenge us with your custom project; from inception to design and development, from prototyping to manufacturing. Our ISO 9001 & ISO 13485 certified facility and our patented technologies ensure high quality products, consistently proven and growing every day.

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Phone: 510 661 2008
www.bayspec.com
BaySpec, Inc., founded in 1999 and located in the Silicon Valley (Fremont, CA), is an OEM fiber-optics company. Based on its proprietary optical technologies, BaySpec has developed a new generation of agile fiber optic modules & sub-systems that significantly improve the cost and performance of current fiber-optic networks.

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Jupiter, FL 33458
Phone: 561 625 0133
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Phone: 978 663 3660
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Bruker offers a comprehensive range of analytical instruments based on Nuclear Magnetic (NMR, EPR) and Vibrational Spectroscopy (FT-IR, Raman), analytical X-Ray (XRD, XRF) and Mass spectrometry. For more information please visit www.bruker.com .

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ChemImage Corporation **Booth 27**
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Manufacturer of high resolution optical and scanning probe microscopes for scientific and industrial applications. A modular product line allows the combination of different microscopy techniques guaranteeing highest flexibility for a wide range of applications. The alpha300 series includes the Confocal Raman Imaging Microscope alpha300 R providing the ability to image the chemical properties of a sample at a resolution down to 200 nm. At each image pixel a complete Raman spectrum can be acquired in less than one millisecond. The resulting multi-spectrum file can then be analysed in order to generate high-resolution Raman images. Combined with the Atomic Force Microscopy capabilities of the alpha300 R, the chemical information can be linked with topographical surface structures. Images with an optical resolution beyond the diffraction limit can be easily obtained with the alpha300 S. The new alpha500 and alpha700 series allow automated Confocal Raman and Atomic Force Microscopy on large samples.

FACSS/SAS WORKSHOPS

Workshops are a valuable component of FACSS and are conducted by leading experts. There is an additional charge for workshops. See on-site registration form for costs. All workshops except for the Hands On Workshops are on the Mezzanine Level.

ANALYTICAL RAMAN SPECTROSCOPY

Brian Marquardt, *University of Washington – CPAC*; **Jeremy Shaver**, *Eigenvector Research, Inc.*; **Ian R. Lewis**, *Kaiser Optical*

Sunday 8:00 – 11:30 AM, *Shasta 2, Mezzanine Level*

The course will provide an overview of modern Raman spectroscopy beginning with an introduction to Raman scattering and the differences between IR and Raman spectra. It will include discussion of sampling, calibration, data analysis methods (pre-treatments and modeling approaches), and successful application developments. Modern instrument configurations and configuration choices will be covered. The course will include a thorough introduction to the major approaches to sample illumination and spectrum collection, emphasizing fiber optic probes and Raman microprobes. Raman imaging will be briefly discussed. The applicability of and successes with Raman will be surveyed with numerous applications examples. This ½ day course will be split 50 / 50 between a) Raman practical considerations and theory and b) applications. Course attendees who wish to either receive a solid background in Raman and current applications information prior to or those who want a follow-up opportunity with hands-on instrument experience will be able to receive this by electing this course and the Hands-on Raman Workshop scheduled for Sunday afternoon.

INFRARED SPECTRAL INTERPRETATION: A STRATEGIC APPROACH

Brian C. Smith, *Spectros Associates*

Sunday, Monday, and Tuesday, 9:00 AM – 5:00 PM, *Teton 1, Mezzanine Level*

A 3 day overview of how to determine unknown molecular structures from infrared spectra. The course begins with how molecules absorb infrared radiation, and what peak positions, heights, and widths mean. Next, a systematic, 10-step approach to successfully interpreting spectra is presented. The bulk of the course is a discussion of the important infrared bands of a number of economically important molecules including alkanes, aromatics, alcohols, esters, and amines. Special discussions of polymers and inorganics are included. The course concludes with a practical discussion of how library searching and spectral subtraction make interpreting spectra faster and easier. Interpretation Workshops, where attendees interpret unknown spectra with the help of the instructor, are held throughout the course. Course attendees receive a copy of Dr. Smith's more than 300 PowerPoint slides that will make learning fast and easy.

ATTACK THE VARIANCE: AN INTRODUCTION TO ROBUST METHOD DESIGN

Drew Manica and Nancy Jestel; *SABIC Innovative Plastics*

Sunday, 9:00 AM – 5:00 PM, *Ruby 2, Mezzanine Level*

This course will help you learn how to fix problems with your existing methods and help develop dependable new methods, no matter what technique you're using. This course will prepare you to go home and uncover what is causing variation in your data, whether it is the operator's technique, the sample itself, some other experimental or environmental variable, or even an interaction of the above. You will then be able to manage these factors to optimize your method. Robust design methodologies accommodate the variability present in the experimental parameters and sample handling in such a way that undesirable variation of the final result is minimized. Consequently, both an accurate and robust measurement system can be developed simultaneously. The class will explore the steps involved in selecting the best experiments to run, executing those experiments properly, analyzing the data, and finally optimizing the method. Some of the tools employed to make sound conclusions from your data include analysis of variance (ANOVA), gauge repeatability and reproducibility (GRR), and several types of design of experiment (DOE) strategies. Each topic will be presented as click-along exercises using Minitab® software (Minitab Inc.) and Design Expert® software (Stat-Ease), followed by independent hands-on exercises to reinforce the practical use of the tools. This course is designed to enhance the applied statistical skills of the intermediate scientist to the advanced level.

CHEMOMETRICS WITHOUT EQUATIONS (OR HARDLY ANY) – HANDS ON

Jeremy Shaver and Neal Gallagher; *Eigenvector Research, Inc.*

Sunday and Monday, 9:00 AM – 5:00 PM, *Ruby 1, Mezzanine Level*

Chemometrics without Equations concentrates on two areas of chemometrics: 1) exploratory data analysis and pattern recognition, and 2) regression for multivariate calibration. Participants will learn to safely apply techniques such as Principal Components Analysis (PCA), Principal Components Regression (PCR), and Partial Least Squares (PLS) Regression. Sample classification with SIMCA and PLS Discriminant Analysis will also be considered. Examples will include problems drawn from process monitoring and quality control, predicting product properties, and others. The target audience includes those who collect and/or manage large amounts of data that is multivariate in nature. This includes bench chemists, process engineers, and managers who would like to extract the most information from their measurements. The course will finish with a short section on how to apply these models for online predictions, Multivariate Statistical Process Control and inferential sensing. Students will work problems using MATLAB and PLS_Toolbox on computers provided (maximum of two students per computer).

PROCESS ANALYTICAL CHEMISTRY: OUT OF THE LAB AND INTO THE PIPE

James Rydzak, *GlaxoSmithKline*

Sunday, 9:00 AM -5:00 PM*, Teton 2, Mezzanine Level*

Process Analyzers are becoming more important to the manufacturing industry by providing improved process quality, yields, uptimes and safety, while reducing hazards and environmental impact. This course will answer a question frequently posed by laboratory analytical chemists: "What is process analytical chemistry and how does it differ from more traditional laboratory-based analysis?" It will introduce basic relevant engineering concepts, and compare process analyzers with laboratory instrumentation. The course will primarily focus on on-line and in-line applications of optical and mass spectrometry, gas chromatography, and titrimetry as they are applied in the refining, chemicals, petrochemicals, food, personal care, pharmaceuticals, and life science industries.

HANDS-ON RAMAN
Exhibitors, Instrumentation Company Representatives
Sunday, No charge
12:30 – 1:30 PM – overview, *S1 extension*
1:30 – 3:30 PM – Hands On, *S 2/3*

Class attendees will get a basic introduction to Raman Spectroscopy and Raman Spectroscopy techniques followed by hands-on experience with a variety of Raman instrumentation from FACSS exhibitors: Ahura, Andor, B&W Tek, Bruker, CDI Pharma, Enwave, Hamilton Sundstrand, Headwall, HORIBA Jobin Yvon, InPhotonics, Kaiser, Lambda Solutions, Ocean Optics, PerkinElmer, Photon Systems, Renishaw, Thermo Scientific, WITec

Hands-On Raman Workshop Agenda:
12:30 – 1:30 PM Overview Presentations
- General/Introduction
- Compact/Fiber Optic
- Process
- Raman Microscopy
- UV & Resonance Raman

1:30 – 3:30 PM Hands-on with the Instrument Companies

HAND-ON LASER ABLATION AND LIBS
Exhibitors, Instrumentation Company Representatives
Sunday, No Charge
1:30 – 1:50 – overview, *S1 extension*
2:00 – 4:30 PM – Hands On, *S 2/3*

Class attendees will get a basic introduction to Laser Ablation and Laser Induced Breakdown Spectroscopy techniques followed by hands-on experience with a variety of LA/LIBS instrumentation from FACSS exhibitors: Avantes, CETAC, Ocean Optics, and Spectra LAse

Hands-On LIBS Workshop Agenda
1:30 – 1:50 PM Overview Presentations
- General Introduction
- Laser Ablation
- LIBS

2:00 – 4:30 PM Hands-on Laser Ablation/LIBS

HANDS-ON IR
Exhibitors, Instrumentation Company Representatives
Sunday, No charge
1:00 – 1:15 PM – Introduction and Overview, *S2/3*
1:15 – 4:30 PM – Hands On, *S 2/3*

Workshop attendees will be given an essential overview of IR techniques followed by hands-on experience with a variety of IR spectroscopic instruments and software products from FACSS exhibitors: Bruker, PerkinElmer, Thermo Fisher Scientific, A2 Technologies, Smiths Detection, Spectra Analysis, Varian and others. Small groups will rotate through instrument locations on a ~20-30 minute timeframe.

Hands-On IR Workshop Agenda:
1:00 – 1:15 PM Overview and Introductions
1:30 – 4:30 PM Rotations through Instrument Locations for Hands-on Experience

RAMAN CHEMICAL IMAGING TECHNOLOGIES AND METHODS
Matthew Nelson and Patrick Treado, *ChemImage*
Monday 9:00 – noon, *Shasta 2, Mezzanine Level*

Chemical Imaging is a rapidly maturing discipline that involves the integration of digital imaging with molecular spectroscopy, relying on Raman, fluorescence, visible, NIR and IR absorption/reflectance techniques. It has evolved as a powerful approach for non-invasive characterization of chemical heterogeneity. Among these techniques, Raman Chemical Imaging is particularly suited for microspectroscopy and imaging due to the inherent selectivity and sensitivity of Raman spectroscopy. Two different imaging approaches, spatial and wavelength scanning, are used to acquire a hyperspectral data cube containing wavelength, intensity, x, y and z- spatial information. This course emphasizes wavelength scanning approaches to Raman Chemical Imaging which enable rapid image acquisition with diffraction-limited spatial resolution. In widefield Raman Chemical Imaging, thousands of Raman spectra are simultaneously collected from a field of view. The spectral data is used to generate chemically-specific images. Intricate image and spectral processing techniques may be applied to the chemical imaging data to produce various qualitative and/or quantitative parameters associated with the often complex sample matrix. This short course is designed as a comprehensive overview of theoretical and practical aspects of Raman Chemical Imaging and associated instrumentation. The special emphasis is placed on Raman Chemical Imaging applications in pharmaceutical and biothreat detection fields. This course will be useful to analytical, forensic, biomedical and materials chemists.

TRAINING: INTRODUCTION TO GRAMS/AI
Diana Pike and Brie Gervin, *Thermo Scientific*
Monday, 9:00 AM – 5:00 PM, *Ruby 2, Mezzanine Level*

This one day basic GRAMS/AI course will help you to develop the knowledge needed for utilizing the GRAMS/AI software effectively for a variety of data display and analysis tasks. Delivered by one of our in-house experts, this course covers the fundamentals of using GRAMS/AI through a combination of classroom instruction and hand-on exercises. You will receive a certificate upon completion of this course as well as comprehensive course notes that can be used as reference material. Upon completion of this course, attendees will have an understanding of:

- The GRAMS/AI user interface
- Workspace customization
- Importing and exporting spectral and chromatographic data
- Using the graphical display features with various data types
- General spectral processing applications
- Advanced applications, including Peak Fitting
- Introduction to ActiveApps
- Using GRAMS/AI with other products from the GRAMS suite

Who should attend:
Scientists and technicians who use GRAMS/AI for data display and analysis. Current users and new hires requiring a certificate on the latest product version

TRAINING: GRAMS CHEMOMETRICS WITH PLSPLUS/IQ
Diana Pike and Brie Gervin, *Thermo Scientific*
Tuesday, 9:00 AM – 5:00 PM, *Ruby 2, Mezzanine Level*

This one day advanced course will help you to develop the basic knowledge needed for utilizing the GRAMS/AI and PLSPlus/IQ software effectively for qualitative and quantitative spectral analysis with multivariate chemometric methods. Delivered by one of our in-house experts, this course builds a fundamental understanding of the chemometric methods and the software tools available with GRAMS/AI and PLSPlus/IQ through a combination of classroom instruction and hand-on exercises. You will receive a certificate upon completion of this course as well as comprehensive course notes that can be used as reference material. Upon completion of this course, attendees will have an understanding of:

- The theory behind the chemometric methods used in PLSPlus/IQ
- The basic steps for building models using PLSPlus/IQ
- How to build an effective training set
- Analyzing and interpreting experimental model results

- Predicting unknowns with the IQ Predict ActiveApp
- Optimizing qualitative and quantitative models
- How to combine qualitative and quantitative techniques

Who should attend: Advanced GRAMS/AI users who are interested in performing chemometric analysis. Current users and new hires requiring a certificate on the latest product version Note that this course assumes a basic familiarity with the GRAMS/AI software. Users are encouraged to view the PLSPlus/IQ tutorial prior to attending this course.

ADVANCED CHEMOMETRICS WITHOUT EQUATIONS - HANDS ON!

Jeremy Shaver and Neal Gallagher; *Eigenvector Research, Inc.*

Tuesday, 9:00 AM – 5:00 PM, *Ruby 1, Mezzanine Level*

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 relevant variation 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. This course focuses on advanced preprocessing methods, including Extended Multiplicative Scatter Correction (EMSC) and Generalized Least Squares (GLS), for improving models. Variable selection techniques, such as interval PLS (iPLS) are also considered. The effect of preprocessing and variable selection on robustness of the final models is also considered. Tools for testing model robustness are demonstrated.

PRACTICAL APPLICATIONS OF LCMS FOR SMALL MOLECULES

Michael P. Balogh, *Waters Corporation*

Wednesday, 9:00 AM – 5:00 PM, *Teton 1, Mezzanine Level*

Comprehensive focus on understanding the fundamentals of the most widely used mass spectrometers and sample inlet technologies: how and where are they employed to the practitioners' best advantage? Examples include how designing the separation and avoiding pitfalls of combining LC, GC and MS can increase analytical success. Discussion includes the latest technologies such as non-LC atmospheric ionization techniques (DESI, DART, ASAP) and incorporates other current topics such as MALDI imaging for tissues. The course is designed for anyone in pharma, industry or environmental practice employing MS for small molecule investigations including: design of experiment considerations (column chemistries, solvents and ionization methods); quantitative considerations; qualitative considerations (spectral interpretation) and identification of target compounds in complex matrices. In addition to course materials, references for further study and a glossary explaining commonly used terms are included. The take-home value of attending for students is gaining an overall view of current mass spectrometry practice and the opportunity to address individual questions.

INDUCTIVELY COUPLED PLASMA- MASS SPECTROMETRY (ICP-MS): INTRODUCTION

R. S. Houk, *Ames Laboratory USDOE, Iowa State University*

Wednesday, 9:00 AM – 1:00 PM, *Ruby 1, Mezzanine Level*

This course is meant for the beginner in ICP-MS. Course Topics: The ICP as an Ion Source Ion Extraction and Beam Formation Operating Principles of Ion Lenses, Quadrupole Mass Analyzers, and Detectors Magnetic Sector Mass Analyzers with the ICP Causes of and Corrections for Spectral Interferences and Matrix Effects Survey of Methods to Remove Polyatomic Ions - Cool Plasma, Collision Cells, Solvent Removal Survey of Applications Designing a Sound Analytical Strategy Using ICP-MS

NEAR INFRARED SPECTROSCOPY: MEASUREMENT PRINCIPLES AND INTERPRETATION

Jerry Workman, *Luminous Medical, Inc.*

Wednesday, 9:00 AM – 5:00 PM, *Ruby, 2 Mezzanine Level*

This workshop is useful for learning how to interpret near infrared spectra for many applications. Near infrared spectroscopy is used for many applications where analytes are measured in the presence of interfering substances, such as high moisture content, or when sampling is constrained to in situ conditions. Near infrared spectra consist of generally overlapping vibrational bands that are non specific and non-resolved. Spectra measured in this wavelength region contain information related to the chemical, optical, and physical properties of materials. This workshop will describe the methods and techniques applied to make effective near infrared measurements for many applications, including: natural products, fine chemicals, pharmaceuticals, hydrocarbons, polymers and rubbers, biotechnology, medical applications, and other materials. In addition, a detailed overview and workshop will be given on interpretation of near infrared spectra, including exercises and practical helps on the use of spectra-structure correlation tables and charts provided to participants.

INDUCTIVELY COUPLED PLASMA MASS SPECTROMETRY (ICP-MS): ADVANCED TOPICS

R. S. Houk, *Ames Laboratory USDOE, Iowa State University*

Wednesday, 1:30 – 5:30 PM, *Ruby 1, Mezzanine Level*

This course is meant for the experienced ICP-MS user, or someone who has completed the Introduction course. Course Topics: Fundamentals of Ion Extraction Micronebulizers & Solvent Removal Droplets, Particles & Noise in the ICP Collision Cells Magnetic Sectors – Applications Multicollector Instruments for Isotope Ratio Measurements Quadrupoles in Alternate Stability Regions TOF Mass Analyzers Speciation by GC, LC and CE with ICP-MS Instrument Survey

FACSS EMPLOYMENT BUREAU

The FACSS Employment Bureau is now online so you can manage your employment efforts anywhere you can connect to the internet! The Employment Bureau is a free service to both job seekers and employers that provides job and applicant listings, message boards, and interviewing booths.

How to register: From the FACSS website (www.facss.org), click on Employment in the top menu.
You can create a Job Target account to manage resumes, search employment opportunities and set up personal job alerts. Post your resume online, anonymously if desired, and create a job alert to email new postings directly to your in-box.

Before the conference:
Search available jobs and resumes, and contact the employer or candidate directly via your Job Target account. Employers (only) can pre-schedule interviews for the week of the conference by creating accounts to manage their on-line recruiting efforts and contact candidates in advance of the conference. **All job descriptions will be posted free of charge for conference attendees from August 1 through December 31, 2008.** Please email erica.kyllo@sabic-ip.com for additional information

At the conference:
Location: The employment bureau is located Nevada 1
Hours: 9:00 AM – 5:00 PM, Monday – Wednesday and 9:00 AM – 3:00 PM on Thursday

Check your Job Target in-box to follow-up on your employment leads. Wireless internet access will be available in the Employment Bureau, the Exhibit Hall, and the Silver State Foyer Foyer. Two desktop computers and a printer will also be available in the Employment Bureau to help you in your job/candidate search. The wireless access ID is FACSS 2008.

Interview rooms (Nevada Office 1 and 2) will be available for 30-minute interviews during Employment Bureau hours. The employer is responsible for scheduling the use of interview rooms by signing on a schedule posted in the Employment Bureau (Nevada 1).

SPECIAL INVITATIONS TO STUDENT ATTENDEES:
Tuesday, 12:30 PM, Roundtable discussion and complimentary lunch for students sponsored by SABIC Innovative Plastics. 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. Employers who are interested in participating in the employment panel, please email drew.manica@sabic-ip.com. **Room Sierra 1/2.** ***Sign up at conference registration desk.***

PROGRAM HIGHLIGHTS

SUNDAY	MONDAY	TUESDAY	WEDNESDAY	THURSDAY
	7:30 Wake up coffee	7:30 Wake up coffee	7:30 Wake up coffee	7:30 Wake up coffee
8:00 AM – 5:00 PM FACSS/SAS Workshops	Plenary Session *S2/3* 8:00 AM James Heath *Professor of Chemistry at Caltech and Professor of Molecular & Medical Pharmacology at UCLA, and Director of the National Cancer Institute NSB Cancer Center*	Plenary Sessions *S2/3* 8:00 AM Charles Mann Award Ian R. Lewis *Kaiser Optical Systems* 8:30 AM ANACHEM Award Scott McLuckey *Purdue University*	Plenary Sessions *S2/3* 8:00 AM SAS Applied Spectroscopy William F. Meggers Award Taka-aki Ishibashi *Hiroshima University* 8:30 AM Lester W. Strock Award Annemie Bogaerts *University of Antwerp*	Plenary Session *S2/3* 8:00 AM Ellis R. Lippincott Award Richard P. Van Duyne *Northwestern Univ.* 8:30 AM Coblentz Clara Craver Award John C. Conboy *University of Utah*
	9:00 AM – 5:00 PM Workshops	9:00 AM – 5:00 PM Workshops	9:00 – 5:00 PM Workshops	
	9:00 AM Break *Silver State Foyer*	9:00 – 10:15 AM Poster Session and Break *S1*	9:00 – 10:15 AM Poster Session and Break *S1*	9:00 – 10:15 AM Poster Session and Break *Nevada Room*
		9:00 AM – 5:00 PM Exhibits Open *S1*	9:00 AM – 3:30 PM and 5:00 7:00 PM Exhibits Open *S1*	
	9:15 – 11.15 AM Oral Symposia	10:15 AM – 12:15 PM Oral Symposia	10:15 AM – 12:15 PM Oral Symposia	10:15 AM – 12:15 PM Oral Symposia
	11:15 Lunch on own	12:15 PM Lunch on own	12:15 PM Lunch on own	12:15 PM Lunch on own
		12:20 PM "What's Hot" Symposium *S1 extension*	12:20 PM "What's Hot" Symposium *S1 extension*	
12:30 – 4:30 PM Hand-On Instrument Workshops *S1 Extension and S2/3*	12:30 – 2:00 PM Poster Session and Break *S1 Extension*	12:30 PM Roundtable Discussion for Students. Sponsored by SABIC Innovative Plastics *Sierra 1/2*		
		1:30 – 3:00 PM Poster Session and Dessert Reception *S1*	1:30 – 3:00 PM Poster Session and Dessert Reception *S1*	1:30 – 3:00 PM Poster Session and Dessert Reception *Nevada Room*
3:40 PM "What's Hot" Symposium *S1 Extension*	2:00 – 4:00 PM Oral Symposia	3:00 – 5:00 PM Oral Symposia	3:00 – 5:00 PM Oral Symposia	3:00 – 5:00 PM Oral Symposia
5:00 – 7:00 PM Welcome Mixer and SAS Sponsored Student Poster Session Coblentz Student Awards FACSS Student Awards *S1 Extension*	4:00 PM Plenary Session Gary Hieftje *Indiana University* *S2/3*	6:00 PM Raman Reception *S2/3*		
	5:00 – 7:00 PM Exhibit Opening Reception *S1*	7:00 PM SAS Reception *(SAS members only)* *Nevada 6/7*	5:00 PM FACSS All Inclusive Wednesday Evening Event *S1*	
	6:45 PM Chemistry of Wines – A Tasting Event, *Sierra 1/2* *Ticket required*		7:30 PM FACSS After Dark *S1 extension*	

SUNDAY

3:40 PM "What's Hot" Symposium **–** oral presentations by FACSS 2008 exhibitors describing some of their latest products, page 43**.** *S1 extension*

5:00 PM Welcome Mixer and SAS Sponsored Student Poster Session, Coblentz Student Awards and FACSS Student Awards, *S1 extension*

MONDAY MORNING

8:00 AM **PLENARY LECTURE,** *S2/3*
New Bioanalytical Technologies for Probing the Paradoxical Relationship of the Immune System and Cancer; **James Heath**, page 44

9:00 AM **SYMPOSIA**

9:15 – 11:15, Symposia, page 44
- Nuclear Magnetic Resonance, *Room N2*
- Terahertz, *Room N3*
- Applications of Atomic Spectroscopy, *Room N4*
- Bioanalytical – Nanoparticles and Nanosensors, *Room N5*
- Fundamentals of Electrospray Ionization, *Room N6*
- Fundamental Advances in Plasma Source Mass Spectrometry, *Room N7*
- Industrial and Environmental Applications of LIBS, *Room N8*
- Raman Imaging: Developments in Instrumentation and Applications, *Room N9*
- Emerging Optical Spectroscopy Techniques and Applications (sponsored by the Society for Applied Spectroscopy), *Room N10*

MONDAY AFTERNOON

12:30 **SYMPOSIA AND POSTER SESSION**
12:30 – 2:00, Posters, *S1 extension,* page 46

2:00 – 4:00, Symposia, page 47
- Bioanalytical – Cellular Analysis, *Room N2*
- Forensics in Food Safety, *Room N3*
- Microplasmas for Life, *Room N4*
- Controlling Nanostrucutres with Atomic Precision: The Ultimate of Nanochemistry, *Room N5*
- Fundamentals of MALDI Mass Spectrometry, *Room N6*
- Archaeometry: Analytical Measurements on Archaeological Samples, *Room N7*
- Advances in Analytical Techniques for Petroleum Industry, *Room N8*
- Developments in Raman Spectroscopy (sponsored by the Society for Applied Spectroscopy), *Room N9*
- A Spectrometer in the Hand is Worth Two in the Lab, *Room N10*

4:00 PM **PLENARY LECTURE,** S2/3
40 Years of Contributions to Atomic Spectroscopy and Analytical Chemistry**, Gary Hieftje**, page 44

TUESDAY MORNING

8:00 AM **PLENARY LECTURES,** *S2/3*
Charles Mann Award, Ian R. Lewis, page 50
ANACHEM Award, Scott McLuckey page 50

9:00 AM **SYMPOSIA AND POSTER SESSIONS**

9:00 – 10:15, Posters, *Exhibit Hall S1,* page 50

10:15 – 12:15, Symposia, page 52
- ANACHEM Award Session Honoring Scott McLuckey, *Room N2*
- Bioanalytical - Raman, *Room N3*
- Forensic Analytical Chemistry Applications of Chemometrics, *Room N4*
- Spectroscopy and Nanomaterials, *Room N5*
- Quantitative Mass Spectrometry I: Peptides and Proteins, *Room N6*
- 40 Years of Atomic Spectroscopy Innovation: A Tribute to Gary Hieftje (sponsored by the Society for Applied Spectroscopy, *Room N7*
- Infrared Imaging, *Room N8*
- Chiral Analysis using Vibrational Circular Dichroism (VCD), *Room N9*
- Ultrafast Vibrational Spectroscopy: Chemistry, Material and Biological Science, *Room N10*

TUESDAY AFTERNOON

12:20 **WHAT'S HOT EXHIBITOR PRESENTATIONS,** *S1 extension,* page 54

1:30 PM **SYMPOSIA AND POSTER SESSIONS**

1:30 – 3:00, Posters, *Exhibit Hall S1,* page 50

3:00 – 5:00, Symposia, page 54
- Pharmaceutical Forensics, *Room N3*
- Sample Introduction: From A to Z, *Room N4*
- Chemometrics Along Spatial and Chemical Dimensions, *Room N5*
- New Developments I Mass Spectrometry, *Room N6*
- 40 Years of Spectroscopy Innovation: A Tribute to Gary Hieftje (sponsored by the Society for Applied Spectroscopy), *Room N7*
- NeSSI – Application of Sensors for Increased Process Control, *Room N8*
- Charles Mann Award Session: Ian R. Lewis awardee, *Room N9*
- NIR Spectroscopy in Pharmaceutical Analysis: Technology Transfer in Action, *Room N10*

PROGRAM OVERVIEW

WEDNESDAY MORNING

8:00 AM **PLENARY LECTURES,** *S2/3*
SAS Applied Spectroscopy William F. Meggers Award, Taka-aki Ishibashi, page 57
Lester W. Strock Award, Annemie Bogaerts, page 57

9:00 AM **SYMPOSIA AND POSTER SESSIONS**

9:00 – 10:15, Posters, *Exhibit Hall S1,* page 57

10:15 – 12:15, Symposia, page 59
Chemometrics in Separations, *Room N2*
Vibrational Spectroscopy, Chemical Imaging and QbD, *Room N3*
LIBS, *Room N4*
Electron Transfer Chemistry and Nanostructured Materials, *Room N5*
Ion Mobility Spectrometry – Recent Applications I, *Room N6*
Lester Strock Award, *Room N7*
Process Analytical Monitoring (sponsored by the Society for Applied Spectroscopy), *Room N8*
Bio and Pharmaceutical Applications of Raman Spectroscopy, *Room N9*
Innovations in Analytical Applications of SERS, *Room N10*

WEDNESDAY AFTERNOON

12:20 **WHAT'S HOT EXHIBITOR PRESENTATIONS,** *S1 extension, page 61*

1:30 PM **SYMPOSIA AND POSTER SESSIONS**

1:30 – 3:00, Posters, *Exhibit Hall S1,* page 57

3:00 – 5:00, Symposia, page 61
Novel But Important Data Analysis Techniques for Analytical Science, *Room N2*
Two-Dimensional Correlation Spectroscopy, *Room N3*
Laser Ablation, *Room N4*
Meggers Award, *Room N5*
Ion Mobility Spectrometry – Recent Applications (sponsored by the Society for Applied Spectroscopy), *Room N6*
FACSS Student Awards, *Room N7*
Spectroscopic and Sensing Technologies in Pharmaceutical Industry, *Room N8*
Raman Spectroscopy and Astrobiology: Terrestrial Analogues & Extraterrestrial Scenarios, *Room N9*
Industrial Applications of SERS, *Room N10*

THURSDAY MORNING

8:00 AM **PLENARY LECTURE:** *S2/3*
Ellis R. Lippincott Award, Richard P. Van Duyne, page 64
Coblentz Clara Craver Award, John C. Conboy, page 64

9:00 AM **SYMPOSIA AND POSTER SESSIONS**

9:00 – 10:15, Posters, *Nevada Room,* page 64

10:30 – 12:30, Symposia, page 66
Classification and Multivariate Calibration for Bioanalytical Applications, *Room N2*
Microanalytical Chemistry, *Room N3*
Applications of Fluorescence Spectroscopy and Related Techniques, *Room N4*
Lippincott Award *Room N5*
Mass Spectrometry and Arrays, *Room N6*
Hidden Isotope Ratio Information – Yours to Discover with MC-ICP-MS *Room N7*
Surface Plasmon Resonance, *Room N8*
Raman in Pharma/Biotech, *Room N9*
Two-Diumensional Correlation Spectroscopy, *Room N10*

THURSDAY AFTERNOON

1:30 PM **SYMPOSIA AND POSTER SESSIONS**

1:30 – 3:00, Posters, *Nevada Room,* page 64

3:00 – 5:00, Symposia, page 64
Spectral and Multiway Patttern Recognition, *Room N2*
Applications of Microscopy and Microanalysis in Forensic Science, *Room N3*
Applications of Fluorescence Spectroscopy and Related Techniques, *Room N4*
Bioanalytical - SERS, *Room N5*
Coblentz Society Clara Craver Award, *Room N6*
Actinide Analysis, *Room N7*
Surface Plasmon Resonance, *Room N8*
Emerging Areas in Raman Spectroscopy, *Room N9*
Mid-IR Imaging: From Basic Developments Towards Clinical Translation, *Room N10*

TECHNICAL PROGRAM OVERVIEW BY TOPIC

AWARD SESSIONS

Tuesday AM
ANACHEM Award – Scott McLuckey (Awardee), *Rm N2*
Tuesday PM
Charles Mann Award – Ian R. Lewis (Awardee), *Rm N9*
Wednesday AM
Lester W. Strock Award – Annemie Bogaerts (Awardee), *Rm N7*
Wednesday PM
Meggers Award – Taka-Aki Ishibashi (Awardee), *Rm N5*
FACSS Student Awards, *Rm N7*
Thursday AM
Lippincott Award – Richard Van Dyne (Awardee), *Rm N5*
Thursday PM
Coblentz Craver Award – John Conboy (Awardee) *Rm N6*

ATOMIC SPECTROSCOPY

Monday AM
Fundamental Advances in Plasma Source Mass Spectrometry *Rm N7*
Applications of Atomic Spectroscopy, *Rm N4*
Industrial and Environmental Application of LIBS, *Rm N8*
Monday PM
Microplasmas for Life, *Rm N4*
Archaeometry: Analytical Measurements on Archaeological Samples, *Rm N7*
Tuesday AM
40 Years of Atomic Spectroscopy Innovation: A Tribute to Gary Hieftje, *Rm N7*
Tuesday PM
Sample Introduction: From A to Z, *Rm N4*
40 Years of Spectroscopy Innovation: A Tribute to Gary Hieftje, *Rm N7*
Wednesday AM
LIBS, *Rm N4*
Lester W. Strock Award – Annemie Bogaerts (Awardee), *N7*
Wednesday PM
Laser Ablation, *Rm N4*
Thursday AM
Hidden Isotope Ratio Information – Yours to Discover with MC-ICP-MS, *Rm N7*
Thursday PM
Actinide Analysis, *Rm N7*

BIOANALYTICAL

Monday AM
Bioanalytical-Nanoparticles and Nanosensors, *Rm N5*
Monday PM
Bioanalytical-Cellular Analysis, *Rm N2*
Tuesday AM
Bioanalytical - Raman, *Rm N3*
Wednesday AM
Bio & Pharmaceutical Applications of Raman Spectroscopy, *Rm N9*
Thursday AM
Microanalytical Chemistry, *Rm N3*
Thursday PM
Bioanalytical-SERS, *Rm N5*

CHEMOMETRICS

Tuesday AM
Forensic Analytical Chemistry Applications of Chemometrics, *Rm N4*
Tuesday PM
Chemometrics Along Spatial and Chemical Dimensions, *N5*
Wednesday AM
Chemometrics in Separations, *Rm N2*
Wednesday PM
Novel but Important Data Analysis Techniques for Analytical Science, *N2*
Thursday AM
Classification and Multivariate Calibration for Bioanalytical Applications, *N2*
Thursday PM
Spectral and Multiway Pattern Recognition, *Rm N2*

FLUORESCENCE

Thursday AM
Applications of Fluorescence Spectroscopy and Related Techniques I, *Rm N4*
Thursday PM
Applications of Fluorescence Spectroscopy and Related Techniques II, *Rm N4*

FORENSICS

Monday PM
Food Safety, *Rm N3*
Tuesday AM
Forensic Analytical Chemistry Applications of Chemometrics, *Rm N4*
Tuesday PM
Pharmaceutical Forensics, *Rm N3*
Thursday PM
Applications of Microscopy and Microanalysis in Forensic Science, *Rm N4*

IMAGING

Monday AM
Raman Imaging: Developments in Instrumentation and Applications, *Rm N9*
Tuesday AM
Infrared Spectral Imaging, *Rm N8*
Thursday PM
MID-IR Imaging, *Rm N10*

MASS SPECTROMETRY

Monday AM
Fundamentals of Electrospray Ionization, *Rm N6*
Monday PM
Fundamentals of MALDI, *Rm N6*
Tuesday AM
Quantitative Mass Spectrometry I: Peptides and Proteins, *Rm N6*
ANACHEM – Scott McLuckey (Awardee), *N2*
Tuesday PM
New Developments in Mass Spectrometry, *N6*
Wednesday AM
Ion Mobility Spectrometry – Recent Applications I, *Rm N6*
Wednesday PM
Ion Mobility Spectrometry – Recent Applications II, *Rm N6*
Thursday AM
Mass Spectrometry and Arrays, *Rm N6*

TECHNICAL PROGRAM OVERVIEW BY TOPIC

IR and NIR MOLECULAR SPECTROSCOPY

Monday AM
Emerging Optical Spectroscopy Techniques and Applications, *Rm N10*
Terahertz Spectroscopy, *Rm N3*

Tuesday AM
Ultrafast Vibrational Spectroscopy: Chemistry, Material, and Biological Science, *Rm N10*
Chiral Analysis using Vibrational Circular Dichroism (VCD), *N9*

Tuesday PM
Chemometrics Along Spatial and Chemical Dimensions, *N5*
NIR Spectroscopy and Calibration Transfer, *N10*

Wednesday AM
Vibrational Spectroscopy, Chemical Imaging and QbD, *Rm N3*

Wednesday PM
Two-Dimensional Spectroscopy I, *Rm N3*
Meggers Award – Taka-Aki Ishibashi (Awardee), *Rm N5*

Thursday AM
Two-Dimensional Spectroscopy II, *Rm N10*

Thursday PM
MID-IR Imaging, *Rm N10*

NANOTECHNOLOGY

Monday AM
Bioanalytical-Nanoparticles and Nanosensors, *Rm N5*

Monday PM
Controlling Nanostructures with Atomic Precision: The Ultimate of Nanochemistry, *Rm N5*

Tuesday AM
Spectroscopy and Nanomaterials, *Rm N5*

Wednesday AM
Electron Transfer Chemistry and Nanostructured Materials, *Rm N5*

Thursday AM
Lippincott Award – Richard Van Dyne (Awardee), *Rm N5*

NMR

Monday AM
NMR, *Rm N2*

PHARMACEUTICAL

Tuesday AM
Chiral Analysis using Vibrational Circular Diochroism (VCD), *Rm N9*

Tuesday PM
Pharmaceutical Forensics, *Rm N3*
NIR Spectroscopy and Calibration Transfer, *Rm N10*

Wednesday AM
Bio & Pharmaceutical Applications of Raman Spectroscopy, *Rm N9*

Thursday AM
Raman in Pharma/Biotech, *Rm N9*

PROCESS, ANALYTICAL

Monday AM
Industrial and Environmental Applications of LIBS, *Rm N8*

Monday PM
Advances in Analytical Techniques for Petroleum Industry, *Rm N8*

Tuesday PM
NeSSI – Application of Sensors for Increased Process Control, *Rm N8*

Wednesday AM
Process Analytical Monitoring – SAS Technical Session, *Rm N8*

Wednesday PM
Spectroscopic and Sensing Technologies in Pharmaceutical Industry, *Rm N8*

RAMAN

Monday AM
Raman Imaging: Developments in Instrumentation and Applications**,** *Rm N9*

Monday PM
Developments in Raman Spectroscopy, *Rm N9*

Tuesday AM
Bioanalytical - Raman, *Rm N3*

Tuesday PM
Charles Mann Award – Ian R. Lewis (Awardee), *Rm N9*

Wednesday AM
Innovations in Analytical Applications of SERS, *Rm N10*
Bio & Pharmaceutical Applications of Raman Spectroscopy, *Rm N9*

Wednesday PM
Raman Spectroscopy and Astrobiology: Terrestrial Analogues and Extraterrestrial Scenarios, *Rm N9*
Industrial Applications of SERS, *Rm N10*

Thursday AM
Raman in Pharma/Biotech, *Rm N9*
Lippincott Award – Richard Van Dyne (Awardee), *Rm N5*

Thursday PM
Emerging Areas in Raman, *Rm N9*
Bioanalytical-SERS, *Rm N5*

SEPARATIONS and MICROFLUIDICS

Wednesday AM
Chemometrics in Separations, *Rm N2*

Thursday AM
Microanalytical Chemistry, *Rm N3*

SURFACE PLASMON RESONANCE

Thursday AM
Surface Plasmon Resonance: Innovation and Application I, *Rm N8*

Thursday PM
Surface Plasmon Resonance: Innovation and Application II, *Rm N8*

YOUNG INVESTIGATORS
Sponsored by the Society for Applied Spectroscopy and The Analyst

Monday

Julie Herberg – Low Cost CE-NMR with Microcoils for Chemical Detection, 9:15 AM, *Room Nevada 2*

Tuesday

George Chan – Mechanistic Study of Analyte Excitation and Matrix Effects in Inductively Coupled Plasma-Atomic Emission Spectrometry, 11:35 AM, *Room Nevada 7*

Nathan VerBerkmoes - Proteomics Approaches for Characterizing Microbial Proteomes, 12:15 PM, *Room Nevada 6*

Steven Ray – Simultaneous Molecular and Elemental Mass Spectrometry for Comprehensive Elemental Speciation Analysis, 4:40 PM, *Room Nevada 7*

James Barnes – Fundamental Ion Diagnostics in Pulsed Glow Discharge Plasmas, Tuesday Poster Board 10

Facundo Fernandez – Host-Guest Reactive Desorption Electrospray Ionization Mass Spectrometry (DESI-MS) for the Rapid and Quantitative Authentication of Tamiflu Capsules, 3:40 PM, *Room Nevada 3*

Wednesday

Facundo Fernandez – Investigation of Alternate-Construction and Variable Duty Cycle Gating Waveforms for Digitally-Multiplexed Atmospheric Pressure Drift Tube Ion Mobility Spectrometry, 11:15 AM*, Room Nevada 6*

Yanxia Chen - Direct Monitoring the Bond Strength of CO at Au@Pt Core-Shell Nano-Particle Electrodes by *in-situ* Electrochemical Surface-Enhanced Raman Spectroscopy, 10:35 AM, *Room Nevada 5*

Thursday

Brian Dable – Detection of Biological Compounds using a Fluorescence-Based Detection System, 3:20 PM, *Room Nevada 4*

Amanda Haes – Engineering Stable Nanostructures for Enhanced Optical Detection, 10:55 AM, *Room Nevada 8*

Jean-Francois Masson – Nanoholes Arrays Sensors Prepared using Lithography, 10:15 AM, *Room Nevada 8*

TECHNICAL PROGRAM - SUNDAY
Workshops - see page 34 and "What's Hot" Exhibitor Presentations

"What's Hot" Symposium, Presider: Brian Dable**,** *Room S1 Extension*

3:40 **Lambda Solutions,** "Spectra to 40 Wavenumbers with the New High Throughput Dimension-P2"

3:50 **Shimadzu,** "More New Spectroscopy Instruments from Shimadzu"

4:00 **BaySpec,** "Low-cost, Handheld, Dispersive NIR Spectrometer – a Benefit from the Telecom Boom and Bust"

4:10 **Polymicro;** "FDP: Highly Stable Deep UV Fiber"

4:20 **Aurora Biomed,** "Automated Liquid-Liquid Extraction System for LC-MS Sample Preparation"

4:30 **Glass Expansion,** "A Portable Device for Real-time Sample Flow Measurement"

4:40 **PerkinElmer,** "New Atomic and Molecular Spectroscopy Options to Enhance Your Research Laboratory"

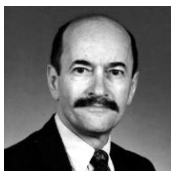
4:50 **HORIBA-Jobin Yvon,** "Multi-line Analysis by ICP-OES: a New Concept for More Reliable Results using a CCD Based ICP"

5:00 PM
WELCOME MIXER
SAS Sponsored Student Poster Session, Coblentz Student Awards, FACSS Student Awards
S1 extension

TECHNICAL PROGRAM – MONDAY
Plenaries 8:00 AM and 4:00 PM and Orals 9:15 – 11:15 AM

8:00 AM Plenary Lecture, S 2/3

(1) New Bioanalytical Technologies for Probing the Paradoxical Relationship of the Immune System and Cancer**. James Heath**, *Professor of Chemistry at Caltech and Professor of Molecular & Medical Pharmacology at UCLA, and Director of the National Cancer Institute NSB Cancer Ctr.*



4:00 PM Plenary Lecture, S 2/3

(2) 40 Years of Contributions to Atomic Spectroscopy and Analytical Chemistry**.** **Gary Hieftje**, *Indiana University*

Monday Morning, Room Nevada 2
NUCLEAR MAGNETIC RESONANCE
Organizer and Presider: Julie Herberg

9:15 (3) **Low Cost CE-NMR with Microcoils for Chemical Detection**; Julie L. Herberg[1], Kristl Adams[1], Vasiliki Demas[1,2], Anthony Bernhardt[3], Vince Malba[3], Lee Evan[3], Christopher Harvey[3], Robert S. Maxwell[1]; [1]Lawrence Livermore National Laborartory, Chemistry, Material, Earth, and Life Sciences, [2]University of California-Berkeley, [3]Lawrence Livermore National Laboratory, Engineeirng Technologies Div., [4]Lawrence Livermore National Laboratory, Physical Science Division

9:35 (4) **Fruit of the Vine, Two Buck Chuck, or Lighter Fluid: Applying NMR and GC/MS to Wine and Homeland Security Problems**; Matthew Augustine; [1]UC Davis

9:55 (5) **NMR as a Forensic Tool for the Organization for the Prohibition of Chemical Weapons**; Sarah Chinn[1], Robert Maxwell[1], Armando Alcaraz[1], Hugh Gregg[1], Bradley Hart[1], Carolyn Koester[1], Richard Whipple[1], Dennis Reutter[1]; [1]Lawrence Livermore National Laboratory

10:15 (6) **Advanced Metabolomics-Based Methods for Biomarker Discovery and Systems Biology Research**; Daniel Raftery[1], [1]Purdue University

10:35 (7) **Hyphenation of Capillary Electrophoresis with Slotted Microstrip NMR Detection**; Roland Hergenröder[1], Hans-Georg Krojanski[1], Jörg LAmbert[11]Institute for Analytical Sciences

10:55 (8) **207-Pb and 13-C Nuclear Magnetic Resonance Spectroscopy of Adducts of 1,10- Phenanthroline with Lead(II) Halides: Solid-State Studies**; Cecil Dybowski[1], Alicia Glatfelter[1], David D. Kragsten[1], Shi Bai[1], Dale L. Perry[2], Scott E. Van Bramer[3]; [1]University of Delaware; [2]Lawrence Berkeley National Laboratory; [3]Widener University

Monday Morning, Room Nevada 3
TERAHERTZ
Organizer and Presider: Mike Claybourn

9:15 (9) **Enantiomeric Dependence of the Far-Infrared Spectra of Polycrystalline Tyrosine and Valine**; Charles Schmuttenmaer[1], Alan True[1], Timothy French[1], Konstanze Schroeck[2]; [1]Yale University, Department of Chemistry; [2]University of Bochum, Chemistry Dept

9:35 (10) **Time-Domain Terahertz Measurements of Pharmaceutical Tablet Mass and Compression Force**; Jeffrey White, Irl Duling, David Zimdars, Greg Fichter; [1]Picometrix LLC; [2]Picometrix LLC; [3]Picometrix LLC; [4]Picometrix LLC

9:55 (11) **Development of Terahertz Time Domain Spectrometer for Gas Phase Spectroscopy**; Hiromichi Hoshina[1], Takamasa Seta[2], Yasuko Kasai[2], Iwao Hosako[2], Chiko Otani[1]; [1]RIKEN; [2]NICT

10:15 (12) **Advanced Terahertz Sources And Imaging Configurations for Rapid Analytical Measurement Applications**; Yao-chun Shen[1], Peter Weightman[2]; [1]The University of Liverpool; [2]The University of Liverpool

10:35 (13) **The Use of Terahertz Pulsed Imaging within the Pharmaceutical Environment;** Philip Taday[1]; [1]TeraView Limited

10:55 (14) **Prototype Inspection System of Hidden Drugs in Sealed Envelopes using Terahertz Wave Scattering and Fingerprint Spectra**; Yoshiaki Sasaki[1], Horimichi Hoshina[1], Masahiro Yamashita[2], Gosei Okazaki[2], Chiko Otani[1], Kodo Kawase[3]; [1]RIKEN; [2]S.I Seiko Co., Ltd.; [3]Nagoya University

Monday Morning, Room Nevada 4
APPLICATIONS OF ATOMIC SPECTROSCOPY
Organizer: Greg Klunder; Presider: David Butcher

9:15 (15) **Certification of Beryllium Mass Fraction in Standard Reference Material 1877 Beryllium Oxide Powder using High-Performance ICP-OES with Exact Matching**; Michael Winchester[1], Gregory Turk[1], Therese Butler[1], Thomas Oatts[2], Charles Coleman[3], Dan Nadratowski[4], Rita Sud[4], Aleksandr Stefaniak[5], Mark Hoover[5]; [1]National Institute of Standards and Technology; [2]Y-12 National Security Complex; [3]Savannah River Site; [4]Bureau Veritas North America, Inc., [5]National Institute for Occupational Safety and Health

9:35 (16) **Exploration of Sample Introduction Systems for Reduction of Calcium Oxide Formation and Increased Sensitivity for Nickel Analysis in Biological Samples**; Melissa Maras[1], Jonathan Good[1], Steve Eckdahl[1], Matthew Hanley[1], Michelle Wermers[1], Matthew Knopp[2]; [1]Mayo Clinic; [2]Elemental Scientific, Inc.

9:55 (17) **Phytoremediation of Arsenic by Hyperaccumulating Plants**; David Butcher[1], Sung-Gun Park[1]; [1]Western Carolina University

10:15 (18) **Fluorescence-Based Studies of Ion Transmission through the Skimmer Cone of an ICP-MS**; Haibin Ma[1], Jeff Macedone[1], Paul Farnsworth[1]; [1]Brigham Young University

10:35 (19) **An Ion Funnel-based Vacuum Interface for Inductively Coupled Plasma Mass Spectrometry (ICPMS)**; Rolf Dietiker[1], Tatiana Egorova[1], Bodo Hattendorf[1], Detlef Guenther[1]; [1]ETH Zurich, Laboratory of Inorganic Chemistry

10:55 (20) **Introduction of Aqueous Samples to High Power Pulse Microplasma Source**; Yoichi Nagata[1], Hidekazu Miyahara[1], Taichi Meguro[1], Ryuichi Shimada[1], Eiki Hotta[1], Akitoshi Okino[1]; [1]Tokyo Institute of Technology

TECHNICAL PROGRAM – MONDAY
Orals 9:15 – 11:15 AM

Monday Morning, Room Nevada 5
BIOANALYTICAL-NANOPARTICLES AND NANOSENSORS
Organizer and Presider: Heather Clark

9:15 (21) **Novel SERS Nanosensors Suitable for One- and Two-Photon Excitation**; Janina Kneipp[2], Harald Kneipp[1], Mark Stockman Stockman[3], Katrin Kneipp[1]; [1]Harvard University Medical School; [2]Humboldt University, Chemistry Departmen; [3]Georgia State University, Department of; [4]Harvard-MIT Division of Health Sciences

9:35 (22) **Nano-Wiffle Balls - Porous Phospholipid Nanoshells for Biological Sensing**; Craig Aspinwall[1]; [1]University of Arizona

9:55 (23) **The Application of Nano-Sensors to the Real-Time Monitoring of Endosomal Ion Fluctuation in Dictyostelium Discoideum during cAMP Stimulation**; Murphy Brasuel[1], Phoebe Lostroh[2], Jessica Hellyer[1], Everett Moding[1]; [1]Colorado College Department of Chemistry; [2]Colorado College Department of Biology

10:15 (24) **Optical Nanosensors for Intracellular Ion Analysis**; Heather Clark[1], J. Matthew Dubach[1], Saumya Das[2], Anthony Rosenzweig[2]; [1]The Charles Stark Draper Laboratory; [2]Beth Israel Deaconess Medical Center

10:35 (25) **Hybrid SERS/Fluorescence Bionanoprobes for the Rapid Detection of Toxic Materials**; Nicole Whitten[1], Dimitra Stratis-Cullum[2], Brian Cullum[1]; [1]University of Maryland Baltimore County; [2]United States Army Research Laboratory

10:55 (26) **Fabrication of Functional Plasmonic Nanoparticles through Layer-by-Layer Assembly on Optical Fiber for Real-Time and Spatially-Resolved Oxygen Measurement**; Veronica Rigo[1], Peter Geissinger[1]; [1]University of Wisconsin Milwaukee

Monday Morning, Room Nevada 6
FUNDAMENTALS OF ELECTROSPRAY IONIZATION
Organzier and Presider: Rachel Ogorzalek Loo

9:15 (27) **Electrospray Mass Spectrometry: How and Why Did We Get Here?**; Richard Cole; [1]University of New Orleans

9:55 (28) **Electrochemistry Fundamentals of Electrospray Ionization**; Gary Van Berkel, Vilmos Kertesz; [1]Oak Ridge National Laboratory

10:15 (29) **Effects of Rapid Analyte/Solvent Mixing for ESI-MS of Peptides and Proteins**; Joseph Loo[1], Ivory Peng[1]; [1]UCLA

10:35 (30) **Ions for Free: Thermally Cycled Pyroelectric Crystals and Electrocuted Liquid Droplets as Ion Sources**; Evan Neidholdt[1], J.L. Beauchamp[1]; [1]California Insitute of Technology

10:55 (31) **Is a Cone-Jet Electrospray the Holy Grail of ESI-MS?**; Ioan Marginean[1], Ryan T. Kelly[1], David C. Prior[1], Brian L. LaMarche[1], Keqi Tang[1], Richard D. Smith[1]; [1]Pacific Northwest National Laboratory

Monday Morning, Room Nevada 7
FUNDAMENTAL ADVANCES IN PLASMA SOURCE MASS SPECTROMETRY
Organizer and Presider; José A. C. Broekaert

9:15 (32) **Evaluation of Penning Ionization in Inductively Coupled Plasma**; Nicholas Taylor, Paul B. Farnsworth; [1]Brigham Young University

9:35 (33) **The Atmospheric Pressure Glow Discharge: A Plasma for Ambient Mass Spectrometry**; Steven Ray[1], Jacob Shelley[1], Greg Schilling[1], Joshua Wiley[1], Gary Hieftje[1]; [1]Indiana University

9:55 (34) **Development of a Hollow Cathode Geometry for Particle Beam Glow Discharge Mass Spectrometry**; R. Kenneth Marcus[1], Joaudimir Castro[1]; [1]Clemson University

10:15 (35) **Advances in Fundamental Understanding and Practical Use of Collision/Reaction Cells in ICP-MS**; Patrick Gray[1], Susan Olesik[1], John Olesik[1]; [1]The Ohio State University

10:35 (36) **Evaluation of Pyrolysis Curves for Volatile Elements in Aqueous Standards and Carbon-Containing Matrices in ETV-ICP-MS**; Margaretha de Loos-Vollebregt[1], Alessandra de Silva[1], Bernhard Welz[2]; [1]Delft University of Technology; [2]Universidade Federal de Santa Catarina

10:55 (37) **Studies on Thermochemical Reagents in ETV-ICP-MS**; José Broekaert; [1]University of Hamburg

Monday Morning, Room Nevada 8
INDUSTRIAL AND ENVIRONMENTAL APPLICATIONS OF LIBS
Organizers: S. Michael Angel and Brian Marquardt;
Presider: S. Michael Angel

9:15 (38) **Industrial LIBS Applications and Approaches to Becoming a More Mainstream Analytical Technology**; Robert Kearton; [1]Ocean Optics, Inc.

9:35 (39) **Overview of LIBS Applications for Real Time Analysis and Process Control**; Mohamad Sabsabi[1], Paul Bouchard[1], René Heon[1], André Hamel[1], Gregg Lithgow[1], François Doucet[1], Stephane Laville[1]; [1]NRC-IMI

9:55 (40) **Laser Induced Breakdown Spectroscopy of Aqueous Solutions**; Scott Goode[1], Shana Williams[1], Amelia Taylor[1]; [1]Dept of Chemistry Univ of So Carolina

10:15 (41) **Optimization of Excitation Conditions for Aqueous Phases LIBS Measurements**; Christopher Gordon[1], Michael Angel[1]; [1]University of South Carolina

10:35 (42) **Remote LIBS of Hydrous Phases of Clay Minerals**; Shiv Sharma[1], Rachel Lentz[1], Anupam Misra[1]; [1]Hawaii Institute of Geophys.& Planetology, UH

10:55 (43) **Multi-Plasma Laser-Induced Breakdown Spectroscopy (Multi-Plasma LIBS): Uses and Applications**; Galan Moore[1], Douglas Jennings[1]; [1]Corning Incorporated

Monday Morning, Room Nevada 9
RAMAN IMAGING: DEVELOPMENTS IN INSTRUMENTATION AND APPLICATIONS
Organizer and Presider: Matt Nelson

9:15 (44) **Towards Automation in the Characterization of Nanostructured Materials and Devices**; Klaus Weishaupt[1], Thomas Dieing[1], Fernando Vargas[1], Ute Schmidt[1]; [1]WITec GmbH

9:35 (45) **Biological Threat Detection with Raman Chemical Imaging**; Ashish Tripathi[1], Jason A. Guicheteau[2], A. Peter Snyder[2], Darren K. Emge[2], Rabih E. Jabbour[1], Steven D. Christesen[2]; [1]SAIC; [2]2-\tECBC, US Army APG

10:15 (46) **Resolution Targets for Chemical Imaging of Pharmaceutical Products**; John Kauffman[1], Sean Gilliam[1], R. Scott Martin[2]; [1]FDA Div. of Pharmaceutical Analysis, St. Louis, MO; [2]Saint Louis University, St. Louis, MO

10:35 (47) **Chemical Imaging of Pharmaceutical Granules by Raman Global Illumination and Near-Infrared Mapping Platforms**; Slobodan Sasic; [1]Pfizer, Analytical R & D

10:55 (48) **Raman Imaging of Sub-Cellular Organization, and Uptake of Drug Delivery Systems into Cells**; Max Diem[1], Christian Matthaeus[1], Tatyana Chernenko[1], Luis Arcesio Quintero Pizo[2]; [1]Northeastern University; [2]University of Puerto Rico

Monday Morning, Room Nevada 10
EMERGING OPTICAL SPECTROSCOPY TECHNIQUES AND APPLICATIONS (sponsored by the Society for Applied Spectroscopy)
Organizers and Presiders: John Chalmers and Pavel Matousek

9:15 (49) **Raman + HPLC = Reduced Fluorescence. Is This Possible?**; Brian Marquardt[1], Nils Christian Afseth[2], Jens Petter Wold[2]; [1]University of Washington; [2]Matforsk, Aas Norway

9:35 (50) **Novel Interface-Selective Even-Order Nonlinear Spectroscopy**; Shoichi Yamaguchi[1], Tahei Tahara[1]; [1]RIKEN

9:55 (51) **Remote Detection of Volatile Organic Compounds by Passive Infrared Spectroscopy**; Gary Small[1]; [1]University of Iowa

10:15 (52) **ATR-FTIR Imaging with Variable Angles of Incidence**; Sergei Kazarian, Andrew Chan; [1]Imperial College London

10:35 (53) **Quantitative Analysis of Pharmaceutical Formulations using Low Frequency Transmission Raman**; Mike Claybourn[1], Jonas Johansson[1], Hanna Matic[1]; [1]AstraZeneca

10:55 (54) **High-Speed, High Resolution, Chemical Imaging using Tunable Laser**; Eli Margalith[1], Lam Nguyen[1]; [1]OPOTEK, Inc.

MONDAY POSTER SESSION
12:30 – 2:00 pm
Exhibit Hall S1 Extension

All Monday posters should be put up between 7:30 – 8:00 AM and removed between 4:30 – 5:00 PM. Odd numbered poster boards present between 12:30 – 1:15 PM. Even numbered poster boards present between 1:15 – 2:00 PM

Atomic Spectroscopy

Board #

1 (55) **Can You Increase ICP Productivity and Performance At the Same Time?**; Jerry Dulude[1], Scott Bridger[2], David Jones[3]; [1]Glass Expansion; [2]Scoan Investments; [3]ALS Chemex

2 (56) **Speciation of Gadolinium Compounds in Gadolinium Based Magnetic Resonance Imaging Agents by HPLC-ICP-OES**; Chethaka Kahakachchi[1], Dennis Moore[1] ; [1]Covidien

3 (57) **Self-Learning, Flexible, Multiline-Based Semi-Quantitative Analysis Tool for a Ccd-Based ICP-AES Instrument**; William Zuccarello[1], Philippe Hunault[1], Jean-Michel Mermet[2], Catherine Wallerand[3], Cendrine Dubuisson[3], Emmanuel Fretel[3], Olivier Rogerieux[3], Sébastien Velasquez[3], Sophie Lebouil[3]; [1]HORIBA; [2]Spectroscopy forever; [3]HORIBA Jobin Yvon

4 (58) **Graphite Furnace Atomic Apsorbtion**; [1]Amina Ali, [1]Kuwait Institue for Scientific

5 (59) **Determination Of Tin Levels**; [1]Rabaa Al-Kandari, [1]Amina Ali, [1]Kuwait Institue for Scientific

6 (60) **Investigation Oo Long-Term Stability On ICP-AES for the Microwave Digestion Analysis in Infant Formula Samples**; Rabaa Al-Kandari[1], Amina Ali[1], [1]Kuwait Institue for Scientific

7 (61) **Comparasion between Two**; Amina Ali[1], Rabaa Al-Kandari[1], [1]Kuwait Institue for Scientific

8 (62) **High Sample Throughput Using a Discrete Sampling Accessory for ICP-AES and ICP-MS**; Fred Smith[1], Paula Doeschot[1], Douglas Webb[1], Jeff Johnson[1], Carolyn Prindle[1]; [1]CETAC Technologies

9 (63) **A New High Performance Graphite Furnace Tube for Routine Analysis of Complex Matrices**; Doug Shrader[1], Kai Robinson[1], John Sanders[1], James Barker[1]; [1]Varian, Inc.

10 (64) **Silicon in Naphthas: A Near Cold Plasma Approach for Sub-PPB Detection Limits on an ICP-MS**; Jonathan Talbott[1], Robert Botto[2]; [1]Varian Inc.; [2]ExxonMobil Refining and Supply

11 (65) **Determination of Au from Nanoparticles in Rat Blood and Tissues**; Lee Yu[1], Laura Wood[1]; [1]National Institute of Standards and Technology

12 (66) **Analysis of Arsenicals and Their Sulfur Analogs in Biological Samples using HPLC with Collision Cell ICP-MS and ESI-MS/MS**; Christina M. Gallawa[1], Kevin M. Kubachka[2], Patricia A. Creed[2], John T. Creed[2], Michael C. Kohan[3], Karen Herbin-Davis[3], David J. Thomas[3] , Tom Van de Wiele[4]; [1]Oak Ridge Research Fellow; [2]US EPA, ORD, NERL, MCEARD; [3]US EPA, ORD, NHEERL, ETD, [4]Ghent University

13 (67) **Monte Carlo Simulation of Ambipolar Electric Field Effects and Trace Elements in the ICP-MS Vacuum Interface**; Ross Spencer[1], Paul Farnsworth[1], Daniel Wilcox[1]; [1]Brigham Young University

14 (68) **The Speciation of Five Arsenic Compounds by HPLC-ICP-MS**; James Koedam[1], Anna Starus[1], Gene Dietz[1]; [1]Access Business Group LLC

15 (69) **Advances in Signal Processing for Inductively Couple Plasma**; Stephen Mangum[1], Paul Krampitz[1], Daniel Jones[1]; [1]PerkinElmer LAS

Bioanalytical

16 (70) **Human Tear Lipid: Compositional, Structural and Functional Relationships using Spectrochemical Analysis**; Douglas Borchman[1], Gary Foulks[1], Marta Yappert[1]; [1]University of Louyisville

17 (71) **Development of Naphthyridine Derivatives to Bind Strongly to Cytosine at an Abasic Site and Their Application to SNPs Analysis**; Yusuke Sato[1], Seiichi Nishizawa[1], Norio Teramae[1]; [1]Tohoku University; [2]JST-CREST

18 (72) **A Mechanism for Water Transport across Endocytic Organelle Membranes in Living Cells**; Kenneth Christensen[1], Adriana Chaurra[1]; [1]Clemson University

Forensics

19 (73) **Post-Collection Processing of FT-IR Images Made Easy**; Samuel White[1], Louis G. Tisinger[1]; [1]Perkin Elmer, Inc

20

21 (75) **Multi-Residue Monitoring of 14 Sulfonamides in Fish Meats using LC-PDA with Confirmation by LC/MS/MS**; Hyesook Chang[1], Hoil Kang[1], Kwangsoo Lee[1], Sangho Lee[1], Soyoung Won[1], Suok Kim[1], Sookhee Ha[1], Yooyoung Jung[1], Sohee Kim[1]; [1]Busan Regional Korea Food & Drug Administration

22 (76) **Simultanious Analysis of Veterinary Drugs in Foods by LC/ESI-MS-MS**; Jae Chun Choi[1], Hee Ju Choi[1], Jong sup Jeon[1], Ji Yoon Eom[1], Hye Won Jeong[1], Hwa Jung Lee[1], Mi Kyung Kim[1], Hee-Yun Kim[1]; [1]Seoul Regional Food & Drug Administration

Mass Spectrometry

23 (77) **Characterization of Monoclonal Antibodies and F(ab')2 using MALDI-TOF-MS and Electrospray Ionization with Q-TOF Mass Spectrometry**; Panfilo Ozaeta[1], Carol Ramsay[1], Lianli Chi[1], Cheng Zhao[1], Jeffrey Fishpaugh[1]; [1]Abbott Laboratories

24 (78) **Fluorescence Microscopy of Surfaces in Desorption Electrospray Ionization (DESI)**; Mike Wood[1], Paul Farnsworth[1], Devin Busby[1]; [1]Brigham Young University

25 (79) **A Two Photon IR/UV Ionization Source for MALDI Mass Spectrometry**; Mark Little[1], Lam Nguyen[1], Eli Margalith[1]; [1]OPOTEK, Inc.

Molecular Spectroscopy

26 (80) **Conformational Stability, R0 Structural Parameters, Barrier to Internal Rotation and Vibrational Assignment of Cyclobutylamine**; Arindam Ganguly[1], Ahmed M. El Defrawy[1], W.A. Herrebout[2], B.J. van der Veken[2], James R. Durig[1]; [1]University of Missouri-Kansas City,USA; [2]Universitair Centrum Antwerpen,Belgium

27 (81) **Fuel Property Modeling for Rapid Quality Surveillance**; Mark Hammond[1], Robert Morris[1], Kevin Johnson[1], Jeffery Cramer[1], Braden Giordano[2], Susan Rose-Pehrsson[1] ; [1]Naval Research Laboratory; [2]Nova Research, Inc.

28 (82) **Raman Spectroscopy in the Palm of Your Hand**; Keith Carron[1], Rick Cox[1]; [1]DeltaNu

29 (83) **A Scanning Electrochemical Microscopy Coupled Flow Injection System for Glucose Analysis**; Hsuan-Jung Huang[1], Jyun-Jie Lai[1]; [1]National Sun Yat-sen University

Nanoscience

30 (84) **Iron(III)-Nickel Nanoparticles Synthesized using Microwave Heating and Characterizations with Atomic Force Microscopy**; Algernon Kelley[1], Nickolaus Flurry[1], Stephanie Daniels[1], Jayne Garno[1]; [1]Louisiana State University

31 (85) **Applying the Chemometrics Tools for Nanomaterials Research: Quantum-Chemical Modeling and QSPR of Fullerene C60 Solubility in Organic Solvents**; Tetyana Petrova[1], Bakhtiyor Rasulev[1], Andrey Toropov[1], Danuta Leszczynska[2], Jerzy Leszczynski[1]; [1]CCMSI, Jackson State University; [2]Civil&Env. Eng, Jackson State University

32 (86) **Evaluation of a Novel Single-Wall Carbon Nanotube Purification Method using Raman Spectroscopy**; Aaron Urbas[1], Steven Choquette[1], Gary Giulian[2], John Marino[1,2]; [1]National Institute of Standards and Technology; [2]University of Maryland

33 (88) **Nanotechnology in food production**; Erastus Gatebe; [1]JKUAT

Process

34 (89) **In-Line Turbidity Measurements for Industrial Processes**; John Groetsch; [1]Mettler Toledo Ingold

Terahertz

35 (90) **Terahertz Imaging Diagnostics of Cancer Tissues with a Chemometrics Technique**; Hiromichi Hoshina[1], Aya Hayashi[1], Norio Miyoshi[2], Chiko Otani[1]; [1]RIKEN; [2]University of Fukui

36 (91) **Time-Domain Terahertz Deconvolution Analysis for Non-Contact Measurement of "Opaque" Layered Samples**; Jeffrey White, Greg Fichter, David Zimdars; [1]Picometrix LLC; [2]Picometrix LLC; [3]Picometrix LLC

Monday Afternoon, Room Nevada 2
BIOANALYTICAL-CELLULAR ANALYSIS
Organizer and Presider: Ken Christensen

2:00 (92) **Analysis of Single Cells using Microfabricated Devices**; Nancy Allbritton[1], Wei Xu[1], Hsuan-Hong Lai[1], Scott Phillips[1], Chris Sims[1]; [1]University of North Carolina, Chapel Hill

2:20 (93) **Visualizing Cholesterol Dynamics in the Living Cell Membrane**; Jerilyn Timlin[1], Amanda Carroll-Portillo[1], Janet Pfeiffer[2], Haitao Li[3], Gary Griffiths[3], Janet Oliver[2], Bridget Wilson[2]; [1]Sandia National Laboratories; [2]University of New Mexico; [3]National Institutes of Health, NHLBI

2:40 (94) **Capillary-Channeled Polymer Films as a Platform for Cellular Analysis**; Kenneth Christensen[1], [1]Clemson University

3:00 (95) **Construction, Figures of Merit, and Testing of a Single-Plankton Fluorescence Excitation Spectroscopy System**; Luisa T.M. Profeta[1], Laura S. Hill[1], Evelyn Lawrenz[1], Tammi L. Richardson[1], Benjamin S. Twinning[1], Christopher J. Hintz[1], Timothy J. Shaw[1], Michael L. Myrick[1]; [1]University of South Carolina

3:20 (96) **Examination of Creatine Deposits and Environs in Brain Tissue from TgCRND8 Mice by Raman and FTIR Microscopy**; Avid Khamenehfar[1], Adriana Szeghalmi[1], Marc Del Bigio[2], David Westaway[3], Robert Julian[4], Kathleen Gough[1]; [1]Department of Chemistry, University of Manitoba; [2]Department of Pathology, University of M; [3]3Centre for Research in Neurodegenerativ; [4]Synchrotron Radiation Centre, University

3:40 (97) **Chemical Imaging using Deep UV Laser Induced Native Fluorescence and Resonance Raman**; Rohit Bhartia[1,3], William F. Hug[2], Everett C. Salas[3], Ray D. Reid[2], Kripa Sijapati[2], Arthur L. Lane[2], Kenneth H. Nealson[3]; [1]Jet Propulsion Laboratory/Caltech; [2]Photon Systems Inc.; [3]University of Southern California

Monday Afternoon , Room Nevada 3
FORENSICS IN FOOD SAFETY
Organizers: Carolyn Koester and Janel Owens;
Presider: Janel Owens

2:00 (98) **Detection of Toxic Chemicals in Human and Pet Foods**; Frederick Fricke; [1]US Food and Drug Agency, Forensic Chemistry Center

2:40 (99) **Quantitation of Abrine, an Indole Alkaloid Marker of the Toxic Glycoproteins Abrin, by LC/MS/MS from Various Beverages**; Janel Owens[1]; [1]Lawrence Livermore National Laboratory

3:00 (100) **Multiplexed Detection of Foodborne Pathogenic Bacteria on SERS Based Immunomicrowell-arrays**; Jian Sun[1], Mikella Hankus[1]; [1]University of Maryland Baltimore County

3:20 (101) **Spectroscopic Imaging for Detection and Discrimination of Different E. Coli Strains**; Michael Gilbert[1], Caleb Frick[1], Andrew Wodowski[1], Frank Vogt[1]; [1]University of Tennessee

3:40 (102) **Extraction of Oxytetracycline and Oxolinic Acid from Food for Fish and its Determination by Derivative Spectrophotometry**; María Inés Toral[1], Sandra Orellana[1], Pablo Richter[2]; [1]University of Chile; [2]University of Chile

Monday Afternoon, Room Nevada 4
MICROPLASMAS FOR LIFE
Organizer and Presider: Akbar Montaser

2:00 (103) **Modeling and Diagnostics of Microplasmas in ExB Fields**; Akbar Montaser[2], Michael Keidar[1], A. Shashurin[1], Maryam Farmand[2]; [1]The George Washington University, Mechanical and Aerospace Engineering; [2]The George Washington University, Department of Chemistry

2:40 (104) **Generation and Applications of Micro Inductively Coupled Plasma Sources**; Mazdak Taghioskoui[1,2], Mona Zaghloul[2], Akbar Montaser[1]; [1]The George Washington University Department of Chemistry; [2]The George Washington University Department of Electrical Engineering

3:00 (105) **Micro Discharges for Science and Engineering**; Yogesh Gianchandani[1]; [1]University of Michigan

3:40 (106) **A Novel Low-Flow Inductively Coupled Plasma Source for Elemental Analysis: Study of Its Fundamental Properties**; Carsten Engelhard[1], George C.-Y. Chan[1], Gerardo Gamez[0], Andy Scheffer[3], Wolfgang Buscher[3], Gary M. Hieftje[1]; [1]Indiana University; [2]Swiss Federal Institute of Technology; [3]University of Muenster

Monday Afternoon, Room Nevada 5
CONTROLLING NANOSTRUCTURES WITH ATOMIC PRECISION: THE ULTIMATE OF NANOCHEMISTRY
Organizer and Presider: Rongchao Jin

2:00 (107) **Chalcogenide Tetrahedral Clusters and their Superlattices**; Pingyun Feng[1]; [1]University of California-Riverside

2:20 (108) **Electron-Electron and Electron-Hole Interactions in Small Metallic Crystallites: The Size-Dependence of the Lowest Optically Excited Electronic States**; Robert Whetten; [1]Georgia Tech

2:40 (109) **Ligand-Protected Gold Clusters – Synthesis, Structures, and Stabilities**; Tatsuya Tsukuda[1,2]; [1]Catalysis Research Center, Hokkaido University; [2]CREST, Japan Science and Technology

3:00 (110) **Metal, Alloy and Core-Shell Nanoparticles and Assemblies for Catalytic and Sensing Applications**; Chuan-Jian Zhong; [1]State University of New York at Binghamton

3:20 (111) **TDDFT Studies of Optical Properties of Silver and Gold Nanoparticles**; Christine Aikens; [1]Kansas State University

3:40 (112) **Development of Hybrid Nanoporous Membranes by Assembling Mesostructured Silica in a Porous Alumina membrane**; Akira Yamaguchi[1], Norio Teramae[1]; [1]Tohoku University

Monday Afternoon, Room Nevada 6
FUNDAMENTALS OF MALDI MASS SPECTROMETRY
Organizer and Presider: Martha M. Vestling

2:00 (113) **Approaches to Post-Translational Modification Analysis using MALDI Tandem Time-of-Flight Mass Spectrometry**; Robert J Cotter; [1]Johns Hopkins University School of Medicine

2:40 (114) **Sample Preparation: Clues to Understanding MALDI Mass Spectrometry**; Martha M. Vestling[1]; [1]University of Wisconsin

3:00 (115) **Substrate Influence on Peptide/Protein MALDI Ion Signals**; Gary Kinsel[1], Lijuan Peng[1]; [1]Southern IL Univ Carbondale

3:20 (116) **Hydrophobic Protein Mixtures Analyzed by MALDI-MS**; Rachel Ogorzalek Loo[1], Jonathan Erde[1], Joseph Loo[1]; [1]UCLA

3:40 (117) **Reactive-Electrospray-Assisted Laser Desorption Ionization (Reactive-ELDI) for Characterization of Peptides and Proteins**; Ivory Peng[1], Rachel Loo[1], Jentaie Shiea[2], Joseph Loo[1]; [1]University of California, Los Angeles; [2]National Sun Yat-Sen University

Monday Afternoon, Room Nevada 7
ARCHAEOMETRY: ANALYTICAL MEASUREMENTS ON ARCHAEOLOGICAL SAMPLES
Organizer and Presider: Mary Kate Donais

2:00 (118) **Raman Microscopy, Pigments, and Interfaces with Art and Archaeology**; Robin Clark[1]; [1]University College London

2:40 (119) **Tracing the Past: Application of LA-ICP-MS for the Assessment of Potential Exposure to Arsenic in Ancient Chinchorro Mummies.**; Dula Amarasiriwardena[1], Sam Byrne[1], Basel Bandak[1], Jennifer Kane[1], Joseph Jones[1], Jorge Yanez[2], Bernardo Arriaza[3,4], Lorena Cornejo[3,4]; [1]Hampshire College, Amherst, USA; [2]Universidad de Concepción, Chile; [3]Universidad de Tarapacá, Arica, Chile; [4]Instituto de Alta Investigación, Chile

3:00 (120) **Micro-Structural Characterization of Archaeological Materials: the Importance of Understanding Scale of Heterogeneity for Analyses of Provenance, Performance and Post-Depositional Alteration**; John Dudgeon[1]; [1]Idaho State University/CAMAS

3:20 (121) **Geochemical Evidence of Ancient Maya Marketplace Activities**; Richard Terry[1], Daniel Bair[1]; [1]Brigham Young University

3:40 (122) **Investigations of Metals in Drainage System Deposit and Lead Pipe in Castel Viscardo**; Mary Kate Donais, Cindy Lebel, Katherine Thibodeau; [1]Saint Anselm College

Monday Afternoon, Room Nevada 8
ADVANCES IN ANALYTICAL TECHNIQUES FOR PETROLEUM INDUSTRY
Organzier and Presider: Wei-Chuan Shih

2:00 (123) **Downhole Fluid Analysis – The Key to Unraveling Reservoir Complexities**; Oliver Mullins; [1]Schlumberger-Doll Research

2:20 (124) **Petroleum Compositional Information Revealed by High Resolution FT-ICR Mass Spectrometry**; Amy M. McKenna[1], Brandie M. Ehrmann[1], Priyanka Juyal[2], Ryan P. Rodgers[1,2], Jeremiah M. Purcell[2], Tanner M. Schaub[2], Alan G. Marshall[1,2]; [1]Department of Chemistry & Biochemistry, FSU; [2]National High Magnetic Field Laboratory

2:40 (125) **Advances in Petroleum Analysis via Comprehensive Two-Dimensional Gas Chromatography**; Christopher Reddy[1], G. Todd Ventura[1], Robert Nelson[1], Soraya Betancourt[2], Gordon Lambertus[2], Oliver Mullins[2], Andrew Pomerantz[2], Bhavani Raghuraman[2]; [1]Woods Hole Oceanographic Institution; [2]Schlumberger-Doll Research

3:00 (126) **Application of FTIR Spectroscopic Imaging to Asphaltenes**; Sergei Kazarian, Feng Tay; [1]Imperial College London

3:20 (127) **Determination of H2S in Natural Gas and other Hydrocarbons by Differential Mobility Spectroscopy**; Eric Kirleis[1], Quan Shi[1]; [1]Sionex Corporation

3:40 (128) **Oil Spill Detection using a Plurality of Spectral Bands**; Wei-Chuan Shih[1], A. Ballard Andrews[1]; [1]Schlumberger-Doll Research

Monday Afternoon, Room Nevada 9
DEVELOPMENTS IN RAMAN SPECTROSCOPY, sponsored by the Society for Applied Spectroscopy
Organizers: Pavel Matousek and Ian R. Lewis;
Presider: Ian R. Lewis

2:00 (129) **Low Frequency Multi-Channel Raman Spectroscopy with an Iodine Vapor Filter**; Hajime Okajima[1], Hiro-o Hamaguchi[1]; [1]School of Science, The University of Tokyo

2:40 (130) **Development of Validated Raman Spectral Libraries using NIST Relative Intensity Correction Standards**; Steven Choquette[1], Aaron Urbas[1], Bruce Benner[1], Michele Schantz[1]; [1]NIST

2:40 (131) **Characterization of Variability in Raman Measurements from Tissues**; Anita Mahadevan-Jansen[1], Elizabeth Kanter[1], Elizabeth Vargis[1], Nicole Gasparino[1], Jennifer Whisenant[1], Mattheus Grimbergen[2], Nicholas Stone[3]; [1]Vanderbilt University, Nashville, TN; [2]University of Utrecht, The Netherlands; [3]Gloucestershire Hospital, United Kingdom

3:00 (132) ***in-vivo* Confocal Raman Spectroscopy: Studying the Effectiveness of Penetration Enhancers to Deliver Retinol through the skin**; Paul Pudney[1], Mickael Mélot[1], Guoping Lian[1], Ann-Marie Williamson[1], Peter Caspers[2], Andre Van Der Pol[2], Gerwin Puppels[2]; [1]Unilever Research; [2]River Diagnostics

3:20 (133) **Image Size Distortions: The Influence of Out of Focus Light on Raman Mapping**; Neil Everall; [1]Intertek MSG

3:40 (134) **Picosecond Raman Spectroscopy for Depth Analysis of Diffusely Scattering Samples: Temporal and Spatial Resolution**; Freek Ariese[1], Heleen Meuzelaar[1], Joost B. Buijs[1], Cees Gooijer[1]; [1]Laser Centre Vrije Universiteit Amsterdam

Monday Afternoon, Room Nevada 10
A SPECTROMETER IN THE HAND IS WORTH TWO IN THE LAB
Organizer and Presider: Richard Crocombe

2:00 (135) **A Rugged High-performance FTIR System in a Handheld Package**; Christopher D. Brown[1]; [1]Ahura Scientific

2:20 (136) **Screeing Consumer Products for Toxic Elements with a Portable XRF Analyzer**; Kenneth Stehr[1]; [1]Thermo Fisher Scientific, NITON Analyzers

2:40 (137) **Bringing the Instrument to the Sample: Use of a Miniature Hand Held FTIR Spectrometer for *in-situ* Sample Measurement**; John Seelenbinder[1]; [1]A2 Technologies

3:00 (138) **Enabling Technologies for Handheld Optical Spectroscopy**; Jouko Malinen[1], Ralf Marbach[1], Mauri Aikio[1], Heimo Keränen[1], Heikki Saari[1], Antti Lamminpää[1]; [1]VTT Technical Research Centre of Finland

3:20 (139) **Compact Liquid Crystal Waveguide Based Fourier Transform Spectrometer for *in-situ* and Remote Gas and Chemical Sensing**; Scott Davis[1], Scott Rommel[1], George Farca[1], Alan Martin[1], Ben Luey[1], Michael Anderson[1], Tien-Hsin Chao[2], Thomas Lu[2]; [1]Vescent Photonics Inc.; [2]Jet Propulsion Laboratory

3:40 (140) **NIR Spectrometers in the Field: Design Considerations for Practical Applications**; Mark Gunning[1], Graham Poulter[1], Forrest Imhoff[2], Dave Coombs[1]; [1]Specac Ltd; [2]Specac Inc

4:00 PM Plenary Lecture, S 2/3

His 40 Years of Contributions to Atomic Spectroscopy and Analytical Chemistry**. Gary Hieftje**, *Indiana University*

TECHNICAL PROGRAM – TUESDAY
Plenary Sessions, Presider: Curt Marcott

Charles Mann Award
8:00 AM Plenary Session, S2/3

Ian R. Lewis
(141) **Shift Happens: Developments in Raman Sampling**
Ian R. Lewis; Kaiser Optical Systems
Refer to page 13 for biographical information

ANACHEM Award
8:30 Plenary Session, S2/3

Scott McLuckey
(142) **Gas-Phase Bio-Ion Reactions and Bioanalysis**
Scott McLuckey; Purdue University
Refer to page 13 for biographical information.

TUESDAY POSTER SESSIONS
9:00 – 10:15 am and 1:30 – 3:00 pm
Exhibit Hall S1

All Tuesday posters should be put up between 7:30 – 8:00 AM and removed between 5:00 – 6:00 PM. The odd numbered poster boards present in the morning and the even numbered poster boards present in the afternoon.

Gary Hieftje Symposia – Invited Posters

Board #

1 (143) **Characterization of an Inductively Coupled Plasma/Electrospray Dual-Source Time-of-Flight Mass Spectrometer for Comprehensive Chemical Speciation**; Duane Rogers[1], Steven Ray[1], Gary Hieftje[1]; [1]Indiana University

2 (144) **Electrode Comparison for Use with Electrochemically Modulated Separations for ICP-MS**; Scott Lehn[1], Martin Liezers[1], Shane Peper[1], Doug Duckworth[1]; [1]Pacific Northwest National Laboratory

3 (145) **Fiber-Optic Chemical Sensing using Cavity Ring-Down Principles**; Jacob Shelley[1], Carsten Engelhard[1], Radislav Potyrailo[2], Gary Hieftje[1]; [1]Indiana University; [2]General Electric Global Research Center

4 (146) **Comparison of Atmospheric-Pressure DC Plasma Sources Used in Ambient Mass Spectrometry**; Joshua Wiley[1], Jacob Shelley[1], Steven Ray[1], Gary Hieftje[1]; [1]Indiana University

5 (147) **Imaging of Proteins on Gel Electropherograms via Radio Frequency Glow Discharge Optical Emission Spectrometry**; Carsten Engelhard[1], Steven J. Ray[1], Gerardo Gamez[1,2], Gary M. Hieftje[1]; [1]Indiana University; [2]Swiss Federal Institute of Technology

6 (148) **Improvement of Isotope Ratio Measurements with an Inductively Coupled Plasma Mattauch-Herzog Mass Spectrograph Equipped with Faraday-Strip Array Detection**; Gregory Schilling[1], Steven Ray[1], Roger Sperline[2], M. Bonner Denton[2], Charles Barinaga[3], David Koppenaal[3], Gary Hieftje[1]; [1]Indiana University; [2]University of Arizona; [3]Pacific Northwest National Laboratory

7 (149) **Analysis of Environmental Samples with Inductively Coupled Plasma-Atomic Emission Spectrometry**; William C. Wetzel[1], Erica C. Goetz[1], Adam W. Reis[1], Corinne E. Weinel[1]; [1]Thomas More College

8 (150) **Integrated Sensing and Processing-Acoustic Resonance Spectroscopy (ISP-ARS) for Rapid Tablet Identification**; David Link[1], Thaddaeus Hannel[1], Robert Lodder[1]; [1]University of Kentucky

9 (151) **Surreptitious Remote Sensing of Blood Alcohol Content: Molecular Factor Computing (MFC) Near-Infrared Spectroscopic (NIRS) Imaging and Laser Speech Detection**; Thaddaeus Hannel[1], David Link[1], Robert Lodder[1]; [1]University of Kentucky

10 (152) **Fundamental Ion Diagnostics in Pulsed Glow Discharge Plasmas**; James Barnes[1], Cris Lewis[1], Megan Dejesus[2], Adam Zocco[3]; [1]Los Alamos National Laboratory; [2]West Virginia University; [3]New Mexico State University

11 (153) **Use of a Flowing Atmospheric-Pressure Afterglow Ionization Source for Sensitive Detection of Fast Transient Signals**; Jacob Shelley[1], Steven Ray[1], Gary Hieftje[1]; [1]Indiana University

12 (154) **Spectroscopic Imaging Microscope**; Michael R. Webb[1], Christopher N. LaFratta[1], David R. Walt[1]; [1]Department of Chemistry, Tufts University

13 (155) **Precise Element Ratios from Noisy Laser Ablation ICP- MS Signals: can Collision/Reaction Cells Help?**; Patrick Gray[1], Susan Olesik[1], John Olesik[1]; [1]The Ohio State University

14 (156) **Spectroscopic Investigation of Hydrophobic Silica Aerogels**; Mary Carroll[1], Christopher Backlund[1], Emily Green[1], Ann Anderson[1]; [1]Union College

15 (157) **Plasma Cavity Ring-Down Spectroscopy for Elemental, Isotope, and Hyperfine Structure Measurement**; Yixiang Duan[1,2,3], Chuji Wang[2], Christopher B. Winstead[3]; [1]Los Alamos National Laboratory; [2]Mississippi State University; [3]University of Southern Mississippi

16 (158) **Real-Time Monitoring of Valproic Acid Intake via Extractive Electrospray Ionization Mass Spectrometry of Exhaled Breath**; Gerardo Gamez[1], Liang Zhu[1], Konstantin Chingin[1], HuanWen Chen[2], Renato Zenobi[1]; [1]ETH Zurich, Zurich, Switzerland; [2]College of Chemistry, Jilin University

17 (159) **Characterization of Nanoscale Vapor Barrier Glass Coatings on Polymer Substrates by Ellipsometry**; Richard Savage[1], Daniel Helms[1], John Felts[2]; [1]Cal Poly State Univesity; [2]Nano Scale Surface Systems

TECHNICAL PROGRAM – TUESDAY
Posters 9:00 – 10:15 and 1:30 – 3:00 PM

Atomic Spectroscopy

Board #

18 (160) **Optimization of a Method to Determinate Metals in Petroleum Products by Direct Injection using ICP-OES**; Mariano Cipollone[1], Fabián Sein[1], Rodolfo Durán[1], María Bernarda Epele[1], María Luján Collivadino[1]; [1]CTA, RepsolYPF

19 (161) **Supersonic Jet Spectroscopic Analysis with Desorption Sample Introduction**; Taylor Cline[1], Amber Johnstone-Gygi[1]; [1]Brigham Young University

20 (162) **Development of Droplet Direct Injection Free-Runnin ICP for Nano, Pico-Liter Analysis**; Taichi Meguro[1], Etsuo Yamagishi[2], Hidekazu Miyahara[1], Naoki Nakashima[1], Eiki Hotta[1], Ryuichi Shimada[1], Akitoshi Okino[1]; [1]Tokyo Institute of Technology; [2]Pearl Kogyo Co., Ltd.

21 (163) **Inductively Coupled Plasma Atomic Emission Spectrometry as a Detection Technique for Liquid Chromatography**; Jose L. Todoli[1], Eduardo Paredes[1], Salvador Maestre[1], Soledad Prats[1]; [1]University of Alicante

Bioanalytical

22 (164) **Direct Chemiluminescent Imaging Detection of Low-Abundant Proteins in Serum by PAGE using Metal Tags**; Jin Ouyang[1], Willy Baeyens[2]; [1]College of Chemistry Beijing Normal University; [2]Ghent University

23 (165) **A Comparison of Efficient Methods (Microwave, Pressure) for Digestion of Therapeutic Proteins**; Lorna Maheu[1], Adam Harder[1], Heather Connelly[1], Steven Cockrill[1]; [1]Amgen

Chemometrics

24 (166) **PyChem: Software for Statistical and Multivariate Analysis**; Roger Jarvis[1], Royston Goodacre[1]; [1]The University of Manchester

Environmental

25 (168) **Identification and Quantification**; Zainab Al-Ballam; [1]Kuwait Institue foe Scientific Research

26 (169) **Low-level Mercury Determination in Wastewater Effluent Using CVAFS**; Maggie Day[1], Jeff Forsberg[1]; [1]CETAC Technologies

Forensics

27 (170) **Detection of Gunshot Residue from Decomposing Tissue Samples and Blowfly Larvae using ICP-MS**; Ruth Waddell Smith[1], Lisa LaGoo[1], David W. Szymanski[1], Brian C. Hunter[2]; [1]Michigan State University; [2]Hurley Medical Center Laboratory

28 (171) **MatLab Simulations for Infrared Visualization of Blood Stains on Fabrics Based on Sensitized Thermal Detectors**; Heather Brooke[1], Megan Baranowski[1], Jessica McCutcheon[1], Anthony Trimboli[1], Stephen Morgan[1], Michael Myrick[1]; [1]University of South Carolina

29 (172) **Validation Experiments for Infrared Visualization of Blood Stains on Fabrics Based on Sensitized Thermal Detectors**; Megan Baranowski[1], Heather Brooke[1], Jessica McCutcheon[1], Anthony Trimboli[1], Stephen Morgan[1], Michael Myrick[1]; [1]University of South Carolina

30 (173) **Human Breath Analysis for the Detection of Chemical Exposure and Pernicious Activity**; Audrey Martin[1,2], George Farquar[1], A. Daniel Jones[2], Matthias Frank[1]; [1]Lawrence Livermore National Laboratory; [2]Michigan State University

31 (174) **Automated Sample Treatment and Fluorescence Derivatization by Sequential Injection for the Determination of Amphetamines in Biological Fluids by Capillary Electrophoresis**; Ahmed O. Alnajjar[1]; [1]King Faisal University

32 (175) **Important Variables in the Classification of OTC Drugs by FTIR/ATR Spectra and Principal Component Analysis.**; Huggins Msimanga; [1]Kennesaw State University

Mass Spectrometry

33 (176) **Inactivation of Microbial Cells and Spores for MALDI-TOF Mass Spectrometry**; Peter Lasch[1], Herbert Nattermann[2], Maren Stämmler[1], Marcel Erhard[3], Roland Grunow[2], Bern Appel[2], Dieter Naumann[1]; [1]Robert Koch-Institut, P25; [2]Robert Koch-Institut, ZBS2; [3]AnagnosTec GmbH

Molecular Spectroscopy

34 (177) **Calibration-Free Quantitative Application of *in-situ* Raman Spectroscopy**; Jeroen Cornel[1], Marco Mazzotti[1]; [1]Institute of Process Engineering, ETH Zurich

35 (178) **Crossed Beam Thermal Lens Spectroscopy for Standoff Detection of Chemical Species**; Tasha Messenger; [1]University of Maryland Baltimore County

36 (179) **Solvent Diffusion Studies through Polymer Membranes by Time Resolved FT-IR/ATR**; James Sloan[1]; [1]U.S. Army Research Laboratory

37 (180) **Looking at Lipid Domains in Stratum Corneum Lipid Models using Vibrational Microspectroscopy**; Michel Lafleur[1], Sungjong Kwak[1], Aicha Ouakrim[1], Amine Touggant[1]; [1]Université de Montréal

38 (181) **Instrument Selection Criteria for Near-Infrared Process Monitoring – Guidelines and Applications**; Roger Schirmer[1], Susan Foulk[1]; [1]Guided Wave, Inc.

39 (182) **Determining Out-Of-Spec (OOS) Conditions with Fieldable FTIR and Raman Spectroscopy**; Robert Brush[1], Robert Green[1], Jeremy Linoski[1], Wayne Jalenak[1], Christopher Brown[1]; [1]Ahura Scientific, Inc.

40 (183) **Applications of a Handheld FT-IR Spectrometer to the Study of Museum Objects;** Steven M. Barnett[1]; Aniko Bezur[2]; [1]A2 Technologies, [2]The Museum of Fine Arts, Houston

41 (184) **Studies of Lead(II) Halide-1,10-Phenanthroline Photosensitive Materials by FT-IR**; Dale L. Perry[1], Cecil R. Dybowski[2], Shi Bai[2], David Kragsten[2], Margaret J. Blake[1], Santiago Segarra[1], Dale L. Perry[1]; [1]Lawrence Berkeley National Laboratory; [2]University of Delaware

42 (185) **Detection of Polymorphs in CL-20 using Infrared and Raman Spectroscopy**; Kathleen Alam, Laura Martin, Thomas Massis, Rachel Carlson; [1]Sandia National Laboratories

43 (186) **Synchrotron Infrared Microspectroscopy of Individual Strands or Cells in Mat Formation of Benthic Algae from Freshwater, Pristine Prairie Source**; Jason Murdock[1], John Reffner[2], David Wetzel[2]; [1]Kansas State University, Biology Division; [2]KSU Microbeam Molecular Spectroscopy Lab

44 (187) **Large Area FT-IR Imaging at High Spatial Resolution - How Differing Levels of Spatial Resolution Can Influence Interpretation**; Frank Weston[1], Jim Steensrud[1], Mustafa Kansiz[1]; [1]Varian, Inc

45 (188) **IR Approaches for Quantitatively Measuring Silanol in Silicones**; Elmer Lipp[1]; [1]Analytical Sciences Dept., Dow Corning Corp.

TECHNICAL PROGRAM – TUESDAY
Posters 9:00 – 10:15 and 1:30 – 3:00 PM and Orals 10:15 AM – 12:15 PM

Nanoscience

Board #

46 (189) **Moisture Migration and Intermolecular Relationships in Carbohydrate Films**; Janiece Hope[1], Allen Muroski[1], Doug Elmore[1], Sean Smith[1], Justin Kruger[1]; [1]Cargill, Inc.

47 (190) **Nanomaterials: Computational and Chemometrics Methods towards "Nanotoxicology"**; Bakhtiyor Rasulev[1], Danuta Leszczynska[2], Jerzy Leszczynski[1]; [1]CCMSI, Jackson State University; [2]Civil&Environ Engineering, JSU, Jackson

48 (191) **Characterization of Self-Forming Nanovesicles by Vibrational Spectroscopic Techniques**; Reinhard Bruch[1], Rajan Bista[1], Emilie Steinhoff[1], Thomas Huser[2]; [1]University of Nevada, Reno; [2]University of California, Davis

49 (192) **Metal-Ion Binding Properties of Phosphoserine Immobilized on Magnetic Nanoparticles**; Anselm Omoike; [1]University of Michigan-Flint

Raman

50 (193) **Assessment of Accuracy for Non-invasive Bone Raman Spectroscopy in Mice**; Kathryn A. Dooley[1], Matthew V. Schulmerich[1], Jacqueline H. Cole[1], Jaclynn M. Kreider[2], Steven A. Goldstein[2], Michael D. Morris[1]; [1]Chemistry, U. Michigan; [2]Orthopaedic Surgery, U. Michigan

51 (194) **Applications of Micro-Raman spectroscopy for Detection of Cancer and Viruses**; Lori Kamemoto[1,2], Shiv Sharma[1], Anupam Misra[1], Qigui Yu[2], Ningjie Hu[2], Hugh Luk[3], Marc Goodman[3], Pavel Zinin[1]; [1]Hawaii Inst. of Geophysics & Planetology; [2]John A. Burns School of Medicine; [3]Cancer Research Center of Hawaii

Tuesday Morning, Room Nevada 2
ANACHEM AWARD SESSION HONORING SCOTT MCLUCKEY
Organizer and Presider: Patsy Coleman

10:15 (195) **Atmospheric Pressure Surface Sampling and Ionization**; Gary Van Berkel; [1]Oak Ridge National Laboratory

10:35 (196) **The Role of Human Salivary Defensin Peptides in Response to Vaccination**; James Stephenson[1], Michael Gardner[1], Megan Rowland[1], Jonathan Bundy[1]; [1]Research Triangle Institute

10:55 (197) **Mass Spectrometry Strategies to Identify Lipid Biomarkers of Disease**; Gavin Reid[1], Todd Lydic[1], Xi Zhang[1], Rheal Towner[2], Julia Busik[1]; [1]Michigan State University; [2]Oklahoma Medical Research Foundation

11:15 (198) **Peptide Fragmentation Assisted by Low Temperature Plasma**; Yu Xia[1], Zheng Ouyang[2], R. Graham Cooks[1]; [1]Department of Chemistry, Purdue University; [2]Weldon School of Biomedical Engineering

11:35 (199) **Towards Nanoscale Chemical Imaging: Investigation of Near-Field Optical Processes for Use in Atmospheric Pressure Desorption/Ionization Mass Spectrometry**; Douglas Goeringer[1], Kent Meyer[1], Olga Ovchinnikova[1], Kin Ng[2]; [1]Oak Ridge National Laboratory; [2]California State University Fresno

11:55 (200) **Space Charge Effects and Ion Motion Control in the Orbitrap Mass Analyzer**; Richard H. Perry[1], Gary A. Salazar[1], Robert J. Noll[1], Wolfgang Plass[2], R. Graham Cooks[1]; [1]Purdue University; [2]II.Physikalisches Institut

Tuesday Morning, Room Nevada 3
BIOANALYTICAL – RAMAN
Organizer and Presider: Jerilyn Timlin

10:15 (201) ***In Situ* Quantitative Evaluation of Saturation vs. Unsaturation in Biodiesel Production**; Dale LeCaptain[1], David Allan[1], Michael Todd[1], Doug Hasso[1]; [1]Central Michigan University

10:35 (202) **Raman Spectroscopic Analysis of Warrior Wound Biopsies: What Happens When Good Wounds Go Bad?**; N. J. Crane[1], T. S. Brown[1], J. S. Hawksworth[1], F. A. Gage[2], D. Tadaki[2,3], P. W. Perdue[2], J. R. Dunne[2], J. W. DeNobile[2], E. A. Elster[2,3]; [1]Naval Medical Research Ctr.; [2]Naval Medical Research Ctr.; [3]Uniformed Services Univ. of Health Science

10:55 (203) **Raman Spectroscopy, a New Tool for Early Diagnosis of Osteoarthritis**; Karen A. Esmonde-White[1], Gurjit S. Mandair[2], Farhang Raaii[4], Francis W.L. Esmonde-White[2], Blake J. Roessler[3], Michael D. Morris[2]; [1]University of Michigan, Biomedical Engineering; [2]University of Michigan, Chemistry; [3]Univ. Mich. Medical School, Rheumatology; [4]Wayne State Univ., Orthopedic Surgery

11:15 (204) **Development of Raman-Based Techniques for Biomedical Spectroscopy and Imaging**; James Chan[1,2]; [1]Lawrence Livermore National Laboratory; [2]NSF Center for Biophotonics, UC Davis

11:35 (205) **Spatially Offset Raman Spectroscopy for Depth-sensitive Measurements in Excised Breast Tissues**; Matthew Keller[1], Anita Mahadevan-Jansen[1]; [1]Vanderbilt University

11:55 (206) **Correlating Cell Biochemistry and Fungal Lifestyle using FTIR, Raman and SERS Spectroscopy**; Kathleen M. Gough[1], Rusty J. Rodriguez[2,3], Regina S. Redman[2], Susan G.W. Kaminskyj[4], Merrill Isenor[1]; [1]Univeristy of Manitoba; [2]University of Washington; [3]US Geological Survey; [4]University of Saskatchewan

Tuesday Morning, Rooom Nevada 4
FORENSIC ANALYTICAL CHEMISTRY APPLICATIONS OF CHEMOMETRICS
Organizer and Presider: Stephen L. Morgan

10:15 (207) **Chemometric Analysis as a Means to Differentiate Class Evidence**; John Goodpaster; [1]IUPUI

10:35 (208) **Chemometric Analysis of LIBS Data: Identification of Explosives**; Candice Bridge[1], Michael Sigman[1], Martin Richardson[1]; [1]University of Central Florida

10:55 (209) **Comparison of Differential Mobility Spectrometry and Mass Spectrometry for Gas Chromatography and Two-way Classification of Ignitable Liquids from Fire Debris**; Yao Lu[1], Peter Harrington[1]; [1]OHIO University

11:15 (210) **Performance Evaluation of a Sensitized Thermal Detector for Infrared Forensic Visualization of Blood Stains on Fabrics using Chemometrics-Driven Simulations**; Heather Brooke[1], Megan Baranowski[1], Jessica N. McCutcheon[1], Anthony R. Trimboli[1], Stephen L. Morgan[1], Michael L. Myrick[1]; [1]University of South Carolina

11:35 (211) **Forensic Applications of Multivariate Statistical Methods for Discrimination of Trace Evidence**; Stephen L. Morgan[1]; [1]University of South Carolia

11:55 (212) **Evaluation of Chemometric Approaches for the Analysis of Textile Fibers via Room-Temperature Fluorescence Excitation-Emission Matrices**; Krishna veni Appalaneni[1], Matthew Rex[1], Hector Goicoechea[2], Andres Campiglia[1]; [1]University of Central Florida; [2]Universidad Nacional del Litoral

Tuesday Morning, Room Nevada 5
SPECTROSCOPY AND NANOMATERIALS
Organizer and Presider: Yat Li

10:15 (213) **Novel Hollow Gold Nanospheres: Synthesis, Structure, Plasmon Absorption, SERS, and Photothermal Cancer Therapy**; Jin Zhang[1], Adam Schwartzberg[1], Tammy Olson[1], Chun Li[2]; [1]UC Santa Cruz; [2]UT M. D. Anderson Cancer Center

10:35 (214) **Two Novel Nanoscale Phenomena**; Ting Guo[1]; [1]University of California, Davis

10:55 (215) **Multilayered Nanospheres As Scattering Probes with Multiple Resonances**; Anil Kodali[1], Rohit Bhargava[1]; [1]University of Illinois

11:15 (216) **Gold and Silver Nanocrescents with Infrared Plasmonic Properties as Tunable Substrates for Surface Enhanced Infrared Absorption Spectroscopy**; Jennifer Shumaker-Parry[1], Rostislav Bukasov[1]; [1]University of Utah

11:35 (217) **Tailoring Gold Nanorods for Laser Desorption/Ionization Mass Spectrometry**; Edward Castellana[1], David Russell[1]; [1]Texas A&M University

11:55 (218) **Raman Studies of CuInS2Nanoparticles**; Lisa Lau, Rene Rodriguez, Joshua Pak, Dennis Strommen; [1]Idaho State University, Dept. of Chemistry

Tuesday Morning, Room Nevada 6
QUANTITATIVE MASS SPECTROMETRY I: PEPTIDES AND PROTEINS
Organizer and Presider:: Christoph Borchers

10:15 (219) **Nano-LC/MS/MS for MRM Quantitation of Peptides**; Christine Miller[1], Ning Tang[1], Ben Collins[2], Thomas Lau[2], Stephen Pennington[2]; [1]Agilent Technologies, Inc.; [2]University College Dublin

10:35 (220) **A Cocktail of Isotopically Labeled Peptide Standards for MRM Based Quantitation of 45 Human Plasma Proteins**; Michael A. Kuzyk[1], Derek Smith[1], Tyra Cross[1], Juncong Yang[1], Angela Jackson[1], Darryl Hardie[1], N. Leigh Anderson[2], Christoph H. Borchers[1]; [1]University of Victoria, Victoria, BC; [2]Plasma Proteome Institute, Washington DC

10:55 (221) **Driving Biological Discovery using Quantitative Mass Spectrometry**; Johns Yates[1]; [1]The Scripps Research Institute

11:15 (222) **Quantitative Proteomics using 18O Labeling**; Catherine Fenselau[1]; [1]University of Maryland

11:35 (223) **Differential Proteome Analysis using Targeted Label-Free Workflows**; A. Kettani[1], W. Jabs[1], M. Lubeck[1], M. Behrens[1], D. C. Chamrad[2], K. Marquart[2], M. Blueggei[2], B. Sitek[3], B. Korte[3], S. Link[3], C. Stephan[3], K. Stühler[3], H. E. Meyer[3], C. Baessmann[1]; [1]Bruker Daltonik GmbH; [2]Protagen AG; [3]Medizinisches Proteom-Center

11:55 (224) **iMALDI for MS-Based Quantitative Proteomics Intended for Clinical Use**; Christoph Borchers[1]; [1]University of Victoria Genome BC Proteomics Centre

12:15 (225) **Proteomics Approaches for Characterizing Microbial Proteomes**; Nathan VerBerkmoes; [1]Oak Ridge National Lab

Tuesday Morning, Room Nevada 7
40 YEARS OF ATOMIC SPECTROSCOPY INNOVATION: A TRIBUTE TO GARY HIEFTJE,
sponsored by the Society for Applied Spectroscopy
Organizer and Presider: John W. Olesik

10:15 (226) **Gary Martin Hieftje: Four Decades of Innovation and Excellence in Analytical Chemistry**; Gary Horlick[1]; [1]Department of Chemistry, University of Alberta

10:35 (227) **Analytical Laser Spectroscopy - An Amazing Journey**; Rick Russo; [1]Lawrence Berkeley National Lab

10:55 (228) **Near Surface Depth Profile Analysis**; Kim Marshall[1], Charles Maul[1], Diane Goodman[1]; [1]LECO Corporation

11:15 (229) **Mapping Argon Metastable Atoms in an ICP-MS using Absorption Depletion Imaging**; Paul Farnsworth[1], Nicholas Taylor[1], Haibin Ma[1]; [1]Brigham Young University

11:35 (230) **Mechanistic Study of Analyte Excitation and Matrix Effects in Inductively Coupled Plasma-Atomic Emission Spectrometry**; George Chan[1], Gary Hieftje[1]; [1]Indiana University, Dept. of Chemistry

11:55 (231) **Some Remaining Questions, Challenges and Potential Advances in ICP-OES and ICP-MS**; John Olesik[1], Patrick Gray[1], Josh Dettman[1], Elodie Linard[1], Anthony Lutton[1]; [1]The Ohio State University

Tuesday Morning, Room Nevada 8
INFRARED IMAGING
Organizer: Curt Marcot;t Presider: Heinz Siesler

10:15 (232) **FT-IR Imaging of Anisotropy by Polarized Radiation: A Novel Polymer Characterization Technique**; Heinz W. Siesler[1], Christian Vogel[1]; [1]University of Duisburg-Essen

10:35 (233) **Application of ATR/FT-IR Hyperspectral Imaging and Chemometrics for Studying the Distribution of Materials Sprayed on Heterogeneous Substrates**; Boiana Budevska; [1]DuPont Crop Protection

10:55 (234) **Imaging ATR Analysis in Non-Square Configurations**; Ellen Miseo[1], Jim Steensrud[1], Frank Weston[1]; [1]Varian, Inc

11:15 (235) **Processing Efficiency and Mass Balance via InSb Image Pixel Counting of Incoming Material and Product and By-Products**; David L. Wetzel[1], Elieser Posner[2], Hulya Dogan[1]; [1]Kansas State University; [2]Posner Grain Milling & Handling Consult

11:35 (236) **Robustness of Histological Recognition in Tissues using Fourier Transform Infrared Spectroscopic Imaging**; Rohith Reddy[1], Rohit Bhargava[1]; [1]University of Illinois at Urbana-Champaign

11:55 (237) **Determination of the Composition of Counterfeit Drugs by Near Infrared Chemical Imaging**; Marta Lopes[1], Jean-Claude Wolff[2], José Bioucas-Dias[1], Mário Figueiredo[1]; [1]Universidade Técnica de Lisboa; [2]GlaxoSmithKline

Tuesday Morning, Room Nevada 9
CHIRAL ANALYSIS USING VIBRATIONAL CIRCULAR DICHROISM (VCD)
Organizer and Presider: Don Pivonka

10:15 (238) **Vibrational Circular Dichroism: Evolution from Instrument Development to Biopolymer Applications. 35 years and Growing**; Tim Keiderling; [1]University of Illinois at Chicago

TECHNICAL PROGRAM – TUESDAY
Orals 10:15 AM – 12:15 PM and 3:00 – 5:00 PM

10:35 (239) **Chiral Analysis using Vibrational Circular Dichroism (VCD)**; Oliver McConnell[1], Yanan He[1]; [1]Wyeth Research

10:55 (240) **Chiral Vibrational Spectroscopy of Amino Acids, Peptides and Ligands**; Karl James Jalkanen; [1]Curtin University of Technology

11:15 (241) **Computational Aspects of VCD**; James Cheeseman[1]; [1]Gaussian, Inc.

11:35 (242) **Examples of 'Missing' Conformers in VCD Calculations, and Strategies for Finding Them**; Steven Wesolowski[1]; [1]AstraZeneca

11:55 (243) **Streamlining the VCD Computational Workflow from Conformer Selection to Structural Assignment**; Don Pivonka[1], Steve Wesolowski[1]; [1]AstraZeneca

Tuesday Morning, Room Nevada 10
ULTRAFAST VIBRATIONAL SPECTROSCOPY: CHEMISTRY, MATERIAL AND BIOLOGICAL SCIENCE
Organizer and Presider: Michael W. George

10:15 (244) **Using Ultrafast Time-resolved Near IR Spectroscopy to Probe Photocatalytic Reactions on TiO2**; Koichi Iwata[1]; [1]The University of Tokyo

10:35 (245) **Picosecond Time-Resolved Spectroscopic Studies of Phototriggers and Polyhalomethanes**; David Lee Phillips; [1]The University of Hong Kong

10:55 (246) **Excited State Photophysics and Photochemistry Probed by Femtosecond Spectroscopy**; Terry L. Gustafson[1], Jessica E. Donehue[1], Nicole M. Dickson[1], Jin Wang[1], Gotard T. Burdzinski[2], Jacek Kubicki[2], Christopher M. Hadad[1], Matthew S. Platz[1], [1]Department of Chemistry, The Ohio State University;[2] Adam Mickiewicz University, Poland

11:15 (247) **Time-resolved IR Measurements in Supercritical Fluids: Probing Alkane and Activation and the Role of the Solvent in Green Chemistry Applications**; Michael W. George[1]; [1]University of Nottingham

11:35 (248) **Monitoring Transition States c/ 2D-IR**; Charles Harris[1], James Cahoon[1], Karma Sawyer[1], Jacob Schlegel[1]; [1]Univ of California at Berkeley

11:55 (249) **Utilizing Two-Dimensional Infrared Spectroscopy in Pursuing an Understanding of Amyloid Aggregation**; David Strasfeld[1], Sang-Hee Shim[1], Yun Ling[1], Martin Zanni[1]; [1]University of Wisconsin

TuesdayAfternoon, S1 extension
"WHAT'S HOT" EXHIBITOR PRESENTATIONS
Organizer: Mike Carrabba; Presider: Brian Dable

12:20 **Spectra Analysis**, "Introducing a Novel LC-IR Spectrometer from Spectra Analysis, Inc., the 2008 R&D 100 Award Winning DiscovIR-LC System"

12:30 **Varian**, "The New 600 Series FTIR from Varian, Inc."

12:40 **Pike**, "Performance Characterizatio of a New Monolithic Diamond ATR for FTIR Spectroscopy"

12:50 **Ocean Optics**, "Jaz – a Community of Stackable, Modular and Autonomous Components that Combine to Create a Family of Smart Sensing Instruments"

1:00 **Thermo Scientific**, "Spectroscopy Simplified"

1:10 **HORIBA-Jobin Yvon**, "Low Cost Raman Microscopy – Taking the Gamble out of Vibrational Spectroscopy"

1:20 **Renishaw**, "TBD"

12:30 PM, Roundtable Discussion and Lunch for Students, sponsored by SABIC Innovative Plastics
Sierra 1/2 Mezzanine Level

TUESDAY AFTERNOON POSTER SESSION
Break and Dessert
1:30 – 3:00 PM
Exhibit Hall S1
Even numbered poster boards present.
See page 50 for a listing of the posters.

Tuesday Afternoon, Room Nevada 3
PHARMACEUTICAL FORENSICS
Organizer and Presider: Mark R. Witkowski

3:00 (250) **Pfizer Pforensics: Intriguing Example Case Studies of Non-Authentic Pharmaceuticals**; Amy Callanan[1]; [1]Pfizer, Inc.

3:20 (251) **Various On-Dosage Anti-Counterfeiting Technologies Which Can Facilitate Field and Forensic Authentication**; David Schoneker[1]; [1]Colorcon

3:40 (252) **Host-Guest Reactive Desorption Electrospray Ionization Mass Spectrometry (DESI-MS) for the Rapid and Quantitative Authentication of Tamiflu Capsules**; Facundo Fernandez[1], Leonard Nyadong[1], Michael Green[2]; [1]Georgia Institute of Technology; [2]CDC Atlanta

4:00 (253) **Analysis of Suspected Counterfeit Drugs: Supporting Prosecution and Enforcement**; Anthony Zook; [1]Merck & Co., Inc.

4:20 (254) **Immediate Field Analyses of Suspect Pharmaceutical Materials by Handheld Raman and FTIR: a Prescription for Action**; Christopher D. Brown[1], Robert C. Brush[1]; [1]Ahura Scientific

4:40 (255) **GC-MS and GC-IRD Studies on Regioisomeric and Isobaric Phenethylamines Related to 3,4-Methylenedioxymethamphetamine**; C. Randall Clark[1], Jack DeRuiter[1], Tamer Awad[1]; [1]Auburn University

Tuesday Afternoon, Room Nevada 4
SAMPLE INTRODUCTION: FROM A TO Z
Organizer and Presider: Akbar Montaser

3:00 (256) **Novel Aerosol Diagnostics for Nebulization Systems and High-Temperatures Plasmas**; William Bachalo; [1]Artium Technologies, Inc.

3:40 (257) **Comparison of Total Sample Consumption Systems for the Analysis of Microsamples through ICP-AES and ICP-MS**; José L. Todolí[1], Jean-Michel Mermet[2]; [1]University of Alicante; [2]Spectroscopy Forever, France

4:20 (258) **Novel Tool for Quantitation of Plant Genomic DNA**; Ryan Brennan[1,2], Savelas Rabb[2], Marcia Holden[3], Michael Winchester[2], Akbar Montaser[1]; [1]GWU Department of Chemistry; [2]NIST Analytical Chemistry Division; [3]NIST Biochemical Science Division

4:40 (259) **Nanoelectrospray and MALDI Combined with Ion Mobility-Mass Spectrometry: Structural Insights from Liquid and Solid Phases**; John A. McLean[1], Sundarapandian Sevugarajan[1], Michal Kliman[1]; [1]Department of Chemistry, Vanderbilt University

TECHNICAL PROGRAM – TUESDAY
Orals 3:00 – 5:00 PM

Tuesday Afternoon, Room Nevada 5
CHEMOMETRICS ALONG SPATIAL AND CHEMICAL DIMENSIONS
Organzier and Presider: Frederick Koehler

3:00 (260) **Enhancing the Tissue Segmentation Capability of Fast Infrared Spectroscopic Imaging via Chemometric Methods**; Rohit Bhargava[1], Frances Pounder[1], Rohith Reddy[1], Xavier Llora[1]; [1]University of Illinois at Urbana-Champaign

3:20 (261) **Kinetic Modeling of Hyperspectral Temporal Images**; Paul Gemperline[1], Patrick Cutler[1], David Haaland[2], Erik Andries[3]; [1]East Carooina University; [2]Sandia National Laboratories; [3]InLight Solutions

3:40 (262) **Modified Alternating Least-Squares as a Flexible Constraint Engine for Multispectral Dermoscopy Image Analysis**; Thomas Hancewicz[1], Jesse Weissman[1]; [1]Unilever R&D

4:00 (263) **Advanced Methods Characterizing Spatial Heterogeneity in Chemical Imaging Data Analysis**; Frederick Koehler[1], Kenneth Haber[1], E. Neil Lewis[1]; [1]Malvern Instruments, Inc.

4:20 (264) **InSb Chemical Imaging of Processed Mixtures Analyzed for Ingredient Identity, Concentration and Distribution**; Lauren Brewer[1], David Wetzel[1], Hayes Charles[1]; [1]KSU Microbeam Molecular Spectroscopy Lab

4:40 (265) **On-Line Attenuated Total Reflectance Fourier Transform Infrared Analysis of an Oligonucleotides Synthesizer Effluent Stream**; Lamar Dewald[1], Mary Beth Seasholtz[1], Randy Pell[1], Wendy Flory[1]; [1]The Dow Chemical Company

Tuesday Afternoon, Room Nevada 6
NEW DEVELOPMENTS IN MASS SPECTROMETRY
Organizer and Presider: Martha Vestling

3:00 (267) **Investigations Into Steroid Analysis Using Surface Assisted Laser Desorption Ionisation Mass Spectrometry**; Georgia Guild[1], Claire Lenehan[1], Stewart Walker[1]; [1]Flinders University

3:20 (268) **In-Line Mass Spectrometry Application for Control of Critical Drying Points**; John Wasylyk[1], William Bartels[1], Ming Huang[1], Robert Wethman[1], Charles Ray[1]; [1]Bristol-Myers Squibb Co.

3:40 (269) **Approaches to Increase Molecular Selectivity in Porous Silicon Based Laser Desorption/Ionisation Mass Spectrometry**; Rachel Lowe[1], Endre Szili[1], Paul Kirkbride[2], Gary Siuzdak[3], Nicolas Voelcker[1]; [1]Flinders University; [2]Australian Federal Police; [3]The Scripps Research Institute

4:00 (270) **GC-MS and Electron Ionization LC-MS with Supersonic Molecular Beams**; Aviv Amirav[1], Alexander Gordin[1], Marina Poliak[1], Kfir Gil[1], Tal Alon[1], Alexander B. Fialkov[1]; [1]Tel Aviv University

4:20 (271) **Fundamental Properties of DC Atmospheric-Pressure Helium Discharges Used in Mass Spectrometry**; Jacob Shelley[1], George Chan[1], Steven Ray[1], Gary Hieftje[1]; [1]Indiana University

4:40 (272) **A Miniature Mass Spectrometer with a Miniature Rectilinear Ion Trap**; Scott Smith[1], Jeffrey Maas[2], Zheng Ouyang[3], William Chappell[2], Robert Cooks[1]; [1]Dept of Chemistry, Purdue Univ.; [2]Dept of Elec & Comp Eng, Purdue Univ.; [3]Dept of Biomedical Eng, Purdue Univ.

Tuesday Afternoon, Room Nevada 7
40 YEARS OF SPECTROSCOPY INNOVATION: A TRIBUTE TO GARY HIEFTJE,
sponsord by the Society for Applied Spectroscopy
Organziers: John Olesik and Steven Ray; Presider: Steven Ray

3:00 (273) **Nanos Gigantum Humeris Insidentes: Approaches For Sensor Development in the 21st Century**; Radislav Potyrailo[1]; [1]GE Global Research

3:20 (274) **Chemistry In-Silica: Sensor Arrays Based on Tailored Xerogel Platforms**; Frank Bright; [1]UB, SUNY

3:40 (275) **Developing Chemical Instrumentation using Microelectronics Fabrication Tools**; J. Michael Ramsey; [1]University of North Carolina at Chapel Hill

4:00 (276) **Eye on Ions - Forays with MS for Isotopic and Metallomic Analyses**; David Koppenaal[1], Charles Barinaga[1], George Hager; [1]Pacific Northwest National Laboratory; [2]Indiana University; [3]University of Arizona

4:20 (277) **Research in the AAA Problems**; Robert Lodder[1]; [1]Spherix Inc.

4:40 (278) **Simultaneous Molecular and Elemental Mass Spectrometry for Comprehensive Elemental Speciation Analysis.**; Steven Ray[1], Duane Rogers[1], Gary Hieftje[1]; [1]Indiana University

Tuesday Afternoon, Room Nevada 8
NESSI-APPLICATION OF SENSORS FOR INCREASED PROCESS CONTROL
Organizer: Mel Koch; Presider: Brian Marquardt

3:00 (279) **NeSSI Based Calibrated Gas Mixing System for Sensor Development and Calibration**; Kent Mann[1], Brian Marquardt[2], Conor Smith[1], Charles Branham[2]; [1]University of Minnesota; [2]University of Washington

3:20 (280) **Parker and NeSSi: Application of Bus Communications and Analytics in Sample Handling Systems**; Mike Cost; [1]Parker Hannifin

3:40 (281) **Combining Analytical Sensors and NeSSI to Improve Process Understanding**; Dave Veltkamp[1], Brian Marquardt[1,2]; [1]CPAC, University of Washington (UW); [2]Applied Physica Lab (APL), UW

4:00 (282) **Calibration and Evaluation of Small Fiber Optic Oxygen Sensors with a NeSSI Gas Generation System**; Charles W. Branham[1], Conor Smith[2], Kent Mann[2], Brian Marquardt[1]; [1]University of Washington; [2]University of Minnesota

4:20 (283) **Dynamic Nuclear Polarization for NMR Signal Enhancement**; Sandra Garcia[1], Jeff Walton[1], Songi Han[2], Michael J. McCarthy[1]; [1]University of California Davis; [2]University of California Santa Barbara

4:40 (284) **New Intrinsically Safe Digital Bus Based Controller Area Network Applicability to Integrated Process Gas Chromatography Sample Handling Systems**; Tracy Dye[1], Patrick Lowery[2]; [1]ABB Process Analytics; [2]CIRCOR

Tuesday Afternoon, Room Nevada 9
CHARLES MANN AWARD SYMPOSIUM
IAN R. LEWIS AWARDEE
Organizer and Presider: Neil Everall

3:00 (285) **Ignoring Pharma: Moving Spectroscopy into the Real World**; Fred LaPlant[1]; [1]3M Inc.

3:20 (286) **Making Do - Weighted Regression Models for Use with Less-Than-Perfect Data**; Jeremy Shaver[1]; [1]Eigenvector Research, Inc.

3:40 (287) **Novel Spectroscopic and Statistical Approaches for Measuring Spatial and Chemical Heterogeneity in 'Sparse' Samples.**; Neil Lewis[1], Kenneth Haber[1], Linda Kidder[1], Frederick Koehler[1], Janie Dubois[1]; [1]Malvern Instruments

4:00 (288) **Practical Applications of Raman Spectroscopy in Pharmaceutical API Process Development**; Robert Wethman[1], John Wasylyk[1], Ming-Hsing Huang[1], Jonathon Haulenbeek[1]; [1]Bristol-Myers Squibb

4:20 (289) **Laser Raman Spectroscopic Technology and Results in Oceanographic Science Applications**; William J Kirkwood[1], Peter G Brewer[1]; [1]Monterey Bay Aquarium Research Institute

4:40 (290) **Process Raman: Challenges and Rewards**; Brian Marquardt[1]; [1]University of Washington

Tuesday Afternoon, Room Nevada 10
NIR SPECTROSCOPY IN PHARMACEUTICAL ANALYSIS: TECHNOLOGY TRANSFER IN ACTION
Organizers and Presiders: Katherine Bakeev and Tony Moffat

3:00 (291) **Combining Calibration Transfer and Preprocessing: What Methods, What Order?**; Charles E. Miller[1], Robert T. Roginski[1], Neal B. Gallagher[1], Barry M. Wise[1]; [1]Eigenvector Research, Inc

3:20 (292) **Practical aspects of PAT Method Transfer in the Pharmaceutical Industry**; Bronwyn Grout[1,2]; [1]Pfizer Inc; [2]School of Pharmacy, University of London

3:40 (293) **Universal Quantitative Standards for the Transfer of Assays of Actives in Intact Tablets using Reflection NIR Spectroscopy**; Nathaporn Hongsrisuk[1], Roger Jee[1], Tony Moffat[1]; [1]The School of Pharmacy, University of London

4:00 (294) **NIR Determination of Crystallization Solvent Composition: Method Development and Transfer from Lab to Pilot Plant**; Charles Goss[1], Seán Sisk[2], Bob Cooley[1], Bobby Glover[1], Rahn McKeown[1], Tom Lovelace[1], Brian Crump[1], Darryl Ertl[1]; [1]GlaxoSmithKline, RTP, NC, USA; [2]GlaxoSmithKline, R&D Lab, Cork, Ireland

4:20 (295) **Augmented Classical Least Squares Methods for Improved Calibration Transfer and Maintenance**; David Haaland[1], David Melgaard[1], Christine Wehlburg[2], Robert Guenard[3], Randy Pell[4]; [1]Sandia National Laboratories; [2]MITRE Corporation; [3]Merck & Company; [4]The Dow Chemical Company

4:40 (296) **Examples of NIR Calibration Transfer Across Identical and Different Hardware Platforms**; Michael Surgeary[1], Ronald Rubinovitz, Ph.D[1]; [1]Buchi Corporation

5:00 **Open Panel Discussion on Calibration Transfer – Speaker and Audience Participation**

TECHNICAL PROGRAM – Wednesday
Plenary Sessions, Presider: Curt Marcott

William F. Meggers Award
8:00 AM Plenary Lecture, S 2/3

Taka-aki Ishibashi

(297) **Development of a Multiplex Spectrometer for Doubly-Sesonant SFG Spectroscopy**

Taka-aki Ishibashi, Toshiki Maeda; Hiroshima University

Refer to page 15 for biographical information

Applied Spectroscopy Lester W. Strock Award
8:30 AM Plenary Lecture, S2/3

Annemie Bogaerts

(298) **Modeling of Plasmas, Plasma-Solid and Laser-Solid Interaction**

Annemie Bogaerts; University of Antwerp

Refer to page 15 for biographical information

WEDNESDAY POSTER SESSIONS
9:00 – 10:15 am and 1:30 – 3:00 pm
Exhibit Hall S1

All Wednesday posters should be put up between 7:30 – 8:00 AM and removed at 3:00 PM The odd numbered poster boards present in the morning and the even numbered poster boards present in the afternoon.

Atomic Spectroscopy

Board #

1 (299) **Analysis of Bismuth in Pharmaceuticals**; Brent Ferguson[1], Rebekah Kimbrough[1], Marina Koether[1]; [1]Kennesaw State University

2 (300) **Thermoelectrically Cooled Cryocell Assisted LA-ICP-MS and Liquid ICP-MS Analysis of Metals in Kidney and Liver Samples from Beached Porpoise**; Matthew Horton[1], Aldemaro Romero[2], Roger Buchanan[2], Robyn Hannigan[3]; [1]CETAC Technologies; [2]Arkansas State Univ., Dept. of Bio. Sci.; [3]Arkansas State Univ. Dept. of Env. Science

3 (301) **Distribution of Cd, Zn, Se and Fe in Prostate Cancer Specimens**; Todor Todorov[1], Alan Koenig[1], Andre Kajdacsy-Balla[4], Andrey Sarafanov[2], Marion Gray[3], Jose Centeno[2]; [1]US Geological Survey; [2]Armed Forces Institute of Pathology; [3]James Cook University, Australia; [4]University of Illinois - Chicago

4 (302) **Calibration-Free Libs Analysis of Space Resolved Spectra from a Cu-Fe-Mn-Ni Alloy Plasma**; Gabriele Cristoforetti[1], José Antonio Aguilera[2], Carlos Aragon[2], Elisabetta Tognoni[1]; [1]CNR-IPCF, Italy; [2]Universidad Publica de Navarra, Spain

Bioanalytical

5 (303) **Cryo-Cell Innovations for Biological Tissue Analysis by Laser Ablation ICP-MS**; Steven Hughes[1], Joseph Brady[1], Robert Fry[1]; [1]Spectr-LAse

6 (304) **Second Order Nonlinear Optical Imaging of Chiral Crystals (SONICC)**; Garth Simp; [1]Purdue University

7 (305) **Investigations of Thermotropic Phase Behavior of Newly Developed Synthetic PEGylated Lipids Using Raman Spectro-Microscopy**; Rajan Bista[1], Reinhard Bruch[1], Aaron Covington[1,2]; [1]Department of Physics, University of Nevada, Reno; [2]Nevada Terawatt Facility, Reno, Nevada

Chemometrics

8 (306) **Chemometrics to Handle and Resolve Time Resolved Spectroscopic Data**; Cyril Ruckebusch[1], Lionel Blanchet[1,2], Ludovic Duponchel[1], Jean-Pierre Huvenne[1]; [1]LASIR CNRS USTLille; [2]Universitat de Barcelona

9 (307) **Use of Harmonized Data Standards to Simplify use of Chemometric Methods for Online Analysis**; Steve Best; [1]Coblentz

10 (308) **Estimation of Myoglobin Oxygen Saturation from Spectra of Cardiac Tissue using Multivariate Curve Resolution**; Francis W.L. Esmonde-White[1], Lorilee S. L. Arakaki[2], Kenneth A. Schenkman[2], Wayne A. Ciesielski[2], David H. Burns[1]; [1]McGill University; [2]University of Washington

11 (309) **Sensor Fusion of IR, NIR, and Raman Spectroscopic Data for Polymorph Quantitation of an Agrochemical Compound**; Jalice Manso[1], Steven Brown[2], Boiana Budevska[1]; [1]DuPont - Crop Protection; [2]University of Delaware

12 (310) **Simultaneous Spectrophotometric Determination of Albendazole and Praziquantel using Two Different Mathematical Spectrophotometric Approaches**; Maria Toral[1], César Soto[2], David Contreras[2], Juanita Freer[2], Sandra Orellana[1]; [1]Universidad de Chile; [2]Universidad de Concepción

Mass Spectrometry

13 (311) **Simultaneous Glycoproteomic Strategies Utilizing Ion Mobility-Mass Spectrometry: New Insights from Structural Separations**; Larissa S. Fenn[1], John A. McLean[1]; [1]Vanderbilt University

14 (312) **Phosphoproteomic Mapping with Two-Dimensional Structural Separations by Ion Mobility-Mass Spectrometry;** Randi L. Gant[1], Thomas J Kerr[1], John A. McLean[1]; [1]Vanderbilt University

15 (313) **Top-Down Sequence Analysis of Antibody Fragments by an Ion-mobility Time-of-flight Mass Spectrometer**; Asish Chakraborty[1], Weibin Chen[1], Carola Dame[2], John Gebler[1]; [1]Waters Corporation; [2]Slotervaart Hospital/The Netherlands

16 (314) **Determination of Protein Conformational Changes by an Ion-Mobility TOF MS**; Asish Chakraborty[1], Weibin Chen[1], John Gebler[1]; [1]Waters Corporation

Pharmaceuticals

17 (315) **Preparation and Characterisation of Solvatomorphs of Rifampicin**; Sushma Gupta[1], Deepika Thakur[1], Poonam Arora[1]; [1]University Institue of Pharmaceutical Sciences

18 (316) **Simple and Rapid Spectrophotometric Method for the Determination of Erythromycin Esters in Pharmaceutical Formulations.**; Dr. Priti Mehta[1], Dr. A. K. Shukla[2]; [1]Institute of Pharmacy; [2]Suvic Pharmaceutical Laboratory

19 (317) **A Multivariate Model Free Approach for Pharmaceutical Tablet Content Uniformity Analysis via NIR**; Yang Liu[1], Sonja Sekulic[1]; [1]Pfizer Global Research and Development

20 (318) **Online PAT Monitoring for Parenteral Process Understanding and Design Space Mapping**; Yang Liu[1], Robert Leasure[2], Fred Carroll[1], Mark Berry[1], Richard Ferraina[1], Joanne Lukaszewicz[1]; [1]Pfizer Global Research and Development; [2]Pfizer Global Manufacturing

21 (319) **Development of an IN-Line API Concentration Determination for Control of Crystallization and Metastable Zone Evaluation**; Ming Huang[1], Robert Wethman[1], Daniel Hsieh[1], John Wasylyk[1]; [1]Bristol-Myers Squibb

22 (320) **Pharmaceutical Hydrate Transformation Kinetics: Effects of Polymer Excipients**; Alan Gift[1], Daniel Brooks[2]; [1]University of Nebraska Omaha; [2]Indiana University South Bend

23 (321) **Evaluation of the Impact of Container Interference for Bulk Material Authentication using a Handheld Raman Spectrometer**; Jeremy Linoski[1], Robert Green[1], Robert Brush[1], Wayne Jalenak[1], Christopher Brown[1]; [1]Ahura Scientific, Inc.

24 (322) **Replacement Method Development for Hazard Solvents Using Method in Korean Pharmaceutical Codex**; Kyung-Yoal Yoo[1], Dal-Hwan Kim[2], Ryoon-Kyung Lee[1], Seung-Hwan Kim[1], Jin-Hee Nam[1], Soon-Han Kim[1]; [1]Dageu Regional Korea Food & Drug Administration; [2]Korea Food & Drug Administration

25 (323) **Application of LC-MSn in Conjunction with Mechanism-based Stress Studies for the Elucidation of Drug Impurity Structure**; Rosario Fico[1], Min Li[1], Mingxiang Lin[1], Abu Rustum[1]; [1]Schering-Plough Corporation

26 (324) **Effects of Formulation and Processing Changes on a NIR PLS Model for Determining Tablet Hardness**; Melissa Mrozek-Morrison[1], Thomas Lang[1], Wencan Chen[1], Angela Olsofsky[1], Charles Yang[1]; [1]Amgen, Inc.

27 (325) **Characterization of Protein Modifications using Liquid Chromatography and Data Independent Acquisition Tandem Mass Spectrometry**; Hongwei Xie[1], Martin Gilar[1], John C. Gebler[1]; [1]Waters Corporation, Milford, MA

Raman

28 (326) **Surface Enhanced Raman Spectroscopy for the Detection of Chemical Agent Surrogates**; Baolong Bai[1], Gary Rayson[1]; [1]New Mexico State University

29 (327) **Photobleaching Behavior in Raman Spectroscopy**; Richard Spragg[1], Robert Alexander[1], Nancy Kawai[2]; [1]PerkinElmer LAS UK; [2]PerkinElmer LAS USA

30 (328) **Confocal Raman Microscopy of the Interfacial Region of Liquid Chromatographic Stationary Phase Materials**; Jennifer L. Gasser-Ramirez[1], Joel M. Harris[1]; [1]Department of Chemistry, University of Utah

31 (329) **Micro-Cavity Resonator: A Novel Method for Improving the Raman Signal without SERS from Sub-Micron Size Materials**; Anupam Misra[1], Shiv Sharma[1], Lori Kamemoto[1,2], Pavel Zinin[1], Qigui Yu[2], Ningjie Hu[2]; [1]University of Hawaii, HIGP/SOEST; [2]Hawaii AIDS Clinical Res. Program, UH

32 (330) **Surface Enhanced Raman (SERS) Nanoparticle Reagent Delivery Device for *in-situ* Sample Analysis**; Thomas Tague[1], Sergey Shilov[1], Marco Leona[2]; [1]Bruker Optics; [2]Metropolitan Museum of Art

Separations

33 (331) **High-Performance Liquid Chromatographic Determination of Bile Acids using Micellar Phase-Transfer Catalysis and Fluorescence Detection**; Suh-Jen Jane Tsai[1], Win-Ya Lee[1], Yu-Sheng Chung[1], Pei-Yin Hsieh[1]; [1]Dept. of Applied Chemistry, Providence Univ.

34 (332) **On-Board Pneumatic Valves for Multiplexed Applications in Microfluidic Devices**; Leanna Levine[1], Jason McDowell[1], Jackie Goldstein[1], William Penrose[2]; [1]ALine, Inc.; [2]Custom Sensor Solutions

35 (333) **Electrophoretic Capture: A New Approach to Separations**; Michelle Meighan[1], Michael Keebaugh[1], Stacy Kenyon[1], Alicia Quihuis[1], Mark Hayes[1]; [1]Arizona State University

36 (334) **Pre-Concentration and Determination of Polycyclic Aromatic Hydrocarbons (PAHs) on Centrifugal Microfluidic Discs**; Josiane P. Lafleur[1], Andrien A. Rackov[1], Scott McAuley[1], Eric D. Salin[1]; [1]McGill University

37 (335) **Purification of Pharmaceutical Candidates From Biological Fluids by Countercurrent Chromatography.**; Jill Hochlowski[1], Jeff Pan[1], Philip Searle[1], Tom Nemcek[1], Dave Blanchard[1], Dave Dingle[1], Steve Spanton[1]; [1]Abbott Laboratories

38 (336) **Measuring Dissociation Constants of Mono-hydroxy Polycyclic Aromatic Hydrocarbons via Capillary Zone Electrophoresis**; Gaston Knobel[1], Andres D. Campiglia[1]; [1]University of Central Florida

39 (337) **Synthesis, Characterization, and Liquid-Liquid Electrochemistry of a New Class of Chiral Hydrophobic Room Temperature Ionic Liquids**; Julie B. Rollins[1], John C. Conboy[1]; [1]University of Utah

40 (338) **The Effect of Temperature Gradients in Solvating Gas Chromatography**; Jordan Smith[1], Nicole Taylor[1], John-David McElderry[1]; [1]Brigham Young University

41 (339) **Development and Validation of Method for Simultaneous Quantification of Different Marker by Reverse Phase HPLC and HPTLC in Sida Species**; Vaibhav Shinde[1], Kamlesh Dhalwal[1], Kakasaheb Mahadik[1]; [1]Poona College of Pharmacy, Bharati Vidyapeeth Univ

42 (340) **Validation of HPLC Method for Simultaneous Determination of Gallic Acid and Ellagic Acid in Herbal Extract and Formulations**; Kamlesh Dhalwal[1], Vaibhav Shinde[1], Kakasaheb Mahadik[1]; [1]poona College of Pharmacy

43 (341) **Analysis of Trans-Fatty Acids by Gas Chromatography/ Infrared Spectroscopy (GC/IR)**; Katsunori Ishii[1], Aya Harada[2], Kouichi Toda[2], Kunio Awazu[1]; [1]Graduate School of Engineering, Osaka University; [2]Technofleet Inc.

44 (342) **Quantification of Pantoprazole by High Performance Liquid Chromatography in Human Plasma**; Patel Alpeshkumar[1], Patel Bhaveshkumar[2], Suhagia Bhanubhai[3], Patel Natwarlal[1]; [1]Shri.B.M Shah College of Pharma. Edu. & Research; [2]K.B. Institute of Pharma. Edu.& Research; [3]L.M.College of Pharmacy, Ahmedabad

45 (343) **Development of a Centrifugal Microfluidic System for Rapid On-Site Analysis of Environmentally Important Species**; Angela LaCroix-Fralish[1,2], Jennifer Clare[1], Cameron Skinner[1], Eric Salin[2]; [1]Concordia University; [2]McGill University

46 (344) **A Powerful New Structural Information Tool for Complex Mixtures and Polymers; Chromatography Hyphenated with Solvent Removal to FTIR**; Tom Kearney[1], William W. Carson[1], Sidney Bourne[1]; [1]Spectra Analysis, Inc.

Wednesday Morning, Room Nevada 2
CHEMOMETRICS IN SEPARATIONS
Organizer and Presider: Frank Gomez

10:15 (345) **Combining Chromatography, Spectroscopy and Chemometrics to Solve Real-World Analytical Problems**; Thomas Hancewicz[1], Dane Drutis[1]; [1]Unilever R&D

10:35 (346) **Chromatographic Alignment for Improved Multivariate Analysis**; Scott Ramos[1], Brian Rohrback[2]; [1]Infometrix, Inc.

10:55 (347) **Chemometrical Experimental Design-Based Optimization Studies in Capillary Electrophoresis Applications**; Frank Gomez, Ruthy Montes, Grady Hanrahan; [1]California State University, Los Angeles; [2]California Lutheran University

11:15 (348) **Application of Experimental Design and Artificial Neural Networks in Modern Separation Studies**; Grady Hanrahan[1], Ruth Montes[2], Joseph Rower[1], Toni Riveros[2], Frank A. Gomez[2]; [1]California Lutheran University; [2]California State University, Los Angeles

11:35 (349) **Experimental Design, Optimization and Pattern Recognition in Chromatography: Applications and Perspectives**; Stephen L. Morgan[1], Sparkle T. Ellison[1], Pakritsadang Kaewsuya[1]; [1]University of South Carolina

11:55 (350) **Multivariate Versus Univariate Optimization of Separation Conditions in Micellar Electrokinetic Chromatography**; Carlos Garcia[1], Jessica Felhofer[1], Grady Hanrahan[2]; [1]UT San Antonio; [2]California Lutheran University

Wednesday Morning, Room Nevada 3
VIBRATIONAL SPECTROSCOPY, CHEMICAL IMAGING AND QBD
Organizer and Presider: Hung Tian

10:15 (351) **Utilization of Chemical imaging during Formulation Design – Identification of Critical Quality Attributes**; Hung Tian[1], Hitesh Chokshi[1]; [1]Roche

10:35 (352) **Quantitative Measures of Spatial Resolution for Chemical Imaging of Pharmaceuticals**; John Kauffman[1], Sean Gilliam[1], R. Scott Martin[2]; [1]FDA Div. of Pharmaceutical Analysis, St. Louis, MO; [2]Saint Louis University, St. Louis, MO

10:55 (353) **NIR Chemical Imaging for Enhanced Understanding of Blending Processes**; Carl Anderson[1], Ma Hua[1], Zhenqi Shi[1]; [1]Duquesne University

11:15 (354) **Terahertz Pulsed Imaging as a Process Analytical Tool for Tablet Film Coatings**; Philip Taday[1]; [1]TeraView Limited

11:35 (355) **Chemical and Morphological Imaging of Pharmaceutical Products: Measuring the Impact of Process Conditions on Finished Tablets**; Janie Dubois[1], Lisa J. Makein[1], Linda H. Kidder[1], Maurizio Valleri[2], E. Neil Lewis[1]; [1]Malvern Instruments; [2]Menarini Pharmaceuticals

11:55 (356) **The Use of Chemical Imaging to Support the Mapping of a Product Design Space**; Stepehen Hammond[1]; [1]Pfizer Inc

Wednesday Morning, Room Nevada 4
LIBS
Organizers: Jose Almirall and Jhanis Gonzalez;
Presider: Jose Almirall

10:15 (357) **Investigation on the Mechanisms Underlying the Signal Improvement Observed in the Double Pulse Laser Ablation**; Gabriele Cristoforetti[1], Stefano Legnaioli[1], Vincenzo Palleschi[1], Elisabetta Tognoni[1]; [1]Institute for Chemical Physical Processes, CNR

10:35 (358) **Experimental and Theoretical Studies of the Dynamics of the Laser Induced Plasma and the Associated Particle Generation Process**; Sy-Bor Wen[1]; [1]Texas A&M University

10:55 (359) **Discrimination of Complex Chemical Substances with Laser Induced Breakdown Spectroscopy**; Jong Yoo[1], Richard E. Russo[1], Xianglei Mao[2], JeeBum Lee[3], Sungho Jeong[4]; [1]Applied Spectra, Inc.; [2]Lawrence Berkeley National Laboratory; [3]Chonnam National University Medical Scho; [4]Gwangju Institute of Science and Technology

11:15 (360) **Overview of Standoff Laser Induced Breakdown Spectroscopy Progress at U.S. Army Research Laboratory**; Frank De Lucia[1], Jennifer Gottfried[1], Chase Munson[1], Andzrej Miziolek[1]; [1]U.S. Army Research Laboratory

11:35 (361) **LIBS Analysis and Imaging of Very Low Mass Lodading of Metals Delivered on Surfaces**; Jose Almirall[1], Cleon Barnett[1], Erica Cahoon[1], Monica Joshi[1]; [1]Florida International University

11:55 (362) **Double-Pulse LIBS Signal Enhancement Correlated to Nanoparticle Size Distributions**; Andrew Effenberger[1], Steven Buckley[2,3]; [1]Dept. of Chemistry, Univ. California, San Diego; [2]Dept of MAE, Univ. California, San Diego; [3]Photon Machines, Inc.

TECHNICAL PROGRAM – Wednesday
Orals 10:15 AM – 12:15 PM

Wednesday Morning, Room Nevada 5
ELECTRON TRANSFER CHEMISTRY AND NANOSTRUCTURED MATERIALS
Organizer and Presider: Shaowei Chen

10:15 (363) **Towards Multicomponent Nanoparticle-Based Catalysts for Solar Hydrogen Generation from Water**; Frank Osterloh[1], Owen Compton[1], F. Andrew Frame[1], Elizabeth Carroll[1], Michael Sarahan[1], Cory Mullet[1], Shirley Chiang[1], Nigel Browning[1], Delmar Larsen[1] ; [1]UC Davis

10:35 (364) **Direct Monitoring the Bond Strength of CO at Au@Pt Core-Shell Nano-Particle Electrodes by *in-situ* Electrochemical Surface-Enhanced Raman Spectroscopy**; Yan Xia Chen[1], Pu Zhang[1], Jun Cai[1], Shao Xiong Liu[1], Jian Feng Li[2], An Wang[2], Ping Ping Fang[2], Xiao Bing Lian[2], Bin Ren[2], Zhong Qun Tian[2]; [1]aHefei National Laboratory for Physical Sciences a; [2]State Key Laboratory of Physical Chemistry

10:55 (365) **Soft X-Ray Spectroscopy of Thin Film Solar Cells – Towards an Understanding of the Chemical and Electronic Structure of Interfaces**; Clemens Heske; [1]UNLV

11:15 (366) **Surface Bottom-Up Synthesis of Redox Molecular Wires and Their Electron Transfer Behavior**; Hiroshi Nishihara[1]; [1]The University of Tokyo

11:35 (367) **Electron Transfer through a Self-Assembled Monolayer of Thiol-End-Functionalized Porphyrins and Metalloporphyrins**; Lu Xiaoquan[1]; [1]Northwest Normal University,P.R.China

11:55 (368) **Metal Nanoparticles Stabilized by Metal-Carbon CovalentBonds**; Shaowei Chen[1]; [1]University of California, Santa Cruz

Wednesday Morning, Room Nevada 6
ION MOBILITY SPECTROMETRY – RECENT APPLICATIONS I
Organizer and Presider: Charles Wilkins

10:15 (369) **Latest Results on High Resolution IMS-MS**; Michael Bowers[1], Paul Kemper[1], Nicholas Dupuis[1], [1]UC Santa Barbara

10:55 (370) **Characterization of an 800 kDa eIF3 Protein Complex: Effects of CID and Solvent Disruption using Ion Mobility MS**; Julie Leary, Matthew Schenauer, Armann Andaya, Raluca Stefanescu; [1]University of California Davis

11:15 (371) **Investigation of Alternate-Construction and Variable Duty Cycle Gating Waveforms for Digitally-Multiplexed Atmospheric Pressure Drift Tube Ion Mobility Spectrometry**; Facundo Fernandez[1], Mark Kwasnik[1]; [1]School of Chemistry and Biochemistry. Georgia Tech

11:35 (372) **A Novel Ion Mobility Device: Overtone Mobility Spectrometry (OMS) and Potential Applications**; Stephen Valentine[1], Ruwan Kurulugama[2], David Clemmer[3]; [1]Predictive Physiology and Medicine, Inc.; [2]Indiana University

11:55 (373) **T Cyclize or Not Cyclize - What is a Peptide Fragment to Do?**; Nicolas Polfer[1]; [1]University of Florida

Wedesday Morning, Room Nevada 7
LESTER STROCK AWARD SYMPOSIUM
Organizer and Presider: Renaat Gijbels

10:15 (374) **Fundamental and Applied Investigations into Glow Discharges**; G.M. Hieftje[1], G. Gamez[1], M.R. Webb[1], G. Chan[1], C. Engelhard[1], S.J. Ray[1]; [1]Indiana University

10:35 (375) **Driving Laser Ablation Fundamentals to Applications**; Rick Russo[1], Xianglei Mao[1], Sy-Bor Wen[1,2], Dayana Gonzalez-Oropeza[1], Jhanis Gonzalez[1]; [1]Lawrence Berkeley National Laboratory; [2]Texas A&M University

10:55 (376) **Laser Induced Plasmas: Prediction of Plasma Composition**; Igor Gornushkin[1,2]; [1]University of Florida, Gainesville, FL, USA; [2]BAM, Germany, USA

11:15 (377) **Aerosol Flow Dynamics and Transport Systems in Laser Ablation Inductively Coupled Plasma Mass Spectrometry**; Detlef Gunther[1], Joachim Koch[1], Jorge Pisonero[2], Markus Waelle[1], Rolf Dietiker[1], Matthias Fricker[1], Robert Kovacs[1], Bodo Hattendorf[1]; [1]ETH Zurich, Laboratory of Inorganic Chemistry, CH-; [2]Department of Physics, University of Ovi

11:35 (378) **RF and Pulsed Glow Discharges, and Crater Formation in Glow Discharges**; Volker Hoffmann[1]; [1]IFW Dresden

11:55 (379) **Molecular Emission in Compositional Depth Profiling using GD-OES**; Arne Bengtson; [1]Swerea KIMAB

Wednesday Morning, Room Nevada 8
PROCESS ANALYTICAL MONITORS, sponsored by the Society for Applied Spectroscopy
Organziers Brandye Smith-Goettler and Edita Botonjic-Sehic; Presider: Edita Botonjic-Sehic

10:15 (380) **Determining Blend Content Uniformity during Manufacturing using NIR in a High Shear Mixer**; Edita Botonjic-Sehic[1], Glenys Foster Roberts[1], Krishna Venkatesh[1], Richard Lienhart[1]; [1]Barr Laboratories, Inc.

10:35 (381) **Implementation of Control Systems for a Fluid Bed Processor**; Brian Zacour[1], Michael Moore[1], Steven Short[1], Zhenqi Shi[1], Robert Cogdill[1], James Drennen[1], Carl Anderson[1]; [1]Duquesne University Center for Pharmaceutical Tech

10:55 (382) **Multivariate Re-Calibration Utilizing QbD Approach to Monitor Blend Uniformity**; Dongsheng Bu[1], Saeed Hashemi[2]; [1]CAMO Software Inc; [2]Wyeth Pharmaceuticals

11:15 (383) **Implementation of QbD/PAT in Pharmaceutical Development and Manufacturing - Some Theoretical and Practical Aspects**; Jun Huang[1], Rina Chokshi[1]; [1]Wyeth

11:35 (384) **PAT in the Pharmaceutical Industry; Looking Forward**; Patrick Rameas[1]; [1]GlaxoSmithKline

11:55 (385) **The Use of Process Analytical Technology (PAT) Tools in Biofuels Production**; Jose Menezes[1], Pedro Felizardo[1], Maria Joana Neiva-Correia[1]; [1]Technical University of Lisbon

TECHNICAL PROGRAM – Wednesday
Orals 10:15 AM – 12:15 and 3:00 – 5:00 PM

Wednesday Morning, Room Nevada 9
BIO & PHARMACEUTICAL APPLICATIONS OF RAMAN SPECTROSCOPY
Organizer: Rina Dukor; Presiders: Rina Dukor and Larry Nafie

10:15 (386) **UV Resonance Raman Discovery of Gibbs Free Energy Landscape for Protein Alpha Helix Folding**; Sanford Asher[1], Alexander Mikhonin[1], Edward Gooding[1], Lu Ma[1], Bhavya Sharma[1], Sergei Bykov[1], Zeeshan Ahmed[1], Nataliya Myshakina[1]; [1]University of Pittsburgh

10:55 (387) **Raman and Raman Optical Activity Studies of Biomecular Structure and Behaviour**; Ewan Blanch; [1]University of Manchester

11:35 (388) **Deep Subsurface Raman Spectroscopy of Biological Tissue and Pharmaceutical Products**; Pavel Matousek[1]; [1]Rutherford Appleton Laboratory

Wednesday Morning, Room Nevada 10
INNOVATIONS IN ANALYTICAL APPLICATIONS OF SERS
Organizer and Presider: Duncan Graham

10:15 (389) **Rapid Characterisation of Biological Systems using SERS and Machine Learning**; Roy Goodacre[1], Roger Jarvis[1], Iqbal Shadi[1], Ketan Patel[1], Yun Xu[1], Mike Anderson[1]; [1]University of Manchester

10:55 (390) **Combining SERS and SEIRA on the Same Substrate**; Naomi Halas; [1]Rice University

11:35 (391) **Surface Enhanced Raman Spectroscopy using Gold Colloidal Nanoparticles for Measurement of Signaling Molecules Used by Quorum Sensing Bacteria**; Jasmine Ervin[1], William Pearman[1], S. Michael Angel[1], Alan Decho[2]; [1]Dept. of Chemistry and Biochemistry; [2]Dept. of Environmental Health Science

11:55 (392) **Tunable Fiber Optic Imaging Bundles for SERS Chemical Imaging Below the Diffraction Limit**; John Kiser[1], Mikella Hankus[1]; [1]University of Maryland Baltimore County

Wednesday Afternoon, S1 extension
"WHAT'S HOT" EXHIBITOR PRESENTATIONS
Organizer: Mike Carrabba; Presider: Brian Dable

12:20 **Avantes,** "AvalLIBS: A Transportable LIBS System for In Situ Analysis"

12:30 **Eigenvector,** "What's New in PLS-Toolbox/Solo 5.0"

12:40 **OPOTEK**, "High Repetition Rate Tunable Lasers"

12:50 **Andor**, "New Raman/LIBS Solutions – Andor 2009"

1:00 **WiTec**, "WiTec alpha500 The First Automated Confocal Raman and Atomic Force Microscope"

1:10 **Kaiser Optical Systems**, "In Situ Raman: New Development in Software and Instrumentation"

1:20 **Photon Systems**, "A New Deep UV Raman and Photoluminescence Spectrometer, Breakin gthe Cost Barrier"

WEDNESDAY AFTERNOON POSTER SESSION
Break and Dessert
1:30 – 3:00 PM
Exhibit Hall S1
Even numbered poster boards present.
See page 57 for a listing of the posters.

Wednesday Afternoon, Room Nevada 2
NOVEL BUT IMPORTANT DATA ANALYSIS TECHNIQUES FOR ANALYTICAL SCIENCE
Organizer and Presider: Karl Booksh

3:00 (393) **Multivariate Curve Resolution: A General Approach for Extracting Real Information from Analytical Data**; Thomas Hancewicz[1], Dane Drutis[1], Jesse Weissman[1]; [1]Unilever R&D

3:20 (394) **Nonlinear Classification in Spectroscopic Imaging by Means of Kernel Principal Component Analysis Applied to Analyses of Bacterial Contaminations**; Frank Vogt[1], Robert Luttrell[1], Eduard Duranty[1]; [1]University of Tennessee, Dept of Chemistry

3:40 (395) **Application of Excitation Emission Matrix Fluorescence to Monitor Flavonoid Aggregation**; Renee JiJi[1], John Simpson[2], Dan Zerjav[1]; [1]University of Missouri

4:00 (396) **Multivariate Prediction of Fuel Quality Parameters: Developing a Robust Capability for the US Navy**; Kevin Johnson[1], Jeffrey Cramer[1], Mark Hammond[1], Robert Morris[1], Susan Rose-Pehrsson[1]; [1]US Naval Research Lab

4:20 (397) **Chemometric Resolution of Fully Overlapped Capillary Electrophoresis Bands: Quantitation of Carbamazepine in Human Serum in the Presence of Several Interferences**; Héctor Goicoechea[1], Luciana Vera Candioti[1], Maria Julia Culzoni[1], Alejandro Olivieri[2]; [1]LADAQ, Universidad Nacional del Litoral; [2]IQUIR, Universidad Nacional de Rosario

4:40 (398) **Multivariate Analysis of Chemical Data using Genetic Algorithms**; Barry Lavine[1], Nikhil Mirjankar[1], Kadambari Nuguru[1], Mehul Vora[1]; [1]Department of Chemistry, Oklahoma State University

5:00 (399) **PARAFAC-SIMCA of Five-way Fluorescence Data for the Classification of Estuarine Water**; Gregory Hall[1], Jonathan Kenny[2]; [1]U.S. Coast Guard Academy; [2]Tufts University

Wednesday Afternoon, Room Nevada 3
TWO-DIMENSIONAL CORRELATION SPECTROSCOPY
Organizer and Presider: Curt Marcott

3:00 (400) **Frontiers of 2D Correlation Spectroscopy**; Isao Noda; [1]The Procter & Gamble Company

3:40 (401) **The Use of Two-Dimensional Correlation Spectroscopy to Study Centrosomal Proteins and Protein Interactions**; Belinda Pastrana[1,2]; [1]University of Puerto Rico; [2]Center for Protein Research

4:00 (402) **Applications of 2D-COS IN VCD Spectroscopy: Protein Fibrillation Dynamics in Insulin**; Laurence A Nafie[1,2], Shengli Ma[1], Rina K Dukor[2], Teresa B Freedman[1]; [1]Syracuse University; [2]BioTools, Inc.

4:20 (403) **Perturbation-Correlation Moving-Window 2D Correlation Spectroscopy and Its Applications to a Series of Vibrational Spectra**; Yukihiro Ozaki[1], Shigeaki Morita[2], Isao Noda[3]; [1]Kwansei Gakuin Univerisity; [2]Nagoya University; [3]Procter & Gamble Co.

4:40 (404) **Dynamic FT-IR Spectroscopy using Continuous Scan Dual Channel Acquisition**; Sergey Shilov[1], Michael Joerger[1]; [1]Bruker Optics

TECHNICAL PROGRAM – Wednesday
Orals 3:00 – 5:00 PM

Wednesday Afternoon, Room Nevada 4
LASER ABLATION
Organizer and Presider: Jhanis Gonzalez

3:00 (405) **The Physics of Femto- and Nanosecond Laser-Generated Aerosols in ICP-MS**; Roland Hergenröder ; [1]Institute for Analytical Sciences

3:20 (406) **Do Laser-Based Analytical Methods Really Go Nano?**; Christopher Latkoczy[1,2], Ralf Kaegi[2], Detlef Guenther[1]; [1]ETH Zurich, D-CHAB; [2]Eawag, SWW

3:40 (407) **Current and Future Directions of Laser Ablation ICP-MS at the US Geological Survey: Application Based Investigations and Reference Materials Development**; Alan Koenig[1]; [1]United States Geological Survey

4:00 (408) **Femtosecond and Nanosecond Laser Ablation–Time-of–Flight Based Inductively Coupled Plasma Mass Spectrometry.**; Jhanis Gonzalez[1], Dayana Oropeza[1], Xianglei Mao[1], Richard Russo[1]; [1]L. Berkeley National Lab.

4:20 (409) **The Forensic Analysis of Gel Ink Pens by Laser Ablation Inductively Coupled Plasma Mass Spectrometry (LA-ICP-MS)**; Benjamin Naes[1], Yaribey Rodriguez[1], Tatiana Trejos[1], Jose Almirall[1]; [1]Florida International University

4:40 (410) **Mainstream Laser Ablation and Technology Innovations**; Steven Hughes[1], Joseph W. Brady[1], Robert Fry[1]; [1]Spectra-LAse

Wednesday Afternoon, Room Nevada 5
MEGGERS AWARD SYMPOSIUM
Organizer: Shoici Yamagushi; Presiders: Koichi Iwata and Terry L. Gustafson

3:00 (411) **Advances in Sum-Frquency Spectroscopy Technique**; Y. Ron Shen[1]; [1]University of California at Berkeley

3:40 (412) **Air-Aqueous Interfaces Studied using Vibrational Sum Frequency Spectroscopy**; Heather Allen[1]; [1]The Ohio State University

4:00 (413) **Sum Frequency Generation Imaging Microscopy of Self Assembled Monolayer Patterns**; Steven Baldelli[1], Katherine Cimatu[1]; [1]University of Houston

4:20 (414) **Precise Structural Analysis of Interfaces and Materials by Nonlinear Optical Stokes Ellipsometry**; Garth Simpson; [1]Purdue University

4:40 (415) **Study of Interfacial Molecule using Novel Non-linear Electronic Spectroscopy**; Pratik Sen[1], Shoichi Yamaguchi[1], Tahei Tahara[1]; [1]Molecular spectroscopy Lab., RIKEN, Japan

5:00 (416) **Label-Free Detection of Drug-Biological Membrane Interaction**; Trang T. Nguyen[1], John C. Conboy[1]; [1]University of Utah

Wednesday Afternoon, Room Nevada 6
ION MOBILITY SPECTROMETRY – RECENT APPLICATIONS II
sponsored by the Society for Applied Spectroscopy
Organizer and Presider: Charles Wilkins

3:00 (417) **Metabolomics by Ion Mobility Mass Spectrometry**; Herbert Hill[1]; [1]Washington St. University; [2]Washington St. University; [3]Washington St. University

3:40 (418) **Emerging Directions for the Structural Analysis of Complex Biological Samples using Ion Mobility-Mass Spectrometry**; John McLean[1]; [1]Vanderbilt University

4:00 (419) **Snapshots of Gas-Phase Separated Complex Polymers for Rapidly Distinguishing Changes in Molecular Makeup**; Sarah Trimpin[1], David Clemmer[2]; [1]Wayne State University; [2]Indiana University

4:20 (420) **Ion Mobility-Mass Spectrometry Studies of Factors that Influence Structure(s) of Gas-Phase Peptide Ions: The Effects of Multiple Charge-Carrying Sites**; David H. Russell; [1]Texas A&M University

4:40 (421) **New Technologies for Standoff Detection of Explosives at Tens of Meters**; M. Bonner Denton[1], Roger P. Sperline[1], Wit T. Wisniewski[1], David A. Jones[2], Christopher A. Gresham[2]; [1]University of Arizona; [2]Sandia National Laboratories

Wednesday Afternoon, Room Nevada 7
FACSS STUDENT AWARDS AND SAS STUDENT POSTER AWARDS
Organizer and Presider: Greg Klunder

3:00 (422) **Design and Implementation of an Efficient and Automated Acoustically Levitated Drop Reactor for Studying Reaction Kinetics**; Christopher Field[1], Zakiah Pierre[1], Alexander Scheeline[1]; [1]Univesrity of Illinois Urbana-Champaign

3:20 (423) **Investigation of Photobleaching and Saturation of Single Molecules by Fluorophore Recrossing Events**; Sean Burrows[1], Randall Reif[1], Dimitri Pappas[1]; [1]Texas Tech University

3:40 (424) **FT-IR and Quantum Cascade Laser Based Trace Gas Sensors**; Christina Young[1], Claire Gmachl[2], Boris Mizaikoff[1,3]; [1]Georgia Institute of Technology; [2]MIRTHE, Princeton University; [3]University of Ulm

4:00 SAS Student Poster Awardee

4:20 SAS Student Poster Awardee

4:40 SAS Student Poster Awardee

Wednesday Afternoon, Room Nevada 8
SPECTROSCOPIC AND SENSING TECHNOLOGIES IN PHARMACEUTICAL INDUSTRY
Organizer and Presider: Radislav A. Potyrailo

3:00 (425) **Streamlining Protein-Drug Research and Formulation with Vibrational Spectroscopy**; Rina Dukor[1], Laurence Nafie[1,2]; [1]BioTools, Inc.; [2]Syracuse University

3:20 (426) **Prediction of Complex Bioprocess Operation Variables by On-Line Acquisition of Different Spectroscopic and Spectrometric Methods**; Karl Bayer; [1]Univ. Natural Res.& Applied Life Sciences Vienna

3:40 (427) **Hybrid Analytical Approaches: Simultaneous Physical and Chemical Characterization as a Tool for Pharmaceutical Quality by Design**; Neil Lewis[1], Kenneth Haber[1], Frederick Koehler[1], Janie Dubois[1], Linda Kidder[1]; [1]Malvern Instruments

4:00 (428) **Implementation of Multiplexed FT-NIR Technology as a PAT Tool to Improve Antibody Manufacture by Mammalian Cell Culture**; Linda M. Harvey[1], Payal Roy Choudhury[1], Ronan D. O'Kennedy[2], Brian McNeil[1]; [1]Strathclyde Fermentation Centre, Glasgow, UK; [2]GSK Biopharm CEDD, Beckenham, UK

4:20 (429) **PAT in Biologics Manufacturing**; Jose Menezes; [1]Technical University of Lisbon

4:40 (430) **New Sensing Concepts for Process Analytical Technology**; Radislav Potyrailo[1]; [1]GE Global Research

Wednesday Afternoon, Room Nevada 9
RAMAN SPECTROSCOPY AND ASTROBIOLOGY: TERRESTRIAL ANALOGUES & EXTRATERRESTRIAL SCENARIOS
Organizer and Presider: Howell G. M. Edwards
Please note early start

2:40 (431) **Raman Spectroscopy of Extremophiles: The Exomars Mission**; Howell GM Edwards[1], Ian J Scowen[1], Michael D Hargreaves[1], Ian Hutchinson[2], Richard Ingley[2]; [1]University of Bradford; [2]Brunel University

3:00 (432) **A Combined Raman-LIBS Spectrometer for the Exomars Mission**; Fernando Rull[1]; [1]Unidad Asociada UVA-CSIC al CAB

3:20 (433) **Sulfates on Mars: Study of Two Structural Polymorphs of MgSO4•H2O by Raman, IR, XRD, and Humidity Buffer Experiments**; Alian Wang[1], John Freeman[1]; [1]Washington University

3:40 (434) **Applications of Time-Resolved Remote Raman and Laser-Induced Native Fluorescence (LINF) Spectroscopy in Astrobiology**; Shiv Sharma[1]; [1]Hawaii Institute of Geophys., UH

4:00 (435) **Application of Non-Destructive Raman Spectroscopic Identification of Organic Minerals and Selected Biomarkers in Astrobiological Areas**; Jan Jehlicka[1], Howell Edwards[2], Petr Vitek[1]; [1]Charles University in Prague, Geochemistry; [2]University of Bradford, Chem and Forens

4:20 (436) **The Potential of Raman Spectroscopy for the Analysis of Diagenetically Transformed Carotenoids**; Craig Marshall[1], Alison Olcott[2]; [1]The University of Sydney; [2]University of Kansas

4:40 (437) **Raman and Raman/Sem Spectroscopic Studies of Terrestrial Materials of Relevance to Mars**; Elizabeth Carter[1], Craig Marshall[1], Peter Lay[1], Michael Hargreaves[2], Howell Edwards[2]; [1]The University of Sydney; [2]University of Bradford; [3]; [4]

5:00 (438) **Deep UV Raman Investigation sof Biological and Meteroitic Samples**; Juergen Popp[1,2]; [1]Friedrich-Schiller University Jena; [2]Institute of Photonic Technology

Wednesday Afternoon, Room Nevada 10
INDUSTRIAL APPLICATIONS OF SERS
Organizer and Presider: Duncan Graham

3:00 (439) **Photonic Bandgap Fiber Enabled Raman Detection of Nitrogen Gas**; Peter Codella[1], Rui Chen[1], Renato Guida[1], Anis Zribi[1], Alexey Vert[1], Radislav Potyrailo[1], Marko Baller[2]; [1]GE Global Research, Niskayuna; [2]GE Global Research, Munich

3:20 (440) ***in vitro* Diagnostics Using Encapsulated, SERS-Active Nanoscale Taggants**; Richard Freeman, Michael Natan; [1]Oxonica Materials, Inc.

3:40 (441) **SERS Platforms: the Next Generation of Ultra-Sensitive and High Throughput Detection Solutions**; Caterina Netti[1], Graeme McNay[1], Karen McCarney[1], Alastair Ricketts[1], Ewen Smith[1], Robert Stokes[2], Karen Faulds[2], Duncan Graham[2]; [1]D3 Technologies Ltd; [2]University of Strathclyde

4:00 (442) **Signal Enhancement in Near Field Raman Spectroscopy**; Richard Bormett, Matthew Bloomfield, Ken Williams

4:20 (443) **Surface-Enhanced Raman Substrate Comparison**; Jason Guicheteau[1], Steven Christesen[1], Augustus Fountain, III[1], Darren Emge[1]; [1]USA RDECOM ECBC

4:40 (444) **A Single Nucleotide Polymorphism Screening Method Based on Surface-Enhanced Raman Scattering**; Mustafa Culha[1], Omer Faruk Karatas[1], Omer Aydin[1], Mehmet Kahraman[1], Omer Faruk Bayrak[1]; [1]Yeditepe University

5:00 (444b)**Quantitative SERS of Anionic and Cationic Species using Off-the-Shelf Colloid,** S. E. J.. Bell, M. McCourt, E. Lozano-Diz, A. C. Dennis

TECHNICAL PROGRAM – THURSDAY
Plenary Sessions, Presider: John Hellgeth

Ellis R. Lippincott Award
8:00 AM Plenary Session, S2/3

Richard P. Van Duyne
(445) **Molecular Plasmonics: Single Molecule SERS, Exploring the Plasmonic Periodic Table, and Plasmon Microscopy**
Richard P. Van Duyne; Northwestern University
Refer to page 20 for biographical information

Coblentz Clara Craver Award
8:30 AM Plenary Session, S2/3

John C. Conboy
(446) **Nonlinear Vibrational Spectroscopy for the Analysis of Biological Membranes**
John Conboy; University of Utah
Refer to page 21 for biographical information

THURSDAY POSTER SESSIONS
9:00 – 10:15 am and 1:30 – 3:00 pm
Nevada Room

All Thursday posters should be put up between 7:30 – 8:00 AM and removed by 5:00 PM The odd numbered poster boards present in the morning and the even numbered poster boards present in the afternoon

Atomic Spectroscopy

Board #

1 (447) **Chemically Modified Electrodes for Rapid On-line Separation and ICP-MS Analysis of Cesium**; Scott Lehn[1], Kate L. Ziegelgruber[1], Shane M. Peper[1], Douglas C. Duckworth[1]; [1]Pacific Northwest National Laboratory

2 (448) **Signal Enhancement in DRC-ICP-MS by Collisional Focussing**; Julian Tyson[1], Maura Mahar[1], Kenneth Neubauer[2], Dennis Yates[2]; [1]University of Massachusetts; [2]PerkinElmer Life and Analytical Sciences

3 (449) **Development of Laser Ablation-Inductively Coupled Plasma-Atomic Emission Spectrometry (LA-ICP-AES) Prototype for Monitoring Vitrification of Hanford Radioactive Waste**; Jinesh Jain[1], Aruna Arakali[1], Thomas Lane[1], Douglas Perkins[1], Cary Seidel[2], Larry Lockrem[2]; [1]Hanford Tank Waste Treatment Plant; [2]222-S Laboratory

4 (450) **Detection Limits Based on Poisson Statistics in ICP-MS**; Martin Tanner[1], Arturo Gomez-Tuena[1]; [1]UNAM Mexico, Centro de Geociencias, Queretaro

Bioanalytical

5 (451) **Electrophoretically Mediated Microanalysis of Alcohol Dehydrogenase Kinetics and Inhibition**; Rachel Henken[1], Li Yang[1], S. Douglas Gilman[1]; [1]Louisiana State University

6 (452) **Correlative Spectromicroscopy and Conventional Microscopy for Exploring Fungal Metabolism**; Merrill Isenor[1], Susan Kaminskyj[2], Merrill Isenor[1], Konstantin Jilkine[1], Catherine Liao[1], Margaret Rak[3], Kathleen Gough[1], [1]University of Manitoba; [2]University of Saskatchewan; [3]European Synchrotron Radiation Facility

Fluorescence

7 (453) **Excited State Electric Dipole Moment of Some Benzene Derivatives through Solvatochromic Shifts**; Neeraja Rani Gaddipati[1], Narasimha Ayachit[1]; [1]SDM College of Eng & Tech., Dharwad, India

8 (454) **Analysis of Complex Samples using a Portable Multi-Wavelength Light Emitting Diode (LED) Fluorescence Spectrometer**; Bai Baolong[1], Dean Anderson[2], Gary Rayson[1]; [1]New Mexico State University; [2]USDA-ARS, JER

9 (455) **Fluorescence Quenching of Polycyclic Aromatic Hydrocarbons Near Gold Nanoparticles**; Huiyong Wang[1], Korina Calimag[1], Andres Campiglia[1]; [1]University of Central Florida, Chemistry Departmen

10 (456) **Single-Molecule Spectroscopic Study of HIV-1 Viral Rev-RRE Interactions**; Hui Wang[1], Yu-Shan Yeh[1], Matthew Daugherty[2], Alan Frankel[2], Paul Barbara[1]; [1]The University of Texas at Austin; [2]University of California, San Francisco; [3]; [4]

11 (457) **Interaction of 4-Amino Benzoic Acid (PABA) with Ionic and Nonionic Micelles by Fluorescense**; Seema Acharya[1], REKHA Soni[1]; [1]J.N.V. University

12 (458) **Chemiluminescence and Fluorescence Signal Variations Due to Water Quality**; Maricar Tarun, Stephane Mabic; [1]Millipore Corp

13 (459) **Solid-Surface Room-Temperature Fluorescence Determination of Biomarkers on Solid-Phase Extraction Membranes**; Korina Jesusa Calimag; Andres Campiglia[1];[1]University of Central Florida

14 (460) **Fabrication of Porous Cladding Materials for Remote Sensing with Crossed-Fiber Sensor Arrays using Microsphere Templating**; Paul Henning[1], Veronica Rigo[1], Peter Geissinger[1]; [1]University of Wisconsin - Milwaukee

15 (461) **Data Analysis Tools for Determining Single Molecule Binding Affinities Using Total Internal Reflection Fluorescence Microscopy**; Eric Peterson[1], Josh Wayment[1], Moussa Barhoum[1], Karl-Heinz Gericke[2], Joel Harris[1]; [1]University of Utah Chemistry Department; [2]Technische Universität Braunschweig

16 (462) **Intracellular Delivery and Localization of Luminescent Conjugated Polymer Nanoparticles**; Kenneth Christensen[1], Prakash Kandel[1], Lawrence Fernando[1], Jason McNeill[1]; [1]Clemson University

17 (463) **Studies of the Fluorescence Excitation Spectroscopy of Phytoplankton at the Single Organism Level**; Laura S. Hill[1], Luisa T.M. Profeta[1], Evelyn Lawrenz[1], Tammi L. Richardson[1], Benjamin S. Twinning[1], Christopher J. Hintz[1], Timothy J. Shaw[1], Michael L. Myrick[1]; [1]University of South Carolina

18 (464) **Quantification of Affinity and Kinetics of Membrane Associated Proteins by Ratiometric Imaging and Flow Cytometry**; Kenneth Christensen[1], Barbara Bull[1], Thomas Caldwell[1]; [1]Clemson University

19 (465) **Detection of Reactive Oxygen Species in Cells using a Fluorescent Probe– Application and Limitation**; Kazunari Kondo[1], Sayaka Ohta[1], Reiko Teshima[1]; [1]National Institute of Health Sciences

20 (466) **Oxytetracycline Determination by Derivative Spectrophotometry Based in the Formation of Ionic-Pair with crystal Violet and Its Spectroscopy Verification**; María Inés Toral[1], Sandra Orellana[1]; [1]University of Chile

21 (467) **Development of Accurate, Real Time and Sensitive Optical Oxygen Sensors for Hydrocarbon Environments**; Mahmoud Shahriari[1], Mike Morris[2]; [1]Ocean Optics Corp.; [2]Spectrecology

22 (468) **Fluorescence Lifetime Global Analysis using a Multiple-Frequency Frequency Domain Fluorometer**; Karen Steege[1], James Mattheis[1], Adam Gilmore[1]; [1]Horiba Jobin Yvon

23 (469) **TCSPC Fluorescence Lifetime Microscope System in the Deep UV-Visible and NIR (240nm - 5:00nm)**; Lin Chandler; [1]Horiba Jobin Yvon, Inc.

24 (470) **CO2 Laser Induced Far-Infrared Fluorescence from Bio-Materials**; Raphael Moon[1], Boris Gelmont[2], Ashish Tripathi[3]; [1]US Army, ECBC, AMSRD-ECB-RT-DL; [2]University of Virginia; [3]Science Applicaitons International Corp

Forensics

25 (471) **Identification of Micro Particles from Bio-Pharmaceutical Manufacture Process using Multiple Micro-Spectroscopes**; Wen Jing[1], Xiaolin Cao[1], Gary Li[1], Zai-qing Wen[1]; [1]Amgen Inc

26 (472) **Differentiation of Paper and Adhesives in Labels by Fourier Transform Infrared Spectroscopy and Linear Discriminant Analysis**; Deidre Krupp[1], Christopher Detloff[1], Mary Carrabba[1], Mark Witkowski[2]; [1]Southern Oregon University; [2]FDA Forensic Chemistry Center

Molecular Spectroscopy

27 (473) **Determining the Sensitivity of our Biological Fluorescent Hyperspectral Images**; Howland Jones[1], David Haaland[1], Michael Sinclair[1], Bryan Carson[1]; [1]Sandia National Laboratories

28

29 (475) **Chemiluminescent Radicals in HN3/H2/O2 Flames**; R. Sausa[1], M. Grams[1]; [1]US Army Research Laboratory

Raman

30 (476) **Super-Resolution and Raman Chemical Imaging: from Multiple Low Resolution Images to a High Resolution Image**; Duponchel Ludovic[1], Ruckebusch Cyril[1], Milanfar Peyman[2], Huvenne Jean-Pierre[1]; [1]University of Lille-Lasir Lab-France; [2]University of California-MDSP Lab-USA

31 (477) **Resolution of Raman Spatial Artifacts using Optical Pre-Processing**; Michael Pelletier; [1]Pfizer

32 (478) **Getting the Most from the Microscope in Your Micro-Raman Spectrometer**; Kathleen Martin[1], Gretchen Shearer[1]; [1]McCrone Associates, Inc.

33 (479) **Combining Raman Spectroscopy and Differential Scanning Calorimetry**; Richard Spragg[1], Robert Alexander[1], Nancy Kawai[2], Kevin Menard[2]; [1]PerkinElmer LAS UK; [2]PerkinElmer LAS USA

34 (480) **Potential-Dependent Acid/Base Chemistry of Silver-Immobilized 2-Mercaptobenzoic Acid Studied by Surface Enhanced Raman Spectroscopy**; Chaoxiong Ma[1], Joel Harris[1]; [1]University of Utah

35 (481) **SRM 2244: Relative Intensity Correction Standard for 1064 nm Excitation**; Steven Choquette[1], Aaron Urbas[1], Stefan Leigh[1]; [1]NIST

36 (482) **Confocal Raman Microscopy of Optically-Trapped Lipid Vesicles: Investigation of the Polymerization of a Diacetylenic Lipid Membrane**; Jonathan Schaefer[1], Christopher Fox[1], Joel Harris[1]; [1]University of Utah

37 (483) **Towards a Practical Clinical Approach for Automated Breast Histopathology**; Frances Pounder[1], Rohit Bhargava[1]; [1]University of Illinois at Urbana-Champaign

38 (484) **Coherent Raman Studies of Germanium Sulfide Thin Film Deposition**; Patrick Whitham[1], Rene Rodriguez[1], BarJean Phillips[1]; [1]Idaho State University

39 (485) **Autocalibration of Process Raman Data Utilizing Multivariate Temperature and Pressure Modeling**; Wesley J. Thompson[1], Brian J. Marquardt[1]; [1]Applied Physics Lab, Univ. of Washington

40 (486) **Raman Spectroscopic Assessment of the Effects of Genetic Abnormalities on Bone Composition in a Mouse Model**; Michael Roberto[1], Jacqueline Cole[1], Chad Novince[2], Laurie McCauley[2], Ramiro Toribio[3], Michael Morris[1]; [1]University of Michigan Department of Chemistry; [2]University of Michigan School of Dentist; [3]Ohio State University College of Vet Med

41 (487) **UV Raman Spectra and Cross Sections of the G-Series Nerve Agents**; Steven D. Christesen[1], Jay Pendell Jones[2], Joseph M. Lochner[1], Aaron M. Hyre[1]; [1]U.S. Army Edgewood Chemical Biological Ctr; [2]ITT Advanced Engineering and Sciences

Surface Plasmon Resonance

42 (488) **Hybrid Electrokinetic Localized Surface Plasmon Resonance Platform For Biomolecule Quantification In Complex Media**; Michael R Malone[1], Raul S Rivera[1], Karl S Booksh[1]; [1]University of Delaware

43 (489) **Designing Novel Interfaces for Probing Protein Interactions with Carbohydrates and Lipids using Surface Plasmon Resonance and SPR Imaging**; Quan Cheng[1], Matthew Linman[1]; [1]Univ of California Riverside

XRF

44 (490) **X-Ray Characterization of Materials in 3D**; Brian Patterson[1], George Havrilla[1], Kimberly Defriend; [1]Los Alamos National Laboratory

45 (491) **Studies of Gadolinium-Doped Zinc Telluride Semiconductors by X-Ray Photoelectron and Auger Spectroscopy**; Dale L. Perry[1], Andrew Olson[3], Erik Topp[2], Zhix Ma[1], Samuel S. Mao[1]; [1]Lawrence Berkeley National Laboratory; [2]University of California, Berkeley; [3]Carleton College

46 (492) **A Prototype Pico Liter Deposition Device to Generate Reference Deposits for Direct Elemental Analysis using Micro X-Ray Fluorescence (MXRF)**; Ursula E. A. Fittschen[1], George J. Havrilla[1]; [1]Los Alamos National Laboratory

Thursday Morning, Room Nevada 2
CLASSIFICATION AND MULTIVARIATE CALIBRATION FOR BIOANALYTICAL APPLICATIONS
Organizer and Presider: Jerry Workman

10:15 (493) **Assessing and Classifying the Spatial Distribution of E. coli Contamination by Means of Spectroscopic Imaging and Chemometrics**; Frank Vogt[1], Michael Gilbert[1], Rebecca Burke[1]; [1]University of Tennessee, Dept of Chemistry

10:35 (494) **Interplay of Chemometrics and Large-Scale Databases**; Brian Rohrback[1], Gregory Banik[2]; [1]Infometrix, Inc.; [2]Bio-Rad Informatics Division

11:15 (495) **Wavelet Transform for Near Infrared Spectral Data Mining – Single Spectrum Disease Diagnosis**; Barry Lavine[1], Nikhil Miranjakar[1], Roumiana Tsenkova[2]; [1]Department of Chemistry, Oklahoma State University; [2]Faculty of Agriculture, Department of Eng

11:35 (496) **The Chemometrics Leading to Robust Calibrations for Low Signal-to-Noise Applications**; Jerry Workman; [1]Luminous Medical Incorporated

Thursday Morning, Room Nevada 3
MICROANALYTICAL CHEMISTRY
Organizer and Presider: Carlos Garcia

10:15 (497) **Developing Micro/Nano Solutions for Bioanalytical Chemistry using Low Resolution Tools**; Emanuel Carrilho[1]; [1]University of São Paulo

10:35 (498) **DNA-Based Diagnosis of Greenhouse Fungal Pathogens on a 96-Channel Microfluidic Microarray Chip**; Paul Li[1], Lin Wang[1]; [1]Simon Fraser University

10:55 (499) **Biomedical Devices and Biosensors Based on Protein Attachment to Nanoparticles**; Alexey Vertegel[1]; [1]Clemson University

11:15 (500) **Smaller is Better: Microfluidics Meet Surfaces**; Carlos D. Garcia[1], Maria Fernanda Mora[1], Carla E. Giacomelli[1,2], Jennifer Wehmeyer[1], Rena Bizios[1], Arturo A. Ayon[1]; [1]UT San Antonio; [2]Univ. Nacional de Cordoba - Argentina

11:35 (501) **Integrated Microfluidic System for Detection of Biomarkers in Biological Samples**; Hsiang-Yu Wang, Weichun Yang, Xiuhua Sun, Adam Woolley; [1]Brigham Young University

11:55 (502) **Active MOS Capacitive Sensor Array for Lab-On-a-Chip Applications**; Manu Sebastian Mannoor[1], Teena James[1]; [1]New Jersey Institute of Technology

Thursday Morning, Room Nevada 4
APPLICATIONS OF FLUORESCENCE SPECTROSCOPY AND RELATED TECHNIQUES
Organizer and Presider: Andres D. Campiglia

10:15 (503) **Luminescent Pyridine-bis(oxazoline) Complexes of Eu(III) and Tb(III)**; Ana de Bettencourt-Dias ; [1]University of Nevada, Reno

10:35 (504) **Mobility and Diffusivity of Molecules Confined in Silica-Nanochannel as Studied By Time-Resolved Fluorescence Spectroscopy**; Toshio Kamijo[1], Akira Yamaguchi[2], Norio Teramae[3]; [1]Tohoku University

10:55 (505) **Multiparameter Fluorescence Fluctuation Spectroscopy for Ultrasensitive Analysis of Nucleic Acids**; Alan Van Orden[1], Jaemyeong Jung[1], Keir Fogarty[1], Jeff McPhee[1], Eric Scott[1]; [1]Colorado State University

11:15 (506) **Assays On-the-Fly: Rapid Identification of Aerosols using Fluorescent Beacons**; Matthew Hart[1], Horn-Bond Lin[1], Casey Jacobsen[1], Jay Eversole[1], Charles Merritt[1]; [1]Naval Research Laboratory

11:35 (507) **Competitive Homogeneous Fluorescence Immunoassay (FIA) for Hapten Detection**; Annette Kupstat[1], Michael U. Kumke[1], Reinhard Niessner[2], Dietmar Knopp[2]; [1]University of Potsdam; [2]Technische Universitaet Muenchen

11:55 (508) **Room-Temperature Fluorescence Excitation-Emission Matrices for Comparing Textile Fibers as Physical Evidence**; Hector Goicoechea[2], Mathew Rex[1], Andres Campiglia[1]; [1]University of Central Florida; [2]Universidad Nacional del Litoral

Thursday Morning Room Nevada 5
LIPPINCOTT AWARD SYMPOSIUM
Organizer and Presider: Michael J. Pelletier

10:15 (509) **Catalytic Transformations of Biological Macromolecules in Single Nanopores Probed by 4ð Single Molecule Cross-Correlation.**; Paul Bohn[2], Travis King[1,2], Zhen Wang[2]; [1]University of Illinois- Urbana-Champaign; [2]University of Notre Dame

10:35 (510) **SERS - a Single Molecule Tool**; Katrin Kneipp[1,2], Harald Kneipp[1]; [1]Harvard University Medical School; [2]Harvard-MIT Division of Health Sciences

10:55 (511) **Extreme Biosensing with Plasmons, Nanoparticles and Surface Enzyme Chemistry**; Robert Corn; [1]Chem Dept, Univ. of California-Irvine

11:15 (512) **Nanoparticle Optical Property Modeling**; George Schatz; [1]Northwestern University

11:35 (513) **Nanoparticulate Quantitation Labels Based on SERS**; Michael Natan[1]; [1]Oxonica Materials Inc.

11:55 (514) **Spectroscopic Studies of Environmentally Important Processes at Aqueous Surfaces**; Geraldine Richmond; [1]University of Oregon

Thursday Morning, Room Nevada 6
MASS SPECTROMETRY AND ARRAYS
Organizer and Presider: Randall W. Nelson

10:15 (515) **Targeted Mass Spectrometric Immunoassays for Population Proteomics**; Dobrin Nedelkov; [1]Intrinsic Bioprobes Inc.

10:35 (516) **Combining Protein Microarrays and Mass Spectrometry**; Robert J Cotter[1], Kenyon M Evans-Nguyen[1], Dwella M Nelson[1], Sheng-Ce Tao[1], Heng Zhu[1]; [1]Johns Hopkins University School of Medicine

10:55 (517) **Performing Enzyme Activity Assays with SAMs & Mass Spectrometry**; Steven Patrie[1,2]; [1]University of Texas Southwestern Medical Center; [2]University of Texas Dallas

11:15 (518) **Interfacing High-performance Separation Systems with New High-speed MALDI-TOF Mass Spectrometry**; Marvin Vestal[1], Stephen Hatton[1], Kevin Hayden[1]; [1]Virgin Instruments Corp.

11:35 (519) **Micropatterned Fluid Lipid Bilayers Created Using a Continuous Flow Microspotter**; Kathryn Smith[1], Bruce Gale[2], John Conboy[1]; [1]Department of Chemistry, University of Utah; [2]Department of Mechanical Engineering

11:55 (520) **Tissue Imaging Of Antitumor Drugs With MALDI-TOF/TOF And MALDI-FTMS**; Emily Creedon[2], Stefen Laukien[2], Paul Kowalski[1], Jane-Marie Kowalski[1], Michael Easterling[1], Katherine Kellersberger[1], Claire Sauvageot[3], Nathalie Agar[4]; [1]Bruker Daltonics; [2]The Rivers School; [3]Dana Farber Cancer Inst., Harvard Med; [4]Brigham & Women's Hospital, Harvard Med

Thursday Morning, Room Nevada 7
HIDDEN ISOTOPE RATIO INFORMATION – YOURS TO DISCOVER WITH MC-ICP-MS
Organizers and Presiders: Ralph Sturgeon and Frank Vanhaecke
Note early start

10:05 (521) **MC-ICPMS: the Year in Review**; Charles Douthitt; [1]Thermo Scientific

10:15 (522) **Lead Isotopic Analysis as a vErsatile Tool for Provenance Determination**; Frank Vanhaecke[1], Eleonora Balliana[1,2], Carlo Barbante[2], Christophe Cloquet[1,3], David De Muynck[1], Esperanza Garcia-Ruiz[4], Paz Marzo[4], Martin Resano[4], Paul Vallelonga[2]; [1]Ghent University, Belgium; [2]Ca\'Foscari Uni + IDPA-CNR, Venice, Italy; [3]CRPG - Nancy, France; [4]University of Zaragoza, Spain

10:35 (523) **Mo Stable Isotope Fractionation: From Marvel to Mechanism**; Laura Wasylenki[1], Tracy Lund[1], Colin Weeks[2], Thomas Spiro[2], John Bargar[3], Ariel Anbar[1]; [1]Arizona State University; [2]University of Washington; [3]Stanford Synchrotron Research Laboratory

10:55 (524) **Advances in High-Precision U-Series Analyses using MC-ICPMS**; Victor Polyak[1], Yemane Asmerom[1]; [1]University of New Mexico

11:15 (525) **Accurate and Precise Determination of Hg Isotope Ratios and Isotope Fractionation Induced by Vapor Generation**; Lu Yang[1], Ralph Sturgeon[1]; [1]NRCC

11:35 (526) **Mass Independent Fractionation of Mercury Isotopes in Environmental Samples**; Holger Hintelmann[1], Wang Zheng[1], Klaus Gantner[2], Derek Muir[2], Xinbin Feng[3]; [1]Trent University, Peterborough ON; [2]Environment Canada, NWRI, Burlington ON; [3]Chinese Academy of Sciences, Guiyang

11:55 (527) **Isotopic Reference Materials for the 21st Century**; Robert Vocke[1], Jacqueline Mann[1]; [1]National Institute of Standards and Technology

Thursday Morning, Room Nevada 8
SURFACE PLASMON RESONANCE: INNOVATION AND APPLICATION I
Organizers: Karl Booksh and Roger Terrill; Presider: Karl Booksh

10:15 (528) **Nanoholes Arrays Sensors Prepared using Lithography**; Jean-Francois Masson[1]; [1]Universite de Montreal

10:35 (529) **SPR Microscopy Combined with a Microfluidic Flow Cell Array as a Platform for Immunogenicity Assays**; Jennifer Shumaker-Parry[1]; [1]University of Utah

10:55 (530) **Engineering Stable Nanostructures for Enhanced Optical Detection**; Amanda Haes[1], Maryuri Roca[1], Kyungtag Ryu[1]; [1]University of Iowa

11:15 (531) **Electrochemical SPR Studies of Acid Thiol Chemisoption**; Roger Terrill[1], Arthur Cheng[1], Shaowei Chen[1]; [1]San Jose State University; [2]UC Santa Cruz

11:35 (532) **Pure Plasmons: The Control of Plasmon Frequency and Bandwidth in Conducting Metal Oxides**; Josh Guske[1], Alina Efremenko[1], Mark Losego[1], Jon-Paul Maria[1], Stefan Franzen[1]; [1]North Carolina State University

11:55 (533) **Designing Novel Interfaces for Probing Protein Interactions with Carbohydrates and Lipids using Surface Plasmon Resonance and SPR Imaging**; Quan Cheng[1], Matthew Linman[1]; [1]Univ of California Riverside

Thursday Morning, Room Nevada 9
RAMAN IN PHARMA/BIOTECH
Organizer and Presider: Manoharan Ramasamy

10:15 (534) **Raman Spectroscopy for Bioprocess Development**; Harry Lee[1], Gustavo Gil[1], Paolo Boccazzi[1], Anthony Sinskey[1], Rajeev Ram[1], Elizabeth Bruce[1]; [1]Massachusetts Institute of Technology

10:35 (535) **Near-Infrared Spectroscopy: A Versatile Tool for the Pharmaceutical Industry**; Christopher John[1], James Roberts[1], Megan Miller[2], Feng Yang[2], Maria Cruanes[1], Manoharan Ramasamy[3]; [1]Merck-MRL-PAC; [2]Merck-MRL-Vaccines and Biologics; [3]Merck-MRL-AS&QT-Specialty Analytical

10:55 (536) **Does Crystal Structure Trump Chemistry? Raman Spectroscopy of Isostructural Solvates**; CJ Pommier[1], Raymond Scaringe[1], John DiMarco[1], Michael Galella[1], Mary Malley[1]; [1]Bristol-Myers Squibb

11:15 (537) **Raman Spectroscopy of Biopharmaceuticals for Counterfeit Detection and Quality Assurance**; John Kauffman[1], John Spencer[1], Connie Gryniewicz[1], Lucinda Buhse[2], Benjamin Westenberger[1], Hongping Ye[1], John Reepmeyer[1], Wei Ye[1]; [1]FDA Div. of Pharmaceutical Analysis, St. Louis, MO

11:35 (538) **Spearman Rank Correlation: a Robust Method for Determining High-throughput Raman and pXRD Crystalline Solid Spectra Statistical Distances**; B. Andre Weinstock[1]; [1]TransForm Pharmaceuticals Inc.

11:55 (539) **Transmission Raman Spectroscopy for Quantitative Analysis**; Olof Svensson[1], Anders Sparén[1], Jonas Johansson[1], Staffan Folestad[1], Mike Claybourn[2]; [1]PAR&D, AstraZeneca R&D Mölndal, Sweden; [2]PAR&D, AstraZeneca R&D Macclesfield , UK

Thursday Morning, Room Nevada 10
TWO-DIMENSIONAL CORRELATION SPECTROSCOPY
Organizer and Presider: Curtis Marcott

10:15 (540) **Two Dimensional Correlation Spectroscopy to Graphically Represent Instrument Similarity for Calibration Transfer**; Franklin Barton[1], James der Haseth[1], Arnold Eilert[2]; [1]Light Light Solutions, LLC; [2]Unity Scientific, Inc.

10:35 (541) **Application of IR Correlation Spectroscopy to Conjugated Polymer Materials**; Georgia Arbuckle-Keil; [1]Rutgers University

TECHNICAL PROGRAM – THURSDAY
Orals 10:15 AM – 12:15 PM and 3:00 – 5:00 PM

10:55 (542) **Characterization of Hydrostatic Pressure Effect on the Phase Transitions of a Weakly Interacting Block Copolymer by Two-Dimensional Correlation Spectroscopy**; Young Mee Jung[1], Hye Jeong Kim[2], Seung Bin Kim[3], Jin Kon Kim[2]; [1]Dept. of Chemistry, Kangwon National University; [2]Dept. of Chemical Engineering, POSTECH; [3]Dept. of Chemistry, POSTECH

11:15 (543) **Enhancing S/N in Nanosecond Time-Resolved IR Emission Spectra from Transient Radicals through 2-D Correlation Analysis**; Hai-Lung Dai[1], Michael Wilhelm[2], Mathew Nikow[2]; [1]Department of Chemistry, Temple University; [2]Department of Chemistry, University of PA

11:35 (544) **New Method for Time-Resolved Structural Characterization with Polarization Modulation FTIR Spectroscopy**; Christian Pellerin[1], Yongri Liang[1], Robert Prud'homme[1], Damien Mauran[1]; [1]University of Montreal

11:55 (545) **Quantitative Study of Protein Conformation and Orientation in Single Silk Fibers by Golden Gate Attenuated Total Reflectance Infrared Spectroscopy**; Michel Pezolet[1], Maxime Boulet-Audet[1], Thierry Lefevre[1], Thierry Buffeteau[2]; [1]Laval University; [2]Universite de Bordeaux

THURSDAY AFTERNOON POSTER SESSION
Break and Dessert
1:30 – 3:00 PM
Nevada Room
Even numbered poster boards present.
See page 64 for a listing of the posters.

Thursday Afternoon, Room Nevada 2
SPECTRAL AND MULTIWAY PATTERN RECOGNITION
Organizer and Presider: Frank Vogt

3:00 (546) **Spatial Compression and Noise Scaling for Improved Multivariate Analysis of Hyperspectral Fluorescence Images**; David Haaland[1], Howland Jones[1], Michael Sinclair[1], Bryan Carson[1]; [1]Sandia National Laboratories

3:20 (547) **Quantification of Synthetic Fuel Content and Property Prediction Compensation in Fuel Blends using Near-Infrared Spectroscopy and Partial Least Squares**; Jeffrey Cramer[1], Robert Morris[1], Mark Hammond[1], Braden Giordano[2], Susan Rose-Pehrsson[1]; [1]U.S. Naval Research Laboratory; [2]Nova Research, Inc.

3:40 (548) **Analytical Chemistry and Multi-Block Modeling for Improved NIR Spectral Interpretation**; Charles Miller; [1]Eigenvector Research, Inc.

4:00 (549) **Identification of Protein Secondary Structure UVRR Spectral Motifs using Trilinear-MCR of 2D Excitation Raman Shift Matrices**; Renee JiJi[1], John Simpson[1]; [1]University of Missouri

4:20 (550) **Pattern Recognition Methods for Real-Time Monitoring Applications of Near-Infrared Spectroscopy**; Gary Small[1]; [1]University of Iowa

4:40 (551) **Two-Dimensional Gas Chromatography / Time-of-Flight Mass Spectrometry with Chemometric Data Analysis**; Jamin C. Hoggard[1], Robert Synovec[1]; [1]University of Washington

Thursday Afternoon, Room Nevada 3
APPLICATIONS OF MICROSCOPY AND MICROANALYSIS IN FORENSIC SCIENCE
Organizer and Presider John A. Reffner

3:00 (552) **Application of the Raman Microscope to Forensic Science**; Sergey Mamedov[1], Eunah Lee[1], Fran Adar[1], Andrew Whitley[1], Jon Goldey[1]; [1]Horiba Jobin Yvon

3:20 (553) **Crystal Tests as a Separation Method for the Rapid Analysis of Illicit Drugs by IR Microspectroscopy**; Pauilne Leary[1]; [1]Smiths Detection

3:40 (554) **FT-IR Microspectroscopy of Individual Starch Granules Detects the Presence of Chemical Modification**; Yanjie Bai[1], Yong-Cheng Shi[1], David Wetzel[1]; [1]KSU Microbeam Molecular Spectroscopy Lab

4:00 (555) **The Challenges of Trace Evidence – In the Field, Laboratory and Court**; John Reffner[1]; [1]Trace Consulting

4:20 (556) **Studies on the Feasibility of using Chemometric Modeling of Spectral Data for the Determination of Post-mortem Intervals on Skeletal Remains**; Patricia Diamond[1], Marianna Busch[1], Kenneth Busch[1], Jody Dogra[1]; [1]Center for Analytical Spectroscopy

Thursday Afternoon, Room Nevada 4
APPLICATIONS OF FLUORESCENCE SPECTROSCOPY AND RELATED TECHNIQUES
Organizer and Presider: Andres Campiglia

3:00 (557) **Laser Induced Fluorescence Spectral Classification and Selective electrostatic Collection of Individual biothreat Aerosol Particles**; Vasanthi Sivaprakasam[1], Jay Eversole[1], Timothy Pletcher[2], David Keller[2]; [1]Naval Research Laboratory; [2]Sarnoff Corporation

3:20 (558) **Detection of Biological Compounds Using a Fluorescence-Based Detection System**; Brian Dable[1], Geoff Wilson[1], Steve Estrada[1], Everett Perry[1], Jim Brady[1], Mike Carrabba[1]; [1]Hach Homeland Security Technologies

3:40 (559) **Unusual Photophysical Behavior of Pyrazolo[3,4-b]quinoline in Low-Temperature n-octane Matrices**; Freek Ariese[1], Joost S. de Klerk[1], Arjen N. Bader[1], Cees Gooijer[1], Monika Sterzel[2], Mariusz Pilch[2], Andrzej Danel[3], Szczepan Zapotoczny[2]; [1]Laser Centre Vrije Universiteit Amsterdam; [2]Jagiellonian University, Krakow, Poland; [3]Agricultural University, Krakow, Poland

4:00 (560) **Single Molecule Fluorescence Anisotropy Measurements to Monitor and Quantify Biomolecular Complexation**; Sean M. Burrows[1], Dimitri Pappas[1]; [1]Texas Tech University

4:20 (561) **In-Capillary Protein Detection using Laser Induced Native Fluorescence of the Aromatic Amino Acids**; Matthew Heywood[1], Paul Farnsworth[1]; [1]Brigham Young University

4:40 (562) **Fluorescence Microscopy Analysis of Surface Immobilized Phospholipid Vesicles**; Emily Heider[1], Moussa Barhoum[1], Karl-Heinz Gericke[2], Joel Harris[1]; [1]University of Utah; [2]Technische-Universitaet Braunschweig

TECHNICAL PROGRAM – THURSDAY
Orals 3:00 – 5:00 PM

Thursday Afternoon, Room Nevada 5
BIOANALYTICAL-SERS
Organizer and Presider: George Chumanov

3:00 (563) **Analytics in a Live Cell using SERS**; Janina Kneipp[3], Harald Kneipp[1], Margaret McLaughlin[2], Burghardt Wittig[4], Dennis Brown[1,2], Katrin Kneipp[1]; [1]Harvard University, Medical School; [2]Renal Unit, Massachusetts General Hospit; [3]Humboldt University, Chemistry Departmen; [4]Institute for Molecular Biology

3:20 (564) **Novel Nanorod Array Substrates for High Sensitivity Biopathogen Sensing**; Richard Dluhy[1], Jeremy Driskell[1], Vinh Hoang[1], Yiping Zhao[1], Paul Rota[2], Ralph Tripp[1]; [1]University of Georgia; [2]Centers for Disease Control

3:40 (565) **Barcoding Bacteria: A SERS Based Methodology for Rapid Bacterial Identification**; Lawrence Ziegler[1], W. Ranjith Premasiri[1], Donald Moir[2], Ishan Patel[1]; [1]Boston University; [2]Microbiotix, Inc

4:00 (566) **Application of SERS to Structure-Functional Characterization of Complex Biosystems**; George Chumanov[1], Jacquitta KaTrina Daniels[2], David Evanoff[1]; [1]Clemson University; [2]Sporian Microsystems, Inc

4:20 (567) **Probabilistic Modeling for Small Molecule Identification in LC-SERS Experiments**; Royston Goodacre[1], Iqbal Shadi[1], Richard O'Connor[1], Roger Jarvis[1]; [1]The University of Manchester

4:40 (568) **Immunoassay Sensor Based on Surface-Enhanced Raman Scattering on Gold SOLS for Detecting Biological Molecules**; Ava Dykes[1], Lori Kamemoto[1,2], Anupam Misra[1], Shiv Sharma[1]; [1]University of Hawaii; [2]John A. Burns School of Medicine

Thursday Afternoon, Room Nevada 6
COBLENTZ SOCIETY CLARA CRAVER AWARD SYMPOSIUM HONORING JOHN CONBOY
Organizer: Mark A. Druy; Presider: John Hellgeth

3:00 (569) **To Charge or Not to Charge: Ions at Aqueous Interfaces**; Geraldine Richmond; [1]University of Oregon

3:20 (570) **Vibrational Spectroscopy of Water Interfaces**; Yuen-Ron Shen[1]; [1]University of California, Berkeley

3:40 (571) **Coupling of Cholesterol-Rich Lipid Phases in Asymmetric Bilayers**; Lukas Tamm[1], Volker Kiessling[1], Chen Wan[1]; [1]University of Virginia

4:00 (572) **Quantitative Determination of Interfacial Populations at the Single-Molecule Level**; Joel Harris[1], Joshua Wayment[1], Christopher Fox[1]; [1]University of Utah

4:20 (573) **A Molecular View of Low Work Function Metal-Organic Contacts in Photonic Devices**; Jeanne E. Pemberton[1], Robert J. Davis[1], Matthew C. Schalnat[1]; [1]University of Arizona

4:40 (574) **Structure, Functional Properties, and Analytical Applications of Poly(Lipid) Bilayer Membranes**; Scott Saavedra[1]; [1]University of Arizona

Thursday Afternoon, Room Nevada 7
ACTINIDE ANALYSIS
Organizer: Greg Klunder; Presider: Stefan Buerger

3:00 (575) **Correcting Isotope Ratio Inaccuracies Encountered with ICP-TOF-MS**; Adam Rowland[1], James Holcombe[1]; [1]University of Texas at Austin

3:20 (576) **Plutonium Isotope Ratio Measurements at Femtogram-Attogram Levels by Single and Multicollector ICP-MS using Inline Selective Electrochemical Preconcentration and Stripping**; Martin Liezers[1], Scott A. Lehn[1], Khris B. Olsen[1], Orville T. Farmer (lll)[1], Douglas C. Duckworth[1]; [1]Pacific Northwest National Laboratory

3:40 (577) **High Accuracy and Precision Multi-Collector TIMS Uranium Isotope Metrology**; Stefan Buerger[1], Rebecca B. Thomas[1], Richard M. Essex[1], Kattathu Mathew[1], Peter Mason[1]; [1]DOE New Brunswick Laboratory

4:00 (578) **Analysis of High Activity Nuclear Waste: Laser Ablation ICP at 100 Million Rads!**; Steven Hughes[1], Joseph W. Brady[1], Robert Fry[1]; [1]Spectra-LAse

4:20 (579) **Trace Element Analysis by DC Arc**; Jeffrey Miller[1], David Gallimore[1], Ning Xu[1]; [1]Los Alamos National Laboratory

4:40 (580) **Site Selective Passive Eu(III) Binding Affinities to Datura innoxia Plant Cell Walls using Saturated Luminescence Spectroscopy**; Jessica Moore[1], Debbie Serna[1]; [1]New Mexico State University, Chemistry Department

Thursday Afternoon, Room Nevada 8
SURFACE PLASMON RESONANCE: INNOVATION AND APPLICATION II
Organziers: Karl Booksh and Roger Terrill;
Presider: Roger Terrill

3:00 (581) **Introducing Molecular Recognition to Surface Plasmon Resonance Sensors using Composite Metal-Polymer Coatings**; Nicola Menegazzo[1], Jing Wang[1], Soame Banerji[1], Wei Peng[1], Yoon-Chang Kim[1], Karl Booksh[1]; [1]University of Delaware

3:20 (582) **Development of Compact Sensing System by the Localized Surface Plasmon Resonance**; Ryosuke Hasui[1], Takeo Nishikawa[1], Satoshi Fujita[1], Hideyuki Yamashita[1], Yutaro Okuno[1]; [1]OMRON Corporation Core Technology Center

3:40 (583) **Combining SPR with Other Analytical and Surface Techniques for Studies and Separation of Proteins**; Feimeng Zhou[1], Yongjun Li[1], Ming Du[1], Juan Xiang[2]; [1]California State University, Los Angels; [2]Central South University, P. R. China

4:00 (584) **A Surface Impedance Imaging Technique**; Kyle Foley[1], Xiaonan Shan[1], Nongjian Tao[1]; [1]Arizona State University

4:20 (585) **Swellable Polymer Particles for Optical Sensing**; Barry Lavine[1], Mary Kim[1], Donald Brown[1]; [1]Department of Chemistry, Oklahoma State University

4:40 (586) **Plasmonic Electrode Assemblies for Multi-Modal Sensing and Intelligent**; Paul W. Bohn[1], Sean P. Branagan[1]; [1]University of Notre Dame

Thursday Afternoon, Room Nevada 9
EMERGING AREAS IN RAMAN SPECTROSCOPY
Organizer and Presider: Pavel Matousek

3:00 (587) **TERS – a Potential Tool for Direct Sequencing**; Volker Deckert[1,2], Elena Bailo[1], Tanja Deckert-Gaudig[1]; [1]ISAS; [2]TU Dortmund

3:20 (588) **Making CARS Better**; Eric Potma[1]; [1]University of California, Irvine

3:40 (589) **Non-invasive Raman Spectroscopy and Mapping of Musculoskeletal Tissue using Spatially-Separated Delivery and Collection Optical Fibers**; Jacqueline Cole[1], Matthew Schulmerich[1], Kathryn Dooley[1], Michael Morris[1]; [1]University of Michigan, Ann Arbor, MI

4:00 (590) **Static Coded Apertures for Diffuse and Imaging Spectroscopy**; David Brady[1]; [1]Duke University

4:20 (591) **SERS-melting: A New Method for Distinguishing Mutations in DNA Sequences**; Sumeet Mahajan[1], James Richardson[1], Tom Brown[1], Phil Bartlett[1]; [1]School of Chemistry, University of Southampton

4:40 (592) **Raman Analysis of Common Gases using a Multi-Pass Capillary Cell (MCC)**; Christopher Gordon[1], William Pearman[1], Chance Carter[2], Michael Angel[1], James Chan[2]; [1]University of South Carolina; [2]Lawrence Livermore National Laboratory

Thursday Afternoon, Room Nevada 10
MID-IR IMAGING: FROM BASIC DEVELOPMENTS TOWARDS CLINICAL TRANSLATION
Organizer and Presider: Rohit Bhargava

3:00 (593) **Detection of Disease in Individual Exfoliated Cells from Oral and Cervical Cytological Samples by Infrared Micro-spectroscopy**; Max Diem[1], Benjamin Bird[1], Miloš Miljkoviæ[1], Jennifer Schubert[1], Kostas Papamarkakis[1], Melissa Romeo[1]; [1]Northeastern University

3:20 (594) **Infrared Chemical Imaging with a Solid Immersion Lens**; Chris Michaels[1]; [1]NIST

3:40 (595) **Vibrational Infrared Spectroscopic Imaging of Protein Acetylation: Pharmacodynamic Assessment of Histone Deacetylase Inhibitors**; Tsoching Chen[1], Jane Trepel[1], Ira Levin[1]; [1]National Institutes of Health

4:00 (596) **FTIR Imaging of Multiple Sclerosis Animal Models**; Donald McNaughton[1], Sally Caine[1], Vivienne Juan[1], Philip Heraud[1], Claude Bernard[1]; [1]Monash University

4:20 (597) **Diagnosis of Colorectal Adenocarcinoma by MIR Microspectroscopic Imaging**; Peter Lasch[1]; [1]Robert Koch-Institute

4:40 (598) **Optimized Mid- IR Imaging for Clinical Translation**; Rohit Bhargava[1], Frances Keith[1], Anil Kodali[1], Jason Ip[1], Michael Walsh[1]; [1]University of Illinois at Urbana-Champaign

ABSTRACTS

(1) **New Bioanalytical Technologies for Probing the Paradoxical Relationship of the Immune System and Cancer**

Gabriel Kwong, Rong Fan, Habib Amad, R.J. Krom, Kiwook Huang, Sean Sarkaria, Caius Radu, Toni Rebus, Owen Witte, Paul Mischel, James R. Heath; Caltech, Division of Chemistry and Chemical Engineering, NanoSystems Biology Cancer Center, and the Geffen School of Medicine, UCLA

The human immune system has a complex relationship with cancer. On the one hand, it constitutes one of the most powerful weapons for battling the disease. On the other hand, many of the hallmarks of cancer, such as angiogenesis and metastasis, are thought to arise out of a process in which the immune system actually reinforces the aberrant nature of cancer. In this general audience talk, I will discuss technologies that we have developed and are applying towards understanding both of these issues. Recent advances in understanding the molecular mechanisms governing the recognition of specific cancer cells by T lymphocytes (a type of white blood cell) have led to a dramatic increase in the number of adoptive cell immunotherapies for melanoma and other cancers. Positive patient responses to such therapies are dependent upon the generation of large and persistent repertoires of tumor-specific cytotoxic T lymphocytes (CTLs), accumulation of these CTLs at the tumor site and acquisition of cytotoxic phenotypes. These studies also indicate that further improvements in the response rates of such immunotherapies are contingent on the availability of new immune monitoring technologies. We have developed a highly multiplexed approach, called Nucleic Acid Cell Sorting or NACS, for such immune monitoring. Preliminary data indicate that, in conjunction with ultrasensitive protein assays (called DEAL) also developed by our groups, NACS allows sorting and functional testing of very low numbers of mouse and human antigen-specific T cells. We have established a tissue bank consisting of samples from patients with metastatic melanoma undergoing treatment with experimental tumor immunotherapy strategies. Our preliminary data indicates that the multiplexing ability, sensitivity and specificity of the combined NACS-DEAL approach will vastly exceed the specifications of existing immune monitoring technologies, including flow cytometry. Recent results from our efforts in this area will be discussed. Solid tumors are complex mixtures of cell types, and often are comprised of from between 20-50% immune cells. It is these cells that are thought to reinforce and promote some of the hallmarks of cancer. We have developed on-chip strategies to monitor several of the proteins that comprise aspects of the tumor/immune system communication network. These proteins are monitored as model cell cultures, consisting of both cancerous and immune cells, are built up, one cell at a time, and as those cultures are 'perturbed' by small molecules. These experiments are allowing us to monitor a number of new and interesting biological phenomena, including emergent behavior in communication between these diverse cell-types. Strategies for unraveling the rules that lead to this emergent behavior, as well as for comparing these measurements against what can be measured in surgically resected human tumors, will be discussed.

(2) **40 Years of Contributions to Atomic Spectroscopy and Analytical Chemistry; Gary Hieftje**, *Indiana University*

Covering 40 years of anything in 40 minutes constitutes a compression ratio of 525,600, a daunting task in anyone's book. Accordingly, the coverage here will necessarily be selective. Greatest emphasis will be placed on work from the past, since many of our current activities will be described by group members in other talks at this meeting. The approach will be to begin with general topics, and to illustrate studies in each topical area with an example or two. A dominant theme will be the people and other resources that made each advance possible. Such resources include top-notch students and other group members, generous collaborators, supportive colleagues, strong machine, electronics, and glass shops, talented clerical and administrative support, an excellent undergraduate and graduate curriculum, and outstanding laboratory facilities.

(3) **Low Cost CE-NMR with Microcoils for Chemical Detection**;

Julie L. Herberg[1], Kristl Adams[1], Vasiliki Demas[1,2], Anthony Bernhardt[3], Vince Malba[3], Lee Evan[3], Christopher Harvey[3], Robert S. Maxwell[1]; [1]Lawrence Livermore National Laborartory, Chemistry, Material, Earth, and Life Sciences, [2]University of California-Berkeley, [3]Lawrence Livermore National Laboratory, Engineeirng Technologies Div., [4]Lawrence Livermore National Laboratory, Physical Science Division

Understanding speciation in solids and solutions is important for environmental and toxicological purposes. Capillary electrophoresis (CE) is a simple rapid separation method that can be used to identify species in solution. One of the challenges with CE is obtaining a method of direct detection that can provide speciation information. Nuclear magnetic resonance (NMR) has been used to identify chemical species in aqueous solutions and has also been coupled to CE. We are developing separation protocols to determine the speciation of chemical complexes in solutions with minimal perturbation to the original sample equilibrium. On-line NMR measurements will be made downstream of the UV detector. We will discuss our development of a low-cost microcoil CE-NMR system for *in situ* characterization of samples of interest. Prepared by LLNL under Contract DE-AC52-07NA27344.

(4) **Fruit of the Vine, Two Buck Chuck, or Lighter Fluid: Applying NMR and GC/MS to Wine and Homeland Security Problems**

Matthew Augustine; [1]UC Davis

With the emergence of a new technique, wine collectors now have a promising procedure for quantifying the amount of spoilage in unopened bottles of fine and, often, expensive wine. Although originally developed to screen for the oxidative spoilage of fine wine, this full bottle nuclear magnetic resonance (NMR) method has recently been extended to the analysis of counterfeit wine without violating the bottle seal. Rapid throughput methods to accomplish both of these NMR measurements will be surveyed and the need for inexpensive spectral resolution solutions mentioned. As the motivation for this work is the wine collector market, a new chromatographic device that non-invasively and non-destructively monitors the amount of cork taint or 2,4,6-trichloroanisole in bottled wine will also be presented. Applications of all of these techniques to airport security will be included.

(5) **NMR as a Forensic Tool for the Organization for the Prohibition of Chemical Weapons**

Sarah Chinn[1], Robert Maxwell[1], Armando Alcaraz[1], Hugh Gregg[1], Bradley Hart[1], Carolyn Koester[1], Richard Whipple[1], Dennis Reutter[1]; [1]Lawrence Livermore National Laboratory

The Organization for the Prohibition of Chemical Weapons (OPCW) is a worldwide association of member states that was established to implement the provisions of the Chemical Weapons Convention in 1997. With the ultimate mission of eliminating the threat of chemical warfare, a number of laboratories around the world are accredited to receive and test suspect samples in the case of challenge inspections due to non-compliance or alleged CW use. To achieve and maintain OPCW accreditation, regular Proficiency Examinations are performed in which a laboratory must analyze a series of test samples and identify all scheduled agents using numerous analytical techniques. Nuclear Magnetic Resonance (NMR) is a routine screening method for all samples due to its ability to nondestructively detect chemical species without the need for additional sample preparation that could potentially chemically

alter the sample. Additionally, the structure-specific nature of the analysis is essential for the identification of different isomers that would otherwise be indistinguishable with other methods. In this presentation, the use of NMR for screening and identification of CW agents will be discussed. Results from standard 1H, 31P{1H}, and 1H{31P} solution state experiments will be shown along with those from more advanced 1D and 2D inverse detection experiments. Finally, sensitivity enhancement methods and additional chemical forensic applications of NMR will be reviewed.

(6) **Advanced Metabolomics-Based Methods for Biomarker Discovery and Systems Biology Research**

Daniel Raftery[1]; [1]Purdue University

While the analysis of biofluid samples by 1D NMR and pattern recognition methods have proven effective at classifying populations such as "disease" and "healthy," these methods tend to focus on the metabolites with high concentration. New NMR approaches such as selective TOCSY experiments and chemical derivatization methods are being developed which focus on both major and minor components to provide an improved ability to discriminate similar samples. We can also combine or correlate the results of NMR with several new and advanced MS methods to provide additional information for identifying putative biomarkers to distinguish diseased and healthy populations and to learn more about perturbed complex biological systems. The combination of NMR and MS improves our ability to classify cohorts and to identify additional potential biomarkers. Mapping the observed changes on to the metabolic pathways provides insight regarding the complex and correlated network of metabolic perturbations that occur in disease. Examples using both small animal and human studies will be discussed.

(7) **Hyphenation of Capillary Electrophoresis with Slotted Microstrip NMR Detection**

Roland Hergenröder[1], Hans-Georg Krojanski[1], Jörg Lambert[1]; [1]Institute for Analytical Sciences

A new NMR microprobe based on microstrip technology has been established. Owing to its planar design, the probe is easily adaptable to the size and geometry requirements of the samples. The sensitivity of the probe is by factor of 70000 better than that of a commercial NMR probe. With the detection volume being in the low nanoliter range, the probe is not only well suited for investigations on volume limited samples, but also as a detector for chromatographic or electrophoretic separation techniques. In addition, the design is well suited to the implementation into microfluidic manifolds. In currently available solenoidal microcoil designs, the sample tube in electrophoretic separations must be oriented perpendicular to the external magnetic field. Hence, electrophoretic currents, following Ampere's law, give rise to a magnetic field gradient in the flow direction deteriorating spectral resolution and causes substantial distortions in the NMR spectral linewidths and peak heights. These pitfalls can be completely avoided with the new microstrip probe allowing the sample tube to be oriented in parallel to the external field. Hyphenation of capillary electrophoresis and NMR detection based on a microstrip NMR detector are therefore expected to give enhanced spectral resolution as compared to solenoidal microcoil detection. This outstanding sensitivity advantage will be exploited for metabolic studies on synchronized cell ensembles that pose high demands on the selectivity and sensitivity of spectroscopic techniques and have therefore been out of reach hitherto. Investigations on synchronized cell ensembles will deliver new insights in the information flow in biological systems.

(8) **207-Pb and 13-C Nuclear Magnetic Resonance Spectroscopy of Adducts of 1,10- Phenanthroline with Lead(II) Halides: Solid-State Studies**

Cecil Dybowski[1], Alicia Glatfelter[1], David D. Kragsten[1], Shi Bai[1], Dale L. Perry[2], Scott E. Van Bramer[3]; [1]University of Delaware; [2]Lawrence Berkeley National Laboratory; [3]Widener University

Solid-state 207Pb and 13-C nuclear magnetic resonance (NMR) studies of 1:1 and 1:2 coordination complexes of lead(II) bromide and lead(II) iodide with 1,10- phenanthroline are reported. The NMR spectra are compared to the spectra of lead salts and pure 1,10-phenanthroline. Significant structural and electronic differences between the 1:1 and 1:2 adducts are reflected in the NMR parameters. Both adducts are holodirected, and the NMR results imply that the 1:2 adduct is more stereochemically active than the 1:1 adduct. The NMR chemical shielding of the isostructural complexes indicates that the electronic state of the lead(II) center depends on the number of ligands and the halogen anion. This work was supported by the Petroleum Research Fund of the American Chemical Society, Grant Number 33633-AC5, the National Science Foundation under Grant CHE-0411790, and the U. S. Department of Energy under Contract Number DE-AC02-05CH11231.

(9) **Enantiomeric Dependence of the Far-Infrared Spectra of Polycrystalline Tyrosine and Valine**

Charles Schmuttenmaer[1], Alan True[1], Timothy French[1], Konstanze Schroeck[2]; [1]Yale University, Department of Chemistry; [2]University of Bochum, Chemistry Dept.

The far-infrared spectra of polycrystalline samples of tyrosine and valine have been measured using THz time-domain spectroscopy. Spectra of the pure enantiomers, both D and L, as well as the DL-racemates have been taken at room temperature and low temperature (77 K). The room temperature spectra of the D and L enantiomers are essentially identical, and are markedly different from the DL-racemates. In addition, a temperature-dependent study of L-valine and D-valine was undertaken wherein the absorption maxima are found to blue-shift as a function of decreasing temperature, and new peaks grow in to the D-valine spectrum at temperatures below 160 K. The vibrational frequencies and intensities were calculated using CHARMM32b1, allowing a tentative assignment of the experimentally observed modes.

(10) **Time-Domain Terahertz Measurements of Pharmaceutical Tablet Mass and Compression Force**

Jeffrey White, Irl Duling, David Zimdars, Greg Fichter; [1]Picometrix LLC

Time-Domain Terahertz (TD-THz) measurements of pharmaceutical products will be presented. Of primary interest is measurement of tablet mass. All measurements will have been made with an automated system consisting of a THz controller and fiber optically coupled sensor to a remote tablet handler system. The tablet handler accommodates a large sample set (~1000 tablets). Thus, this system and the results will mimic on-line measurements of such products. The measurement method is to inspect tablets for reflections of the ps wide THz pulse off interfaces of the sample. The data is recorded in time domain with approximately 2 fs resolution. Somewhat similar to ultrasound measurements, the THz reflection's Time-of-Flight (ToF) values are used to determine the extents of the sample. Picometrix has previously demonstrated the capability to determine a sample's mass from the measured ToF values. As the tablet sample set will be large (~ 1000 tablets), statistical results will be presented. Additional information available from the same time-domain measurement data includes crack detection (presence of an interior "interface"). These measurements are envisioned as enabling

Process Analytical Technology (PAT) efforts which encompasses "…timely measurements (i.e., during processing) of critical quality and performance attributes of raw and in-process materials and processes with the goal of ensuring final product quality." (FDA PAT website).

(11) **Development of Terahertz Time Domain Spectrometer for Gas Phase Spectroscopy**

Hiromichi Hoshina[1], Takamasa Seta[2], Yasuko Kasai[2], Iwao Hosako[2], Chiko Otani[1]; [1]RIKEN; [2]NICT

The development of femtosecond lasers has led to the time-domain spectrometer (TDS) becoming a widespread spectrometry tool in the THz region. Since a THz-TDS system detects signals with femtosecond time window and is less affected by thermal noise, it works without liquid helium cooling and enables relatively easy experiments in THz. In addition, the detector has a better signal-to-noise ratio and a higher dynamic range (106 ~108) than conventional Fourier transform infrared spectrometers (FT-IR) in the 0.3-4.0 THz frequency region, because the THz-TDS system is more stable than the combination of a mercury lamp and a Si bolometer. Due to these advantages, THz-TDS has been recently used for various spectroscopic studies in the THz region. In this study, we have built a THz-TDS for gas phase spectroscopy. Since long optical path is required for the measurement of absorption spectrum of gas phase molecules, a White-type multi-pass cell with a path-length of 2 m was combined with a conventional THz-TDS in the frequency region of 0.5-3.5 THz. With this system, we have measured the pressure broadening parameters of water vapor with N2 and O2 gas. Due to better signal-to-noise ratio of this system, the parameters of more than 30 lines were obtained for each gas, and their precision was much better than that of conventional results by FT-IR. The obtained parameters were compared with the theoretical values, and the quantum number dependence of the obtained parameters was observed for the first time. Our result shows the potentiality of THz-TDS for gas phase spectroscopy. We developed the system for high-resolution spectroscopy. The present status of our research will be reported.

(12) **Advanced Terahertz Sources and Imaging Configurations for Rapid Analytical Measurement Applications**

Yao-chun Shen[1], Peter Weightman[2]; [1]The University of Liverpool; [2]The University of Liverpool

The terahertz region of the electromagnetic spectrum (0.1 – 10 THz, 3.3 – 333 cm-1) has a unique combination of properties in that terahertz waves can propagate through most pharmaceutical materials; many excipients and active ingredients show characteristic spectral features in the terahertz region; and the radiation is nonionizing and is safe to use. Terahertz pulsed spectroscopic imaging has been demonstrated to have unique capability of three-dimensional structure and chemical mapping, making it a powerful analytical tool for non-destructively evaluating the critical quality attributes of pharmaceutical tablets [1-2]. The state-of-the-art terahertz instrument can record a terahertz spectrum in less than 20 ms, and a whole terahertz pulsed imaging data set in minutes. Greater acquisition rate, which is necessary for some specific applications such as real time on-line measurement, is possible if more terahertz power is available (currently less than 1μW for a typical table top terahertz system). In this talk, I will present recent advances in terahertz source including (1) a powerful photoconductive terahertz source with non-planar structures for rapid terahertz imaging; (2) an ultra-broadband terahertz source for drug discovery and formulation; (3) the high intensity terahertz source being developed at Daresbury, UK (ALICE—accelerators and lasers in combined experiments, previously named as 4GLS—the 4th generation of light source). This source is ideal for single shot terahertz spectroscopic imaging, in addition to many other important physical, biological, chemical and medical applications. References: (1)Y.C. Shen, P.F. Taday, Development and Application of Terahertz Pulsed Imaging for Non-destructive Inspection of Pharmaceutical Tablet, (invited paper), J. Selected Topics in Quantum Electronics, 14 (2008) 407-415 (2)L. Ho, R. Müller, M. Römer, K.C. Gordon, P. Kleinebudde, M. Pepper, T. Rades, Y.C. Shen, P.F. Taday, J.A. Zeitler, Applications of terahertz pulsed imaging to sustained-release tablet film coating quality assessment and dissolution performance, J. Controlled Release, 127 (2008) 79-87

(13) **The Use of Terahertz Pulsed Imaging within the Pharmaceutical Environment**

Philip Taday[1]; [1]TeraView Limited

Tablet coatings are of great importance to both the consumer and the pharmaceutical manufacturer. By controlling the release of the active pharmaceutical ingredient (API) tablet coatings ensure bioavailability, minimise harmful effects and the waste of the drug by delivering it at the specific site and at the optimum level. These functions may be compromised if a coating is non-uniform or has defects. The exceptional properties of terahertz radiation, such as ability to penetrate most non-polar materials that can be opaque for visible light or low contrast for x-rays and very importantly, low photon non-ionising energies, make this radiation very attractive tool for aiding understanding the pharmaceutical materials and products. Until recently, the analysis of coating thickness relied on indirect techniques and it was usually determined by the weight gain of the coated tablet compared to the uncoated tablet core. Near-infrared and Raman spectroscopic and imaging techniques developed in recent years to yield information about the quality and integrity of the coatings are usually restricted to the outer surface of the tablet. In order to test the coating for uniformity or to analyse buried structures or even multiple layers within the tablet, the tablet has to be cut and spectroscopic images to be acquired for each layer. However, in contrast to the near-infrared and mid-infrared regions of the electromagnetic spectrum, many of the excipients used for coating solid dosage forms are transparent or semi-transparent to terahertz radiation. Moreover, terahertz radiation can easily penetrate commonly used coating polymers. This in turn means that, unlike aforementioned techniques, terahertz pulsed imaging non-destructively provides spatially resolved information from below the surface of the tablet. Consequently, terahertz measurements are arguably more suited than any of the aforementioned techniques to monitor key quality attributes of the pharmaceutical solid dosage forms during the manufacturing. In this paper we explore the capability of the technique in detecting the film coatings on tablets assessing their effect on dissolution.

(14) **Prototype Inspection System of Hidden Drugs in Sealed Envelopes using Terahertz Wave Scattering and Fingerprint Spectra**

Yoshiaki Sasaki[1], Horimichi Hoshina[1], Masahiro Yamashita[2], Gosei Okazaki[2], Chiko Otani[1], Kodo Kawase[3]; [1]RIKEN; [2]S.I Seiko Co., Ltd.; [3]Nagoya University

Applications to the inspection related to security and safety are strongly required because of recent serious social and political situations in the world and inside Japan. The absence of practical technologies to detect illicit drugs or hazardous substances hidden in sealed envelopes by nondestructive methods has made it extremely difficult to prevent them from being smuggled domestically and across international borders. We are developing a prototype apparatus that can identify these substances concealed inside sealed mail without opening it, by taking advantage of the ability of terahertz waves. However, in an actual inspection, more than 100,000 envelopes must be processed in a day. Therefore, the introduction of a fast preliminary process to pick up the suspicious

envelopes is essential. In this paper, we introduce our recent developments of this application and the prototype apparatus for the inspection. For the inspection, we have proposed the following procedure: First, X-ray pre-inspection is carried out to distinguish the mail including only papers and the ones in which some substance is included; second, the measurement of scattered THz waves is applied to pick up suspicious mails because the scattering is an good indicator of the presence of powders in them; and, third, the identification of the drugs is done by spectral fingerprinting for the suspicious mails. The first and second steps can be achieved by an apparatus to screen the mails. The running speed of the envelopes will be at most 100 meter per minute, corresponding to about 2 envelopes per second or 7 thousands per hour. For the third stage of the apparatus where THz spectroscopy below 3 THz is applied, the absorbance by the powders is the important issue in the measurements and identification. We have introduced the THz-TDS system for the spectroscopy, and the short-pulse excitation is more appropriate to obtain the good signal-to-noise ratio in the high frequency range. The absorbance spectra were measured from 0.3 to 3 THz with 15 GHz frequency resolutions. We will present and discuss a current status of the development, the system configuration, the performance and the limitation of the prototype.

(15) **Certification of Beryllium Mass Fraction in Standard Reference Material 1877 Beryllium Oxide Powder using High-Performance ICP-OES with Exact Matching**

Michael Winchester[1], Gregory Turk[1], Therese Butler[1], Thomas Oatts[2], Charles Coleman[3], Dan Nadratowski[4], Rita Sud[4], Aleksandr Stefaniak[5], Mark Hoover[5]; [1]National Institute of Standards and Technology; [2]Y-12 National Security Complex; [3]Savannah River Site; [4]Bureau Veritas North America, Inc., [5]National Institute for Occupational Safety and Health

For technological and health reasons, validated analytical methods are needed for quantification of Be. Historically, beryllium has been quantified using methods validated with solution reference materials. However, the full efficacy of these methods remains unknown, largely due to the absence of particulate beryllium reference materials. In response, the National Institute of Standards and Technology (NIST) recently issued Standard Reference Material (SRM) 1877 Beryllium Oxide Powder. SRM 1877 consists of high-fired, crystalline beryllium oxide, with primary particle diameter of approximately 200 nm, in aggregated clusters that have been size separated to pass a 20-mesh screen. The Be mass fraction in SRM 1877 was certified using a recently improved version of a methodology that we refer to as "High-Performance" (HP-) ICP-OES. HP-ICP-OES incorporates a judiciously chosen internal standard, an efficient drift correction methodology, and gravimetric solution preparation, all within a robust experimental design. The improved version of HP-ICP-OES incorporates careful matching of the nominal analyte mass fractions, the nominal internal standard element mass fractions, and the acid matrices among the calibration standards and samples. When first introduced, the HP-ICP-OES protocol involved only approximate matching of these quantities. Our recent experience shows that "exact matching" significantly improves the performance of HP-ICP-OES for many analytes. Owing to the significant toxicity hazards posed by the BeO powder, we found it necessary to modify the sample preparation approach that is usually applied for certification of a NIST SRM. Preparations of calibration and sample solutions were performed by collaborating laboratories with the necessary experience and equipment to handle beryllium-containing powders safely. The solutions were then shipped to NIST for HP-ICP-OES analyses. A challenge in terms of the careful matching of acid matrices was posed by the fact that each collaborating laboratory used a unique digestion protocol, with one laboratory using different protocols for the BeO sample and the Be metal calibration material. In this presentation, we will discuss the certification of the Be mass fraction in SRM 1877. The implementation of HP-ICP-OES with exact matching will be described in detail. The approaches used to overcome the challenge of carefully matching the acid matrices will be delineated.

(16) **Exploration of Sample Introduction Systems for Reduction of Calcium Oxide Formation and Increased Sensitivity for Nickel Analysis in Biological Samples**

Melissa Maras[1], Jonathan Good[1], Steve Eckdahl[1], Matthew Hanley[1], Michelle Wermers[1], Matthew Knopp[2]; [1]Mayo Clinic; [2]Elemental Scientific, Inc.

Calcium oxide (44Ca16O) formation is a significant obstacle for the analysis of nickel in biological matrices by inductively coupled plasma mass spectrometry (ICP-MS). The primary species responsible for polyatomic interference for 60Ni is 44Ca16O. To correct for this interference a mathematical correction factor for oxide formation is currently calculated by standard addition of Calcium (0-500 mg/L) into a biological matrix while monitoring 44Ca16O formation- seen as increased counts per second (CPS) at atomic mass 60. This calculated factor is multiplied by the CPS at 60Ni and then subtracted from the total CPS. The factor is calculated numerous times throughout an analytical run to monitor changes in 44Ca16O rate of formation and make adjustments as needed. Nebulizer flow is often decreased to reduce oxide formation, which results in decreased sensitivity. Reduction of 44Ca16O formation below 3 percent and increased sensitivity is desirable. An ESI SC-2 FAST sample handling system on PerkinElmer ELAN ® DRC II ICP-MS is currently utilized for Ni analysis. Two systems will be explored to see which meets the needs of both reduction of 44Ca16O formation and increased sensitivity in the Ni assay. The first system being ESI's PC3 which is a compact Peltier Cooled inlet system, PFA-ST Microflow nebulizer, and corresponding ESI cyclonic spray chamber, compared to the second system, ESI's APEX Q High Sensitivity Sample Introduction System, CTFE (high flow) valve, PFA Microflow nebulizer, and corresponding cyclonic spray chamber. Results from the exploration of the two systems will be examined. The successful system will be validated and implemented for routine clinical analysis.

(17) **Phytoremediation of Arsenic by Hyperaccumulating Plants**

David Butcher[1], Sung-Gun Park[1]; [1]Western Carolina University

Recent studies suggest that phytoremediation (remediation using green plants) is a viable method of cleaning large areas of soil and that it may be an effective alternative to current soil cleanup methods. The principal advantage of phytoremediation compared to conventional remediation techniques (e.g., soil excavation and removal, solvent extraction) is cost. Additionally, the total volume and mass of waste may be reduced to as low as 1% of the original contaminated soil. Phytoremediation techniques may also be more publicly acceptable, aesthetically pleasing, and less disruptive than current techniques. Our laboratory has conducted a number of projects involving the use of phytoremediation at Barber Orchard, NC, a United States EPA Superfund site in Haywood County. These include the use of Chinese brake ferns (Pteris vittata) and moonlight ferns (Pteris cretica cv Mayii) for the removal of arsenic, the use of x-ray absorption spectroscopy to characterize arsenic species in plant tissue, and the investigation of the interaction between arsenic species and thiol containing compounds by electrospray ionization mass spectrometry.

(18) **Fluorescence-Based Studies of Ion Transmission through the Skimmer Cone of an ICP-MS**

Haibin Ma[1], Jeff Macedone[1], Paul Farnsworth[1]; [1]Brigham Young University

It is a simple matter to observe the changes in signal level that accompany changes in sample matrix or instrument operating parameters in an inductively coupled plasma mass spectrometer (ICP-MS). It is much more difficult to determine where in the complex train of processes that are required to convert a sample to an analytical signal the changes occur. Changes that occur in the vacuum interface that connects the plasma to the mass analyzer are particularly difficult to track because of the closed nature of a typical interface. To address the challenge we have developed a vacuum interface that allows us to directly monitor flow through the skimmer cone using laser-induced fluorescence. The interface allows us to monitor two regions simultaneously. The first region is immediately upstream from the tip of the skimmer cone. The second region will be downstream from the skimmer cone at a position controlled by xyz motorized stages. Measurements in the upstream region will allow us to directly observe any shock structure attached to the upstream tip of the skimmer cone. Measurements in the downstream region, normalized to simultaneous upstream measurements, will allow us observe changes in transmission efficiency into the second vacuum stage caused by scattering, space charge, or other physical phenomena. We will describe the design of the interface and present the initial results obtained with it.

(19) **An Ion Funnel-Based Vacuum Interface for Inductively Coupled Plasma Mass Spectrometry (ICPMS)**

Rolf Dietiker[1], Tatiana Egorova[1], Bodo Hattendorf[1], Detlef Guenther[1]; [1]ETH Zurich, Laboratory of Inorganic Chemistry

Inductively coupled plasma mass spectrometry (ICPMS) is an established technique for trace and ultra-trace element determinations in a large range of applications. It offers very high sensitivity for almost the entire periodic table with a wide dynamic range and a flexible coupling to many existing sample introduction techniques. Nonetheless the detection efficiency of current instruments is limited to about 0.1% at best, which is at least partly a result of the design of the vacuum interface required to transfer the ions from the ICP to the high vacuum in the mass spectrometer. The transmission of current sampler-skimmer configurations has been estimated to be between 1 and 3% of the ions entering the sampler orifice, which obviously is a substantial limitation to the sensitivity that could in principle be obtained by ICPMS. Another approach to transfer ions through a differential pumping stage, which is used in particle physics and organic MS is the implementation of a so called “ion funnel” or “fair wind gas cell”, which operate as an ion guide at pressures in the mbar-range. It is formed by an Rf-voltage applied to stack of ring electrodes with decreasing inner diameter, located inside the first vacuum stage of the MS. Unity transmission was reported for ions of m/z > 80 (1) when connected to an electrospray source. Due to these promising characteristics we built and tested a prototype instrument with an ion funnel interfaced to a conventional ICP ion source. Ions are extracted from the ICP via a standard sampler followed directly by the funnel to transfer the ion beam towards an exit aperture of 2 mm ID. This prototype setup has been used to first characterize the transmission, kinetic energy distribution and angular spread of the ion beam exiting the funnel in dependences on its operating conditions (Rf-frequency and amplitude, pressure, electrode spacing and DC gradient). First results and implications from these studies will be discussed in this presentation. (1) A.V. Tolmachev et al., Int. J. Mass Spectrom. 203 (2000) 31–47

(20) **Introduction of Aqueous Samples to High Power Pulse Microplasma Source**

Yoichi Nagata[1], Hidekazu Miyahara[1], Taichi Meguro[1], Ryuichi Shimada[1], Eiki Hotta[1], Akitoshi Okino[1]; [1]Tokyo Institute of Technology

Inductively coupled plasma (ICP) is widely used as an ionization or excitation source for elemental analysis. It has been one of the most powerful tools for trace elemental analysis because of its excellent sensitivity. Recent years, target of the elemental analysis has been shifted to smaller samples such as nano-particles, bio cells, etc. However, conventional ICP system consumes too much sample solution (~1 mL/min) to analyze these targets. To analyze small amount samples more efficiently, we have developed a microplasma source for elemental analysis. DC discharge to generate the microplasma had been used but the analytical figure of merit was not enough high because the input power was limited by damage of the electrodes. To increase the input power without the electrode damage, a high-power pulsed microplasma was developed.

(21) **Novel SERS Nanosensors Suitable for One- and Two-Photon Excitation**

Janina Kneipp[2], Harald Kneipp[1], Mark Stockman[3], Katrin Kneipp[1,4]; [1]Harvard University Medical School; [2]Humboldt University, Chemistry Departmen; [3]Georgia State University, Department of; [4]Harvard-MIT Division of Health Sciences

Nanosensors based on surface enhanced Raman scattering (SERS) have exciting potential capabilities to address almost all aspects for ultrasesnsitive and high resolution sensing, particularly also in biological environment. Raman spectroscopy provides rich molecular structural information, based on the vibrational fingerprint of matter. Extremely strong enhancement of the Raman signal in the local optical fields of silver and gold nanostructures enables Raman measurements at the single molecule level. Since the signal enhancement appears in strongly confined local fields around the nanostructure, SERS sensors enable molecular structural probing at the nanometer scale, two orders of magnitude better than the diffraction limit. Two-photon excitation is gaining rapidly in interest and significance in sensing. Surface enhanced hyper Raman scattering is the two-photon is analogous to one-photon-excited SERS. SEHRS provides structurally sensitive vibrational information complementary to those obtained by SERS and combines the advantages of two-photon spectroscopy with the structural information of vibrational spectroscopy and the high-sensitivity and nanometer-scale local confinement of plasmonics-based spectroscopy. A key question in all SERS sensing modalities are nanostructures that provide a high level of electromagnetic field enhancement. Moreover, for biosensing, the structures should be mobile and small enough to cross biological membranes and they should enable probing biological structures without inducing perturbation or toxicity. Self-similar structures formed by gold nanospheres of different sizes, so-called “nanolenses” are potent enhancing structures. Gold nanolenses are generated by laser ablation from solid gold into water. The “chemically clean” preparation process provides several advantages over chemically prepared nanoaggregates.

(22) **Nano-Wiffle Balls - Porous Phospholipid Nanoshells for Biological Sensing**

Craig Aspinwall[1]; [1]University of Arizona

We have developed a new class of nanometer-sized polymeric shell-type structures utilizing cross-linked phospholipid architectures for biological sensing and delivery applications. The resultant unilamellar, polymer-lipid vesicles are chemically and environmentally stabilized, biocompatible and protect components

that are loaded into the aqueous interior from interfering species in the exterior environment. This novel architecture allows delivery of protected protein and enzyme cargos into the intracellular environment for use as chemical sensors and/or therapeutic agents. Here, we will outline the design, characterization and utilization of these structures for a range of biological delivery and sensing applications.

(23) **The Application of Nano-Sensors to the Real-Time Monitoring of Endosomal Ion Fluctuation in Dictyostelium Discoideum during cAMP Stimulation**

Murphy Brasuel[1], Phoebe Lostroh[2], Jessica Hellyer[1], Everett Moding[1]; [1]Colorado College Department of Chemistry; [2]Colorado College Department of Biology

PEBBLEs (Photonic Explorers for Biomedical use with Biologically Localized Embedding) for pH measurement were fabricated, characterized and utilized for determining the role of endosome ion pumps in Dictyostelium discoideum chemotaxis. Ion signaling plays a crucial role in cellular interactions, including, but not limited to signal transduction, and control of cellular growth and differentiation. Dictyostelium discoideum has been widely used as a model organism for the study of the chemical and ion signaling that promote and control chemotaxis and cell differentiation. Dictyostelium cAMP stimulation has been shown to elicit a proton efflux which establishes cell polarity during chemotaxis, generating internal asymmetries in aggregating cells that promote efficient movement towards chemoattractants. Previous work by Flaadt, Schaloske, and Malchow established that the proton flux is independent from cytosolic pH [1]. PEBBLEs clearly show acidification of endosomes during cAMP stimulation (pH rapidly drops from 7 to 5 in the endosomes) clearly suggesting endosomal mediated proton efflux. 1. Flaadt, H., R. Schaloske, and D. Malchow, Mechanism of cAMP-induced H+-efflux of Dictyostelium cells: a role for fatty acids. Journal of Biosciences, 2000. 25(3): p. 243-252. Novelty: Moving beyond proof-principle into bioanalytical applications of nano-ion sensors.

(24) **Optical Nanosensors for Intracellular Ion Analysis**

Heather Clark[1], J. Matthew Dubach[1], Saumya Das[2], Anthony Rosenzweig[2]; [1]The Charles Stark Draper Laboratory; [2]Beth Israel Deaconess Medical Center

The use of fluorescent dyes such as Fura-2 to study the dynamics of intracellular calcium fundamentally advanced our knowledge of calcium signaling in excitable cells. Sodium flux through voltage-gated sodium channels is responsible for initiating action potentials in excitable cells. However, little is known about the compartmentalization and dynamics of sodium fluxes in cells with complex cyto-architecture such as cardiomycoytes. Here we describe novel nanosensors that can report sodium concentration with microsecond response time, high intensity, and minimal photobleaching. Furthermore we demonstrate the feasibility of studying sodium fluxes in cardiomyocytes. We previously reported polymer nanosensors that accurately report sodium concentration {Dubach et al., Nano Lett 2007; 7(6):1827-31}. The sensors are ~ 100 nm in diameter and fluorescently report sodium concentration with a kD near 10 mM. Previous studies have shown loading of fluorescent indicator dye molecules and dextran conjugates though a whole cell patch clamp seal. The nanosensors used here were able to load though the seal in a similar manner. Once loading was achieved, electrical control of the membrane channels was performed using patch clamp. The electrical whole cell membrane response and optical sodium flux response were simultaneously monitored. The sensors were loaded into cells via picoinjection or patch pipette and pharmacological and electrical channel responses were measured by monitoring optical changes of the sensors. The responses were verified by simultaneous electrical recording in the whole cell patch experiments. Control experiments showed that loading the nanosensors through the patch pipette did not alter the electrical recording or control of the cell membrane voltage gated channels during IV curve generation and steady state recovery experiments. IV curve experiments were performed 20 minutes after whole cell patch was achieved to verify that cell viability was not altered by the presence of the nanosensors. Changes in the fluorescent intensity were recorded when the cell was depolarized to open the voltage gated sodium channels. Results showed very little delay between optical response of the nanosensors and electrical response from the patch clamp. We have created sodium sensitive nanosensors that are exquisitely specific for sodium ions, have favorable dynamics for studying kinetics of sodium fluxes through voltage gated sodium channels and can be introduced into cells. This tool will yield fundamental knowledge about the biology of excitable cells.

(25) **Hybrid SERS/Fluorescence Bionanoprobes for the Rapid Detection of Toxic Materials**

Nicole Whitten[1,2], Dimitra Stratis-Cullum[2], Brian Cullum[1]; [1]University of Maryland Baltimore County; [2]United States Army Research Laboratory

With the enhanced threat of biological agents over the past several years, there is a clear need for the development of a compact sensing technology, for both biomedical and defense organizations, capable of providing sensitive, accurate and rapid identification and detection of a wide array of biological agents. Current methods for the point-detection of both genetic and non-genetic biological materials tend to false alarm frequently, and the associated analyses required subsequent to false-alarming are expensive and time-consuming. To prevent these costly and dangerous situations, we have developed an economically-practical biosensing platform which integrates surface enhanced Raman scattering (SERS) substrates with aptamer-based bionanoprobe receptors. The combination of these two elements allows for the ultratrace (down to single molecule) detection of a wide variety of pathogenic or toxic substances in a rapid (seconds to minutes), reliable (two-channel transduction), and inexpensive manner. The SERS substrates are fabricated and optimized for uniformity, reproducibility, stability, and sensitivity. By adjusting the nanoparticle spacing and size, the wavelength at which the maximum electromagnetic field, or surface plasmon resonance (SPR), occurs can be tuned. By adjusting the type of metal used (i.e. Cu/Ti and Au/Ag) and the thickness and layering of these metals, the stability and sensitivity of the substrates can be maximized. The spectroscopic investigation of rhodamine B, rhodamine red and Bodipy 630/650 for use as SERS and fluorescence labels will be discussed, in addition to DNA hybridization and thrombin protein results in relation to the proposed transduction mechanism.

(26) **Fabrication of Functional Plasmonic Nanoparticles through Layer-by-Layer Assembly on Optical Fiber for Real-Time and Spatially-Resolved Oxygen Measurement**

Veronica Rigo[1], Peter Geissinger[1]; [1]University of Wisconsin Milwaukee

We report a novel oxygen sensor comprised of a nanoscale system of silver nanoparticles which were covalently attached to the core of an optical fiber and labelled with luminescent sensor molecules. The particular combination of metallic nanostructures, providing large enhancement of luminescence via localized plasmon resonance, and optical fiber technology, providing fast, remote and real time detection capabilities, allow for the fabrication of versatile sensor. Sensing is based on luminescence quenching of a ruthenium complex in presence of molecular oxygen. To take advantage of the

metal-enhancement effects in our sensor arrays, the ruthenium complex was kept at an appropriate distance from the silver nanoparticles by spacer layers assembled using the well-established Layer-by-Layer (LbL) technique. Varying the number of non-luminescent polyelectrolyte spacer layers allow for placing luminophores at varying distances from the metal nanoparticles and, thus, for optimizing the metal enhancement effect. We used high-resolution TEM imaging and optical spectroscopy to corroborate that the resulting luminescently-labelled nanostructures were stable during their construction and also to study the relationship of geometrical features of individual silver nanostructures and their optical plasmon resonant properties. This allows for matching of the plasmon resonance frequencies to the spectral properties of the luminophore, which is crucial to successfully employ the metal-enhancement effect, and to develop ultra-sensitive chemical sensors. The plasmonic-based sensor was tested using a two-crossed-fiber sensor array with two regions excited with a dye laser (465 nm) pumped by a nitrogen laser. The second region was used as intensity reference. The sensor was mounted in a home-built flow chamber where both oxygen and nitrogen were pumped into the chamber at different partial pressures. The luminescence emitted by the sensor molecules was captured by a second fiber at right angle to the fiber carrying the excitation light. We measured calibration curves for this sensor system and determined detection limits.

(27) **Electrospray Mass Spectrometry: How and Why Did We Get Here?**

Richard Cole; [1]University of New Orleans

Electrospray has been a principal driver for the transformation of mass spectrometry as an analytical tool primarily useful for small molecules into a primary resource for characterization of large biomolecules. Electrospray has thus served as an enabler for the biological revolution. This presentation will examine the important milestones in the development of electrospray from its early beginnings to the present day. Fundamental aspects of the electrospray process will be highlighted, with particular emphasis placed on the importance of electrochemical phenomena relevant to the production of gas-phase ions.

(28) **Electrochemistry Fundamentals of Electrospray Ionization**

Gary Van Berkel, Vilmos Kertesz; [1]Oak Ridge National Laboratory

Electrochemical reactions are inherent to the operation of the electrospray ion source. Control over these reactions is critical in obtaining experimental results free from electrochemically-generated artifacts of the analyte or in utilizing the inherent electrochemistry to analytical advantage. Our recent efforts have focused on the use of alternative emitter electrode designs and new methods to control the electrochemistry of electrospray. Potential of the working electrode is the governing factor to determine the spectrum of products in an electrochemical system. The control of the working emitter electrode potential was achieved by incorporating a three-electrode, controlled-potential electrochemical cell into the controlled-current ES emitter circuit. This potential control provided the ability to efficiently reduce analytes in positive ion mode and oxidize analytes in negative ion mode, in addition to the ability to control analyte oxidation in positive ion mode (or reduction in negative ion mode). Also, the system was used to selectively ionize analytes with different standard electrochemical potentials within mixtures to different charge states to overcome overlapping molecular ion isotopic clusters. Less precise control over the electrochemical reactions in electrospray was achieved with a battery-powered, controlled-current, two-electrode emitter cell. This cell system provided the ability to control the extent of analyte oxidation in positive ion mode in the electrospray emitter by simply setting the magnitude and polarity of the current at the working electrode. The above mentioned systems both utilize multiple electrodes in the solvent flow path. Unfortunately, the auxiliary electrode in these setups may affect the solution composition via uncontrolled electrochemical reactions at lower flow rates due to more efficient mass transport to this electrode. A novel approach to eliminate these undesired Faradaic processes using one-electrode emitter systems will be discussed.

(29) **Effects of Rapid Analyte/Solvent Mixing for ESI-MS of Peptides and Proteins**

Joseph Loo[1], Ivory Peng[1]; [1]UCLA

ESI-MS is a standard method for peptide and protein characterization. Typically, analyte solutions are introduced into an ESI source via HPLC or direct injection. Recently, our laboratory has been investigating the fundamentals and potential applications of electrospray-assisted laser desorption ionization (ELDI), a soft ionization method that combines features of both electrospray ionization (ESI) and matrix-assisted laser desorption ionization (MALDI) to generate ESI-like multiply charged molecules. The ELDI process is based on merging ESI-generated, charged droplets with particles UV-laser desorbed from dried or wet sample deposits. This presentation will discuss the performance of reactive-ELDI to support chemical reactions, such as protein disulfide bond reduction, during the ELDI process. A comparison of ESI and ELDI mass spectra of proteins reveals many similarities, but also some differences that may reflect on the effects of analyte/solvent mixing, desolvation, and timescale of the desorption/ionization events of ESI.

(30) **Ions for Free: Thermally Cycled Pyroelectric Crystals and Electrocuted Liquid Droplets as Ion Sources**

Evan Neidholdt[1], J.L. Beauchamp[1]; [1]California Insitute of Technology

The ambient pressure pyroelectric ion source (APPIS) and field induced droplet ionization (FIDI) are new techniques we have developed which expand ionization and sampling capabilities in mass spectrometry. APPIS comprises a z–cut lithium niobate or lithium tantalate crystal with an attached resistive heater. Positive and negative ion formation at a single crystal face alternately result from thermally cycling the crystal over a narrow temperature range, typically less than 30 K from ambient. Ionization of 2–(butylamino)-ethanethiol or diethyl phosphoramidate, simulants for the CBW agents VX and Tabun, respectively, results in the detection of singly protonated monomers or dimers of each in the positive ion mass spectrum. Ionization of 1,1,1,3,3,3–hexafluoroisopropanol or benzoic acid results in observation of the singly deprotonated species and their clusters in the negative ion mass spectrum. Ion formation results mainly from electrical "microdischarges" occurring on the surface of the crystal. FIDI mass spectrometry allows for the direct sampling of ions from neutral and charged liquid droplets in the 250 micron to 2 mm size range. This is accomplished by application of a high electric field, leading to elongation of the droplet with simultaneous formation of Taylor cones emitting positively and negatively charged nanodroplets in opposite directions. Ions are sampled directly from the surface of the parent droplet. This facilitates the study of surface and bulk phase activity of dissolved molecules, and an examination of interfacial chemical reactions. The latter is typically accomplished using a hanging droplet that can be exposed to highly reactive gases. Several examples will be presented of the interfacial reactions of ozone with molecular species such as fatty acids and hydrophobic peptides at the surface of liquid droplets. Of particular interest is the observation of significant differences between interfacial and solution phase reactions in several instances.

(31) **Is a Cone-Jet Electrospray the Holy Grail of ESI-MS?**

Ioan Marginean[1], Ryan T. Kelly[1], David C. Prior[1], Brian L. LaMarche[1], Keqi Tang[1], Richard D. Smith[1]; [1]Pacific Northwest National Laboratory

It is commonly accepted that an electrospray used as ionization source for mass spectrometry (MS) delivers the best performance in the cone-jet regime. Our measurements with rigorously monitored electrospray operating regime show that this observation should not be accepted as a general rule. We characterized the low-flow electrospray as ionization source for mass spectrometry using solvents typical for reversed-phase liquid chromatography. Contrary to conventional wisdom, the pulsating regime consistently provided better ESI-MS sensitivity than the cone-jet regime in the experimental conditions studied. This observation was supported by additional measurements showing that the heated capillary interface afforded more efficient sampling and transmission for the charged aerosol generated by a pulsating electrospray. The pulsating electrospray provided relatively constant MS signal intensities over a wide range of voltages, while the signal decreased slightly with increasing voltage for the cone-jet electrospray. The MS signal also decreased with increasing emitter-interface distance for both pulsating and cone-jet electrosprays due to the expansion of the electrospray plume. At flow rates below 100 nL/min the MS signal increased with increasing flow rate due to increased number of gas-phase ions produced. At flow rates greater than 100 nL/min, the signal reached a plateau due to decreasing ionization efficiency at larger flow rates. These results bridge the gap between common electrospray practice with high-flow electrospray and the improved performance reported for low-flow electrosprays. They also suggest methodologies to improve MS performance for low-flow (nano- to micro-) electrosprays.

(32) **Evaluation of Penning Ionization in Inductively Coupled Plasma**

Nicholas Taylor, Paul B. Farnsworth; [1]Brigham Young University

Inductively coupled plasmas (ICP's) are widely recognized as a highly efficient ionization source for atomic mass spectrometry. However, there is still some debate over which ionization mechanisms are major contributors to the overall ionization of the analyte. Of particular interest is Penning ionization, since it has been shown to be an important mechanism in other types of discharges and plasmas. It is the purpose of this work to demonstrate the magnitude Penning ionization has on an ICP by direct experimental evidence. The present experimental scheme involves use of an intense dye laser tuned to the Arm (argon metastable) state, rapidly depleting the Arm state when operated under saturated conditions. The degree of depletion is recorded as changes in the absorbance of a diode laser beam that propagates collinearly with the pulsed dye laser. If Penning ionization is important, removal of Arm state atoms should reduce the contribution of Penning ionization to the population of excited ionic states. Therefore, time-resolved ionic emission measurements from various excited ionic states of Ca, Ba, V, Ti, Y, Mg, Mn, and Cr, coincident with pulsed laser depletion of Arm atoms, under various operating conditions allows better understanding of the impact Penning ionization has on the overall excitation/ionization of the analyte.

(33) **The Atmospheric Pressure Glow Discharge: A Plasma for Ambient Mass Spectrometry**

Steven Ray[1], Jacob Shelley[1], Greg Schilling[1], Joshua Wiley[1], Gary Hieftje[1]; [1]Indiana University

A new ionization strategy has recently been developed that seeks to exploit the strengths of mass spectrometry in everyday settings. Ambient mass spectrometry techniques employ specialized ionization sources that are applied directly to the sample at hand without any pretreatment, removing molecules from the sample surface and ionizing them for subsequent analysis. This strategy is advantageous in that analyte molecules are removed directly from their original chemical environment without the dilution or chemical modification that can occur in sample pretreatment or extraction schemes. Thus, critical chemical information is preserved with spatial resolution, and in analyses that can be accomplished very rapidly. Further, these ion sources often operate within the ambient atmosphere, opening the way for mass spectrometry to be used routinely within a wide variety of settings. The flowing afterglow of an atmospheric pressure glow discharge (APGD) is investigated here as an ionization source for ambient mass spectrometry. A helium-supported APGD sustained in a simple cell is used to create high-energy reagent ions, which then exit the APGD cell in an afterglow plume. When gaseous, liquid, or solid samples are placed within this afterglow plume, analyte molecules are desorbed into the gas phase, ionized, and subsequently analyzed by mass spectrometry. The mass spectra produced by the AGPD source are dominated by the molecular ion with little or no fragmentation observed. Further, the spatial distribution of analyte molecules across the sample surface can be determined by rastering the afterglow plume across a sample. Experimental details of the APGD plasma and the analytical potential of this technique will be examined in a variety of applications.

(34) **Development of a Hollow Cathode Geometry for Particle Beam Glow Discharge Mass Spectrometry**

R. Kenneth Marcus[1], Joaudimir Castro[1]; [1]Clemson University

This laboratory has been developing glow discharge (GD) ion sources for the comprehensive speciation of metals in botanical extracts (i.e., nutraceuticals). Along this way, it has also become clear that the ion sources perform superbly in the profiling of active in these materials as well. The coupling of a liquid chromatography (LC) separation to the GD ion source is accomplished through a particle beam (PB) interface, in such a way that system performance is independent of the actual separation mechanism (e.g., reversed-phase, ion exchange, etc.). We have begun the design of a more efficient hollow cathode (HC) GD geometry as a means of improving the sensitivity of the methods, even though sub-nanogram detection limits are routine. We will report on the progress of the new source and compare it to the first generation GD ion source.

(35) **Advances in Fundamental Understanding and Practical Use of Collision/Reaction Cells in ICP-MS**

Patrick Gray[1], Susan Olesik[1], John Olesik[1]; [1]The Ohio State University

A large fraction of the ICP-Quadrupole MS instruments sold in the last five years have collision/reaction cells to overcome spectral overlaps. Two different approaches are used: ion-molecule reactions and kinetic energy discrimination. Ion-molecule reaction selectivity is easiest to predict when the ions are thermalized. In contrast, kinetic energy discrimination requires that elemental ions maintain higher kinetic energies after colliding with neutral gas than molecular ions at the exit of the collision cell. This has direct implications on attainable improvements in detection limits, the types of spectral overlaps that can be overcome and analysis accuracy for samples that produce spectral overlap ion signals that depend on variable sample composition. We will assess the current fundamental understanding of collision and reaction cells for ICP-MS. Direct connections between kinetic rate constants reported in the literature from Selected Ion Flight Tube MS will be discussed. Ion-molecule reactions for both singly charged and doubly charged ions will be considered. The based on thermalized ion-molecule reactions and those due to collisionally induced dissociation will be

assessed. We will compare approaches to overcome spectral overlaps based on ion-molecule reactions and kinetic energy discrimination with the use of higher mass spectral resolution provided by sector field MS.

(36) **Evaluation of Pyrolysis Curves for Volatile Elements in Aqueous Standards and Carbon-Containing Matrices in ETV-ICP-MS**

Margaretha de Loos-Vollebregt[1], Alessandra de Silva[1,2], Bernhard Welz[2]; [1]Delft University of Technology; [2]Universidade Federal de Santa Catarina

Pyrolysis curves in Electrothermal Atomic Absorption Spectrometry (ET AAS) and Electrothermal Vaporization Inductively Coupled Plasma Mass Spectrometry (ETV-ICP-MS) have been compared for As, Se and Pb in lobster hepatopancreas Certified Reference Material using Pd/Mg as the modifier. The ET AAS pyrolysis curves confirm that the analytes are not lost from the graphite furnace up to a pyrolysis temperature of 800 oC. Nevertheless, a downward slope of the pyrolysis curve was observed for these elements in the biological material using ETV-ICP-MS. This could be related to a gain of sensitivity at low pyrolysis temperatures due to the matrix which can act as carrier and/or promote changes in the plasma ionization equilibrium. Experiments with addition of ascorbic acid to the aqueous standards confirmed that the higher intensities obtained in ETV-ICP-MS are related to the presence of organic compounds in the slurry. Pyrolysis curves for As, Se and Pb in coal and coal fly ash were also investigated using the same Pd/Mg modifier. Carbon intensities were measured in all samples using different pyrolysis temperatures. It was observed that pyrolysis curves for the three analytes in all slurry samples were similar to the corresponding graphs that show the carbon intensity for the same slurries for pyrolysis temperatures from 200 oC up to 1000 oC.

(37) **Studies on Thermochemical Reagents in ETV-ICP-MS**

José Broekaert; [1]University of Hamburg

Electrothermal vaporization is an important technique for sample introduction in ICP-MS, especially when it comes to working with minute amounts of sample or when in powders, which are difficult to bring into solution, determinations have to be performed. In both cases thermochemical reagents are very helpful so as to accomplish trace matrix separation but also to improve the aerosol transport. In the analysis of ceramic powders such as alumina or silicon carbide a.o. slurry sampling into a graphite furnace combined to plasma optical emission or mass spectrometry enables the direct determination of a larger number of trace elements including Fe down to the sub-µg/g level. The signals often can be considerably increased by using thermochemical reagents such as halides or Pd/Mg salt mixtures. By this measure also the occurrence of double peaks often can be avoided. The results of optimizations of the type of salt and its concentration will be shown for several halides and Mg/Pd-salt mixtures and results for real samples of alumina resented both in the case of optical emission and mass spectrometry. The both methods were shown to be accurate and their results were in good agreement. With optical emission spectrometry detection limits were at the µg/g level whereas with ICP-MS the detection limits with respect to the powders often were considerably lower. The question whether the improvement of the signals is due to enhancements of the volatilization or to the improvement of the transport efficiencies has been cleared by radiochemical measurements. Experiments were made with alumina powders which were activated in a nuclear reactor and then contained Cr, Co, Fe and Zn radioisotopes of which the gamma-spectra were recorded after volatilization experiments in the presence of different thermochemical reagents. It could be shown that the volatilization of these elements from mg amounts of the powders studied at the trace level was rather complete also without the addition of thermochemical reagents. However, it also could be impressively shown by trapping the aerosol on filters that the transport efficiencies greatly could be increased when any type of salts was added at some larger concentrations.

(38) **Industrial LIBS Applications and Approaches to Becoming a More Mainstream Analytical Technology**

Robert Kearton; [1]Ocean Optics, Inc.

The first reported work on LIBS was reported in the late 1980's, however it was deemed too expensive since the spectrometers where big and myopic, and impractical for most applications due to cost and weight factors, plus analysis techniques were uncertain and limited. The introduction of low cost, high resolution spectrometers has enabled the commercialization of LIBS systems for a wide variety of industrial and R&D applications. Commercialization and improvements to the hardware, software, and collection optics were made in large part through government contract awards for specific LIBS systems, and collaboration with individuals within the LIBS community. Today LIBS is used primarily as a "finger print" technique for qualitative and semi-quantitative analysis for applications ranging from metal alloy analysis to gem stone characterization. LIBS continues to evolve and is becoming more of a mainstream technology as we learn more about the plasma thermodynamics, and improve techniques for quantification. Key components to this are sensitivity improvement and plasma reproducibility. To that end OOI has teamed with Envimetrics (Princeton, NJ) to integrate standard LIBS with microwave technology that has proven to sustain the plasma in duration and size without the concern for laser flash to flash variation. This is being called LAMPS (Laser Assisted Microwave Plasma Spectroscopy). In this presentation we will discuss the evolution of LIBS technology, various industrial applications, technological barriers, and plans going forward for making LIBS/LAMPS a better quantitative technique.

(39) **Overview of LIBS Applications for Real Time Analysis and Process Control**

Mohamad Sabsabi[1], Paul Bouchard[1], René Heon[1], André Hamel[1], Gregg Lithgow[1], François Doucet[1], Stephane Laville[1]; [1]NRC-IMI

Laser Induced Breakdown Spectroscopy is a method of optical emission spectroscopy that uses a laser-generated plasma as the source of vaporization, atomization and excitation. Basically, a LIBS measurement is carried out by forming plasma on or in the sample and then collecting and spectrally analyzing the plasma light. Since the plasma is formed by optical means, the LIBS technique offers unique features compared to conventional techniques that use an adjacent physical device. Among these attributes is its ability to interrogate samples *in situ* and remotely without preparation of the sample, and to realize fast analysis with the capability to determine nearly all elements of the periodic table. Although the LIBS method has been in existence for more than 40 years, prior to 1980, interest in it centered mainly on the basics of plasma formation. A few instruments based on LIBS have been developed but have not found widespread use. Recently, there has been renewed interest in the method for wide range of applications. This is due to the result of significant technological developments in the components (lasers, spectrometers, detectors) used in LIBS instruments as well as emerging needs to perform measurements under conditions not feasible with conventional techniques. In this presentation, we will give an overview about LIBS applications for on-line measurements where LIBS systems are established and routinely used in industry, as well as novel LIBS applications being studied in R&D projects. Examples for different LIBS applications in our laboratory and elsewhere will be presented: molten

materials, metal ore processing, effluents, slurries, liquids, scanning surface microanalysis, LIBS for nuclear industry, pharmaceutics etc. Beyond the industrial applications, further areas of LIBS applications will be also discussed such as the detection of explosives, art work, archaeology and environmental applications.

(40) **Laser Induced Breakdown Spectroscopy of Aqueous Solutions**

Scott Goode[1], Shana Williams[1], Amelia Taylor[1]; [1]Dept of Chemistry, Univ of So Carolina

Laser induced breakdown spectroscopy has holds several advantages it holds over traditional atomic spectroscopy techniques, including remote and field portable analysis. LIBS is quite effective for the elemental analysis of solids and gases, but not particularly useful for liquids, for which methods like inductively coupled plasma atomic emission spectrometry (ICP-AES) or inductively coupled plasma mass spectrometry (ICP-MS) are widely used. The ICP, however, requires particulate-free liquids than can require extensive handling and/or corrosive acids. We present the results of a systematic study of LIBS for a number of different aqueous solutions. Laser-induced breakdown spectroscopy is performed on chromium with the laser breakdown at the surface of an aqueous sample, in aerosols, and on the surface of ice blocks. In most cases, sampling is matrix dependent and adding internal standards improves reproducibility. Limits of detection vary by an order of magnitude, from 0.6 ppm for ice to 25 ppm for surface analysis, and are consistent with published results. Limits of detection, ease of implementation and comparison to traditional atomic spectroscopy techniques are evaluated. The effect of dissolved particulate matter on the LIBS plasma intensity has been investigated. We compare LIBS results from undigested particulate-loaded solutions to those obtained by acid dissolutions analyzed by ICP. In addition, we investigate the affects of different colored absorbers present in the solution along with the analyte.

(41) **Optimization of Excitation Conditions for Aqueous Phases LIBS Measurements**

Christopher Gordon[1], Michael Angel[1]; [1]University of South Carolina

The possibility of expeditionary oceanographic research requires the development of new *in situ* methods of analysis. One that has shown promise for the use in high-pressure bulk aqueous analysis is LIBS. Studies have shown the ability of LIBS in detecting many group I and group II elements, as well as some transition metals such as zinc and manganese, however further methods of signal enhancement as well as the ability to detect elements such as chlorine and bromine that are critical to the chemistry that occurs in these deep oceanic environments are still necessary for LIBS to be a successful method for *in situ* analysis. One way to enhance the LIBS signal is to use sequential laser pulses. In this technique a vapor bubble is formed in solution by a first laser pulse. A second laser pulse is used to excite a plasma in the vapor bubble once it reaches its maximum expansion diameter. This technique requires careful control over the size and position of the vapor bubble and overlap with the focus of the second laser pulse. We have found that the stability of the initial plasma, vapor bubble and second plasma depend on a number of experimental parameters including laser energy, mode quality and focusing optics. For example changing the laser energy can change the nature of the variability in the intensity of the initial laser plasma and subsequent vapor bubble. At some laser energies the intensity variation seems to follow a normal distribution while at other laser energies an extreme value distribution is observed. In this study, an intensified charge coupled device (ICCD) is used to image the plasma and vapor bubble as the excitation conditions are varied. Variations in the size, intensity and position of the plasma and vapor bubble are described.

(42) **Remote LIBS of Hydrous Phases of Clay Minerals**

Shiv Sharma[1], Rachel Lentz[1], Anupam Misra[1]; [1]Hawaii Institute of Geophys.& Planetology, UH

Remote laser-induced breakdown spectroscopy (LIBS) provides an alternative chemical analysis technique for elemental analysis of natural and synthetic materials. In the present work the authors have analyzed a number of hydrous phases of clay minerals at 8.5 meter distance using both 1064 nm and 532 nm laser beams. The laser beam was focused with a 5x or 10 x beam expander and collected emission light from the plasma with 5-inch or 8-inch diameter telescope. The spectra were analyzed with grating spectrographs equipped with intensified CCD detector. Remote LIBS spectra of clay minerals including montmorillonite, nontronite, hectorite, kaolinite and halloysite, sepiolite, and palygorskite have been analyzed. In addition, we have also analyzed combined Raman and LIBS spectra of various hydrous minerals, including gypsum and hydrous sulfate minerals. LIBS spectra in the UV (240-320 nm) and visible-Near-IR (556-850 nm) wavelengths region show strong, sharp LIBS peaks of all major elements (e.g., Si, Al, Mg, Fe, Ca) and several minor elements (K, Na, Li). All the hydrous mineral spectra show a broad hydrogen band at 657.28 nm. Combination of Raman and LIBS spectra offers a complete analysis of molecular and atomic species in these minerals. At the University of Hawaii, we have developed a combined remote LIBS and Raman spectroscopic instrument with 532 nm laser as excitation source for analyses of various materials including minerals and rocks on planetary surfaces. Advantages of combined Raman and LIBS technique for remote chemical analysis will be discussed.

(43) **Multi-Plasma Laser-Induced Breakdown Spectroscopy (Multi-Plasma LIBS): Uses and Applications**

Galan Moore[1], Douglas Jennings[1]; [1]Corning Incorporated

LIBS can analyze localized areas of heterogeneous materials and, with increased sampling, can give quantitative information about the bulk material. However, often materials to be sampled, particularly in production, are in motion and only a small portion of the material can be analyzed. This problem can be alleviated by creating more than one plasma or an array of plasmas. In Multi-Plasma LIBS, a single energetic laser pulse is divided it into several reduced energy laser pulses in order to form multiple nearly identical laser-induced plasmas. Each plasma contains information about its localized environment so by increasing the number of plasmas taken simultaneously a second spatial dimension to describe a material's homogeneity can be obtained. Multi-Plasma LIBS also allows the sampling of several independent materials simultaneously and can be used for single shot calibration and sampling.

(44) **Towards Automation in the Characterization of Nanostructured Materials and Devices**

Klaus Weishaupt[1], Thomas Dieing[1], Fernando Vargas[1], Ute Schmidt[1]; [1]WITec GmbH

The characterization of nanostructured materials implies knowledge about their chemical and structural properties, leading to a growing demand for characterization methods for heterogeneous materials on the nanometer scale. However, certain properties are difficult to study with conventional characterization techniques due to either limited resolution or the inability to chemically differentiate materials without inflicting damage or using invasive techniques such as staining. By combining various analytical techniques such as Raman spectroscopy, confocal microscopy and AFM in one instrument, the same sample area can

be analyzed with all implemented methods, leading to a better understanding of nanostructured materials. Raman spectroscopy, a chemical analysis technique, combined with confocal microscopy enables the unique Raman imaging of heterogeneous materials. The power of Raman imaging stems from the high chemical information content of molecular vibrational spectra. In the Raman spectral imaging mode, a complete Raman spectrum is recorded at every image pixel, leading to a two-dimensional array consisting of ten-thousands of complete Raman spectra. From this array images are extracted by analyzing various spectral features (sum, peak position, peak width, etc). Differences in chemical composition, although completely invisible in optical images, will be apparent in the Raman image and can be analyzed with a lateral resolution down to 200 nm. If higher resolution is required, by simply turning the microscope turret, the confocal Raman microscope can be transformed in to an AFM. Using this imaging technique, structures below the diffraction limit can be visualized from the same sample area. For the analysis of various devices formed on a support, an automated sample positioner with a travel accuracy better than 5 µm is incorporated in the instrument. Special scripting functions allow the automated execution of predefined measurement sequences on any user defined selection of measurement points on the sample, guaranteeing the most comprehensive surface analysis tool for systematic and routine research tasks.

(45) **Biological Threat Detection with Raman Chemical Imaging**

Ashish Tripathi[1], Jason A. Guicheteau[2], A. Peter Snyder[2], Darren K. Emge[2], Rabih E. Jabbour[1], Steven D. Christesen[2]; [1]SAIC; [2]ECBC, US Army APG

We present a strategy to detect complex biological samples with Raman Chemical Imaging Microscopy (RCIM). Liquid Crystal Tune-able Filter (LCTF) based RCIM translates every pixel or a binned group of pixels as an independent Raman spectrograph. Thus, bacterial samples can be detected without any spectral influence from surrounding Raman active particulates. We demonstrate that the RCIM based detection strategy is not influenced by physical variations of particle size or the water quality leading to positive identification of a target analyte regardless of a strong Raman active interferant. Finally, we demonstrate that detection of bacterial mixture with RCIM can be achieved.

(46) **Resolution Targets for Chemical Imaging of Pharmaceutical Products**

John Kauffman[1], Sean Gilliam[1], R. Scott Martin[2]; [1]FDA Div. of Pharmaceutical Analysis; [2]Saint Louis University

Resolution targets composed of polyethylene glycol (PEG) lines on silicon substrates have been prepared using the method of micromolding in capillaries (MiMIC). The MiMIC process uses standard photolithographic techniques to emboss a pattern of microchannels in a poly(dimethylsiloxane) stamp. The stamp is then placed on a silicon substrate, and molten PEG is drawn into the microchannels by vacuum-assisted capillary action. When the stamp is removed, raised patterns of PEG remain on the silicon substrate. Patterns of three parallel lines with equal width and spacing have been prepared, with widths between 5 and 25 microns. Raman chemical images of the PEG-on-silicon devices as well as the metal-on-glass masks used to prepare the devices were measured. The Raman images were used to determine the impulse response of the instrument by comparing the measured images to model functions prepared by convolution of a test impulse function with the object functions of the devices. Best fit impulse function widths were determined using a grid search over a range of impulse widths and impulse functional forms. Impulse widths for PEG-on-silicon targets were approximately two times greater than impulse widths for metal-on-glass targets. The results provide a quantitative measure of the influence of light-matter interactions on the spatial resolution achievable with chemical imaging instruments. This work shows that microfluidic channels can be used to produce robust patterns of PEG on silicon, and these patterns are realistic resolution targets for spectroscopic chemical imaging of pharmaceutical materials.

(47) **Chemical Imaging of Pharmaceutical Granules by Raman Global Illumination and Near-Infrared Mapping Platforms**

Slobodan Sasic; [1]Pfizer, Analytical R & D

Raman global illumination and near infrared (NIR) mapping instruments were used to chemically image pharmaceutical granules obtained by the wet granulation process in order to determine whether the API was mixed with the major excipient or granulates on its own. The granules were randomly distributed onto a microscope slide and an average area of about 3.5 x 3.5 mm2, covering 50 – 100 granules, was analyzed by both instruments. Light microscopy images of the separated granules were collected before the spectroscopic data acquisition. Both Raman and NIR signals of API and major excipient (mannitol) were easily detected by both techniques which allowed the chemical structure of the granules to be characterised. Most of the granules were found to contain both API and mannitol but pure mannitol and a few pure API granules were also identified. Raman global illumination was found to provide a comprehensive insight into chemical structure of the granules being able to more clearly determine the API in comparison with NIR mapping. Owing to the differences in shapes of the particles and reflection characteristics, visual microscopy and methods based on reflection can be potentially useful for analyzing this particular formulation.

(48) **Raman Imaging of Sub-Cellular Organization, and Uptake of Drug Delivery Systems into Cells**

Max Diem[1], Christian Matthaeus[1], Tatyana Chernenko[1], Luis Arcesio Quintero Pizo[2]; [1]Northeastern University; [2]University of Puerto Rico

Modern Raman Micro-spectroscopic instrumentation permits the acquisition of confocal hyperspectral data sets of individual human cells at a spatial resolution given by the dif-fraction limit. Various approaches of multivariate analysis, among them hierarchical cluster analysis (HCA) and vertex component analysis (VCA), were utilized to recon-struct pseudo-color images from these data sets. These images rival those obtained from confocal fluorescence microscopy; but are based on the inherent vibrational signa-tures of the molecular components, and do not require the use of extrinsic labels for visualization. We have used this methodology to detect mitochondria in cells, and to track the uptake of nanoparticle drug delivery systems into cells. In particular, we have followed the up-take of deuterated liposomes into cells, and have followed their fate over time scales ranging from 1 to about 48 hours. In addition, we have used micelles that incorporate long poly (ethylene glycol) (PEG) chains, and were able to detect the presence of the micelles by the specific signature of PEG. Finally, we have incorporated partially deuterated ceramide, a pro-apoptotic signaling molecule, into poly-å-caprolactone nanoparticles, and detected both the intact nanoparticles, as well as the released drug cargo.

(49) **Raman + HPLC = Reduced Fluorescence. Is This Possible?**

Brian Marquardt[1], Nils Christian Afseth[2], Jens Petter Wold[2]; [1]University of Washington; [2]Matforsk, Aas Norway

A novel real-time liquid-core Raman waveguide detector designed for liquid chromatographic applications will be described. The Raman waveguide detector provides enhanced sensitivity and

selectivity over typical high performance liquid chromatography (HPLC) detectors. The waveguide detector greatly improves the sensitivity of a typical Raman measurement without resorting to surface enhancement or resonance approaches and is compatible with the typical peak width volumes eluted by microbore and minibore HPLC (packed 1 to 2 mm i.d. columns). Detection limit enhancements of over 1000 fold have been achieved for the measurement of alcohols in the aqueous phase with the Raman cell utilizing liquid core waveguide technology. The low refractive index of the polymer material allowed HPLC separations with Raman detection to be performed with an aqueous mobile phase. By coupling the temporal separation achieved by HPLC with the vibrational information gleaned from Raman detection, an information rich multivariate data matrix is obtained that can be deconvoluted to provide chemical speciation even when the HPLC resolution is poor. A second benefit to performing a fast LC separation is that highly fluorescent samples can be effectively analyzed. The use of an HPLC separation can also increase the utility of Raman spectroscopy by separating complex mixtures and isolating fluorescing contaminants from the matrix to allow for collection of Raman data in an otherwise difficult sample. This presentation will describe the physical and optical design of the Raman waveguide detector coupled with an LC column and demonstrate its capabilities for the analysis of highly fluorescent liquid samples.

(50) **Novel Interface-Selective Even-Order Nonlinear Spectroscopy**

Shoichi Yamaguchi[1], Tahei Tahara[1]; [1]RIKEN

New interface-selective second-order (X(2)) and fourth-order (X(4)) nonlinear spectroscopic techniques have been developed. X(2) electronic sum frequency generation (ESFG) spectroscopy enables us to obtain interfacial electronic spectra with an unprecedented high signal-to-noise ratio and dense wavelength data points. Frequency- domain X(4) Raman spectroscopy provides vibrational spectra of interfaces for a very wide wavenumber range covering the whole fingerprint region. Because these new even-order electronic and vibrational nonlinear spectroscopies utilize only visible and/or near-infrared laser pulses, they are applicable to a variety of "buried" interfaces that are not readily accessed by the other existing methods.

(51) **Remote Detection of Volatile Organic Compounds by Passive Infrared Spectroscopy**

Gary Small[1]; [1]University of Iowa

The detection of airborne chemicals is a key capability in a variety of environmental monitoring scenarios. For these applications, passive infrared remote sensors collect infrared emissions from natural and manmade sources such as the radiant emission from the earth or emissions from the stacks of a chemical plant. Chemical compounds absorb or emit infrared energy at characteristic wavelengths, and the profile of these absorption or emission signatures can be used to identify a chemical and to estimate the amount present. Passive infrared remote sensors can be implemented in either imaging or non-imaging configurations and can be constructed to acquire infrared emission data in either multispectral or hyperspectral modes. Implementing these measurements successfully requires the construction of rugged and portable instruments capable of being mounted on platforms such as moving aircraft or ground vehicles. In addition, sophisticated computer processing techniques must be designed to allow the automated analysis of the large quantities of data acquired by these sensors. The research presented here describes the development of novel signal processing and pattern recognition methodology for application to multispectral imaging data and to non-imaging data acquired with a hyperspectral instrument. Remote sensing data were collected with these instruments mounted on an aircraft platform. Controlled releases of several volatile organic compounds were made with a heated stack, and data were also collected at an industrial site. These remote measurements will be used to evaluate the data analysis methodology and to assess the strengths and weaknesses of the imaging and non-imaging remote sensing approaches.

(52) **ATR-FTIR Imaging with Variable Angles of Incidence**

Sergei Kazarian, Andrew Chan; [1]Imperial College London

This talk will present the research we are developing in the area of ATR (Attenuated Total Reflection)-FTIR spectroscopic imaging. The method based on ATR-FTIR imaging with a variable angle ATR accessory is introduced to demonstrate a possibility of obtaining spatially resolved chemical images from different depths within the polymeric sample. The depth range is between fractions of micrometer to several micrometers. The use of variable angle ATR-FTIR imaging overcomes the diffraction limit of light in the z-direction and opens up new opportunities in spectroscopic imaging of heterogeneous materials. The talk will present two approaches using different ATR accessories to obtain images with variable angles if incidence. The demonstrated methods open a possibility of chemical imaging combined with depth profiling which may be particularly valuable in the imaging of polymeric materials and biomedical samples.

(53) **Quantitative Analysis of Pharmaceutical Formulations using Low Frequency Transmission Raman**

Mike Claybourn[1], Jonas Johansson[1], Hanna Matic[1]; [1]AstraZeneca

Transmission Raman has been demonstrated to be a reliable approach to quantitative analysis of pharmaceutical formulations such as tablets or capsules. This gets around the issue of subsampling in back-scattering mode which has limited the reliability of the technology. The reported data focuses on the normal mode region of the spectrum, which is sufficient for many purposes. However, the low frequency response associated with phonon modes (inter-molecular) of the drug substance within the formulation gives a better selectivity to the morphology of the material since the phonon frequencies are related to the crystalline structure. A comparison of nomal mode and phonon mode transmission Raman responses for tablet and capsule formulations shows the low frequency to have clear advantages in terms of sensitivity and quantification.

(54) **High-Speed, High Resolution, Chemical Imaging using Tunable Laser**

Eli Margalith[1], Lam Nguyen[1]; [1]OPOTEK, Inc.

We present a Chemical Imaging instrument based on tunable laser technology, specifically, Optical Parametric Oscillator (OPO). The OPO beam is collected by a fiber bundle and delivered to the target to provide uniform illumination. The wavelength range is defined by the camera of choice and dictated by the application. The visible range can covered with a simple CCD, whereas longer wavelengths require the use of FPA cameras such as InGaAs, InSb, or MCT. We present data collected from various samples over a wide spectral range with different type cameras. The system is capable recording targets with a wide range of magnifications, covering various Field-of View (FOV) from 13 mm (M=1) to 20 cm (M=15). The selection of the magnification is done automatically by computer control. The system records the actual wavelengths and the reflectance signal is calibrated and corrected for linearity at each wavelength in real-time, without the need for calibration curves. Other advantages of the OPO based Chemical Imaging will be presented and discussed, e.g. no heating of samples; fast data acquisition rates; and high spectral resolution.

(55) **Can You Increase ICP Productivity and Performance at the Same Time?**

Jerry Dulude[1], Scott Bridger[2], David Jones[3]; [1]Glass Expansion; [2]Scoan Investments; [3]ALS Chemex

A number of approaches have been utilized for improving the productivity of an ICP spectrometer, most of which involve shortening of the rinse and sample loading steps. This paper describes an accessory which combines and optimizes these approaches with an additional mechanism for improving both the accuracy and precision of the analysis. During an analytical cycle, a significant portion of the time is spent loading the sample into the sample line before it reaches the nebulizer. In addition, once the analytes have been measured, significant time is spent to clear the previous sample from the sample line and the sample introduction system including the nebulizer, spray chamber, and injector. The device described here uses the analytical portion of the previous cycle to load a sample loop which is then injected into the nebulizer at the appropriate time. This approach by itself provides the maximum sample throughput without adversely affecting analytical performance. The method of sample injection used here provides a more constant flow than can be achieved by conventional peristaltic pumps. To accomplish this, the device is configured with a syringe driven pump. We will demonstrate the improvement in consistency achieved. This is particularly important for ICP-MS applications due to the nature of data acquisition. Most modern commercially available optical emission spectrometers use charge transfer detectors and collect charge over a relatively large time (5 to 30 seconds), while ICP mass spectrometers continually scan the amu range. Because of this distinction, the pulsations inherent from a peristaltic pump have a greater impact on the precision of an ICP-MS analysis. Using the device described here allows the operator to choose between higher productivity (shorter scan times with the same detection limits), better performance (improved detection limits at the same scan time), or lower maintenance (more dilute samples with the same detection limits). A second syringe drive can be used to precisely deliver the internal standard in line. In comparison to pumped in-line systems, this device can be programmed to deliver a wide range of ratios of internal standard to sample without changing tubing. The high precision of the internal standard and sample syringe drives provides improved performance for both ICP-OES and ICP-MS applications.

(56) **Speciation of Gadolinium Compounds in Gadolinium Based Magnetic Resonance Imaging Agents by HPLC-ICP-OES**

Chethaka Kahakachchi[1], Dennis Moore[1]; [1]Covidien

Gadolinium(III) polyaminopolycarboxylate complexes are commonly used as magnetic resonance contrast media (MRCM) for magnetic resonance imaging (MRI) studies. Typically these MRCM solutions have been analyzed for purity with chromatographic methods using ultraviolet (UV) detectors, evaporative light scattering detectors (ELSD) and various mass spectrometry (MS) detectors. However, these detection modes require the presence of chromophoric and/ or ionizable groups in the structure of the gadolinium(III) complexes, resulting in methods of poor or limited sensitivity for the desired species. We report the development of a procedure for the determination of gadolinium species in magnetic resonance contrast media by reversed-phase high-performance liquid chromatography with detection by inductively coupled plasma optical emission spectrometry (HPLC-ICP-OES). The analytical performance characteristics studied, including method detection limits and chromatographic parameters for OptiMARK™ (gadoversetamide) and several MRCM solutions containing gadolinium(III) complexes will be presented.

(57) **Self-Learning, Flexible, Multiline-Based Semi-Quantitative Analysis Tool for a CCD-Based ICP-AES Instrument**

William Zuccarello[1], Philippe Hunault[1], Jean-Michel Mermet[2], Catherine Wallerand[3], Cendrine Dubuisson[3], Emmanuel Fretel[3], Olivier Rogerieux[3], Sébastien Velasquez[3], Sophie Lebouil[3]; [1]HORIBA; [2]Spectroscopy Forever; [3]HORIBA Jobin Yvon

Qualitative analysis aims at ascertaining the presence or absence of an element through the observation of the usually most intense lines. A further step can be performed by trying to evaluate at least the order of magnitude of the concentration, using the so-called semi-quantitative analysis. However, semi-quantitative analysis is a poorly defined concept, because a concentration should be provided within a given accuracy (trueness and precision). Acquisition of entire uv-visible spectra using multi-channel detection allows the use of several to many lines per element. An automatic baseline correction (ABC) algorithm permits the obtaining of net signals. Previously stored single or multi-standard calibrations, possibly in some key matrices, are used for concentration determination. Possible outlier results resulting from spectral interferences are eliminated by using the median of the results. It is then possible to significantly improve the quality of the results and to become close to what can be obtained when using quantitative analysis. Reprocessing is possible, providing full flexibility as a function of the nature of the sample. Besides, for a given field of application, semi-quantitative analysis can be self-learning, that is by only keeping the most adequate lines after a few experiments. Such a tool, SMARTVIEW, has been developed by HORIBA Jobin Yvon for its ACTIVA instrument family. Possibilities of SMARTVIEW will be illustrated with examples including solar silicon, glass, environmental samples, biofuels, etc.

(58) **Graphite Furnace Atomic Apsorbtion**

Amina Ali; [1]Kuwait Institue for Scientific

A study of lead amounts in blood carried out at Al- Jahra Hospital, showed that 3 out of 400 children with lead in their blood which came from mothers using Kohl as cosmetics applied to themselves and their children. Although lead has been banned it can still be found in many products. Kohl is a gray or black eye cosmetic that can contain up to 83% lead. In some cultures, it is common for parents to apply kohl to the eyes of infants and children. Infants of mothers who use kohl sometimes have elevated levels of lead in their blood, yet unlike some sources of exposure to lead, this form can be easily avoided by not using kohl with high lead level. Graphite Furnace Atomic Absorption Spectrometry (GF-AAS) provides reliable results for lead presence and level determination in different kinds of kohl. The results show some kohl samples marketed into the local market with relatively high levels of lead. Quality control samples were analyzed through out the study to insure reliable results.

(59) **Determination of Tin Levels**

Rabaa Al-Kandari, Amina Ali; [1]Kuwait Institue for Scientific

The tin coating is an essential component of the can construction and plays an active role in extending shelf-life. The most important aspect of the tin coating on the internal surface is that it protects the steel base-plate (the structural component of the can) from corrosion by the can contents. Without a coating of tin, the exposed iron would be attacked by the product causing serious discoloration and off-flavors, such as tomato-based products. Concentration of tin in canned food must be under the 200mg/kg limit. Inductively coupled plasma Mass Spectroscopy (ICP-MS) technique will be used to analyze tin concentration in canned products.

(60) **Investigation of Long-Term Stability on ICP-AES for the Microwave Digestion Analysis in Infant Formula Samples**

Rabaa Al-Kandari[1], Amina Ali[1]; [1]Kuwait Institue for Scientific

Inductively Coupled Plasma-Atomic Emission Spectrometry (ICP-AES) is one of the best techniques for characterization of the elemental composition of samples and offers a unique tool for food analysis. This study concentrates on the instrument warm-up time which is defined as the time taken from igniting the plasma until the system is stabilized and ready for analysis. Long term stability was measured by performing a calibration on a multi-element standard and a reagent blank, then continuously measuring the standard solution as a sample every 15 minutes without recalibration. For the analytical method microwave digestion was used (MARS 5 Microwave) for the preparation of two milk samples; Nido -1-milk powder, and Milupa-3 milk powder. For test accuracy of the method a Reference Standard Material Non-Fat Milk Powder 1549 was used. One can observe that the sample concentration values are very close to the certified values of the reference material and the study's analysis was very close to the analysis done by the analytical laboratory for Shimadzu Company. The results show that Microwave method has less contamination, consumption of reagents, and take less time to carry out the analysis. One of the factors in improving productivity is to shorten the equipment warm-up time. While waiting for the equipment to warm up, Ca and Mg analysis took about 20 minutes to stabilize ICP-AES, whereas for Fe, Zn and P it took about 5 minutes to stabilize, while Na needed 25minutes to stabilize. The axially-viewed ICP provides excellent long term stability for Ca, Fe, Mg, Mn, Na, P and Zn (4 hour) using standard sample introduction systems.

(61) **Comparasion Between Two**

Amina Ali[1], Rabaa Al-Kandari[1]; [1]Kuwait Institue for Scientific

The main objective of this study was to compare between two preparation method first by acid digestion and second by microwave method for plant leaves .it has been used standard reference material to check about preparation method .The result obtain by microwave was more accurate and short time consumed after analysis by inductively coupled plasma .

(62) **High Sample Throughput using a Discrete Sampling Accessory for ICP-AES and ICP-MS**

Fred Smith[1], Paula Doeschot[1], Douglas Webb[1], Jeff Johnson[1], Carolyn Prindle[1]; [1]CETAC Technologies

Conventional sample introduction for ICP-AES and ICP-MS employs a dedicated peristaltic pump that brings sample solutions from an autosampler. In addition to the actual sample measurement time, the time segments required for sample uptake, stabilization, and washout are significant parts of the total analysis time. A discrete sampling accessory will be described that can minimize the above listed time segments and greatly reduce the overall analysis time. Other advantages include less ICP argon consumption, less exposure of the ICP-AES and/or ICP-MS hardware to the sample matrix, and elimination of memory effects from sample contact with peristaltic pump tubing. System performance and capabilities will be described, including more rapid washout for trace levels of mercury.

(63) **A New High Performance Graphite Furnace Tube for Routine Analysis of Complex Matrices**

Doug Shrader[1], Kai Robinson[1], John Sanders[1], James Barker[1]; [1]Varian, Inc.

Since the introduction of graphite furnace atomizers for atomic absorption in the early 1970's, the technique has provided excellent sensitivity for the determination of elements in a variety of matrices. It has permitted elemental determinations at levels hundreds of times lower than attainable with routine flame AAS. The introduction of Zeeman background correction techniques provided correction for structured background absorption. However, since the introduction of the GF-AAS technique there has been little ongoing research and development of the graphite tube. Early tubes where simple tubes that utilized wall atomization. The next generation of tubes saw the introduction of a graphite platform or "L'vov" type platform onto which the sample was injected for atomization. This type of platform configuration lead to reduced vapour phase interferences. A variety of platform designs have been tried over the years, some of these having limitations such as sample volume, atomization temperature limits, and tube life. A newly developed graphite tube with integral platform has addressed these limitations, allowing for better furnace operation. It has resulted in improved sensitivities and detection limits compared to previous tube designs. And, the new Omega tube design has increased tube lifetime significantly. In this presentation the new Omega platform tube design and performance will be discussed. Results for a range of complex matrices will be presented.

(64) **Silicon in Naphthas: A Near Cold Plasma Approach for sub-PPB Detection Limits on an ICP-MS**

Jonathan Talbott[1], Robert Botto[2]; [1]Varian Inc.; [2]ExxonMobil Refining and Supply

The determination of silicon in naphthas and oils is important for the petrochemical industry because silicon can easily poison hydrocracking catalysts at levels even as low as a few mg/kg and is a serious threat when contaminating gasoline feedstocks. Silicon, along with other metals, is traditionally determined by direct aspiration of the organic matrix into either an ICP-AES or an ICPMS at an elevated RF power 'hot plasma' mode with an oxygen bleed to enhance operability in the organic matrix. Silicon determination, however, is somewhat problematic in this matrix because the element has a relatively high ionization potential, is easily contaminated by glass components of the instrument and because numerous polyatomic interferences occur on all of the isotopes of Si. A new, near Cold Plasma approach at 700 watts on the Varian 820 ICPMS with an Inert Introduction System and a PFA nebulizer was used. This approach, which likely is unique to the Varian ICP-MS due to the highly-efficient, Turner Interlaced load coils of the Varian unit, also uses an oxygen bleed to avoid soot build up on the cooler cones and hydrogen from the Collision Reactive Interface to remove polyatomic interferences on Si. Under these unconventional conditions, the Si-to-background signal was maximized allowing unprecedented, sub-ppb detection limits to be observed in some organic matrices. Further details of the analysis and of the determination of numerous other metals will be presented.

(65) **Determination of Au from Nanoparticles in Rat Blood and Tissues**

Lee Yu[1], Laura Wood[1]; [1]National Institute of Standards and Technology

We have determined gold in blood and tissue samples from rats in support of a study on the efficacy of a gold nanoparticle based, new pharmaceutical candidate. Researchers treated rats with the candidate material. Blood samples were taken at predetermined intervals. The rats were sacrificed after 24 h and the organs and muscles were harvested. As a proxy of the pharmaceutical candidate material, gold was determined in the blood and tissue samples. The blood and tissue samples from rats were digested in a microwave oven with a mixture of nitric acid and hydrochloric acid. Gold in the digests was determined with inductively coupled plasma mass spectrometry (ICP-MS). NIST Reference Material

RM 8012 Gold Nanoparticles was used for quality assurance for the determinations. The results will be presented and discussed.

(66) **Analysis of Arsenicals and Their Sulfur Analogs in Biological Samples using HPLC with Collision Cell ICP-MS and ESI-MS/MS**

Christina M. Gallawa[1], Kevin M. Kubachka[2], Patricia A. Creed[2], John T. Creed[2], Michael C. Kohan[3], Karen Herbin-Davis[3], David J. Thomas[3], Tom Van de Wiele[4]; [1]Oak Ridge Research Fellow; [2]US EPA, ORD, NERL, MCEARD; [3]US EPA, ORD, NHEERL, ETD, [4]Laboratory of Microbial Ecology and Technology, Ghent University

Recent arsenic speciation studies have indicated that the sulfur analogs of the more common arsenic oxides are present in environmental and biological systems. This discovery was previously impeded due to the strong affinity of these arsenic-sulfides for the stationary phases typically used in arsenic oxide based speciation studies. The presence of thiolated arsenicals adds to the chromatographic resolution requirements essential for elemental-based detection (ICP-MS), mainly because misidentifications of an unknown can be made when relying solely on retention time matching when using element specific detection systems. The need for complementary molecular based information using techniques, like LC-ESI-MS/MS, have proven beneficial for assigning molecular structures to unknown arsenicals within complex matrices. The need is also especially important in indentifying the thiolated arsenicals, because primary standards of the neat materials are not commercially available. The detection of thiolated arsenicals as urinary metabolites in both animals and humans has raised questions regarding how and when these species are produced within the metabolic pathway of arsenic. The authors have previously indicated that the microflora in the cecum of a mouse are able to biotransform an arsenosugar oxide (a tri-alkyl substituted arsenic oxide) to its corresponding sulfide [1]. This biotransformation raises questions regarding the conversion of structurally similar arsenic oxides, such as dimethylarsinic acid (DMA, di-alkyl substituted arsenic oxide). This presentation will summarize the analytical data from both LC-ICP-MS and LC-ESI-MS/MS that confirms the production of dimethylthioarsinic acid (DMTA) in the cecum of a mouse. The presentation will also report on the use of an isotopically enriched sulfur label to distinguish between proposed metabolic pathways. Finally, some preliminary research on the conversion of inorganic arsenic to its sulfur analogs will be presented. [1] Conklin, S.; Ackerman, A.; Fricke, M.; Creed, P.; Creed, J.; Kohan, M.; Herbin-Davis, K.; Thomas, D. *In vitro* biotransformation of an arsenosugar by mouse anaerobic cecal microflora and cecal tissue as examined using IC-ICP-MS and LC-ESI-MS/MS. Analyst: 2006, 131, 648-655. Although this work was reviewed by EPA and approved for publication, it may not necessarily reflect official Agency policy.

(67) **Monte Carlo Simulation of Ambipolar Electric Field Effects and Trace Elements in the ICP-MS Vacuum Interface**

Ross Spencer[1], Paul Farnsworth[1], Daniel Wilcox[1]; [1]Brigham Young University

We have recently developed a version of our Direct Simulation Monte Carlo simulation (FENIX) that uses the parallel computing capabilities of the BYU Supercomputing Center. This improved capability allows us to include trace elements in our simulation. We will discuss the effects of ambipolar electric fields on ion transmission through the vacuum interface as well as the physics of secondary shock and re-expansion in the skimmer throat. We will also discuss the details of the transition from continuum flow to kinetic flow on the transmission of trace elements of different masses, including the effects of a secondary shock at the skimmer.

(68) **The Speciation of Five Arsenic Compounds by HPLC-ICP-MS**

James Koedam[1], Anna Starus[1], Gene Dietz[1]; [1]Access Business Group LLC

Arsenic is one of several heavy metals that need to be monitored in consumable raw materials and finished products. As Arsenic can be found as either inorganic or organic, with the different forms posing a different toxicity risk, it was of interest to develop a method that would quantify the different species of Arsenic. Since fish oils are one category of food ingredients that may have some risk of Arsenic contamination, we chose this matrix for our method development. The fish oil samples were extracted into water and alcohol using homogenization. Diarsenic Trioxide (AsIII) and Sodium Hydrogenarsenate (AsV) are extremely toxic while Arsenobetaine (AsB), monosodium acid methane arsonate (MMA) and Dimethyl Arsinic acid (DMA) are not known to be toxic in humans. Using HPLC-ICP-MS these 5 species were separated and quantitated. Through the extraction process spiked samples yielded recoveries of 97-108%. The amount of inorganic toxic Arsenic in fish oil was a very small percentage compared with the total Arsenic levels.

(69) **Advances in Signal Processing for Inductively Couple Plasma**

Stephen Mangum[1], Paul Krampitz[1], Daniel Jones[1]; [1]PerkinElmer LAS

Advances in signal processing for Inductively Couple Plasma (ICP) will be discussed as well as demonstrating the advantages of these advances as they apply to environmental analysis. Universal Data Acquisition (UDA) is a software feature that uses total signal processing and solid state detector technology. The utility of UDA will be demonstrated utilizing EPA method 200.7. This discussion will include examples of data validation, processing of alternate analyte information, instrument and method detection limit determinations as specified in EPA 200.7, and Inter-Element Correction Factor (IEC) determinations. The flexibility of UDA when applied to all of these examples will also be shown.

(70) **Human Tear Lipid: Compositional, Structural and Functional Relationships using Spectrochemical Analysis**

Douglas Borchman[1], Gary Foulks[1], Marta Yappert[1]; [1]University of Louyisville

Knowledge of compositional, structural, conformational and functional relationships in tear film lipid could facilitate the development of therapies to treat symptoms of meibomian gland dysfunction and dry eye disease. Toward this goal, we evaluated IR, NMR, UV and MALDI-TOF mass spectral data to generate a foundation for future studies designed to explore the effect of age, sex and meibomian gland dysfunction on tear lipid composition, structure and function. We first measured lipid composition and conformation using infrared (IR) spectroscopy. With 1H-NMR spectroscopy, we quantified the major lipid classes. Double-bond conjugation, a measure of lipid oxidation, was estimated from UV spectra. Finally, MALDI-TOF mass spectrometry was applied to identify and quantify specific lipid species. 1H-NMR results confirmed our IR data showing wax esters to be the predominant lipid in human meibum (82 %). A significant rise in cholesterol esters was observed in all 17 patients with meibomian gland dysfunction. Using FTIR we found that changes in lipid composition induced a decrease in the strength of lipid-lipid interactions with age. At physiological temperature, lipid order (stiffness) decreased with increasing age. With FTIR we also detected compositional changes in meibum lipid from patients with dry eye symptoms. Compared to normal age-matched subjects, lipid order and phase transition temperatures were significantly

higher to those measured in meibum from normal subjects. The degree of C=C conjugation calculated from UV spectra of meibum lipid did not change with age or with meibum gland dysfunction. By manipulating the matrix composition and cation added to tear lipid samples for MALDI-TOF MS analysis, we were able to quantify and identify lipid components such as cholesterol, phospholipids, hydrocarbons and wax esters with a sensitivity of 9 pmoles. This work highlights the power and complementary nature of spectroscopic methods in the characterization of tear film lipid composition-structure-function relationships and lipid-protein interactions that will be applied in future studies in relation to age, sex and dry eye symptoms.

(71) **Development of Naphthyridine Derivatives to Bind Strongly to Cytosine at an Abasic Site and Their Application to SNPs Analysis**

Yusuke Sato[1], Seiichi Nishizawa[1, 2], Norio Teramae[1, 2]; [1]Tohoku University; [2]JST-CREST

The binding of ligands to DNA has been extensively studied due to their importance as effective pharmaceutical agents. Recently we have discovered the series of new DNA-binding ligands including naphthyridines derivatives, pteridines derivatives, alloxazine derivatives and diaminopyrazine derivatives that can bind cytosine, guanine, adenine and thymine, respectively. As compared to the traditional DNA-binding ligands such as intercalators and groove-binders, our ligands are characterized as the binding to the specific nucleotide opposite an abasic site (AP site) in a DNA duplex. The nature of the binding has successfully been applicable to the analysis of single nucleotide polymorphisms (SNPs). Among these ligands, we previously reported that 2-amino-5-methyl-naphthyridine (AMND) could selectively bind with cytosine at the AP site in a DNA duplex with a binding constant of >106 M-1. In this work, we examined the binding behavior between cytosine and four kinds of naphthyridine derivatives, i.e., 2-amino-naphthyridine (AND), AMND, 2-amino-5,7-dimethyl-naphthyridine (ADMND), 2-amino-5,6,7-trimethyl-naphthyridine (ATMND) by fluorescence and ITC (isothermal titration calorimetry) measurements. Fluorescence titration experiments were performed firstly to examine the ligand-cytosine interaction. All ligands exhibit significant quenching of their fluorescence upon addition of DNA duplexes containing cytosine opposite the AP site, while almost no responses are observed even in the presence of normal duplexes containing no AP sites. The changes in fluorescence intensity can be analyzed by a 1:1 binding isotherm model, by which binding constants (K11) of naphthyridine derivatives with cytosine are estimated. As compared to the binding constant of AND (2.8 „e 105 M-1), the binding constant does increase by a factor of 9, 20, and 64, for AMND (2.7 „e 106 M-1), ADMND (5.8 „e 106 M-1), and ATMND (1.8 „e 107 M-1), respectively. This result clearly indicates that the introduction of methyl groups to naphthyridine does enhance the binding affinity to cytosine at the AP site despite such simple modification. We demonstrate the potential use of these ligands to the analysis of C-related SNPs of PCR (polymerase chain reaction) amplification products.

(72) **A Mechanism for Water Transport across Endocytic Organelle Membranes in Living Cells**

Kenneth Christensen[1], Adriana Chaurra[1]; [1]Clemson University

We have developed a method for measuring water transport across membranes of endocytic organelles in living cells based on rapid superfusion with D2O-based buffers and organelles loaded with Lucifer Yellow dextran. Few studies of organelle water transport have been reported. Most have studied water transport in isolated organelles rather than intact cells. Here, we report measurements of water permeability coefficients in lysosomal and macropinosomal membranes of J774.A1 and RAW 264.7 murine macrophage-like cells. Diffusional water permeability coefficients (Pd) measured in J774.A1 lysosomes had a value of 6.9 ± 0.2 x 10-3 cm/s (mean ± sem) suggesting the presence of aquaporin (AQP) in the organelle membrane. Alternatively, Pd values in early macropinosomes had values of 1.2 ± 0.1 x 10-3 cm/s. The lower Pd value implies that water movement in and out of the early macropinosomes occurs by simple diffusion through the membrane, but Pd increased to 5.2 ± 0.5 x 10-3 cm/s for late macropinosomes. The increase in the Pd value during macropinosome maturation can explained in terms of the activation of AQP under the acidic conditions present in the lysosomal environment. We systematically examined gene expression of the 10 known AQP's using RT-PCR and found gene expression of AQP9 at the mRNA level. AQP9 was also shown to be localized in the endocytic organelle membranes by immunofluorescence microscopy. Finally, Pd was measured in lysosomes of macrophages loaded with Lucifer Yellow and treated with 10 mM NH4Cl to rapidly increase the lysosomal pH. Reduction of the Pd values in lysosomes to early macropinosome levels was observed. These data suggest that AQP9 exhibits pH-dependent function and controls water transport across subcellular organelle membranes. Previously, only AQP6 was reported to have pH-dependent function.

(73) **Post-Collection Processing of FT-IR Images Made Easy**

Samuel White[1], Louis G. Tisinger[1]; [1]Perkin Elmer, Inc.

FT-IR images typically contain many unique spectra; the large amount of data precludes single-spectrum evaluation. Typical routines for analysis have included spectral band distributions, single wavenumber distributions, band ratio images, etc. In addition, least-squares fit of pure component spectra is sometimes done to assess the distribution of whole spectral components, particularly when the chemical composition of a sample is generally known. Frequently, only a few unique spectra are sought in an image containing thousands of spectra. To that end, more complicated routines are used, such as principle component analysis (PCA), which classifies regions with unique chemistries within an image. Unfortunately, unique spectral features within an image are often masked by baseline effects, noise, and spectral sampling artifacts, such as specular reflectance contamination, all of which preclude accurate data interpretation. Another complication is noise due to the low energy return in the image collection, especially in diffuse reflectance and ATR. Consequently, the biggest hurdle in image interpretation tends to be the data extraction process. Many available image analysis programs are available, but they are complicated and difficult to use. This paper will present a processing technique that greatly simplifies data reduction and interpretation of chemical images, using a single push-button approach. The benefit of this technique will be demonstrated in images collected using the different FT-IR sampling modes, i.e., transmission, diffuse reflectance, and ATR.

(75) **Multi-Residue Monitoring of 14 Sulfonamides in Fish Meats using LC-PDA with Confirmation by LC/MS/MS**

Hyesook Chang[1], Hoil Kang[1], Kwangsoo Lee[1], Sangho Lee[1], Soyoung Won[1], Suok Kim[1], Sookhee Ha[1], Yooyoung Jung[1], Sohee Kim[1]; [1]Busan Regional Korea Food & Drug Administration

The analysis of residual amounts of veterinary drugs in food from animal origin is important for quality control of products. For this purpose, Maximum Residue Limits (MRLs) and a simultaneous analysis for 14 sulfonamides (sulfadiazine, sulfathiazole, sulfamerazine, sulfamethazine, sulfamethoxypyridazine, sulfachloropyridazine, sulfamethoxazole, sulfamonomethoxine, sulfisoxazole, sulfadoxine, sulfaphenazole, sulfachloropyrazine, sulfadimethoxine, and sulfaquinoxaline) using liquid chromatography with photodiode array detector (LC-PDA) have been recently updated on Korean food code. Since detected

sulfonamides in fish meats using LC-PDA have to be confirmed with liquid chromatography tandem mass spectrometry (LC/MS/MS), we focused on the establishment of the condition of LC/MS/MS for the confirmation of 14 sulfonamides. Fish samples (approximately 1g) including flatfish, jacopever, sea bream, abalone, common eel, blue crab and shrimp were pretreated by dispersive solid phase extraction (DSPE). After solvent evaporation and sample reconstitution, 14 sulfonamides were analyzed by LC-PDA using CAPCELL PAK C18 MG II (4.6 x 250mm) column. The mobile phase was 5mM potassium dihydrogen phosphate (pH 3.70) and methanol with the gradient elution method. The limits of quantification (LOQs) by LC-PDA were no higher than 18microg/kg for all of the compounds and repeatabilities, expressed as relative standard deviations (RSD), were lower than 2%. We also confirmed 14 sulfonamides by LC/MS/MS using electrospray ionization (ESI) in positive ion mode with acetonitrile/water mobile phase containing 5mM formic acid with the gradient elution method. The cone voltage was 32 V for all the sulfonamides, except sulfadimethoxine of 35 V. This multiple reaction monitoring (MRM) method generated two structurally significant transitions per compound and it was designed to conform to U.S. Food and Drug Administration MS confirmation guidelines. The limits of detection (LOD) and quantification (LOQ) by LC/MS/MS were 0.3~3 and 1~8 microg/kg, respectively and sulfamerazine had the highest sensitivity while sulfachlorpyrazine had the lowest sensitivity. The proposed method was applied to fish meat samples purchased at the markets in Korea. Sulfadiazine was detected by LC-PDA in one sample (flatfish, 15microg/kg) of 118 and confirmed with LC/MS/MS. The multi-residue monitoring of sulfonamides in fish meats is still under investigation.

(76) **Simultanious Analysis of Veterinary Drugs in Foods by LC/ESI-MS-MS**

Jae Chun Choi[1], Hee Ju Choi[1], Jong sup Jeon[1], Ji Yoon Eom[1], Hye Won Jeong[1], Hwa Jung Lee[1], Mi Kyung Kim[1], Hee-Yun Kim[1]; [1]Seoul Regional Food & Drug Administration

Rapid and sensitive simultaneous analytical method based on LC/ESI-MS-MS has been developed for determination of ofloxacin, pefloxacin, enrofloxacin, ciprofloxacin, chloramphenicol, oxytetracyclin, clenbuterol, zeranol, diethylstilbestrol, flumequin, albendazole, spiramycin, spectinomycin, thiamphenicol, oxolinic acid, penicillin G, ampicillin, amoxicillin, danofloxacin, norfloxacin, malachite green, leucomalachite green, crystal violet, leucocrystal violet and 11 sulfa drugs including sulfisoxazole in foods. Under the optimized analytical conditions of LC/ESI-MS-MS using cadenza 5CD-C18(150*2mm, 5um) column, flow rate of 0.2ml/min and 0.1% acetic acid in distilled water and 0.1% acetic acid in methanol as mobile phase, the method provided L.O.D(L.O.Q) of 0.004~16.9ug/L(0.01~56.2ug/L) for 32 compounds in positive mode[M+H]+ and L.O.D(L.O.Q) of 0.01~0.6ug/L(0.034~1.8ug/L) for 4 compounds in negative mode[M-H]-, respectively. The results showed that the method can be used as a routine method for analysis of veterinary drugs in foods.

(77) **Characterization of Monoclonal Antibodies and F(ab')2 using MALDI-TOF-MS and Electrospray Ionization with Q-TOF Mass Spectrometry**

Panfilo Ozaeta[1], Carol Ramsay[1], Lianli Chi[1], Cheng Zhao[1], Jeffrey Fishpaugh[1]; [1]Abbott Laboratories

MALDI-TOF-MS is routinely used in our laboratory to analyze mass profile comparisons of different preparations of monoclonal antibodies and F(ab')2. Q-TOF tandem mass spectrometry with capillary HPLC is used to provide an additional mass spectrometric method to characterize monoclonal antibodies and F(ab')2. Molecular weight profiles of the intact monoclonal antibody and its reduced light and heavy chains were determined using Q-TOF mass spectrometry with electrospray ionization. Q-TOF mass spectrometry determined the characteristic glycosylation mass profiles of the intact monoclonal antibody and the reduced heavy chain. The monoclonal antibody was then deglycosylated and the mass profiles of the reduced light and heavy chains provided additional post-translational modification information. Both MALDI-TOF-MS and Q-TOF mass spectrometry were also used to characterize the F(ab')2 prepared from the monoclonal antibody. MALDI-TOF-MS provided protein solution molecular weight profiles while the Q-TOF mass spectrometry provided post-translational modification information specific to the monoclonal antibodies and F(ab')2. The combination of these MALDI-TOF-MS and Q-TOF mass spectrometry methods afforded mass spectrometric characterization of different preparations of monoclonal antibodies and corresponding F(ab')2.

(78) **Fluorescence Microscopy of Surfaces in Desorption Electrospray Ionization (DESI)**

Mike Wood[1], Paul Farnsworth[1], Devin Busby[1]; [1]Brigham Young University

Desorption Electrospray Ionization (DESI) is a rapidly emerging technology for atmospheric sampling of surfaces in mass spectrometry. In order to understand the mechanisms of this ionization source we have developed a system that allows us to microscopically image the surface that is being sprayed while simultaneously collecting ions through an extension of the mass spectrometers atmospheric-pressure interface. The images acquired provide information to the nature of the solvent-surface interaction. These images can also be used to determine the rates at which the analyte is removed from the surface. Images of fluorescent dyes on hydrophilic surfaces show very rapid removal of the dye from the surface in droplets that form at the ends of narrow rivulets in the dye coating. Removal of sample from porous surfaces is much slower and less exhaustive. Our early results on glass surfaces are consistent with a droplet pickup mechanism for sample removal from the surface.

(79) **A Two Photon IR/UV Ionization Source for MALDI Mass Spectrometry**

Mark Little[1], Lam Nguyen[1], Eli Margalith[1]; [1]OPOTEK, Inc.

The authors have developed a novel laser ionization source that can generate both IR and UV pulses. The optical arrangement has been designed such that switching from UV to IR MALDI and vice versa is accomplished by simply flipping a shutter. A direct comparison of the two techniques will be carried out to show the advantages and disadvantages of using IR versus UV light. In addition, the dual wavelength functionality of the source will be used to investigate practical benefits of two-photon IR/UV MALDI such as increased sensitivity, resolution and the greater ablation potential of IR laser light followed by enhanced efficiency of UV ionization. The laser source is an optical parametric oscillator (OPO) capable of generating simultaneous IR and UV nanosecond laser pulses. IR laser light is tunable from 2.8 micrometers to 3.1 micrometers and UV laser light is fixed at 355 nm. Delay between IR and UV pulses for two photon experiments will be accomplished by using an optical delay line. A custom-built reflectron time-of-flight mass spectrometer will be used for all experiments. Samples will consist of both matrix and matrix-free preparations. In addition to commonly used matrices such as DHB, an analysis of ionic liquid (IL) matrices will be used to investigate analytes embedded in a deep medium. Preliminary two photon MALDI work has been carried out in the author's previous laboratory. In this case, 337 nm/ 10.6 micrometer and 337 nm/2.94 micrometer laser light was used. An enhancement of analyte signal was found in both cases. Further work will test IR wavelength dependence for two photon MALDI.

Also, experiments will be carried out to investigate whether the greater ablation potential of IR light followed by UV ionization for enhanced efficiency will provide further advantages for two photon MALDI using IL matrices. ILs matrices are provided by Dr. Dan Armstrong of the University of Texas at Arlington. Preliminary results indicate that ILs can be used for IR MALDI in vacuum. Final experiments will test a novel ionization geometry where samples will be irradiated with IR light from behind (transmission geometry) followed by front illumination by UV light.

(80) **Conformational Stability, r0 Structural Parameters, Barrier to Internal Rotation and Vibrational Assignment of Cyclobutylamine**

Arindam Ganguly[1], Ahmed M. El Defrawy[1], W.A. Herrebout[2], B.J. van der Veken[2], James R. Durig[1]; [1]University of Missouri-Kansas City,USA; [2]Universitair Centrum Antwerpen,Belgium

The infrared spectra (3600-100 cm^{-1}) of gaseous and solid cyclobutylamine, c-$C_4H_7NH_2$ have been recorded, as well as, the far infrared (600-60 cm^{-1}) spectra in krypton solutions at variable temperatures (-103.3 to -136.4 ºC). From this latter study, the enthalpy difference has been determined to be 225 ± 26 cm^{-1} (2.7 ± 3 kJ/mol) between the most stable equatorial-*gauche* (Eq-g) conformer and the equatorial-*trans* (Eq-t) form. Only 25% of the Eq-t form is present at ambient temperature. The potential function governing the conformational interchange of the NH_2 moiety of the equatorial conformer has been determined with the following potential coefficients (cm^{-1}): V_1= -165 ± 34, V_2 = -179 ± 42, V_3 = 737 ± 9 and V_4 = 64 ± 17 with barriers of 788 cm^{-1} for *gauche* to *gauche* and 838 cm^{-1} for *gauche* to *trans* form. A complete vibrational assignment is proposed for the (Eq-g) conformer based on the infrared band contours, infrared intensities, Raman activities and group frequencies which is supported by normal coordinate calculations utilizing the force constants from *ab initio* MP2(full)/6-31G(d) calculations. Proposed assignments are also made for several fundamentals of the (Eq-t) form. No evidence was obtained for a third conformer. These experimental and theoretical results are compared to the corresponding quantities of some similar molecules.

(81) **Fuel Property Modeling for Rapid Quality Surveillance**

Mark Hammond[1], Robert Morris[1], Kevin Johnson[1], Jeffery Cramer[1], Braden Giordano[2], Susan Rose-Pehrsson[1]; [1]Naval Research Laboratory; [2]Nova Research, Inc.

The Naval Research Laboratory has been engaged in an initiative to develop rapid automated shipboard fuel quality surveillance technologies. This approach is based upon deriving the mathematical relationships between analytical fuel data and measured specification properties. We have implemented novel chemometric methodologies to develop a prototype analyzer based on near-infrared spectroscopy that provides real-time estimates of a range of critical specification fuel properties of jet and Naval distillate fuels. Each incoming fuel is classified as jet (JP-5, JP-8, Jet A) or diesel (F-76, MGO), and the relevant properties for each type are calculated and reported. Additionally diesel fuel is further checked for detection as an ultra-low sulfur diesel and for the presence of biodiesel fuel. Since synthetic Fischer-Tropsch (FT) fuels will be introduced into the Navy fuel supply when they become available, we are currently working to extend the capabilities of this device to FT fuels and blends with petroleum-based fuels.

(82) **Raman Spectroscopy in the Palm of Your Hand**

Keith Carron[1], Rick Cox[1]; [1]DeltaNu

Material recognition is essential for commercial manufacturers and law enforcement investigators. In the past few years, Raman spectrometer form factors have been miniaturized to accommodate portable applications. These devices can be used to provide rapid feedback from manufacturing processes, sorting lines, shipping and receiving terminals, and medical devices. Field deployable Raman devices are used routinely by first responders and criminal investigators. The size and form factor for Raman spectrometers are rapidly changing. The system we developed in 2001 weighed 4.5 lb, and this was considered rather small for its time. A most recent development has produced a palm-sized form factor that weighs a mere 11 oz. We will compare the signal-to-noise, resolution, and other performance characteristics of this device to larger benchtop and portable versions.

(83) **A Scanning Electrochemical Microscopy Coupled Flow Injection System for Glucose Analysis**

Hsuan-Jung Huang[1], Jyun-Jie Lai[1]; [1]National Sun Yat-sen University

By modifying glucose oxidase (GOx) and horseradish peroxidase/ferrocenecarboxylic acid (HRP/Fc) on the tip and substrate electrodes of a SECM system respectively, a positive feedback effect for the catalytic reactions of GOx and HRP was found after the tip electrode has approached to the substrate electrode closely enough. The positive feedback effect can be enhanced by applying a rather positive potential on the substrate electrode. This enhancing effect provides a different method for the analysis of glucose with a SECM system. After coupling the SECM to a FIA system, glucose was determined amperometrically by monitoring the reduction current at the GOx tip electrode. A linear concentration range of 0.01 to 1.0 mM with a satisfactory linear relationship (R2 = 0.9959) and a detection limit of 0.007 mM were obtained. Glucose in real samples was analyzed with the developed SECM system and results obtained matched well with those obtained by using a well established spectrophotometry method.

(84) **Iron(III)-Nickel Nanoparticles Synthesized using Microwave Heating and Characterizations with Atomic Force Microscopy**

Algernon Kelley[1], Nickolaus Flurry[1], Stephanie Daniels[1], Jayne Garno[1]; [1]Louisiana State University

Microwave synthesis can be used to develop Green chemistry methods using less energy and smaller volumes of reagents. Industrial and academic research laboratories have implemented microwave systems for sample digestions, extractions and for organic synthesis. With widespread public concern for the disposal of chemicals or wastes it is necessary for chemists to develop environmentally friendly or "Green chemistry" methods. The benefits of microwave ovens for sample preparation and synthesis include improved safety, speed, smaller reagent volumes and increased product yields in comparison to traditional methods. The goal of this project was to design an accelerated method for producing high quality, monodisperse magnetic nanoparticles using microwave heating. Working within time constraints of six hours of research per week, an LSU undergraduate developed a method for synthesizing magnetic nanoparticles using microwave heating. The student scaled the methods to produce a few milliliters of product in aqueous solution, and optimized temperature and pressure parameters to produce uniform nanoparticles. We hypothesized that precise control of temperature and pressure inside microwave vessels would produce higher quality nanoparticles with better monodispersity. The Fe(Ni)3 particles were imaged and characterized by atomic force microcopy to

investigate the morphology and size distributions for samples prepared with different synthetic conditions. A hydrothermal process was used to synthesize magnetic nanoparticles in a microwave equipped with high pressure Teflon vessels. The microwave synthesis enables precise control of the temperature and pressure within a sealed container using a fiber optic thermocouple and a pressure transducer. Microwave synthesis produced nanoparticles much more rapidly than conventional radiative heating. Microwave synthesis was accomplished within 45 minutes as compared to 15 hours with a conventional oven. As the size of nanoparticles change, the magnetic properties of nanoparticles have been shown to exhibit new phenomena such as giant magnetoresistance (GMR) and superparamagnetism. In addition to the inherent benefits of Green chemistry, microwave systems provide a promising approach for better control of synthetic parameters and sizes of composite metal nanoparticles

(85) **Applying the Chemometrics Tools for Nanomaterials Research: Quantum-Chemical Modeling and QSPR of Fullerene C60 Solubility in Organic Solvents**

Tetyana Petrova[1], Bakhtiyor Rasulev[1], Andrey Toropov[1], Danuta Leszczynska[2], Jerzy Leszczynski[1]; [1]CCMSI, Jackson State University; [2]Civil&Env. Eng, Jackson State University

Fullerenes are sparingly soluble in many solvents. The dependence of fullerene's solubility on molecular structure of the solvent must be understood in order to efficiently separate different members of the fullerene family from each other and from their precursors or derivatives. Quantum-chemical calculations and quantitative structure-activity/property relationship (QSAR/QSPR) tools were used to model the solubility of fullerene C60 in organic solvents. Quantum-chemical calculations were performed with ab initio and semiempirical methods taking into account the solvent properties by self-consistent isodensity polarized continuum model (SCI-PCM). A hybrid method of genetic algorithm and multiple regression analysis (GA-MLRA) was applied to generate correlation models. The quantum-chemical study reveals a correlation of solvent properties and C60 solubility. The important parameters of solvents that affect the C60 solubility have been also evaluated by the QSPR analysis. The employed GA-MLRA approach augmented by application of quantum-chemical calculations yields reliable results, allowing one to build simple, interpretable and transparent models that can be used for future predictions of C60 solubility in various organic solvents and that they provide basics for understanding of this mechanism.

(86) **Evaluation of a Novel Single-Wall Carbon Nanotube Purification Method using Raman Spectroscopy**

Aaron Urbas[1], Steven Choquette[1], Gary Giulian[2], John Marino[1,2]; [1]National Institute of Standards and Technology; [2]University of Maryland

In this work, Raman spectroscopy was used to qualitatively characterize single-wall carbon nanotube (SWNT) enrichment of a commercially obtained material to evaluate a novel large-scale purification technique. At the present, purified SWNT materials are not economical for many potential commercial applications. Most large-scale SWNT fabrication methods require metal catalysts, which are invariably present in the end product. Additional by-products of these fabrication methods include graphitic and amorphous carbon species, fullerenes and multi-wall nanotubes. The raw carbon nanotube materials are relatively inexpensive but there is still great demand for cost-effective purification techniques to produce high purity, homogenous SWNT fractions in high yield. Drawbacks to existing purification methods include efficiency, incomplete purity removal and defect generation in the purified SWNTs. In brief, the purification method evaluated in this work involves (1) a mechanical processing of raw CNT material using "green" water-based chemistry, (2) continuous micron-scale size separation of CNTs with self-cleaning mesh filters, (3) magnetic gradient fractionation in a glycerol gradient and (4) a power-dialysis step to remove < 0.5 nm amorphous carbon species. The poster will focus on the spectroscopic characterization of the raw, intermediate and purified SWNT materials using Raman spectroscopy.

(88) **Nanotechnology in Food Production**

Erastus Gatebe; [1]JKUAT

Can nanotechnology be used to solve world food crisis? We report a new protocol to investigate the effects of nanomaterials to the overall food production and its subsequent high production. With the mounting global food crisis, a new and efficient method of boosting food production and mitigating looming hunger is necessary. In our protocol, we have varied the materials required to support crop production and allowed only those nutrients that are in nano dimensions to be absorbed. The purpose was to investigate whether we can shorten the time frame required for the maturation of crops without using any other methods such as genetically modified techniques. In this new protocol, spectroscopic methods and analysis reveals high nutrients intake and shortening of production period. This is a novel phenomena.

(89) **In-Line Turbidity Measurements for Industrial Processes**

John Groetsch; [1]Mettler Toledo Ingold

In-line turbidity analyzers have been successfully used for many years to measure the suspended solids and/or emulsions levels in liquid process streams in real time. The technique employed is the measurement of light scattering at various angles from the light source and at various wavelengths. The data from these in-line analyzers has helped to optimize and reduce upsets in industrial processes. This paper gives an overview of the light scattering turbidity techniques used and why certain methods perform best in specific applications. Sensor fouling or coating can be a concern, therefore automatic in-place cleaning will be discussed. Calibration is an integral part of any in-line analyzer; the calibration methods used will be presented and compared. Data from both on-line and off-line turbidity analyzers will be reviewed along with the sample conditioning challenges encountered.

(90) **Terahertz Imaging Diagnostics of Cancer Tissues with a Chemometrics Technique**

Hiromichi Hoshina[1], Aya Hayashi[1], Norio Miyoshi[2], Chiko Otani[1]; [1]RIKEN; [2]University of Fukui

Terahertz (THz) spectroscopic images of paraffin-embedded cancer tissues have been acquired with a THz time-domain spectrometer (THz-TDS). The difference between cancer tissues and normal ones was distinguished in the THz images. However, it was difficult to diagnose cancer area systematically from the THz images, because they change drastically with the sample condition. For the systematic identification of cancer tumors, the principal component analysis (PCA) and the clustering analysis were applied. In three of four samples, the cancer tissue was recognized as an aggregate of the data points in the principal component (PC) plots. By agglomerative hierarchical (AH) clustering, the data points were well categorized into cancer and normal tissues. This method can be also applied to various kinds of automatic discrimination of plural components by THz spectroscopic imaging. Recently we started the THz imaging of the frozen samples. Since ice is more transparent in the THz range than water, the imaging spectroscopy of frozen tissues may shorten the sample preparation time and enable rapid cancer diagnosis. The present status of our research will be reported.

(91) **Time-Domain Terahertz Deconvolution Analysis for Non-Contact Measurement of "Opaque" Layered Samples**

Jeffrey White, Greg Fichter, David Zimdars; [1]Picometrix LLC

Time-Domain Terahertz (TD-THz) measurements, and subsequent deconvolution analysis, of single and multilayer samples will be presented. Results of interest are the sample or layer's thickness and material's refractive index values for both transparent and nominally "opaque" materials. The specific method described is a deconvolution of the Time-Domain THz data technique. In general, deconvolution transforms a poorly defined pulse (an asymmetric 2-3 ps THz pulse in this case) into a well defined pulse shape (sinc-shaped pulse 0.5 picoseconds or less). The choice of an appropriate filter (Weiner, Tikhonov) to optimize the deconvolution for THz frequency spectra will be discussed. The deconvolved waveform can then be decomposed into multiple layers using curve-fitting of the resulting sinc-shaped pulses. This process allows significant improvements for the measurement of thin films or layers (less than 10 um, <1/50 of the probing wavelength). Multiple examples will be presented. A key aspect of THz measurements is the capability to inspect "opaque" materials. Most dielectric materials (e.g., paper, paint) are transparent to THz. Thus inspection of a very wide range of samples, including very thick materials, is possible. Additionally, THz measurements can be made at much higher rates (demonstrated 4 kHz), which permits additional measurement capabilities. Samples include paint and coatings, including specialty materials (e.g., extremely high iron content polyurethane) and coatings for aerospace applications. Plastic and paper manufactured products are other measurement applications. Less traditional measurements include penetration of coatings into thick porous substrates (sand castings).

(92) **Analysis of Single Cells using Microfabricated Devices**

Nancy Allbritton[1], Wei Xu[1], Hsuan-Hong Lai[1], Scott Phillips[1], Chris Sims[1]; [1]University of North Carolina, Chapel Hill

Advances in analytical techniques have made the performance of biochemical assays on individual mammalian cells possible. We are currently engaged in developing, microanalytical assays to track cell signaling, migration or phenotype. Devices are fabricated from a variety of different polymers including SU-8, 1002F, and poly(dimethylsiloxane). Inexpensive, disposable, polymer chips are an effective strategy to handle biological solutions such as cellular matrixes or lysed cells. Cells in these devices are manipulated by focused laser beams or fluid streams. We will present recent results on the development of surface coatings, on strategies to rapidly lyse cells , and on the separation of single cells or their contents with microfabricated devices.

(93) **Visualizing Cholesterol Dynamics in the Living Cell Membrane**

Jerilyn Timlin[1], Amanda Carroll-Portillo[1], Janet Pfeiffer[2], Haitao Li[3], Gary Griffiths[3], Janet Oliver[2], Bridget Wilson[2]; [1]Sandia National Laboratories; [2]University of New Mexico; [3]National Institutes of Health, NHLBI

Cells communicate with their surrounding environment via membrane receptors. Ligands associate specifically with receptors initiating critical spatial reorganization of receptors and membrane components, including lipids and proteins, to result in activation of a cascade of signals in response to the environmental trigger. Cholesterol is known to play an important structural role in the living cell membrane creating stiffness and fluidity through local concentration gradients, but the spatial and temporal details of it's interaction with receptors during the cell signaling process remain elusive. For example, cholesterol in the inner leaflet has been shown to concentrate in the area around receptors following receptor crosslinking in Rat Basophilic Leukemia (RBL) cells and subsequent cell fixation and electron microscopy. Bioanalytical techniques capable of real-time visualization of cholesterol in a living cell membrane would have a significant positive impact for understanding cellular signaling events. Unfortunately, capturing the location and concentration of cholesterol in the living cell membrane relative to other membrane components is difficult due to the lack of specific probes for cholesterol and limited-speed of multicolor imaging with membrane specificity. Using the well characterized system of FcåRI (IgE receptor) in the RBL cell membrane we will present the application of a dual-color CCD-based total internal fluorescence (TIRF) microscope and assess the utility of several novel cholesterol probes for highlighting cholesterol dynamics in the living cell. The TIRF-based imaging system provides video-rate time sequences with membrane specificity and permits us to assess spatial reorganization of cholesterol in the outer leaflet of the cell membrane in response to cell stimulation and receptor crosslinking.

(94) **Capillary-Channeled Polymer Films as a Platform for Cellular Analysis**

Kenneth Christensen[1]; [1]Clemson University

Capillary-channeled polymer (C-CP) fibers and films have unique geometries that provide spontaneous wicking that can be used to drive cell-based separations, flow cytometry, and bioassays in a compact, portable, and very simple format. The first generation of C-CP films contains a total of 30 open channels that range from 10 – 100 ìm in diameter that can be used in tandem or as individual elements of a multiplexed bioanalytical method. A uniform flow of cells is achieved within all of the channels in the C-CP films, with dispersion rates on the order of mm/sec, without the use of any fluid pumping or electrophoretic forces! The use of the natural wicking action of the films, the size selectivity of the channels, and the ability to modify the surface chemistry within the channels provide a great deal of flexibility to perform a variety of cellular analyses in a low-cost package.

(95) **Construction, Figures of Merit, and Testing of a Single-Plankton Fluorescence Excitation Spectroscopy System**

Luisa T.M. Profeta[1], Laura S. Hill[1], Evelyn Lawrenz[1], Tammi L. Richardson[1], Benjamin S. Twinning[1], Christopher J. Hintz[1], Timothy J. Shaw[1], Michael L. Myrick[1]; [1]University of South Carolina

Optical traps provide a powerful and noninvasive mechanism for the exploration of small individual particles. During the last three decades, optical traps have allowed for analysis of particles such as nanoparticles, colloidal microparticles and cells. Setting up an optical trap within an inverted microscope system allows for collection of fluorescence measurements from cellular systems. Previous optical trap studies have performed single wavelength fluorescence measurements on phytoplankton. In this study the setup and operation of a continuous wavelength fluorescence optical trap is described for phytoplankton evaluation. The identification of two-photon fluorescence as a secondary effect from the optical trap laser is also elucidated.

(96) **Examination of Creatine Deposits and Environs in Brain Tissue from TgCRND8 Mice by Raman and FTIR Microscopy**

Avid Khamenehfar[1], Adriana Szeghalmi[1], Marc Del Bigio[2], David Westaway[3], Robert Julian[4], Kathleen Gough[1]; [1]Department of Chemistry, University of Manitoba; [2]Department of Pathology, University of M; [3]3Centre for Research in Neurodegenerativ; [4]Synchrotron Radiation Centre, University

Alzheimer Disease (AD) is a progressive neurodegenerative disorder characterized by memory loss and dementia. The pathological hallmarks of AD include extracellular deposits of Beta-Amyloid peptides, derived from proteolytic cleavage of

amyloid precursor protein (APP) by Beta- and Gamma-secretase, and neurofibrillary tangles (NFTs). Both energy metabolism and the function of creatine kinase are known to be affected in Alzheimer diseased brain and in cells exposed to the Beta-amyloid peptide. Synchrotron Fourier Transform infrared (sFTIR) and Raman microspectroscopy imaging techniques have proved to be important methods for *in situ* investigation of tissue sections from a transgenic mouse model for AD. The higher sensitivity, lower integration time and better spatial resolution achievable with the synchrotron light source make it the first choice for FT-IR microspectroscopy. With this technique, we have discovered extensive deposits of crystalline creatine (Cr) in the brain tissue of TgCRND8 mice, an AD model expressing doubly mutant (K670N/M671L and V717F) amyloid precursor protein, and displaying robust pathology from an early age. Raman spectra obtained at higher spatial resolution (1 μm) can be used for the precise delineation of the Cr microdeposits and their environs. In this work, Raman spectroscopic results are compared and discussed in conjunction with the prior sFTIR data and with standard histological tests for relevant targets.

(97) **Chemical Imaging using Deep UV Laser Induced Native Fluorescence and Resonance Raman**

Rohit Bhartia[1,3], William F. Hug[2], Everett C. Salas[3], Ray D. Reid[2], Kripa Sijapati[2], Arthur L. Lane[2], Kenneth H. Nealson[3]; [1]Jet Propulsion Laboratory/Caltech; [2]Photon Systems Inc.; [3]University of Southern California

We present a tagless imaging modality that uses native fluorescence emissions ranging from 260-500nm excited with deep UV lasers (224nm) to detect organics and microbes on a variety of surfaces with single bacterial cell detection limits. This is a result of point spectroscopy analyses that have shown native fluorescence alone can be used as a non-contact, non-invasive, non-destructive method for detection a wide array of organics and biological materials when coupled to chemometric methodologies. Traditionally, fluorescence obscures Raman signatures when using visible excitation wavelengths. This combined methodology of Raman and fluorescence only becomes possible with excitation below 250nm where the fluorescence and Raman spectral regions are separate. Simultaneous acquisition of both regions coupled with chemometric analysis enables detection and characterization of organics, bacteria (cells/spores), and a variety of chemical precipitates with both exquisite sensitivity and a high degree of specificity. Detection of bacterial cells and spores is associated to the unique combinatorial signature of aromatic and non-aromatic compounds. In addition this methodology enables detection of mineral by-products as indicators of microbial activity such as nitrates, carbonates, sulfates, and phosphates We will present two methods, Raster Scanning and Array imaging, that we have used to obtain native fluorescence and Raman images. We have coupled this spectroscopic information with chemometric techniques to determine the presence of organics and microbes in Antarctic ice core and on opaque surfaces from natural environments.

(98) **Detection of Toxic Chemicals in Human and Pet Foods**

Frederick Fricke; [1]US Food and Drug Agency, Forensic Chemistry Center

The U.S. Food and Drug Administration is responsible for ensuring the safety and security of the Nations food supply. One aspect of this responsibility is the development of methodology to detect toxic chemicals in human food, pet food, and dietary supplements. These chemicals may have been introduced into the food intentionally or accidentally. Minimal sample preparation procedures have been developed and coupled with LC-MS, GC-MS, ICP-MS, Raman, FTIR, Ion Chromatography, and ELISA, to screen for toxic chemicals in a variety of food matrices. Case studies will be presented describing the development of these techniques for application to: The detection of the chemical in pet food that resulted in numerous cat fatalities, the detection of the causative agent that sickened and killed many cows at a large dairy farmthe, detection of ricin in baby food, the detection of sildenafil, tadalifil, vardenafil, and their analogs in dietary supplements, the detection of methanol in infant formula and analyses of associated evidence to link the suspect to the product tampering.

(99) **Quantitation of Abrine, an Indole Alkaloid Marker of the Toxic Glycoproteins Abrin, by LC/MS/MS from Various Beverages**

Janel Owens[1]; [1]Lawrence Livermore National Laboratory

Abrin is a class of highly toxic glycoproteins from the seed of the Rosary pea plant, Abrus precatorius. Abrin is homologous to ricin both in structure and mode of action, though abrin is more toxic than ricin. Given its high toxicity, its extraction and analysis from food and beverage matrices are of interest. A procedure for the clean-up of abrine, an indole alkaloid marker of abrin, by both solid phase extraction (SPE) and liquid-liquid extraction (LLE) from various beverages, including bottled water, bottled tea, cola, orange juice, juice drink, and skim milk, with quantitation by liquid chromatography tandem mass spectrometry (LC/MS/MS) is described. The utility of both C18 and mixed-mode cation exchange SPE cartridges from various manufacturers was investigated. Adjustment of sample pH to 3 – 6 with clean-up by strata-X™ C18 SPE (Phenomenex) resulted in optimal recoveries at ranging from 101 to 110 % for abrine standards in water with a relative standard deviation of 7 % or less. The extraction efficiency of abrine from beverages by SPE clean-up was then compared to a liquid-liquid extraction clean-up protocol modified from a previously published method for chemical warfare agent analysis in foods (Kolakowski, Anal Chem, 2007). This method allows for precise quantitative recovery of abrine from beverages by SPE and useful qualitative screening by LLE at low levels. This work performed under the auspices of the U.S. Department of Energy by Lawrence Livermore National Laboratory under Contract DE-AC52-07NA27344. LLNL-ABS-403348.

(100) **Multiplexed Detection of Foodborne Pathogenic Bacteria on SERS Based Immunomicrowell-arrays**

Jian Sun[1], Mikella Hankus[1]; [1]University of Maryland Baltimore County

Quick and sensitive detection techniques for on-site monitoring in the food industry are in great demand for both food processing and food safety reasons. A novel surface enhanced Raman scattering (SERS)-based immunomicrowell-array has been developed for multiplexed detection of pathogenic bacteria. We will present the fabrication and characterization of the SERS based immunomicrowell-array. The immunomicrowell-array is prepared by immobilizing optical addressable immunomagnetic beads into microwells on one end of a fiber optic bundle. These immunomagnetic beads consist of 1-micron polystyrene magnetic microbeads coated with SERS active dye molecules as Raman labels, and antibodies specific to the target bacteria. Characterization and validation of the antibody and dye binding is performed via multi-spectral imaging of the beads. The method of ligand coating is optimized based the immunomagnetic separation efficiency of target bacteria. The microwell array is fabricated by etching the polished end of a fiber optic bundle containing 30,000, 4-micron fiber elements with 25% HF, with the depth of the microwells controlled by the etching time. SEM images of these bundles show that the microwell array is composed of highly ordered and uniform microwells, each characterized by a fiber core surrounded by six cladding peaks. When the cladding peaks are coated by silver, the microwell array acts as a SERS substrate with

uniform surface roughness and SERS enhancement across the entire array. Multiplexed bacteria detection is carried out by employing SERS as the transduction mechanism. Various immunomagnetic beads, each having a different Raman label corresponding to a different target bacteria, can be excited by a single HeNe laser operating at 632.8 nm and their corresponding SERS spectra can be identified discretely due to the narrow bandwidth of SERS peaks.

(101) **Spectroscopic Imaging for Detection and Discrimination of Different E. Coli Strains**

Michael Gilbert[1], Caleb Frick[1], Andrew Wodowski[1], Frank Vogt[1]; [1]University of Tennessee

Food contaminations with E. coli bacteria are a major concern for public health. Current techniques are based on sample extractions, time-consuming sample preparations and labor-intensive analyses. In this study we present an approach and first results that are based on FTIR spectroscopy using little to no sample preparation and thus has online capabilities. For such analyses it is also important not only to detect E. coli but also classify which strain has been found; some E. coli contaminations are harmless while others are toxic, even fatal, at a level of tens of bacteria. However, due to the chemical similarity of different E. coli strains, all spectra contain very similar features. This makes visual discrimination difficult, leading to the need for support by statistical data analyses. Three non-toxic strains have been used in this proof-of-principle study: E. coli B, C and K12. Two types of experiments have been performed. (1) Different samples of the same strain have to be classified as identical. (2) Samples from different strains must be found as such. To demonstrate both requirements, experiments are based on correlations of spectra from different E. coli samples. To generate a sufficiently large set of test spectra, ten spectra were measured from each sample. For experiment (1), spectra from two samples of the same strain were acquired and correlated with the spectra from within one sample. By means of t-tests it was found that the correlation coefficients, i.e. the measure of similarity, among both samples are not significantly different compared to those obtained from correlating the spectra within one sample. From this it was concluded that both samples contain the same strain. Experiment (2) followed a similar correlation approach and now it was observed that the correlation among different strains is significantly lower than within a strain. Thus there must exist significant differences between the spectra of different strains that allow discrimination.

(102) **Extraction of Oxytetracycline and Oxolinic Acid from Food for Fish and Its Determination by Derivative Spectrophotometry**

María Inés Toral[1], Sandra Orellana[1], Pablo Richter[2]; [1]University of Chile, P.O.Box 653; [2]University of Chile, P.O.Box 233

In this work is proposed an extraction method of oxytetracycline (OTC) and oxolinic acid (OA) from fish food and its determination by derivative spectrophotometry (DS). For the extraction of each drug, it was considered its polarity and the capacity of OTC to form complexes. Based on these considerations and preliminary studies, were selected acetonitrile for the extraction of OA and buffer HPO4-2/H2PO4 – 0.1M (pH 7.2) and EDTA 0.1M as complexing agent for extraction of OTC. The enriched samples were prepared starting from 20 g of food with 5.0 mg of each one of the drugs, which corresponding to 250 mg/Kg of OTC and OA. This sample was powdered and homogenized in a mortar by 1 hour. Then different fractions of this sample were weighed and different quantities of food were added in order to obtain solid dilutions of concentrations between 125 and 25 mg/Kg. These foods, enriched with OTC and OA, were extracted in parallel. For the extraction of OTC were added 20 mL of buffer, 4 mL of EDTA and then agitated for 40 min. The extract was centrifuged to 2,000 rpm by 5 min, and the supernatant was filtered to the vacuum. To extract OA 25 mL of acetonitrile was added and then agitated for 40 min. Finally, both extracts were evaluated by DS, in order to ovoid the mutual interference if something of the other drug is extracted. The selected spectral variables, for the determination of OTC and OA, were: first derivative, smoothing factor 16,000, amplification factor 10,000 and the wavelengths, were 380.2 nm and 275.8 nm, respectively. A sequential extraction was also carried out where was extracted the OTC previously and then the OA, however the efficiency of the extraction of OA was smaller, besides requiring a bigger time in the total protocol. Summarize of the obtained results: Parallel extraction: Recovery 106 ± 4% (OTC) and 95 ± 5% (OA) Sequential extraction: Recovery 118 ± 4% (OTC) and 52 ± 5% (OA) In both cases the extraction limit was of 25 mg/Kg. Acknowledgement: FONDECYT Project Nº 1070905, CONICYT Doctoral Scholarship.

(103) **Modeling and Diagnostics of Microplasmas in ExB Fields**

Akbar Montaser[2], Michael Keidar[1], A. Shashurin[1], Maryam Farmand[2]; [1]The George Washington University, Mechanical and Aerospace Engineering; [2]The George Washington University, Department of Chemistry

Devices based on a closed electron drift in ExB fields are currently applied several areas including plasma immersion ion implantation for surface modification, magnetron discharge for plasma processing, and electric thrusters for spacecraft propulsion [1]. Although having different applications, these technologies are based on the same physical phenomena of electrostatic acceleration of ions in partially magnetized plasma with closed electron drift. One important consequence of the E„eB field configuration is the formation of a large electron drift current. A multi-scale model of the discharge in ExB fields is developed in which kinetic treatment will be used for electron component while 2-D macroscopic model will be employed for ion and neutral component analysis. The dielectric wall effect is considered by introducing an effective coefficient of secondary electron emission. Partial electron thermalization is taken into account and it was found that it has very strong effect on global discharge characteristic. Thermalization leads to peak electron temperature saturation, while in the case of a partial thermalization peak electron temperature increases linearly with discharge voltage. Importantly, the electron temperature (in the range of 20-60 eV) can be controlled by discharge voltage. This feature is exceptionally important for chemical analysis of various species [2]. Plasma number density will be measured using a simple and convenient resonator method developed previously described [3] for the local measurements using the small-size quarter-wave resonator. The principal of probe operation consists in shifting of the resonance frequency of the probe inserted to plasma due to the plasma dielectric permittivity in comparison with resonance frequency without plasma. This probe was recently applied for the spatially resolved measurements of the plasma density distribution under strong turbulence in magnetic filed [4]. [ ] M. Keidar and I. Beilis, IEEE Trans Plasma Sci., 4, 2006, p. 804-814. [2] A. Montaser, Editor, Inductively Coupled Plasma Mass Spectrometry, Wiley, 964 pages, 1998. [3] R. L. Stenzel, Rev. Sci. Instrum., 47: 603-607, 1976. [4] A. V. Kostrov, A. V. Shashurin, A. V. Strikovsky, Plasma Phys. Rep. 27(2): 137-142, 2001.

(104) **Generation and Applications of Micro Inductively Coupled Plasma Sources**

Mazdak Taghioskoui[1,2], Mona Zaghloul[2], Akbar Montaser[1]; [1]The George Washing University, Department of Chemistry; [2]The George Washington University Department of Electrical Engineering

Inductively Coupled Plasma (ICP) sources are of great importance for wide range of applications, including but not limited to micro and nano fabrication, chemical analysis, and plasma processing. Portable and battery-operated instruments can be developed using a miniaturized micro ICP chip considering the low-power and low-voltage requirement of micro ICPs. To the best of author's knowledge, this is the first report for generation of a micro ICP on a chip with size of nearly 1 mm using a planar coil with diameter of 800 μm. A novel method for chemical analysis on Mars is presented using miniaturized carbon dioxide inductively coupled plasma optical emission spectroscopy (miniaturized-ICP-OES). Importantly, the conditions of the Martian atmosphere allow for plasma generation without the need for a gas tank and vacuum pump to operate the device. The generation and characterization of miniaturized ICP sources under conditions mimicking the atmosphere of Mars were studied. Circuit design considerations for miniaturized ICP generation are also investigated. The background emission spectrum of a miniaturized carbon dioxide ICP showed an interference-free spectrum from 420 to 900 nm, making it favorable for chemical analysis in the visible region. The feasibility of chemical analysis was examined by introducing ethylene, neon, and hydrogen while monitoring the peaks at 431, 585, and 656 nm, respectively. This method enables the future development of a chemical analyzer for Mars missions with equipment sizes comparable to that of a matchbox, operating at power of 2 - 10 W with the lifetime of several months.

(105) **Micro Discharges for Science and Engineering**

Yogesh Gianchandani[1]; [1]University of Michigan

Preliminary studies have made it clear that microplasmas and micro-discharges differ in some important ways from larger scale discharges. Both differences from and similarities to larger scale discharges can be exploited for manufacturing and sensing modalities. For one, they provide structural and material diversity: microplasmas ignited between thin film metal patterns permit selective localized etching and deposition of materials; micro-arcs permit stainless steel and other metals to be machined in ways that are lithography compatible. Beyond manufacturing issues, the ability to predict and control microdischarges permits them to be exploited in transduction schemes. Spectroscopic sensing of chemicals in both gas and liquid phase is an obvious application. For example, microdischarges to liquid microchannels have been used to detect inorganic contaminants such as lead and chrome in water. However, the converse application, which is the use of liquids to serve as inexpensive but tunable sources for radiation wavelengths that are otherwise not easy to generate, may also offer value. Gas-phase discharges are useful for radiation sensing, such as by micromachined beta-particle counters. The RF emissions emanating from these discharges are in the ultra wideband spectrum, and can be detected by common AM/FM radios, creating some interesting opportunities for wireless networking. Micro-discharges have been used in actuation as well, notably as Ti sputter-ion pumps for cavity pressure control. This talk will address outline some of the challenges and opportunities for microsystems that result from scaling this state of matter.

(106) **A Novel Low-Flow Inductively Coupled Plasma Source for Elemental Analysis: Study of Its Fundamental Properties**

Carsten Engelhard[1], George C.-Y. Chan[1], Gerardo Gamez[1,2], Andy Scheffer[3], Wolfgang Buscher[3], Gary M. Hieftje[1]; [1]Indiana University; [2]Swiss Federal Institute of Technology; [3]University of Muenster

The inductively coupled plasma (ICP) is a popular and powerful tool for elemental and speciation analysis. Recent advances in ICP instrumentation have produced greater spectral resolution, lower detection limits and have made hyphenated techniques more readily available. However, the basic design of the ICP source itself has remained nearly unchanged over the years. As a consequence, the main drawback of this technique, the high argon gas consumption of up to 20 L min-1 - resulting in high operating costs - persists. Recently, however, a novel low-flow inductively coupled plasma source with a total argon consumption of only 0.6 L min-1 was developed. The plasma was sustained in the SHIP torch (Static High Sensitivity ICP), which was designed for optical emission spectrometric detection. This presentation will deal with the fundamental properties of this novel plasma source. Excitation temperatures, rotational temperatures, ionization temperatures, electron temperatures and electron number densities were determined by use of methods based on optical emission. These parameters were investigated in a laterally resolved manner and at selected observation heights in the plasma. Excitation, rotational and ionization temperatures were found to be in the range of 5000 – 8000 K, 3100 – 4000 K, and 6250 – 7750 K, respectively. Electron temperatures were determined to be as high as 9000 K in the analytical channel. Electron number densities were obtained by means of the hydrogen-beta line method and found to be in the range of 5 – 8 x 1015 cm-3 at 1.1 kW radio frequency power. In addition, spatially resolved argon and analyte emission maps will be presented. Moreover, the introduction of wet aerosols into the discharge will be discussed. Previously developed low-flow ICP designs were limited to dried aerosol sample introduction. With a nebulizer tailored for low sample carrier gas flow rates (0.2 – 0.5 L min 1) and modifications to the plasma source design, stable plasma operation was achieved. Signal-to-background ratios and robustness were used to identify optimal operating conditions for trace element analysis. Current analytical figures of merit will be presented.

(107) **Chalcogenide Tetrahedral Clusters and Their Superlattices**

Pingyun Feng[1]; [1]University of California-Riverside

Chalcogenide tetrahedral clusters and their superlattices represent an interesting class of materials that combines uniform porosity with high electrical conductivity and tunable optical properties. They consist of single-sized tetrahedral clusters that act as molecular building blocks in the formation of well-ordered superlattices from zero to three dimensions. Tetrahedral clusters can be joined directly to produce purely inorganic frameworks or by multidentate organic ligands to form inorganic-organic hybrid frameworks. A number of main-group and transition metals have been incorporated into clusters to allow the modification of structural and physical properties. The structural analysis based on single crystals reveals detailed information that could help the structural elucidation of larger colloidal nanostructures. The synthesis, structures, and various properties such as porosity, photoluminescence, photocatalytic property, and fast ion conductivity will be discussed.

(108) **Electron-Electron and Electron-Hole Interactions in Small Metallic Crystallites: The Size-Dependence of the Lowest Optically Excited Electronic States**

Robert Whetten; [1]Georgia Tech

Large metallic crystals have intrinsic electronic properties calculable from the bulk band structure.[1] As the crystal becomes small, a regime is entered in which the electronic properties (bound excited-states and ionization energies) vary strongly with crystallite size and shape. In this regime, the low-energy excited states and ionization processes acquire a molecular character, reflecting the quantized motion of the electron and hole in a confined space. However, diffraction of conduction electrons by the periodic lattice potential remains essential to the crystallite's quantitative electronic structure. Here we consider systematically how the initial optical absorption bands vary with crystallite dimension, D. Semi-quantitatively, one expects the onset of resonant absorption at an energy hvF/L, where vF is the Fermi velocity, and the path-length L ~ πD relates to the crystallite's circumference. Thus, for crystallites of the good metals and alloys, onset bands should appear typically in the near-infrared (NIR) region, i.e. 0.4 to 2 eV for crystallites of circumference (diameter) range of 15 (5) to 3 nm (1 nm).[2] We deduce an elementary model for the lowest optically allowed transitions of small metal crystallites, embedded in a vacuum or dielectric medium. The quantum states are treated at the same level of approximation as used in the analysis of bulk crystalline electron-hole states and of quantum-well states of thin metallic crystals.[3] The effects include the kinetic energy, modeled within the effective-mass approximation, the electron-hole interaction, as modified by dielectric and metallic screening, and the phase-shift, reflecting the penetration into the surrounding dielectric. The results are free of adjustable parameters. Special attention is given to the case of closed electronic shells, where the absorption is dominated by the transitions |n=1,l=lF-1/2> to |1,lF+1/2>, where lF is the Fermi angular momentum. An approximate formula is given for the excitation energy. The fraction (f) of the integrated oscillator strength of this band, strongly diminishes (as D-2) with increasing size, due to metallic screening. But the absence of the Fermi-liquid damping allows it to be sharply defined and long-lived. These characteristics are distinguished from other optical absorption phenomena, such as plasmons and interband transitions (in metallic crystallites), as well as from the analogous theory of excitons in small semiconductor crystallites.[4] We critically examine evidence for such absorption-onset resonances in the NIR absorption and emission spectroscopy of single metal crystallites, and of crystallographically defined ensembles of metal crystallites. NIR resonant multiphoton spectroscopy of (-)charged metallic crystallites may sensitively detect and characterize these transitions. Extensions to nonlinear NIR-optical processes are also indicated. [1] N. W. Ashcroft, N. D. Mermin, Solid State Physics, (Harcourt Publishers, 1976), Chap. 17. [2] R. B. Wyrwas, et al. Eur. Phys. J. D43, 91-95 (2007). [3] C. M. Wei, M. Y. Chou, Phys. Rev. B66, 233408 (2002). [4] L. E. Brus, J. Phys. Chem. 90, 2555-2560 (1986).

(109) **Ligand-Protected Gold Clusters – Synthesis, Structures, and Stabilities**

Tatsuya Tsukuda[1,2]; [1]Catalysis Research Center, Hokkaido University; [2]CREST, Japan Science and Technology

Metal clusters smaller than 2 nm show novel properties absent in the corresponding bulk and their properties evolve dramatically with the numbers of the constituent atoms (cluster size). Because of these unique features, metal clusters have attracted much attention as a potential candidate for the building unit of functional nano-materials. The biggest challenge for the development of cluster-based materials is to synthesize a series of metal clusters with atomically-defined sizes. We have developed an experimental method to synthesize a family of ligand-protected gold clusters with well-defined compositions. Crucial step for our precision synthesis is to fractionate as-prepared, polydisperse gold clusters by size using polyacrylamide gel electrophoresis, size exclusion chromatography, or solvent extraction. Charge states and molecular formulas of the fractionated clusters were determined by electrospray-ionization mass spectrometry. In the present contribution, we discuss the structures and stabilities of the gold clusters protected by phosphines and thiolates.

(110) **Metal, Alloy and Core-Shell Nanoparticles and Assemblies for Catalytic and Sensing Applications**

Chuan-Jian Zhong; [1]State University of New York at Binghamton

A key to the exploitation of nanostructured materials for catalytic and sensing applications is the ability to synthesize and assemble the nanoscale building blocks with controllable size, shape, composition and spatial properties. We have been investigating molecularly engineered and mediated synthesis and assemblies of nanoparticles as a general bottom-up pathway towards this ability. This presentation discusses some of the recent findings of our investigations of the synthesis and assembly of metal, alloy and core@shell nanoparticles for catalytic and sensing applications. The size, shape, composition, surface, and spatial properties of the nanoparticles and assemblies are controlled by a combination of capping, mediating or templating molecules and processing strategies. The electronic, optical and magnetic properties of the nanoparticles and assemblies are tuned by manipulating the nanoparticle, the mediator, and the interparticle structures and interactions. The characterizations of these nanostructures and properties and the examples of applying these nanostructured materials for fuel cell catalysis and chemical or biological sensing will be described.

(111) **TDDFT Studies of Optical Properties of Silver and Gold Nanoparticles**

Christine Aikens; [1]Kansas State University

Noble metal nanoparticles are characterized by sharp peaks in their extinction spectra called surface plasmon resonances. Experimentally and theoretically, clusters such as Ag20 have also been shown to exhibit sharp peaks in their absorption spectra. Time-dependent density functional theory has been employed to calculate the absorption spectrum for neutral and charged tetrahedral Agn (n = 10, 20, 35, 56, 84, 120) clusters. Orbital and shell fillings are important considerations in order to obtain sharp absorption spectra. For silver tetrahedra, the peak location is found to extrapolate linearly with 1/L, where L is the length of a side of the tetrahedron, and with 1/N3, where N is the number of electrons in the cluster. This extrapolation agrees well with results from discrete dipole approximation calculations. Silver nanorods also exhibit similar size dependence. The wavelength of their absorption maxima extrapolates linearly with aspect ratio (e.g. length). The nanorod orbitals and length dependence agree with a simple particle-in-a-box model. Self-assembled arrays of silver tetrahedra and nanorods can potentially possess well-defined excitation energies. The TDDFT predicted red/blue shifts, oscillator strengths, and longitudinal/transverse characterizations in these arrays agree qualitatively with those for larger particles. Small (< 2 nm) gold nanoparticles display multiple peaks in their optical absorption spectra rather than the strong plasmon resonance peak of larger nanoparticles. This characteristic is likely due in part to the structure of these systems. Recent crystal structure determination of the Au102 and Au25 nanoparticles is currently enabling in-depth research into the properties and reactivity of these systems. In this presentation, the level of theory required to accurately compute the core structure and optical absorption spectrum of the Au25 nanoparticle will be discussed. Precise core

geometries are required in order to obtain good predictions for the splitting between the first two spectral peaks. The model potential used to compute the excitation spectrum is critical. Solvent effects play a relatively minor role.

(112) **Development of Hybrid Nanoporous Membranes by Assembling Mesostructured Silica in a Porous Alumina Membrane**

Akira Yamaguchi[1], Norio Teramae[1]; [1]Tohoku University

Surfactant-templated mesostructured silica has a potential use for a separation of molecules and a sensor device because of its uniform pore-diameter with molecular dimensions and high adsorption capacity. For a practical use of the mesostructured silica for membrane based separation and sensor, it has been strongly required to control of pore arrangement as well as morphology of mesoporous silica membrane, which allows mass transport across the membrane. Recently, we have been developed a method to fabricate a hybrid nanoporous membrane composed of the mesostructured silica in a porous anodic alumina membrane (Ya,aguchi et al., Nature Mater. 2004, 3, 337), and the hybrid nanoporous membranes have been applied for nanofluidic systems toward separation science, bio-reactor, and synthesis of metallic nanowire arrays. The hybrid mesoporous membrane can be fabricated as follows: an alumina membrane is set in an ordinary membrane filtration apparatus and an acidic precursor solution containing silica source and surfactants is introduced into the columnar alumina pores under moderate aspiration. The pore diameter of the mesostructured silica inside the alumina pores has been able to tuned ranging from 3 to 12 nm by choosing a template surfactant and the pore size distribution is narrow. In addition, the pore structure and arrangement can be regulated by controlling temperature and composition of the precursor solution. When the hybrid mesoporous membrane was mounted in a U-tube permeation cell, transport of molecules, of which molecular size was larger than pore diameter of the mesostcutured silica, was completely rejected. This result confirmed that the hybrid mesoporous membrane could be used for a membrane separation with a capability of nanometer-order size-exclusive separation. In addition, the hybrid mesoporous membrane could function for a chromatographic column in HPLC system to separate small molecules. These experimental results suggest that the present hybrid nanoporous membrane has a potential application in separation science.

(113) **Approaches to Post-Translational Modification Analysis using MALDI Tandem Time-of-Flight Mass Spectrometry**

Robert J Cotter; [1]Johns Hopkins University School of Medicine

Matrix-assisted laser desorption/ionization (MALDI) has enabled the structural analysis of large proteins and peptides, and is used for the identification and quantitation of proteins that compose the human proteome using MS analysis of tryptic fragments (mass fingerprinting) and MS/MS amino acid sequence analysis of specific peptides. MS/MS analysis also provides the opportunity to identify and locate post-translational modifications, and in this paper we illustrate the application of a tandem time-of-flight (TOF) mass spectrometer to the analysis of lysine acetylation, ubiquitylation and SUMOylation in histones. Quantitation of hyperacetylated isoforms of histone H4 is achieved by deutero-acetylation and subsequent cleavage by trypsin which then cuts only at arginine residues. Protein ubiquitylation is identified following N-terminal sulfonation of the branched tryptic peptide products by the loss of two sulfonation tags, while SUMOylated peptides are identified following successive digestions with trypsin and chymotrypsin. The evolution and development of a unique tandem instrument using a curved-field reflectron is described.

(114) **Sample Preparation: Clues to Understanding MALDI Mass Spectrometry**

Martha M. Vestling[1]; [1]University of Wisconsin

MALDI sample preparation methods will be divided into five categories: four solid, one liquid. The categories are: i) dried drop, thin film, small crystals methods ii) precipitation/electrospray deposition methods, iii) solvent-free methods, iv) surface (Tanaka) methods, and v) liquid methods. The common features of the first four categories will be described. In each example to be presented there is a substance that absorbs the laser light (the matrix). And in all cases the matrix to analyte ratio is quite large as the amount of analyte is quite small. It is commonly observed that unlike electrospray ionization, positive mode MALDI spectra are dominated by +1 ions. To choose the best method for a particular analyte, it is important to pick a matrix that absorbs the laser light and to select an ionization method for the analyte. Most comprehensive descriptions of the MALDI process, like that of Knochenmuss (1) deal with gas phase interactions. In the past too little attention has been paid to the charge state and ionic interactions in the solid state before the laser hits even though sample preparation is at the heart and soul of a successful MALDI experiment. (1) R. Knochenmuss, A quantitative model of ultraviolet matrix-assisted laser desorption/ionization including analyte ion generation, Analytical Chemistry 75: 2199-2207 (2003).

(115) **Substrate Influence on Peptide/Protein MALDI Ion Signals**

Gary Kinsel[1], Lijuan Peng[1]; [1]Southern IL University, Carbondale

This presentation will provide a comprehensive evaluation of the influence of the substrate on the peptide/ protein ion signals observed in a MALDI MS experiment. Previous research in our laboratory has shown that protein binding to the substrate in a MALDI experiment leads to significant loss in protein ion signal. In our recent work we have explored a number of methods to reduce this effect of protein binding by depositing the protein on surfaces with intrinsic protein non-fouling properties including PEG modified polymers, albumin coated surfaces and surfaces modified with non-fouling radio frequency plasma polymers. In addition, we have explored the influence of the phsical properties of the substrate coating material on the ionization efficiency of species deposited on top of the coating material. The influence of these various approaches on the limits of detection for a given intact protein, on the sequence coverage observed for a tryptic digest of a given protein and on the range of species observed in complex mixture analysis will be presented.

(116) **Hydrophobic Protein Mixtures Analyzed by MALDI-MS**

Rachel Ogorzalek Loo[1], Jonathan Erde[1], Joseph Loo[1]; [1]UCLA

MALDI-MS is a simple, rapid, and sensitive method for analyzing complex mixtures of proteins. A well-known shortcoming is that spectra obtained from complex mixtures; e.g., bacterial cells, do not reflect protein abundances faithfully, a limitation often attributed to "ion suppression." Recognizing that abundant, "suppressed" proteins are often readily analyzed by MALDI-MS when presented as single components, yet vanish in mixtures, we optimized sample/matrix preparation to favor their detection from complex mixtures. While MALDI-MS of Escherichia coli cells desorbed from standard sinapinic acid matrix displayed 94 (M+H)+ ions, 119 were observed from our formic acid-based matrix with no more than 10 common to both. Formic acid matrix revealed many lipoproteins and an 8282 m/z ion proposed to be the abundant, water-insoluble ATPase proteolipid. Various formic acid-based cocktails were examined, seeking ones yielding the slowest rate of serine/threonine formylation, covalent modifications arising from exposure to high concentrations of formic acid. We have also

developed methods to mass analyze intact proteins embedded in dried IEF gels. Replacing the SDS-PAGE dimension of classical 2D-analysis by MALDI-MS links intact mass measurements to discrete 2D gel spots. Although hydrophobic proteins are ill-suited to 2D gel electrophoresis, the fault is attributed to poor transfer across the isoelectric focusing (IEF) dimension to the SDS-PAGE 2nd dimension. Thus, membrane proteins should be separable by IEF, if detergents are selected carefully. To investigate membrane protein separations, we separated an E. coli membrane protein fraction by performing isoelectric focusing under denaturing conditions, employing CHAPS detergent, urea, and thiourea. The resulting IEF gels were prepared and subsequently analyzed by MALDI-MS. The intact mass information obtained applies to every previous and subsequent 2D gel, linking to other isoform-specific measurements enabled by 2D-PAGE (e.g., antibody blots, carbohydrate composition, synthesis/degradation rates, and abundance).

(117) **Reactive-Electrospray-Assisted Laser Desorption Ionization (Reactive-ELDI) for Characterization of Peptides and Proteins**

Ivory Peng[1], Rachel Loo[1], Jentaie Shiea[2], Joseph Loo[1]; [1]University of California, Los Angeles; [2]National Sun Yat-Sen University

Electrospray-assisted laser desorption ionization (ELDI) is a soft ionization method for mass spectrometry (MS) and combines features of both electrospray ionization (ESI) and matrix-assisted laser desorption ionization (MALDI) to generate ESI-like multiply charged molecules. The ELDI process is based on the merging of ESI-generated charged droplets and sample particles desorbed by UV laser irradiation from dried or wet samples deposited on a sample plate. ELDI is amenable for MS-based protein identification using top-down and bottom-up techniques, and is capable of tandem MS up to MS4 for top-down characterization of large proteins up to 29 kDa carbonic anhydrase. Multiply charged proteins generated by the ELDI mechanism can be shifted to higher charge state by increasing the organic content in the ESI solvent to denature the protein molecules, or by the addition of m-nitrobenzyl alcohol (m-NBA) into the ESI solvent. Ribonuclease A (RNase A)-CTP noncovalent complex can be generated in the gas phase during the ELDI process, either by ESI of RNase A in its native condition and laser desorbing CTP, or by ESI of CTP and laser desorbing RNase A. Reactive-ELDI allows chemical reactions to occur during the ELDI process. Preliminary reactive-ELDI data for on-line disulfide bond reduction using dithiothreitol (DTT) for oxidized glutathione and insulin were shown to be effective. These data provide evidence that the laser desorbed particles effectively merge with the ESI-generated charge droplets to effect chemical reactions prior to on-line MS detection. This should allow other chemical and enzymatic reactions to be exploited for on-line tools for protein characterization, as well as for tissue screening and imaging. Also, these reactive-ELDI disulfide reduction experiments provide a possibility for direct top-down protein identification for proteomic study, without the necessity of laborious, time-consuming sample preparation such as in-solution reduction and alkylation.

(118) **Raman Microscopy, Pigments, and Interfaces with Art and Archaeology**

Robin Clark[1]; [1]University College London

Raman spectroscopy is a light scattering technique primarily used in the characterisation of vibrational modes of molecules and therefore in assessing the structure and composition of materials. When a light source such as a laser is coupled to a microscope, the resulting technique – Raman microscopy (RM) – is now recognised to provide a very effective means for the identification of micrometre-sized grains of any material such as a pigment. The technique has the great attributes of specificity, sensitivity, reproducibility and high spectral (c. 1 cm-1) and spatial (c. 1 micrometre) resolution, along with those of being non-destructive and applicable *in situ*. It is thus appropriate to artwork and artefacts from which sampling is either undesirable or prohibited. The lecture will be illuminated initially with studies leading to the rapid and effective identification of pigments on manuscripts, paintings, papyri, icons and maps, leading to the establishment of artists' palettes at different periods and in different localities, together with comments on related scientific studies at the Arts/Science interface bearing upon restoration, conservation and dating of artwork and with the detection of forgeries. Reference will be made to the Lindisfarne Gospels (715 AD), Gutenberg Bibles (c.1455 AD), Vermeer paintings (c. 1670 AD), postage stamps (1847 AD), and papyri, etc. The lecture will then develop onto applications of the technique to the identification of pigments on archaeological artefacts such as Chinese sherds (4200 BC), Iraqi stuccoes (9th century AD), Puebloan ceramics (1100-1300 AD), etc. Attention will be given to date-marker pigments such as anatase (TiO2), Prussian blue and phthalocyananine blue which are of importance in both art and archaeology. Rarely has an optical technique made such a rapid impact on seemingly unrelated disciplines.

(119) **Tracing the Past: Application of LA-ICP-MS for the Assessment of Potential Exposure to Arsenic in Ancient Chinchorro Mummies**

Dula Amarasiriwardena[1], Sam Byrne[1], Basel Bandak[1], Jennifer Kane[1], Joseph Jones[1], Jorge Yanez[2], Bernardo Arriaza[3,4], Lorena Cornejo[3,4]; [1]Hampshire College, Amherst, USA; [2]Universidad de Concepción, Chile; [3]Universidad de Tarapacá, Arica, Chile; [4]Instituto de Alta Investigación, Chile

The natural water in the Atacama region in Northern Chile is laden with arsenic [1]. The world's oldest mummies, the Chinchorros, [2] were found in these arsenic endemic areas. Hair tissue is a unique bio-monitor that can offer an archival record of past exposure to arsenic and other toxic elements [3]. In this project we investigated the potential exposure of the Chinchorros to arsenic through laser ablation inductively coupled plasma mass spectrometry (LA-ICP-MS) analysis, using a single strand of mummy hair. Hair samples were cleaned of external contamination and examined microscopically to inspect hair tissue for any debris. Hair strands were mounted on a mounting tape before laser ablation. Arsenic and other elements were determined by LA-ICP-MS. Both linear and spot ablations were evaluated and it was determined that linear scans were more suitable for quantitative analysis of arsenic. The 13C signal was used as an internal standard to compensate for any ablation variations. A set of contemporary human hair strands with known arsenic concentrations from the same region [3] where the Chinchorros had lived was used for calibration of LA-ICP-MS. Linear calibration functions obtained from these standards were used for quantitative determination of mummy hair from four burial sites. Highly elevated As concentrations (> 20.5 µg/g) were found in mummies from the Camarones valley where the As in the potable water is the highest in the region (1000µg/L). The statistical analysis of As concentration in mummy hair from different sites demonstrated significant differences in arsenic concentrations at $p = 0.04$. Long-term distribution of trace metals in a full single strand of mummy hair reflecting the trace metal exposure during the last few days of an individual's life will be presented. This method requires a small portion of a single strand of hair and the sample throughput is very high, which makes this approach very attractive for archeometry. [1]. J. Yáñez, V. Fierro, H.Mansilla, L. Figueroa, L. Cornejo, R.M. Barnes., J. Environ. Monit., 7 1335-134, (2005). [2]. B. Arriaza and V.G. Standen, Death, Mummies, Ancestral Rites: The Chinchorro Culture,

Universidad de Tarapacá, Chile, (2002). [3]. S. Steely, D. Amarasiriwardena, J. Jones, J.Yañez, Microchemical J., 81, 201-208, (2007).

(120) **Micro-Structural Characterization of Archaeological Materials: The Importance of Understanding Scale of Heterogeneity for Analyses of Provenance, Performance and Post-Depositional Alteration**

John Dudgeon[1]; [1]Idaho State University/CAMAS

Due to its high sensitivity and large suite of elements analyzed, as well as its success in other earth sciences, ICP-MS has emerged as a useful tool for archaeological research. In particular, laser ablation (LA) sample introduction methods have set new benchmarks for minimally-destructive testing of a wide range of elements and isotopes with explanatory significance for archaeologists. While this enthusiasm within the archaeology community is largely warranted, several important theoretical and methodological caveats need to be considered when applying LA-ICP-MS analysis to geological and biological artifacts. These include the scale of variation and the effects of post-depositional alteration on archaeological materials. Understanding and acknowledging the continuum of chemical variation and its causes increases the specificity of LA-ICP-MS for archaeology and tempers typologically-driven interpretations of archaeological phenomenon, in favor of more complex—but more appropriate—distributional explanations.

(121) **Geochemical Evidence of Ancient Maya Marketplace Activities**

Richard Terry[1], Daniel Bair[1]; [1]Brigham Young University

Ancient markets are difficult to identify as most utilitarian items and consumables were perishable. Our objective was to use geochemical analyses of extractable phosphorus and metallic residues in soils to distinguish the unique geochemical patterns of market plazas from other types of plazas within the Maya area of Central America. Geochemical techniques in conjunction with locational and archaeological data have provided lines of evidence for Marketplace activities.

(122) **Investigations of Metals in Drainage System Deposit and Lead Pipe in Castel Viscardo**

Mary Kate Donais, Cindy Lebel, Katherine Thibodeau; [1]Saint Anselm College

A drainage system and lead pipes were recently discovered at the Castel Viscardo excavation site near Orvieto, Italy. Samples of deposits from inside the drainage system as well as a small sample of the lead pipe itself were collected in the hope of determining whether the two were connected at one point in time. Acid digestion followed by flame atomic absorption spectroscopy, inductively coupled plasma mass spectroscopy, inductively coupled plasma atomic emission spectroscopy, and glow discharge mass spectrometry were used to determine the composition of both samples. It was found that aluminum, silicon, calcium, iron, carbon, oxygen, and lead made up most of the drainage system deposit sample. The lead pipe sample included mostly lead with some tin, antimony, and copper. Agreement among method results was observed. Based on preliminary lead isotope ratio values for both samples, no conclusion could be made if the lead in the two samples is from the same source.

(123) **Downhole Fluid Analysis – The Key to Unraveling Reservoir Complexities**

Oliver Mullins; [1]Schlumberger-Doll Research

In recent years, there has been a growing realization that improper treatment of reservoir complexities such as compartmentalization and fluid compositional variation commonly lead to gross inefficiencies in facilities design, production strategies and predicted production; new methods are mandated. Previous working assumptions of homogeneous distributions of hydrocarbons in giant reservoir 'tanks' are now understood to be uncommon; one must prove not assume the value of the reservoir. The central questions arise: how can we identify fluid compositional variations in the reservoir and how can we use these measured variations to understand reservoir architecture (all within an acceptable cost structure)? Downhole Fluid Analysis (DFA) is the key. DFA is a new invention with rapidly expanding applications; DFA is used in virtually all market conditions today. By performing DFA measurements on fluid properties *in-situ* in oil wells, one can match the complexity of the hydrocarbon column to the complexity of the fluid analysis program. The operating company pays only for what they need. The methodology is now developed to obtain a 'continuous downhole fluid log.' In petrophysics, continuous logs are the norm, but the oil column is not similarly respected, just a few station measurements typically prevail - ironic in that we are in the oil business, not the rock quarry business. By understanding the variation of fluid properties, we can often identify compartments and other reservoir complexities. For example, density inversions, higher density fluids higher in the column, strongly imply sealing barriers. In addition, connectivity can be strongly implied under certain circumstances. For example, we have recently discovered an asphaltene gradient in a large fluid column. Any newly penetrated sand with a contained fluid on this gradient has a good chance of being hydraulically connected. As will be described, the optimal DFA process involves partnership of the service company with the operating company.

(124) **Petroleum Compositional Information Revealed by High Resolution FT-ICR Mass Spectrometry**

Amy M. McKenna[1], Brandie M. Ehrmann[1], Priyanka Juyal[2], Ryan P. Rodgers[1,2], Jeremiah M. Purcell[2], Tanner M. Schaub[2], Alan G. Marshall[1,2]; [1]Department of Chemistry & Biochemistry, FSU; [2]National High Magnetic Field Laboratory

The depletion of light, sweet crude oils has shifted current and future oil production into medium and heavy petroleum materials. Although abundant, heavy crude oils contain a higher fraction of heteroatoms (nitrogen, oxygen and sulfur) and higher boiling species that must be addressed in the refining processes. Therefore, detailed compositional information of the crude and associated distillate fractions is important in the optimization/design of current/future upgrading procedures. Recent advances in mass spectrometry and ionization methods have resulted in significant gains in the compositional knowledge of heavy crudes.[1,2] The inherent high resolution and high mass accuracy of FT-ICR mass spectrometry make it ideally suited for complex mixture analysis. Simply, high resolution enables multiple isobaric species determination for species that differ in mass by 3 milliDalton or less, while the high mass accuracy (sub ppm) combined with Kendrick mass sorting allows for unambiguous molecular formula assignment.[3] Three soft ionization methods, Atmospheric Pressure PhotoIonization (APPI), ElectroSpray Ionization (ESI) and Atmospheric Solids Analysis Probe (ASAP) serve to highlight acidic, basic and nonpolar species found in heavy crude oils. Limited structural information is provided through detailed compositional analysis in conjunction with known class based ionization trends. Here we describe the compositional information

available through high resolution FT-ICR mass spectrometry and numerous current and future applications.

(125) **Advances in Petroleum Analysis via Comprehensive Two-Dimensional Gas Chromatography**

Christopher Reddy[1], G. Todd Ventura[1], Robert Nelson[1], Soraya Betancourt[2], Gordon Lambertus[2], Oliver Mullins[2], Andrew Pomerantz[2], Bhavani Raghuraman[2]; [1]Woods Hole Oceanographic Institution; [2]Schlumberger-Doll Research

Comprehensive two-dimensional gas chromatography (GCxGC) is a promising technology for analyzing petroleum hydrocarbons. GCxGC instruments produce high-resolution chromatographic separations because each petroleum compound is subjected to two different stationary phase selectivities. Most often, the first dimension separation uses a non-polar phase to separate petroleum compounds mainly by volatility differences, and the second dimension uses a more polar phase to separate first dimension coeluters by polarity differences. The resulting two-dimensional chromatogram can have thousands of resolved peaks sorted according to their volatility and polarity properties. A GCxGC chromatogram has compound peaks grouped by carbon number along the x-axis and by chemical class along the y-axis. For petroleum, this produces separated chemical classes such as alkanes, cycloalkanes, and one-, two-, and multi-ring aromatics, with additional groupings showing homologous series within each class. Because of the information afforded by this technique, GCxGC is ideally suited for studies on petroleum exploration, geochemistry, and pollution especially when coupled to either a flame ionization detector or time-of-flight mass spectrometer. Applications for this technology regarding petroleum exploration will be presented via several cases studies. They will include efforts focusing on drilling mud contamination, biodegradation, reservoir connectivity, abiotic weathering, and more highly refined inventories of hydrocarbons present in select oils. In summary, GCxGC holds great promise for revolutionizing the analysis of petroleum hydrocarbons.

(126) **Application of FTIR Spectroscopic Imaging to Asphaltenes**

Sergei Kazarian, Feng Tay; [1]Imperial College London

This study investigated the feasibility of using Attenuated Total Reflectance Fourier Transform Infrared (ATR-FTIR) spectroscopic imaging to aid in the characterisation of asphaltenes. Pre-heat train fouling is a major economic problem in the crude oil business. Asphaltenes has been closely linked and related to levels of fouling in heat exchangers. The magnitude and significance of crude oil fouling have led to a number of studies but the fundamentals of the complex fouling process are not fully understood. The recent emergence of FTIR spectroscopic imaging has allowed the *in situ* chemical examination of heterogeneous materials. This paper will introduce novel applications of combining macro-ATR and micro-ATR modes of such an advanced imaging technique to characterize asphaltenes. Using different ATR accessories for the macro (diamond) and micro (Germanium coupled to an infrared microscope) modes, FTIR images, of size 700 µm x 500 µm and 65 µm x 65 µm respectively, yield important information about the spatial distribution of different components in asphaltenes. The sensitivity of the 2 modes of measurement with different spatial resolutions allows spatial and chemical information to be obtained and analyzed at different domains of interest. An *in situ* approach to study crude oil heating was developed for the analysis of the chemical changes occurring in crude oil during heating. Characteristic infrared spectral bands of asphaltene were observed to increase in absorbance during the experiment which could be interpreted as asphaltene precipitation. Compositional changes in the crude oil were followed *in situ* during heating to 200 ºC for three hours. This work has demonstrated the potential of ATR-FTIR spectroscopic imaging to understand how molecular and chemical structures of the deposits relate to components of the crude oil. This application of FTIR spectroscopic imaging to characterize asphaltene deposits will provide new insight and understanding of the fouling process.

(127) **Determination of H2S in Natural Gas and Other Hydrocarbons by Differential Mobility Spectroscopy**

Eric Kirleis[1], Quan Shi[1]; [1]Sionex Corporation

Abstract: Sionex Corporation has developed a micro fabricated chip-type differential ion mobility sensor (DMS) which is used as the engine for a number of sensitive analytical devices. This device can measure chemical warfare agents, explosive materials, organic sulfur-containing compounds, and other toxic industrial compounds. Here we coupled a fast gas chromatograph with DMS for a field portable instrument to measure H2S in natural gas and hydrocarbons. High selectivity of DMS for H2S eliminates the interference of hydrocarbons to H2S. Based on H2S unique differential ion mobility coefficient in high and low electric fields, DMS is able to exactly identify H2S in the presence of other compounds. We have demonstrated that we are able to measure 0.1 to 10 ppmv of H2S in natural gas based on simple fixed volume injection. The total analysis time can be as fast as 60 seconds. With usage of pre-concentrator, we also demonstrated that we can detect low ppbv level (~ 5 ppbv) of H2S in ethylene and propylene.

(128) **Oil Spill Detection using a Plurality of Spectral Bands**

Wei-Chuan Shih[1], A. Ballard Andrews[1]; [1]Schlumberger-Doll Research

The objective of this study is to achieve automated detection of hydrocarbon seeps using passive optical methods, i.e., without an artificial light source, against a background substance. This detection technology can be applied in hydrocarbon exploration, production, and refinery. The contrast in different optical spectral bands stems from different physical principles. In the visible and near-infrared bands, the detected light originates mainly from specular and diffuse reflectance of the direct and diffuse solar radiation. Thus the hydrocarbon optical properties play an important role in creating the contrast, as well as the observation angle and sky conditions, such as sun or clouds. In the thermal-infrared band the detected light originates from thermal emission of the objects in the scene within the depth of focus. Thus, the difference in specific heat and intrinsic emissivity between hydrocarbons and the background substance governs the contrast during day and night time, respectively. In several studies of crude oil spillage, it has been observed that the apparent day time contrast of native and crude oil covered sea surfaces depends on the thickness of the oil film. On sunny days, differential heating causes oil to be raised to a higher temperature than the surrounding water because of its higher absorption of solar radiation and lower specific heat, giving rise to the commonly observed contrast of native and crude oil covered sea surfaces in day time remote sensing of oil spills. It has also been observed that a reversal occurs when the oil film is thinner than around 50-150 microns. A plausible explanation to this is that since the oil film is thin, it is essentially in thermal equilibrium with the water underneath and thus the oil appears cooler because of its intrinsically lower bulk emissivity. In this paper, we investigate the thickness dependent thermal contrast using thin film interference theory, and show that the optical interference effect plays an important role in the oil-water contrast. In addition, we demonstrate that thickness variation alone can indeed introduce the historically observed contrast reversals.

(129) **Low Frequency Multi-Channel Raman Spectroscopy with an Iodine Vapor Filter**

Hajime Okajima[1], Hiro-o Hamaguchi[1]; [1]School of Science, The University of Tokyo

Low frequency spectroscopies, which measures the wavenumber region below 200 cm-1, enables us to investigate intermolecular motions that are useful for studying solid and liquid structures. Many low frequency spectroscopies, both frequency-domain and time-domain, have been developed so far. They all employ the single-channel detection to obtain the signal point by point. They require a long measurement time, typically more than an hour, to scan a spectrum. Moreover, each portion of the spectrum is not simultaneously measured. Therefore, these single-channel low frequency spectroscopies are not suitable for real-time dynamical studies of intermolecular motions, such as changes of lattice vibrations during a melting process. In this study, we have newly developed a multi-channel low frequency Raman spectrometer, using iodine vapor as a narrow "notch" filter. Iodine vapor has many absorption lines in the visible region. One of these absorption lines exactly coincides with a longitudinal mode of the 514.5 nm line of the Ar ion laser. Therefore, when we use this longitudinal mode as a Raman excitation source, Rayleigh scattering can be selectively eliminated by the iodine absorption. This technique was used in 1970s with scanning monochromators. We combine this iodine vapor filter with a polychromator to construct a multi-channel low frequency Raman spectrometer. In our experiment, we put iodine in a 10 cm length of cylindrical cell and heat it to 400 K. The transmittance of Lasing light at this temperature is less than 10-5, while the averaged transmittance of continuum light is about 10-1. The Rayleigh reduction efficiency of our iodine vapor filter is thus over 104. The Raman signal, which is transmitted through the filter, is detected by a 60 cm single polycromator. With this multi-channel setup, low frequency vibrational bands of solids and liquids are measured with high S/N ratios. We were able to measure the low frequency band of 9.7cm-1 from l-cystine. The accumulation time is less than 30 seconds, which is shorter than 1/100 of the accumulation time of the single-channel measurement.

(130) **Development of Validated Raman Spectral Libraries using NIST Relative Intensity Correction Standards**

Steven Choquette[1], Aaron Urbas[1], Bruce Benner[1], Michele Schantz[1]; [1]NIST

Raman spectroscopy is a reagent-less analytical identification technique that is enjoying rapid growth because it can provide chemical sample identification in real-time and with a minimum of sample preparation. Because a useable Raman spectrum can be acquired through many types of packaging, a number of forensic laboratories are using the technique as a first-line analytical screening method for unknown compounds. Raman spectrometers are now being used at crime scenes, chemical spills, and other sites where remote or through-the-container analysis of an unknown may be important in protecting the safety of the investigative response team. Although the Raman method is not definitive, it can provide a rapid assessment of sample identity or sample class—often discerning the bad stuff from benign substances Field deployable Raman instruments typically employ vendor-supplied Raman libraries. Comparing results between systems or within the same instrument under field conditions requires considerable expertise and experience on the part of the user and may not be possible if the spectrometer is routinely calibrated. Our goal is to provide both the physical standards and the validated Raman spectral libraries necessary to impart confidence in these Raman measurements, to provide measurement traceablity to national standards, and to ensure evidentiary acceptance of these measurements. This talk will discuss the generation of instrument-corrected Raman libraries, namely for Toxic Industrial Chemicals (TICs). The first step involves the qualification of the materials and the spectrometers used to generate the reference library. This process is modeled after the program to accept reference data into the OPCW (Organization for the Prevention of Chemical Warfare) database. This database and methods for accepting data were formed by an international treaty with nearly universal UN member state buy-in. The second step is the promulgation of this reference data and a new NIST/DHS supported website model will be discussed.

(131) **Characterization of Variability in Raman Measurements from Tissues**

Anita Mahadevan-Jansen[1], Elizabeth Kanter[1], Elizabeth Vargis[1], Nicole Gasparino[1], Jennifer Whisenant[1], Mattheus Grimbergen[2], Nicholas Stone[3]; [1]Vanderbilt University, Nashville, TN; [2]University of Utrecht, The Netherlands; [3]Gloucestershire Hospital, United Kingdom

Recently, the application of Raman spectroscopy for the detection of disease *in vivo* has seen tremendous progress. Numerous researchers have begun to develop RS as a diagnostic tool particularly in the skin, cervix and GI. However, inhenerent to these measurements is the vaiability that exists in Raman spectra acquired from different systems for the same tissue. In order for RS to be an effective diagnostic tool, the origins and relative contributions of such spectral variation must be understood. Sources of variation include effect of instrumentation such as excitation wavelength and collection geometry, effect of normal tissue state such as hormones, socio-econimic factors amongst others. This paper will address some of these factors that contribute to the measured RS of tissues *in vivo* and present results on the application of RS for disease detection while incorporating such variability.

(132) ***In-vivo* confocal Raman Spectroscopy: Studying the Effectiveness of Penetration Enhancers to Deliver Retinol through the Skin**

Paul Pudney[1], Mickael Mélot[1], Guoping Lian[1], Ann-Marie Williamson[1], Peter Caspers[2], Andre Van Der Pol[2], Gerwin Puppels[2]; [1]Unilever Research; [2]River Diagnostics

Raman spectroscopy is uniquely placed to be able to measure biological processes *in-vivo*. Explicitly its light in, light out non-invasive nature, its inherent chemical sensitivity (without labels) and its ability to be able to do confocal depth profiles add up to unique combination of properties. It has been shown previously that the inherent skin components can be measured and characterised non invasively by Raman spectroscopy1. Here we concentrate on the delivery of the skin health active retinol which is known to increase collagen synthesis (an 'anti -wrinkle' agent). Delivery of active molecules to skin, can be extremely difficult to execute, and problematic to confirm and measure. Here we show that it can successfully be measured using Raman spectroscopy. Initially the method was tested with a highly effective model delivery system identified from *ex-vivo* experiments i.e. retinol in PG/ethanol. The retinol was successfully measured penetrating into the skin of the volar forearm, initially into the stratum corneum and then into the viable epidermis. This was monitored over a 12 hours period after which no retinol could be observed. The penetration of the retinol was also observed to be highly correlated with the depth of penetration of the PG. This was followed by investigating delivery from a non skin penetrating oil commonly used in skin creams2, myritol, with and without the use of penetration enhancers. The two penetration enhancers, believed to act by different mechanisms were chosen, a lipid 'fluidiser' Oleic acid and a lipid 'extractor' Triton-x-100. The Raman measurements showed different rates of penetration of retinol from these systems. These measurements have also recently been made fully quantitative.

These results will also be compared to a model on skin penetration. The SC is modelled a heterogeneous media using the "bricks and mortar" model, with the barrier properties of the lipid and corneocytes predicted directly from the fundamental physical and chemical properties3 1) PJ Caspers, GW Lucassen, EA Carter,HA Bruining, and GJ Puppels.. J. Invest. Dermatol. 116 (3), 434-442 (2001) 2) PDA Pudney, ME Melot, PJ Caspers,. A Van Der Pol , GJ Puppels Applied Spectroscopy 61, 804-811 (2007) 3) Guoping Lian, Lonjian Chen, Paul D.A.Pudney, Mickaël Mélot, Lujia Han. Journal of Pharmaceutical Sciences submitted

(133) **Image Size Distortions: The Influence of Out of Focus Light on Raman Mapping**

Neil Everall; [1]Intertek MSG

In this presentation we discuss the influence of out of focus laser light on the fidelity of Raman mapping. While most of the Raman signal is generated from a tight laser focus of the order of a few cubic micrometres, an extended illumination volume exists which can generate significant contributions from material positioned far from the laser focus. In thick, transparent samples, this results in many strange artefacts which (a) complicate the interpretation of micro-Raman data obtained either near the surface of a sample, or at the edge of cross sections, and (b) degrade the surface specificity [1]. In addition, it can badly distort the apparent size and shape of particles, according to their distance from the laser focus. This presentation will highlight these effects, and show how they can be modelled quantitatively. Note, these effects are not those which are well known to arise from spherical aberration when focusing uncorrected objectives below a sample surface [2]; they are an inevitable consequence of Raman microscopy, irrespective of the degree of aberrations which are present. [1] N Everall, Appl. Spectrosc., in press (June 2008) [2] N Everall, J Lapham, F Adar, A Whitley, E Lee and S Mamedov, Appl. Spectrosc. 61, 251-259 (2007)

(134) **Picosecond Raman Spectroscopy for Depth Analysis of Diffusely Scattering Samples: Temporal and Spatial Resolution**

Freek Ariese[1], Heleen Meuzelaar[1], Joost B. Buijs[1], Cees Gooijer[1]; [1]Laser Centre Vrije Universiteit Amsterdam

A depth profiling approach is demonstrated for various layers of non-transparent (diffusely scattering) white polymers. The technique is based on the temporal discrimination between Raman photons emitted from the surface and Raman photons originating from a deeper layer. Excitation is with a 3-ps Ti-sapphire system (400 nm; 76 MHz repetition rate). Time-resolved detection is carried out with an intensified CCD camera that can be gated with a 250-ps gate width. The polymer test samples were machined in blocks of 1-mm and 2-mm thickness and included Arnite (polyethylene terephthalate), Delrin (polyoxymethylene), Polythene and Teflon (polytetrafluoroethylene). These blocks were pressed together in different configurations in order to study the time difference in such media corresponding with several mm of extra net migration distance. We also studied to what extent spatial contrast can be observed between two different second layers. With this technique, molecular spectroscopic information can be obtained through a diffusely scattering surface layer of a few mm thickness. The results obtained with this relatively straightforward setup will be compared with measurements on similar samples using Kerr-gated detection or spatially offset Raman spectroscopy.

(135) **A Rugged High-Performance FTIR System in a Handheld Package**

Christopher D. Brown[1]; [1]Ahura Scientific

In this talk we discuss a handheld FT mid-intrared (FTIR) spectrometer capable of operating at better than 4 wavenumber resolution with a novel diamond ATR sampling interface. The device was specifically designed for use in very challenging field environments by non-experts, and through a number of examples we highlight the performance attributes of the system in a variety of applications, from material identification to quantitative analysis.

(136) **Screeing Consumer Products for Toxic Elements with a Portable XRF Analyzer**

Kenneth Stehr[1]; [1]Thermo Fisher Scientific, NITON Analyzers

Recent commercial developments have brought into the public view the need for a rapid method for testing consumer products for toxic elements. Adaptation of accepted hand-portable X-ray fluorecence (XRF) devices to the screening of finished products and the raw materials from which they are made, provides manufacturers and regulators a method to quickly verify product compliance to established and forth coming consumer product safety standards. A brief overview of hand-portable XRF instrumentation will be presented along with actual use of the instrumentation for the testing of electonic components for RoHS compliance and toys for toxic element composition. Unique capabilities utilizing imaging of the analysis area and variable analysis areas will also be discussed.

(137) **Bringing the Instrument to the Sample: Use of a Miniature Hand Held FTIR Spectrometer for *in-situ* Sample Measurement**

John Seelenbinder[1]; [1]A2 Technologies

Infrared spectroscopy is an excellent technique for chemical characterization of composites and surfaces. By nature, the measurement is non-destructive; however, samples are often too large to bring to a standard laboratory FTIR. The development of truly hand held mid-infrared spectrometers has brought infrared to areas where it was previously unusable. The analysis of composites and surfaces for damage and degradation is now viable on real parts without the need to remove samples or destroy the parts to fit onto a laboratory instrument. In the last few years, FTIR spectrometers have evolved from large, bench based instruments to portable equipment which can be both held and operated with one hand. This has allowed for the measurement of large surfaces through both ATR and reflection sampling technology in any orientation without samples preparation. This paper will focus on the development of portable and handheld FTIR spectrometers and their use in the analysis large surfaces; both identification and quantization of coatings will be discussed along with monitoring oxidation of composite surfaces. Examples of degradation to composite resins as well as determination of surface coatings and coating thickness will be covered. Real world examples of the use of portable and handheld FTIR instrumentation will be discussed.

(138) **Enabling Technologies for Handheld Optical Spectroscopy**

Jouko Malinen[1], Ralf Marbach[1], Mauri Aikio[1], Heimo Keränen[1], Heikki Saari[1], Antti Lamminpää[1]; [1]VTT Technical Research Centre of Finland

Recent developments in electrical, optical, mechanical and signal processing technologies have changed our everyday life, thanks to mobile communication, hand-held media players and similar devices. These enabling techniques can equally well be exploited for developing hand-held optical measurements, e.g., composition analyzers or surface inspection device. Challenges remain in the efficient and reliable use of various optical, electrical and mechanical design tools that have the potential to optimize the design in minimum time and avoid costly prototype iterations. Another challenge in exploiting these techniques for fancy hand-held optical instrument may be business related: current businesses tend to be oriented more towards laboratory or process

measurements rather than hand-held applications. This presentation reviews recent experiences of applying multiple enabling techniques in hand-held applications based on activities carried out at VTT Technical Research Centre of Finland. The optical sensor element is the core component for these measurement devices and recent results with MEMS mirrors, Fabry-Perot filters, LED arrays and imaging detector techniques are discussed. Integration of optics into 3D mechanical designs using metal mirror and plastic techniques is one important area. Possibilities of multilayer ceramic substrates using LTCC (Low Temperature Co-Fired Ceramics) techniques are illustrated using recent design examples. Finally, practical examples of hand-held designs are briefly introduced, including a "GrainGun" grain analyser, an oil film measurement instrument for metal sheets, reader modules for test stripes, as well as optical accessories for mobile phones.

(139) **Compact Liquid Crystal Waveguide Based Fourier Transform Spectrometer for *in-situ* and Remote Gas and Chemical Sensing**

Scott Davis[1], Scott Rommel[1], George Farca[1], Alan Martin[1], Ben Luey[1], Michael Anderson[1], Tien-Hsin Chao[2], Thomas Lu[2]; [1]Vescent Photonics Inc.; [2]Jet Propulsion Laboratory

Vescent Photonics Inc. and Jet Propulsion Lab are jointly developing an innovative ultra-compact (volume < 10 cm^3), ultra-low power (<10^{-3} Watt-hours per measurement and zero power consumption when not measuring), completely non-mechanical electro-optic Fourier transform spectrometers (EO-FTS) that will be suitable for a variety of remote-platform, *in-situ* measurements. These devices are made possible by a novel electro-evanescent waveguide architecture, enabling "chip-scale" EO-FTS sensors. The potential performance of these EO-FTS sensors include: i) a spectral range throughout 0.4-5 μm (25000 – 2000 cm^{-1}), ii) high-resolution ($\Delta\lambda \leq$ 0.1 nm), iii) high-speed (< 1 ms) measurements, and iv) rugged integrated optical construction. This performance potential enables the detection and quantification of a large number of different atmospheric gases simultaneously in the same air mass and the rugged construction will enable deployment on previously inaccessible platforms. The sensor construction is also amenable for analyzing aqueous samples on remote floating or submerged platforms. To date a proof-of-principle prototype EO-FTS sensor has been demonstrated in the near-IR (range of 1450-1700 nm) with a 5 nm resolution. This performance is in good agreement with theoretical models, which are being used to design and build the next generation of EO-FTS devices.

(140) **NIR Spectrometers in the Field: Design Considerations for Practical Applications**

Mark Gunning[1], Graham Poulter[1], Forrest Imhoff[2], Dave Coombs[1]; [1]Specac Ltd; [2]Specac Inc

This paper draws on practical experience in respect to the application of NIR spectroscopy in the field. Consideration is given to spectroscopic measurement applications which have moved from a laboratory to a field environment, and how instruments can be designed to meet these needs. Factors are discussed which relate to optical system performance criteria for taking a measurement process out of the laboratory, as well as design considerations for ensuring the most appropriate sample interface for the application in the given environment. Further considerations relate to the instrument ergonomics and functionality, the instrument control interface, and data processing and results feedback.

(141) **Shift Happens: Developments in Raman Sampling**

Ian R. Lewis[1]; [1]Kaiser Optical Systems

Approximately 80 years ago the discovery of the Raman Effect was published by Professor C.V. Raman and his student. Despite this length of time, it is only recently that Raman spectroscopy could be considered a main stream analytical tool. Over the last twenty years instrumentation for Raman Spectroscopy has dramatically changed and this has allowed new problems to be probed using Raman spectroscopy both inside and outside the laboratory. In this presentation a discussion of the capabilities of Raman for studies of real-world process and quality control applications will be given. Examples for chemical and pharmaceutical problems from the areas of solids sampling, *in situ* reaction analysis, and gas-phase sampling will be given with discussions of why Raman was chosen.

(142) **Gas-Phase Bio-Ion Reactions and Bioanalysis**

Scott McLuckey; [1]Purdue University

The advent of ionization methods that enable the formation of ions derived from large biomolecules has revolutionized the practice of analytical mass spectrometry. While traditional applications in elemental and organic analysis have remained strong, the ability to make high accuracy mass measurements of biological molecules has enabled the development of new fields, such as proteomics and metabolomics. Much of the subsequent development in mass spectrometric instrumentation has been driven by the needs in bioanalysis for higher mass measurement accuracy, greater speed, particularly for coupling with on-line separations, and higher mass range. The mass measurement alone, however, provides no direct structural information. Historically, mass spectrometry has relied on gas-phase ion chemistry, specifically fragmentation reactions, to provide ion structure information. For this reason, the gas-phase ion chemistry of bio-ions in mass spectrometers has been the subject of widespread investigation. A number of new developments in gas-phase bio-ion chemistry have taken place within the past decade that have played a major role in the rapidly expanding role of mass spectrometry and tandem mass spectrometry in bio-analysis. This presentation relates these developments with particular emphasis on the unimolecular, ion/molecule, and ion/ion reactions involving multiply charged ions. These developments are placed into context with other advances in mass spectrometry. Examples of new types of experiments that have been enabled by advances in ion chemistry are related with special emphasis placed on ion/ion reaction studies conducted by the author and co-workers over the past fifteen years.

(143) **Characterization of an Inductively Coupled Plasma/ Electrospray Dual-Source Time-of-Flight Mass Spectrometer for Comprehensive Chemical Speciation**

Duane Rogers[1], Steven Ray[1], Gary Hieftje[1]; [1]Indiana University

In recent years the importance of chemical speciation, i.e. the determination of an element amongst its various oxidation states and molecular or complex forms, has been recognized as more relevant than total elemental concentration. Although the total elemental concentration is often easier to evaluate, the bioavailability and toxicological information it yields is inherently limited. It has been demonstrated that chromatographic separation alone cannot provide sufficient qualitative information for native biological samples, due to the unknown nature of the sample. For this reason, researchers have begun employing two separate instruments to obtain the elemental and molecular information from such samples. However, employing multiple instruments for the analysis of a given sample has several disadvantages. In the work presented here, a single time-of-flight mass spectrometer (TOFMS) will be described that utilizes two sources to obtain comprehensive atomic and molecular information simultaneously. The dual-source TOFMS has been designed and constructed in our laboratory. The current arrangement for the instrument utilizes an inductively coupled plasma to obtain elemental, isotopic, and quantitative information. Meanwhile, an electrospray source is operated in parallel to provide molecular information. Due to the wide mass

range and high spectral-generation rate of TOFMS, ions from both sources can simultaneously be sampled by a single mass analyzer to provide excellent temporal resolution of transient signals, while simultaneously simplifying peak assignment from a chromatographic separation. In addition, since only a single chromatographic separation is necessary for the atomic and molecular channels, sample requirements, preparation time, and analysis time can be significantly reduced. The discussed work will describe the advantages of the dual-source TOFMS for transient analysis.

(144) **Electrode Comparison for use with Electrochemically Modulated Separations for ICP-MS**

Scott Lehn[1], Martin Liezers[1], Shane Peper[1], Doug Duckworth[1]; [1]Pacific Northwest National Laboratory

Electrochemically modulated separations (EMS) have been demonstrated to provide an effective method of pre-concentration of uranium and plutonium for analysis by inductively coupled plasma mass spectrometry (ICP-MS) using anodized glassy carbon (AGC) as the working electrode. Other carbon-based electrodes may provide better performance and flexibility in certain applications. Several different working electrodes such as printed electrodes, reticulated vitreous carbon of various porosities, pyrolitic graphite, carbon paste, and others will be investigated. The results of these studies as they relate to different applications will be presented.

(145) **Fiber-Optic Chemical Sensing using Cavity Ring-Down Principles**

Jacob Shelley[1], Carsten Engelhard[1], Radislav Potyrailo[2], Gary Hieftje[1]; [1]Indiana University; [2]General Electric Global Research Center

Cavity ring-down spectroscopy (CRDS) is widely used as an ultra-sensitive method for trace detection of gases via absorption of laser light. The major advantages of CRDS over conventional absorption methods are that a large number of repeated absorption events from a single light pulse are measured in a short amount of time, increasing the effective path length and sensitivity. In addition, the technique does not require a steady light source or reference beam. Recently, the basic principles of CRDS have been adapted to an optical fiber formed into a loop. This fiber-loop ring-down (FLRD) technique has been used for detection of analytes from a capillary electrophoresis (CE) effluent. In this configuration, light was injected into a bend in the fiber with the sample passing through the splice that forms the loop. Light scattered from the core of the fiber was then detected at another bend in the fiber. However, the poor light-coupling efficiency (10^{-12}) required a large number of averages ($\sim 10^4$) to obtain a ring-down trace, which in turn requires a steady light source. In addition, because the sample was placed into the splice, the absorption cross-section was largely reduced, causing a drop in sensitivity compared to typical CE absorption detection. Both the light-coupling and absorption cross-sections in FLRD can be improved by using evanescent wave absorption at the core/cladding interface, such as in fiber-optic chemical sensing. In the present study, two novel fiber-loop methods for fiber-optic chemical sensing are demonstrated. In both, the sensing agent of interest (e.g. phenol red for the detection of ammonia) is uniformly doped into the plastic cladding of the fiber. The first configuration uses a single fiber spliced end-to-end with laser light being injected into the splice, significantly increasing the coupling efficiency. The second design employs a nanosecond-pulsed LED to inject light into a doped fiber wrapped around a photomultiplier tube (PMT) numerous times. The amount of light traveling through the core declines exponentially, analogous to FLRD but without the requirement of fiber splicing and thereby improving light injection. The result is a very compact (~20 cm^3), inexpensive, and sensitive (<1 ppm for ammonia) sensing system.

(146) **Comparison of Atmospheric-Pressure DC Plasma Sources used in Ambient Mass Spectrometry**

Joshua Wiley[1], Jacob Shelley[1], Steven Ray[1], Gary Hieftje[1]; [1]Indiana University

A multitude of new atmospheric-pressure ionization sources have recently been developed for mass spectrometry. The resulting new field, termed ambient mass spectrometry (AMS), refers to any open-air ionization source that enables the direct mass spectral analysis of samples with little or no pre-treatment. These sources include desorption electrospray ionization (DESI), direct analysis in real time (DART), desorption atmospheric-pressure chemical ionization (DAPCI), and flowing atmospheric-pressure afterglow (FAPA). Of all of the AMS sources, over half utilize an electrical discharge as a means to desorb, directly ionize, or indirectly ionize (by reagent-ion generation) analytes from a sample surface. However, little is known about the fundamental processes in these sources and how these processes affect their capabilities. Accordingly, a direct comparison of these atmospheric-pressure plasma ionization sources seems desirable. In the present study, two different operating modes of a direct-current atmospheric-pressure discharge in helium were compared by means of a variety of methods. One mode, a corona discharge, corresponds to the general operation of the DART source. The other is a true glow discharge such as is used in the FAPA source. These two discharges were compared in terms of reagent ions generated and mass spectra of analytes that are introduced into the source. In addition, infrared thermography was employed to obtain temperature profiles from each source, features that are important in understanding desorption capabilities and optimal sample positioning. For a more thorough comparison, a complete DART source, containing the additional filtering electrodes and heater, was constructed and compared with the FAPA source with a variety of test compounds with different chemical properties. Finally, the issues of matrix effects and quantitation will be discussed in detail.

(147) **Imaging of Proteins on Gel Electropherograms via Radio Frequency Glow Discharge Optical Emission Spectrometry**

Carsten Engelhard[1], Steven J. Ray[1], Gerardo Gamez[1,2], Gary M. Hieftje[1]; [1]Indiana University; [2]Swiss Federal Institute of Technology

Gel electrophoresis (GE) is the most popular procedure for the separation, resolution and purification of biopolymers in complex mixtures. In 2-D GE, separation is achieved according to the electrophoretic mobility of the constituents in one direction and the isoelectric point along the second. The result is an array of biopolymers separated according to both mass and chemical composition. Detection and quantitation is then achieved by staining or developing the gel. A multitude of staining and analysis techniques are available, including densitometry, phosphorescence, fluorography or autoradiography. However, these methods suffer from low limits of detection, limited linear dynamic range or even radioactive waste. Moreover, elemental analysis usually requires gel excision and digestion or electroelution before such analyses can be performed. Recently, a radio frequency (rf) glow discharge (GD) was coupled to a monochromatic imaging spectrometer to perform surface elemental imaging of electropherograms [1]. Here, a 2-D gel separation is subjected to sputtering and excitation by a glow discharge source. The rf energy is applied in short pulses (<250 μs) to reduce the diffusion of sputtered atoms before they emit. This technique allows the identification of biological metal associations, e.g. the study of metalloproteins after separation under

native conditions, or can be used with established staining agents that are based on various elements. A novel instrument design with a larger GD cell will be presented here that enables the direct analysis of targets such as minigels or microarrays. The influence of a variety of parameters (cell pressure, forward power, pulse width, etc.) will be discussed. Laterally resolved emission maps of selected proteins stained with silver-enhanced colloidal gold have been obtained and current analytical figures of merit will be presented. [1] G. Gamez, S. J. Ray, F. J. Andrade, M. R. Webb, G. M. Hieftje, Anal. Chem., 79 (2007) 1317-1326. [a]Present address: Department Of Chemistry and Applied Biosciences, Swiss Federal Institute Of Technology (ETH Zurich), Zurich, Switzerland.

(148) **Improvement of Isotope Ratio Measurements with an Inductively Coupled Plasma Mattauch-Herzog Mass Spectrograph Equipped with Faraday-Strip Array Detection**

Gregory Schilling[1], Steven Ray[1], Roger Sperline[2], M. Bonner Denton[2], Charles Barinaga[3], David Koppenaal[3], Gary Hieftje[1]; [1]Indiana University; [2]University of Arizona; [3]Pacific Northwest National Laboratory

Isotope-ratio measurements are important in many areas, including analysis of nuclear samples, radioactive waste and environmental monitoring, geological dating, and medical applications. Ordinarily, thermal ionization mass spectrometry (TIMS) is considered the standard for such analyses due to its high degree of stability and outstanding precision. However, TIMS often requires tedious sample preparation and very long signal integration periods to achieve such precise measurements. Furthermore, a global set of operating conditions for multiple elements does not exist in TIMS. Therefore, inductively coupled plasma mass spectrometry (ICPMS) using multiple ion collectors has started to take over some of the workload for such analyses. In addition to ICPMS providing near unity ionization efficiencies across the atomic mass range, it also permits much simpler sample preparation and shorter analysis times. A logical step, just being realized in such analyses, is the use of an array detector. An array of detectors enables any number of isotope ratios to be precisely determined for multiple elements simultaneously within a single measurement. Such an array detector has been developed and coupled to a Mattauch-Herzog mass spectrograph. The array consists of 128 gold Faraday strips that are 45-µm wide on a 50-µm pitch, thus permitting the simultaneous collection of a range of m/z values. With this arrangement, duty cycle is greatly improved, spectral skew is eliminated when transient signals are examined, and correlated noise sources, such as ICP fluctuations, can be dramatically reduced through the use of ratioing. The current presentation focuses on experiments aimed at improving the isotope ratio precision that can be achieved using the array detector device. The chosen experiments include the determination of the isotope ratio precision for Ag as a function of peak shape, various detector parameters, and data analysis methods. Precision levels have been shown to be in the 100 ppm range.

(149) **Analysis of Environmental Samples with Inductively Coupled Plasma-Atomic Emission Spectrometry**

William C. Wetzel[1], Erica C. Goetz[1], Adam W. Reis[1], Corinne E. Weinel[1]; [1]Thomas More College

Inductively coupled plasma-atomic emission spectrometry (ICP-AES) has demonstrated utility for determining trace metals in a variety of aqueous solutions. In particular, the ability of ICP-AES to provide simultaneous multielemental information, low (ppb) limits of detection for most elements on the periodic table, and a linear working range over several orders of magnitude makes this technique well-suited to determine the atomic composition of environmental samples. In this study, ICP-AES has been employed for the analysis of various plant and animal tissues. Since the elemental fingerprint of a living organism is influenced by its surroundings, determination of trace metal concentrations ultimately provides information about the environment in which the organism has lived. Sample preparation, results, and comments on the growth environment of various plants (broccoli) and small animals (zebra mussels and cicadas) will be discussed.

(150) **Integrated Sensing and Processing-Acoustic Resonance Spectroscopy (ISP-ARS) for Rapid Tablet Identification**

David Link[1], Thaddaeus Hannel[1], Robert Lodder[1]; [1]University of Kentucky

Fourier transform acoustic resonance spectroscopy (FTARS) is well established and has been shown to differentiate drugs, powders, and liquids. FTARS is nondestructive and complete scans can be made in seconds, therefore it is a prime candidate for use as a process analytical technique (PAT). However, FTARS relies on intensive computer processing following data collection due to the amount of information gained in each scan. An AR spectrum recorded over the interval of 20 Hz to 20 kHz with a sample rate of 44.1 kHz for one second generates a substantial amount of data (1 s x 44.1 kHz = 44100 data points). Chemometric analysis of multiple FTARS data sets can become computationally demanding and could limit the production rate of tablets, especially if 100% tablet inspection is considered. Integrated sensing and processing acoustic resonance spectroscopy (ISP-ARS) is a novel approach to acoustic spectroscopy that can be implemented using instruments as simple as an MP3 player. In ISP-ARS, an ISP acoustic excitation waveform is created that comprises only the distinguishing spectral details associated with an analyte. FTARS is used to develop ISP acoustic waveforms employed in differentiating D-tagatose, a new oral drug in phase 3 clinical trials for treatment of type 2 diabetes, from other toll-manufactured drugs. The ISP detector output is a voltage that can be read immediately and corresponds only to the analyte under investigation. ISP acoustic waveforms composed of 10, 100, and 1000 frequencies were used to identify several drugs. The tablets used in this study were aspirin, acetaminophen, D-tagatose, ibuprofen, vitamin B, and vitamin C. The average accuracy of prediction was 98.47, 97.45 and 95.41 percent for the 10, 100 and 1000 frequency component acoustic waveforms respectively.

(151) **Surreptitious Remote Sensing of Blood Alcohol Content: Molecular Factor Computing (MFC) Near-Infrared Spectroscopic (NIRS) Imaging and Laser Speech Detection**

Thaddaeus Hannel[1], David Link[1], Robert Lodder[1]; [1]University of Kentucky

Alcohol abuse is a major problem in the United States. Common alcohol monitoring techniques include the sampling of breath, urine, saliva, or blood followed by various analyses to assess the alcohol level in each. While many of these techniques provide adequate sensitivity, they are intrusive and have various disadvantages. This work will describe two noninvasive experiments to estimate breath alcohol content (BrAC, known to be highly correlated to blood alcohol content). An IRB-approved clinical trial with cross validation tested the hypothesis that NIR hyperspectral imaging of exposed skin based on molecular factor computing (MFC, a method of integrated sensing and processing) and remote laser interferometry for speech detection could be used to noninvasively measure BrAC. These approaches have the potential to estimate alcohol impairment unobtrusively, remotely and in real-time. MFC-NIRS imaging measurements for standard error of prediction (SEP) for a global model relative to blood alcohol was 8.1 mg/dL (0.0081%) with r2 = 0.99. The laser interferometer for speech measurements resulted in an SEP for a global model relative to blood alcohol at 16.0 mg/dL (0.016%) with

r2 = 0.82, however the SEP for individual phrases and words was much lower.

(152) **Fundamental Ion Diagnostics in Pulsed Glow Discharge Plasmas**

James Barnes[1], Cris Lewis[1], Megan Dejesus[2], Adam Zocco[3]; [1]Los Alamos National Laboratory; [2]West Virginia University; [3]New Mexico State University

Fundamental ion diagnostics of a millisecond pulsed glow discharge plasma operated using different noble gasses (He, Ne, Ar, Kr, Xe) will be presented. Observations have been made at various times during the pulsing cycle of the relative populations of support gas ions, including singly charged, doubly charged, and dimer ions using a time of flight mass spectrometer. The effects of operating parameters, such as applied potential, anode-cathode spacing, and operating pressure, have been determined. From these data, information about the plasma processes and energetics can be elucidated.

(153) **Use of a Flowing Atmospheric-Pressure Afterglow Ionization Source for Sensitive Detection of Fast Transient Signals**

Jacob Shelley[1], Steven Ray[1], Gary Hieftje[1]; [1]Indiana University

The recent development of a wide variety of atmospheric-pressure ionization sources for mass spectrometry (AMS), termed ambient mass spectrometry, has allowed fast, simple analysis of many different sample types. These sources have numerous advantages, including little or no sample pre-treatment, simple mass spectra, and direct analysis of solids and liquids. For these reasons, AMS has become an important tool in cleaning validation, forensic analyses, and drug discovery. However, two major problems with AMS sources have prevented them from becoming more widely used. First, quantitation is difficult to achieve because of changes in analyte desorption and the necessity of precisely positioning the sample with respect to the source. Second, preferential ionization of easily ionizable analytes or more abundant analytes creates problems when mixtures containing a broad range of analyte concentrations must be analyzed. For complex samples, the latter problem can be overcome by introducing the sample as a fast transient (from laser ablation, LA, or gas chromatography, GC). In the present study, the flowing atmospheric-pressure afterglow (FAPA) ionization source is applied as a novel ionization source for fast transient signals from GC, LA, and capillary electrophoresis. The FAPA source uses ionic and excited neutral species from an atmospheric-pressure glow discharge in helium to generate reagent ions in ambient air, which have the capability to desorb/ionize the analytes. The resulting ions are then detected with a LECO Unique® time-of-flight mass spectrometer. The fast response time of the FAPA source (~1 ms) and the fast spectral acquisition rate of the Unique® (100 Hz) make it possible to collect an entire mass spectrum at each point along the fast transient. Additionally, the simple construction of the FAPA source allows it to be easily coupled to many types of sample introduction systems. The result is a very sensitive (LOD = 5 fmol for caffeine) and rapid detection system for solid, liquids, and gases. The ability to obtain MS/MS information with a TOF-MS via orifice-induced dissociation will also be demonstrated.

(154) **Spectroscopic Imaging Microscope**

Michael R. Webb[1], Christopher N. LaFratta[1], David R. Walt[1]; [1]Tufts University

Microscopic imaging is widely used across a variety of disciplines, as is spectroscopy. Combining these two technologies can lead to more powerful analytical platforms. Commonly, simple filters are used to isolate spectral bands in microscopy. However, this approach lacks flexibility. Poor matching of a filter's transmission band to the analytical problem can lead to interference between the analyte's spectrum and those of other components. Further, detailed spectra are often of interest for diagnosing such overlaps, for identifying analytes, or for observing spectral shifts. However, acquiring spectra at even modest wavelength resolution requires a large number of fixed-bandpass filters. Tunable filters are available, but have disadvantages of their own, including high cost and poor rejection of light from outside the selected wavelength band. Grating-based monochromators do not suffer from any of these problems. The bandpass and central wavelength can be easily tuned to suit a particular application, or the wavelength can be scanned so that a spectrum can be acquired. Ordinarily, grating-based monochromators are used for observing the average spectrum of a small area, rather than for acquiring spectra from many points in a two-dimensional image. We present here a simple, grating-based imaging system with aspects of both a monochromator and a microscope. Compared to other monochromator-microscope hybrid systems, the present instrument shows advantages in simplicity, image quality, and cost. Spatial resolution in the low micron range and spectral resolution in the low nanometer range are both possible.

(155) **Precise Element Ratios from Noisy Laser Ablation ICP-MS Signals: Can Collision/Reaction Cells Help?**

Patrick Gray[1], Susan Olesik[1], John Olesik[1]; [1]The Ohio State University

Precise element concentration ratios, measured with tens of micrometer spatial resolution, in structures such as corals and fish otoliths can provide a history of temperature and local water chemistry. Corals can provide information on sea temperature, river water flow into oceans and upwelling while otolith microchemistry can be used to identify migration patterns of fish. Laser ablation ICP-MS signals are easily detectable from major, minor and trace elements in structures such as corals and otoliths. However, LA-ICP-MS signals produced from heterogeneous, porous materials such as coral skeletons can fluctuate by 50% due variations in the amount of material ablated and to incompletely vaporized particles. In contrast, element concentration ratio precision better than 1% is needed to use Sr/Ca to estimate water temperature with sufficient resolution. Large signal fluctuations due to vaporizing particles occur on the 100 μs time scale. Variations in the signal due to sample structure heterogeneity can be observed on the ms to seconds scale. In ICP-quadrupole-MS, one m/z is measured at a time, but with a short settling time (1 ms). ICP-sector field-MS provides flat topped peaks and greater sensitivity than ICP-Q-MS, but has magnet settling time of greater than 10 ms. A pressurized reaction cell placed between the plasma and the analyzer quadupole in an ICP-Dynamic Reaction Cell-MS can force ions to take a random path due to collisions with the collision/reaction gas so that different ions have variable flight times through the cell. This results in temporal homogenization on a time scale to several ms so that peak hopping measurements can be made faster than the homogenized ion signal changes. We will compare ICP-DRC-MS, ICP-SF-MS and simultaneous detection by ICP-OES to obtain precise element ratios. The influence of reaction gas properties (weight, polarizability and dipole moment) and instrument parameters will be discussed. The effect of temporal homogenization on element ratio precision of both homogeneous (CRM) and structurally complex materials (coral) will be examined.

(156) **Spectroscopic Investigation of Hydrophobic Silica Aerogels**

Mary Carroll[1], Christopher Backlund[1], Emily Green[1], Ann Anderson[1]; [1]Union College

Aerogels have many interesting physical properties, including high surface area and porosity, which render them particularly attractive for sensing and chemical spill clean-up applications. Silica aerogels with hydrophobic, and in some cases super-hydrophobic surfaces, can be formed from sol-gel precursor mixtures that include organically modified silanes. But does the surface hydrophobicity of an aerogel monolith render this highly porous structure impermeable to water? We report here on a series of spectroscopic experiments designed to ascertain the extent to which water vapor permeates hydrophobic silica aerogels. We make aerogels via a novel one-step, contained-mold rapid supercritical extraction (RSCE) technique, in a hydraulic hot press. Aerogels fabricated from a base-catalyzed recipe that includes a mixture of tetramethoxysilane (TMOS) and either the methyl-, ethyl- or propyl- derivative of TMOS are super-hydrophobic. Sessile drop tests yield contact angle measurements above 150 degrees and, for some materials, as high as 170 degrees. When a thermally stable luminescent probe is included in the sol-gel precursor mixture placed into the mold, the resulting aerogels contain the probe moieties. There are no solvent-extraction steps in the process and, therefore, there is little opportunity for the probe to leach out of the sol-gel matrix. We have successfully entrapped a variety of luminescent probes in silica aerogels prepared via the RSCE process. We will describe the results of our spectroscopic evaluation of humidity-sensitive probes entrapped within hydrophobic silica aerogels that are exposed to varying levels of water vapor.

(157) **Plasma Cavity Ring-Down Spectroscopy for Elemental, Isotope, and Hyperfine Structure Measurement**

Yixiang Duan[1,2,3], Chuji Wang[2], Christopher B. Winstead[3]; [1]Los Alamos National Laboratory; [2]Mississippi State University; [3]University of Southern Mississippi

We have been exploring highly sensitive techniques for elemental and isotope measurements using cavity ring-down spectroscopy (CRDS) combined with a compact plasma source as an atomic absorption cell. The research work marries the high sensitivity of CRDS with a low power plasma source to develop new instrument that gives high sensitivity and capability for elemental and isotope measurements. CRDS, which uses a single laser pulse ringing down inside the cavity over a thousand times, provides several orders of magnitude more sensitive than conventional absorption techniques. Additional benefit is gained from a compact microwave plasma source that possesses advantages of low power and low plasma gas flow rate, which benefit for atomic absorption measurement. A laboratory CRDS system consisting of a tunable dye laser/diode laser is used in this work for testing and building a science base and to demonstrate the feasibility of the new instrument. A laboratory designed and built sampling system for solution sample introduction is used for the new instrument testing. The ring-down signals are monitored using a photomultiplier tube (PMT) and recorded using a digital oscilloscope interfaced to a computer. Several elements, isotopes, and hyperfine structure were tested and reported.

(158) **Real-Time Monitoring of Valproic Acid Intake via Extractive Electrospray Ionization Mass Spectrometry of Exhaled Breath**

Gerardo Gamez[1], Liang Zhu[1], Konstantin Chingin[1], HuanWen Chen[2], Renato Zenobi[1]; [1]ETH Zurich, Switzerland; [2]College of Chemistry, Jilin University

Monitoring the levels of pharmaceuticals and their metabolites is of utmost importance. This is especially true when there are changes in dosage, clinical condition or concomitant medications. For example, if the antiepileptic drug valproic acid is below therapeutic levels it will not manage seizures efficiently and above a certain threshold adverse effects become more frequent. Thus, frequent blood tests are required to supervise the plasma concentration. However, blood sampling is painful, invasive, requires specialized personnel, and produces hazardous waste. An alternative that overcomes these disadvantages is breath analysis. Recently, extractive electrospray ionization (EESI) mass spectrometry was successfully applied in our laboratory for analysis of breath. Basically, the volunteers exhale through a tube that guides the breath to the area where a pure solution is electrosprayed onto a MS sampling interface. Here, the compounds in the breath can be ionized and later analyzed. This technique requires no sample storage or pretreatment, thus analysis can be performed in real-time. We have found that unique features in the EESI mass spectral fingerprints of individuals under valproic acid can be used for monitoring its intake and perform pharmacokinetic studies. Current work towards identifying these biomarkers and how they relate to the valproic acid plasma concentration is underway. However, it is evident that EESI MS of exhaled breath allows the real-time measurement of drugs intake in a pain-free and non-invasive manner, which will ultimately permit better patient therapy management in the clinical setting.

(159) **Characterization of Nanoscale Vapor Barrier Glass Coatings on Polymer Substrates by Ellipsometry**

Richard Savage[1], Daniel Helms[1], John Felts[2]; [1]Cal Poly State Univesity; [2]Nano Scale Surface Systems

Recent manufacturing processes have made it possible to deposit thin (< 20 nm thick) films of SiOx onto polymer substrates uniformly and efficiently. These films can serve as vapor barriers and have been utilized in the food and beverage industries to extend product shelf-life. The permeability of small gas molecules like CO2 and O2 through polymer containers presents a major problem to many products and can be greatly diminished by the conformal deposition of thin glass films on polymer substrates. They can also serve as chemical barriers in biomedical testing micro-plates. The films are deposited using plasma enhanced chemical vapor deposition processing and require on-line monitoring of their thickness for quality assurance. The focus of this project was to characterize the thickness of the thin glass films on polymer substrate such as polyethylene terephthalate (PET) using ellipsometry based measurement techniques. A simple ellipsometer constructed of a linearly polarized helium-neon (HeNe) laser, quarter waveplate, linear polarizer, and photodetection system was developed along with a signal analysis algorithm for rapidly measuring the thickness of 100 to 200 angstrom films. Measurement results for SiOx on PET will be compared against those obtained with thermally grown oxides and gold films on silicon substrates, typically employed in microfabrication processing.

(160) **Optimization of a Method to Determinate Metals in Petroleum Products by Direct Injection using ICP-OES**

Mariano Cipollone[1], Fabián Sein[1], Rodolfo Durán[1], María Bernarda Epele[1], María Luján Collivadino[1]; [1]CTA, RepsolYPF

In this work we perform a simple and rapid method for the simultaneous determination of several metals and non metals in middle distillate fuels, volatile fuels and other kind of samples by ICP-OES simply diluting the sample in xilene, kerosene and naphtha. This method is very important in the ptrochemical industry in order to reduce the times of analysis, the costs and the errors. To improve the figures of merit of the method we search the best conditions for the more important factors by a factorial analysis. These factors are: power of RF, nebulizer flux and temperature of spray chamber. These better conditions are determined analyzing the behavior of mentioned factors against the BEC (Background equivalent concentration). Also we make a comparison between the solvents used in order to find the best in each case. To introduce directly naphthas and volatiles samples we use a refrigered spray chamber Particulary we extend the scope of applications to samples more complicated like FCC feed, LAB, FAME, naphthas and heavy fractions. Considering the viscosity of the final solutions we perform a table with recommended weights for each kind of sample. This table was probed using the internal standard method. Finaly we make a description of the most importants applications that can be solved by this method, the advantages against an acid treatment and a brief description of recommendations to work with this system.

(161) **Supersonic Jet Spectroscopic Analysis with Desorption Sample Introduction**

Taylor Cline[1], Amber Johnstone-Gygi[1]; [1]Brigham Young University

Analysis of large molecules in complex matrices requires analytical methods with high sensitivity and high discriminating power. One method that meets these requirements is Supersonic Jet Spectroscopy (SJS). A supersonic jet reduces spectral broadening and permits high-resolution analyses. However, the resolving power of SJS is not sufficient for complex samples, and chemical separation must be employed. We will report on the use of simple separations employing thermal desorption and supercritical fluid density programming coupled with SJS for high-resolution analysis of a laboratory-prepared sample and a real sample.

(162) **Development of Droplet Direct Injection Free-Running ICP for Nano, Pico-Liter Analysis**

Taichi Meguro[1], Etsuo Yamagishi[2], Hidekazu Miyahara[1], Naoki Nakashima[1], Eiki Hotta[1], Ryuichi Shimada[1], Akitoshi Okino[1]; [1]Tokyo Institute of Technology; [2]Pearl Kogyo Co, Ltd.

Inductively coupled plasma mass spectrometry (ICP-MS) and ICP atomic emission spectrometry (ICP-AES) have attracted widespread interest because of their analytical figures of merit. Recent years, the target of the elemental analysis has been shifted to smaller amount of samples such as single cell, nano–particles, etc. However, in all sample introduction systems have been developed, aqueous solution was introduced to the plasma as a group of liquid mist. And solution was introduced continuously, so large volume of sample solution was used for analysis. Therefore, it was difficult to analyze these smaller amount samples. To overcome this problem, we developed a droplet direct injection nebulizer (D-DIN) system. In this system, aqueous solutions are not nebulized but directly injected into the plasma with single small droplet shape. The volume of the droplet can be controled by the injection tip hole diameter and the applied back pressure. Therefore, very small and accurate sample introduction can be achieved. In AES using single droplet, the absolute detection limit of magnesium solution was 0.076 fg. However, at this time, the lowest limit of the droplet volume is 700 pL and this is about 100 times larger than the droplets in the mist from conventional nebulizers. Therefore, the plasma fluctuated or disappeared sometime when the droplets are introducing by D-DIN. To avoid the plasma disappearance, we developed a free-running ICP system for droplet direct injection. In the free-running ICP, the impedance shift by introducing the droplet is automatically cancelled by shift of resonant frequency of the entire system. The original resonant frequency of the system is about 40.68 MHz. The frequency shift in Ar-ICP by introducing a droplet of 5 nL was about 30.8 kHz. The frequency came back to the base frequency in about 130 ms.

(163) **Inductively Coupled Plasma Atomic Emission Spectrometry as a Detection Technique for Liquid Chromatography**

Jose L. Todoli[1], Eduardo Paredes[1], Salvador Maestre[1], Soledad Prats[1]; [1]University of Alicante

The determination of the concentration of carbohydrates, carboxylic acids, alcohols, water-soluble vitamins and metals in foods is important for several reasons: the knowledge of the nutritional power of the product, toxicity, nutritional labeling, authenticity studies, etc. Carbohydrates, carboxylic acids, alcohols and water-soluble vitamins are usually determined by HPLC. On the other hand, metals use to be determined by atomic spectrometry techniques such as ICP-AES or ICP-MS. The aim of the present work is developing an analytical method to carry out the determination of these analytes through HPLC-ICP-AES hyphenation in a single chromatographic run. Chromatographic separation conditions for organic compounds, carbon detection conditions by ICP-AES and sample introduction system were studied in order to achieve high resolution and sensitivity for organic compounds. The determination of these compounds in a single chromatographic run was possible by means of a double injection. Firstly, the sample or a standard containing the organic compounds was injected in the column. Afterwards the sample or a standard containing the metals was injected by means of an injection valve placed at the exit of the column. This injection allowed the detection of metals during the time elapsed from the first injection and the time at which the first organic compound left the column. Then, the organic compounds were monitored by ICP-AES by measuring a set of replicates for a carbon emission line. The huge amount of data obtained by this coupling can be employed for the discrimination of different varieties of a given food, thus allowing the detection of fraud. Moreover, this coupling is advantageous in terms of time of analysis when both organic compounds and metals must be determined. In the present work, the methodology developed has been used for the quality control of multivitamin and mineral complexes. In order to achieve an additional reduction in the analysis time, several calibration methods have been proposed as an alternative to conventional external calibration. Calibration process in chromatographic techniques requires long time and the consumption of large quantities of reagents. For these reasons, calibration step is not usually carried out daily in routine analysis. ICP-AES detector provides similar sensitivities for different non-volatile organic compounds when peak area is plotted against carbon concentration. Therefore, calibration can be performed by means of the injection of a single standard containing a set of non-volatile organic compounds at different concentration levels. This calibration method is known as SICA and has been applied also to other chromatographic detectors. In these cases, a signal correction for the different compounds was required. Other two methodologies have been developed to carry out the calibration process using a single standard. These methods are based on the use of peak shape for obtaining the calibration plot. Results obtained with the three

methodologies developed were not significantly different to those obtained by external calibration. Moreover, these calibration methods allowed a significant reduction in the analysis time.

(164) **Direct Chemiluminescent Imaging Detection of Low-Abundant Proteins in Serum by PAGE using Metal Tags**

Jin Ouyang[1], Willy Baeyens[2]; [1]College of Chemistry Beijing Normal University; [2]Ghent University

A novel method based on chemiluminescent image for the detection of low-abundant proteins in serum after polyacrylamide gel electrophoresis is developed. Several metal tags whether coordinating with organic dyes or not have been evaluated. The proteins with different phenotypes have been well identified. The method could be well matched with mass spectrometry for protein identification in subsequent process.

(165) **A Comparison of Efficient Methods (Microwave, Pressure) for Digestion of Therapeutic Proteins**

Lorna Maheu[1], Adam Harder[1], Heather Connelly[1], Steven Cockrill[1]; [1]Amgen

The ability to reduce the time required for analytical proteolysis of proteins represents a large potential cost-savings to protein researchers. Furthermore, reducing the quantity of enzyme employed for a digest provides potential consumable cost savings, and improved analytical data due to diminished background peaks. Conventional proteolysis of a therapeutic monoclonal antibody was compared to digestion with microwave and pressure cycling technologies. Efficient digestion of proteins using both technologies has been reported in the literature; however there has been limited application to protein therapeutics. A complex protein was digested with endoprotease Lys-C using microwave, pressure, and conventional digestion procedures. The degree of digestion (number of missed cleavages), time to achieve complete digestion and effectiveness at reduced enzyme to substrate ratios were investigated for each technique, with conventional digestion used at the control for all experiments performed.

(166) **PyChem: Software for Statistical and Multivariate Analysis**

Roger Jarvis[1], Royston Goodacre[1]; [1]The University of Manchester

The analysis of complex samples such as biological material, using vibrational spectroscopic techniques, often relies upon mathematical pattern recognition methods to answer questions of the data. Even with Raman spectra, where peaks are typically narrower than their IR counterparts, the biochemical complexity of typical biological samples such as prokaryotic or eukaryotic cells, blood or urine, means that this advantage is often lost and only strongly resonance enhanced components can be identified accurately. Multivariate analysis (MVA) methods use the full spectrum to determine categorical or quantitative trends in spectral data, for both exploratory data analysis and predictive purposes. In combination with classical statistical methods, it is also possible to determine which components in a complex spectrum correlate strongly with the hypothesis being tested. MVA and univariate statistics are used widely in the spectroscopy community; but the tools available require either specialist computational knowledge, or cost large sums of money to purchase. The PyChem[1] software is a freely available open source graphical tool for univariate and multivariate analysis and can be downloaded from http://pychem.sf.net/. It provides modules for running principal components analysis (PCA), canonical variates analysis (CVA), partial least squares (PLS1 & PLS2), PLS-discriminant analysis (PLS-DA), parametric and non-parametric statistical tests for sample variance and a test for linearity using the correlation coefficient. In addition, more advanced evolutionary computing methods[2] are deployed with the package that can be used to mine spectral data and determine the variables most important for discrimination or quantification. The graphical output of the software uses representations of results that are not available elsewhere, and figures copied from the software are of publication quality. We will demonstrate example workflows that can be utilized within PyChem for analyzing vibrational spectroscopic data representing categorical and calibration problems. [1] Jarvis, R.M., et al. (2006) PYCHEM: a multivariate analysis package for Python. Bioinformatics 22, 2565-2566 [2] Jarvis, R.M. & Goodacre, R. (2005) Genetic algorithm optimisation for pre-processing and variable selection of spectroscopic data. Bioinformatics 21, 860-868.

(168) **Identification and Quantification**

Zainab Al-Ballam; [1]Kuwait Institue for Scientific Research

The type and concentration of hydrocarbon compounds are important parameters for determining the quality of water. It is, therefore, important to have some knowledge about the nature and amount of hydrocarbon compounds in the ground water of Kuwait. In view of the close association of huge accumulations of natural petroleum hydrocarbons in the rock sequence of Kuwait and the possibility of contamination of the aquifers from the large oil spills that occurred on the ground during the 1991 Gulf War, the matter has gained added urgency. The analysis is made by gas chromatography-mass spectrometry (GC/MS) and liquid chromatography-mass spectrometry (LC/MS). The level of hydrocarbon contaminated in the area where a water soluble fraction (WSF) of the crude oil surface contamination appears to be slowly leaking in to the fresh water lenses.

(169) **Low-Level Mercury Determination in Wastewater Effluent using CVAFS**

Maggie Day[1], Jeff Forsberg[1]; [1]CETAC Technologies

Both local and regional regulations may require lower mercury detection limits for wastewater effluent, prompting more sensitive analytical techniques. Current regulatory standards do not require detection at the low-level; therefore, low-level reporting data is labeled 'non-detect'. This reporting could potentially result in biased data and does not give a true representation of the total mercury in the effluent. The current determinative technique, cold vapor atomic absorption spectrometry (CVAAS), does not allow for sub-ppt mercury quantitation. This paper will present low-level mercury determination of wastewater effluent using cold vapor atomic fluorescence spectrometry (CVAFS). This technique allows for analysis over a large dynamic range to obtain accurate, quantitative data, with minimal analysis time and detection limits ranging from 0.05ppt to 100ppb. Calibration, quality controls and digested wastewater effluent samples will be analyzed to compare and contrast single amalgamation and non-amalgamation with CVAFS using both EPA Method 245.7 and EPA Method 1631, Revision E.

(170) **Detection of Gunshot Residue from Decomposing Tissue Samples and Blowfly Larvae using ICP-MS**

Ruth Waddell Smith[1], Lisa LaGoo[1], David W. Szymanski[1], Brian C. Hunter[2]; [1]Michigan State University; [2]Hurley Medical Center Laboratory

Forensic identification of GSR uses scanning electron microscopy with energy dispersive X-ray spectroscopy (SEM-EDS) to determine the presence of the three elements considered to be characteristic of GSR: antimony (Sb), barium (Ba), and lead (Pb). However, in decomposed bodies, death by gunshot wound can be difficult to discern since visual identification of the wound is complicated by decomposition and larval activity. Hence, an efficient and sensitive method for the chemical, rather than visual,

identification of gunshot wounds is necessary. In this presentation, the development of an inductively coupled plasma-mass spectrometry (ICP-MS) method for the identification of GSR directly from decomposing tissue samples and larvae is demonstrated. A euthanized pig was shot multiple times using a Glock™ handgun and allowed to decompose. Wounds were collected throughout the sampling period and larvae were collected when present. Wounds and larvae were microwave-digested in nitric acid and hydrogen peroxide and subsequently analyzed by ICP-MS using selected ion monitoring for 121Sb, 138Ba, and 208Pb. The study was conducted twice; once during the late summer (37 day sampling period) and again during the winter (60 day sampling period) to assess the effects of temperature on decomposition and GSR persistence. Tissue concentrations ranged from 56.5-0.59 µg 121Sb/g tissue, 164-1.21 µg 138Ba/g tissue, and 123-1.09 µg 208Pb/g tissue throughout the late summer sampling period. For larvae, the three elements were only detected on days 3 and 4 after death during summer, potentially due to inclement weather. In the winter months, tissue concentrations ranged from 35.6-5.23 µg 121Sb/g tissue, 126-34.9 µg 138Ba/g tissue, and 503-81.3 µg 208Pb/g tissue. No larvae were collected during the winter study. Tissue samples were also analyzed by SEM-EDS for comparison with the developed ICP-MS method. Due to adverse weather conditions, GSR was only detected in wounds one day after death in both the late summer and winter sampling periods. Hence, ICP-MS method offers a sensitive means for GSR determination that is unaffected by weather.

(171) **MatLab Simulations for Infrared Visualization of Blood Stains on Fabrics Based on Sensitized Thermal Detectors**

Heather Brooke[1], Megan Baranowski[1], Jessica McCutcheon[1], Anthony Trimboli[1], Stephen Morgan[1], Michael Myrick[1]; [1]University of South Carolina

Work has been done to create a new instrument for detecting blood on various background surfaces. The proposed idea is to design a camera with a thermal detector that has been sensitized to specific spectral regions for blood. A number of MatLab simulations have been carried out to determine the validity of this method, as well as to determine the most appropriate materials for sensitizing the detector and filtering the light. We show that by choosing a good set of film materials, we can distinguish between samples of fabrics with bloodstains and the neat fabric using linear discriminate analysis (LDA). Preliminary experimental studies were also done and are described in another presentation.

(172) **Validation Experiments for Infrared Visualization of Blood Stains on Fabrics Based on Sensitized Thermal Detectors**

Megan Baranowski[1], Heather Brooke[1], Jessica McCutcheon[1], Anthony Trimboli[1], Stephen Morgan[1], Michael Myrick[1]; [1]University of South Carolina

We have theoretically shown that it is possible to distinguish bloodstained fabrics from neat fabric, using an infrared camera system based on a sensitized thermal detector and infrared filtering. In this report, we show experimental results to validate the development of this instrument. Using a Merlin un-cooled microbolometer camera we took infrared images of different fabrics with and without bloodstains. With no alterations to the camera system, we are able to see differences between substrates as well as distinguish bloodstains. Using this same camera, we show the results of experiments using an infrared filtering system to compare with what we predicted in our MatLab simulations (shown in another presentation).

(173) **Human Breath Analysis for the Detection of Chemical Exposure and Pernicious Activity**

Audrey Martin[1,2], George Farquar[1], A. Daniel Jones[2], Matthias Frank[1]; [1]Lawrence Livermore National Laboratory; [2]Michigan State University

Human health and chemical exposure can be non-invasively monitored via breath analysis. The alveolar air of the lung is separated from the bloodstream by the alveolar pulmonary membrane. Compounds, particularly volatile organic compounds (VOCs), can partition between the two compartments across this barrier; thus, the alveolar air of the lung can be considered the headspace of the blood. Collection and analysis of breath can provide information on the chemical species of both exogenous and endogenous origins present in the human body. This proves to be a challenging analysis, as these VOCs are typically present in concentrations of ppbv and below. Several methods have proven successful for the collection and preconcentration of breath samples. The current work uses solid phase microextraction (SPME) to preconcentrate, and GC/MS to analyze and identify these VOCs in breath samples obtained from human subjects using a modified commercial breath sampling system. Presented herein are studies focused on the detection of exogenous compounds in human breath caused by chemical exposure in a variety of manners. Breath samples were obtained before and after inhalation exposure during the application of nail polish at a salon. While many endogenous compounds were present in both breath samples, additional compounds were identified in samples obtained after exposure, specifically camphor. Camphor is a common ingredient in many nail-care products, and was a listed ingredient on the nail polish used in the study. Preliminary data from exposures simulating pernicious activity, such as drug use and explosives synthesis, are also presented. Breath samples obtained before and after consumption of over-the-counter pharmaceuticals were analyzed, and compounds relating to the parent drug were detected. Breath samples were also obtained before and after working in the laboratory with compounds commonly used in the synthesis of explosives. These data serve as an early indication of the potential application of human breath analysis in a forensic or homeland security setting. This work was performed under the auspices of the U.S. Department of Energy (DOE) by Lawrence Livermore National Laboratory in part under Contract W-7405-Eng-48 and in part under Contract DE-AC52-07NA27344.

(174) **Automated Sample Treatment and Fluorescence Derivatization by Sequential Injection for the Determination of Amphetamines in Biological Fluids by Capillary Electrophoresis**

Ahmed O. Alnajjar[1]; [1]King Faisal University

A sequential injection (SI) manifold was constructed to automate on-line sample treatment and fluorescence derivatization for amphetamines in human urine. For sample treatment, solid-phase extraction (SPE) was conducted to perform sample clean-up, extraction and preconcentration in a home-made C18 microcolumn installed in the SI manifold. Fluorescence derivatization was based on the reaction of amphetamines with NBD-F, which was conducted in a reaction coil installed in the SI manifold. Experimental conditions significantly control SPE process including volumes of solvents and sample, and flow rate were optimized to gain good recovery, preconcentration and rapidity. Volume and concentration of NDB-F were also optimized to enhance the fluorescence derivatization reaction. As the following, the treated samples were subjected to capillary electrophoresis with laser induced fluorescence (CE-LIF) detector for separation and detection. CE parameters including electrolyte concentration, electrolyte pH, injection time, separation voltage and temperature were optimized to develop separation and detectability.

Microfluidic techniques used in this method, i.e. SI and CE, offers short analysis time, reduction in reagents and sample consumption and thus better safety to the environment. Furthermore, the automation of SI enhance rapidity and repeatability; and provide safety in reagents and sample. [1] Fang, Z.L., 1999. Trends of flow injection sample pretreatment approaching the new millennium, Anal. Chim. Acta 400: 233-247. [2] Grassi, V., Dias, A.C.B., Zagatto, E.A.G., 2004. Flow systems exploiting in-line prior assays, Talanta 64: 1114-1118. [3] Economou 2005, Sequential-injection analysis (SIA): A useful tool for on-line sample handling and pre-treatment, TrAC 24: 416-425. [4] Alnajjar, A.O., Idris, A.M., Multzenberg, M., McCord, B., 2007. Development of a capillary electrophoresis method for the screening of human urine for multiple drugs of abuse. J. Chromatogr. B 856: 62-67. [5] Idrisa, A.M., 2007. On-line coupling of solid-phase extraction, derivatization and spectrophotometry by sequential injection analysis: application to trifluoperazine assay in human urine. J. Pharmacol. Toxicol. Methods 56: 330-335. [6] Idris A.M., Alnajjar A.O., 2008, Exploiting sequential injection analysis technique to automate on-line sample treatment and quantitative determination of morphine in human urine. Talanta (In press).

(175) **Important Variables in the Classification of OTC Drugs by FTIR/ATR Spectra and Principal Component Analysis**

Huggins Msimanga; [1]Kennesaw State University

The FTIR/ATR spectra of reference compounds (benzoic acid, 3-nitrobenzoic acid, and 4-nitrobenzaldehyde) were acquired and analyzed by principal component analysis in order to establish whether these compounds could be classified successfully or not, and to understand the underlying variables used by PCA to classify the spectra. The goal was to eventually develop a protocol for classifying and identifying illicit drugs in a forensic lab. FTIR spectrum provides fingerprint information about the sample under investigation. PCA helps to pull out all correlated spectra into one group for further identification, if needed. For the above compounds, fourty-five spectra were acquired in the 650 – 4000 cm-1 region using 8 cm-1 resolution. Visual differences in the spectra at specific wave-numbers were noted, and compared with the variables as sorted out by PCA. With the insight obtained from the three reference compounds, four brands of Tylenol (Tylenol PM, Pain Relief-8 Hour, Pain Relief Extra Strength, and Tylenol Children's) were studied as above. These brands contain acetaminophen as the active ingredient, and a variation of excipients. The spectra were normalized before analysis in order to correct for differences in the concentrations of acetaminophen. Children's Tylenol differed the most from the other brands. Important variables via PCA arose from the variations in the amounts and types of excipients (cellulose, providone, stearic acid, dyes, etc). Results for both the reference compounds and Tylenol brands showed distinct classifications of the spectra, with Euclidean distances more than unity between the brands.

(176) **Inactivation of Microbial Cells and Spores for MALDI-TOF Mass Spectrometry**

Peter Lasch[1], Herbert Nattermann[2], Maren Stämmler[1], Marcel Erhard[3], Roland Grunow[2], Bern Appel[2], Dieter Naumann[1]; [1]Robert Koch-Institut, P25; [2]Robert Koch-Institut, ZBS2; [3]AnagnosTec GmbH

Identification of microorganisms specifically of vegetative cells and spores by intact cell mass spectrometry (ICMS) is an emerging new technology. The technique provides specific biomarker profiles which can be employed for bacterial identification at the genus, species, or even at the subspecies level holding the potential to serve as a rapid and sensitive identification technique in clinical or food microbiology and also for sensitive detection of biosafety level (BSL) 3 microorganisms. However, the development of IMCS as an identification technique for BSL-3 level microorganisms is hampered by the fact, that no MALDI-ToF compatible inactivation procedure for microorganisms, and particularly for bacterial endospores, has been evaluated so far. In this report we describe a new methodology for effective inactivation of microorganisms which is compatible with the analysis of microbial protein patterns by MALDI-ToF mass spectrometry. The main challenge of this work was to define the conditions that ensure microbial inactivation and permit at the same time comprehensive analysis of microbial protein patterns. Among several physical, chemical and mechanical inactivation procedures, inactivation by trifluoroacetic acid (TFA) proved to be the best method in terms of bactericidal capacity and information content of the mass spectra. Treatment of vegetative cells by 80% TFA alone for 30 min assured complete inactivation of microbial cells under all conditions tested. For spore inactivation, the "TFA inactivation protocol" was developed which is a combination of TFA treatment with basic laboratory routines such as centrifugation and filtering. This MALDI-ToF/ICMS compatible sample preparation protocol is simple and rapid (30 minutes) and assures reliable inactivation of vegetative cells and spores of highly pathogenic (BSL-3) microorganisms. In the presentation we will give two examples from the genera Bacillus and Yersinia that demonstrate the dicriminative potentials of the new technique.

(177) **Calibration-Free Quantitative Application of *in-situ* Raman Spectroscopy**

Jeroen Cornel[1], Marco Mazzotti[1]; [1]Institute of Process Engineering, ETH Zurich

Identification and characterization of the different kinetic phenomena in crystallization and precipitation are essential for process understanding, allow process modeling and enable process design, optimization and control. Real-time characterization of the liquid and the solid phase properties, e.g. liquid phase concentration, solid phase composition and particle size distribution, is of great importance to obtain accurate and robust estimations of the kinetic parameters. *In-situ* Raman spectroscopy has been recognized as a crucial technique enabling simultaneous estimation of the solid as well as of the liquid phase composition. The quantitative application of Raman spectroscopy, however, is known to be challenging due to influences of many process parameters, e.g. suspension density and particle size and shape. Using an extensive calibration set and multivariate data analysis tools such as PLRS and PCR, it has been shown that accurate and robust estimations of the solid composition as well as the solute concentration can be obtained. However, the development of such a calibration requires many calibration samples and inevitably a significant amount of work. In this paper, *in-situ* Raman spectroscopy has been applied in a quantitative manner to monitor a solvent-mediated polymorph transformation without the use of a calibration model. Based on the linear dependency of the Raman signal intensity on the solute and the solid concentrations, a detailed process model has been fitted directly on the measured Raman spectra. The resulting kinetic parameters have been compared to parameters obtained through the conventional pathway, i.e. obtained through fitting on the solid phase composition profiles resulting from a multivariate calibration model. The discrepancy between the obtained model parameters was found to be small and essentially the same descriptive process model was obtained. However, by fitting directly on the multivariate Raman spectra, a significant amount of calibration effort can be avoided. The applicability of this novel approach has been demonstrated thoroughly through the application to simulations of unseeded and seeded solid-state transformations as

well as through the application to various seeded polymorph transformations.

(178) **Crossed Beam Thermal Lens Spectroscopy for Standoff Detection of Chemical Species**

Tasha Messenger; [1]University of Maryland Baltimore County

Achieving reliable chemical standoff detection is a challenge and important goal for many applications, with direct implications to military safety. The armed forces currently employ an array of methods for the detection and dissemination of chemical warfare agents (CWAs). However, many of these systems require point-sampling and do not offer the added safety of standoff detection. Photothermal lens spectroscopy (TLS) offers a potentially powerful approach to CWA detection. We have developed a dual beam thermal lens spectroscopy system for the potential identification of chemical agents at range. A nanosecond pulsed Nd:YAG laser with a tunable OPO pumps the analyte of interest while a 780nm diode laser probes the sample. By using a 780nm diode laser as the probe beam, background interferences can be significantly minimized. As the excited target molecules relax from wavelength specific absorption by the pump beam, the localized temperature change associated with the non-radiative relaxation of these molecules results in a thermal gradient. This gradient alters the pathlength dependent scattering of the probe beam and triangulation of the crossed beams as well as the return time of the scattered light can be used to accurately determine the position and distance of the analyte. Model compounds have been evaluated for species detection, photodegradation, spatial resolution, and sensitivity employing both collinear and crossed beam geometries. While the collinear geometry shows higher sensitivity compared to the crossed beam configuration, due to the increase in spatial overlap of the two beams, the crossed beam system is capable of providing superior spatial resolution with only a small decrease in sensitivity. In addition, this paper will also discuss the application of this thermal lensing system for the detection of CWAs at range.

(179) **Solvent Diffusion Studies Through Polymer Membranes by Time Resolved FT-IR/ATR**

James Sloan[1]; [1]U.S. Army Research Laboratory

In order to understand membrane transport and thereby develop suitable membranes for protection and separation, there are a few characteristics of the membrane and the diffusing constituents that must be known. These include the molecular states of the diffusing components, their diffusion coefficients, fluxes and the membrane selectivity. The fundamental physical property required designing and optimizing polymers used as barriers and membranes or in polymer processing operations is the mutual diffusion coefficient. For many years, polymer/penetrant mutual diffusion coefficients have been measured using dip and weigh, GC and vapor sorption experiments. Neither of these methods allows the transport of two or more components to be monitored. Diffusion of small solvent molecules through polymer membranes has been studied by FT-IR-ATR. Polymer samples were deposited onto a horizontal IRE crystal and a challenge liquid mixture consisting of two penetrants was allowed to flow over the sample. The IR spectra at the polymer/crystal interface were monitored using conventional GC software allowing the kinetics of the transport process to be evaluated. The utility of this technique is illustrated by following the diffusion of a mixture of water and acetonitrile through a polymer material. The hydroxyl stretch at 3440 cm-1 and the cyano stretch at 2250 cm-1 were used to follow the water and acetonitrile diffusion. Such data allows the polymer materials to be evaluated as potential separation membranes. In another system, diffusion coefficients for various solvents in two different phase separated polymer systems are determined using time resolved FTIR-ATR spectroscopy. The diffusion coefficients were determined using a Fickian diffusion model in a framework for binary systems. In one system, we monitor the diffusion of various small alcohol molecules through a polar ionic polymer. In another case, we look at a polymer-penetrant pair that demonstrates strong molecular interactions.

(180) **Looking at Lipid Domains in Stratum Corneum Lipid Models using Vibrational Microspectroscopy**

Michel Lafleur[1], Sungjong Kwak[1], Aicha Ouakrim[1], Amine Touggant[1]; [1]Université de Montréal

The impermeability of the skin is intimately related to the structure of the stratum corneum (SC), the top layer of the epidermis. The fact that a considerable fraction of the lipids in this layer exists under a solid/crystalline form is believed to be a key factor in the low permeability of the skin barrier. We have characterized, using Raman and infrared microspectroscopies, the mixing properties of model mixtures that included ceramide, free fatty acids, and sterol, the 3 main lipid components of SC. We show that, in ternary mixtures with palmitic acid and cholesterol, the transformation of sphingomyeline, a precursor of ceramide, into ceramide leads to an increase of the heterogeneity of the spatial lipid distribution, in parallel with a significant increase of the conformational order of the acyl chains. Therefore the enzymatic conversion of sphingomyeline into ceramide leads to the transformation of a homogeneous and relatively disordered matrix into a heterogeneous matrix containing crystalline domains. These findings suggest that this transformation is a key event in the formation of the skin barrier. The heterogeneity in lipid composition for the ceramide/cholesterol/fatty acid system is observed by Raman micro-spectroscopy, from the microscopic local variations of the relative areas of the C-H stretching and the C-D stretching bands, the fatty acids being deuterated in our model mixtures. The thermal evolution of the mixing properties of the ceramide/palmitic acid/cholesterol mixtures indicated that an increase in temperature (above 50 °C) leads to the disordering of the fatty acid and, to a lesser extent, of ceramide. In parallel to this melting, a mixing of the lipid species is observed. By recording 196 spectra over a surface of 40 x 40 micrometers2, it was possible to establish that the areas enriched in palmitic acid were also enriched in cholesterol. These results suggest the formation of a fluid phase mainly composed of palmitic acid and cholesterol; this phase may ensure the cohesion between the solid domains. The recording of Raman spectra from several microscopic voxels provides a unique description of the phase composition and distribution of these model mixtures.

(181) **Instrument Selection Criteria for Near-Infrared Process Monitoring – Guidelines and Applications**

Roger Schirmer[1], Susan Foulk[1]; [1]Guided Wave, Inc.

Near-Infrared (NIR) spectroscopy has proven to be a valuable tool in monitoring many different process applications ranging from refinery measurements to pharmaceuticals to chemical production to sterilization. One key consideration when developing a NIR process measurement application is the wavelength range of the spectrophotometric analyzer. A full scanning spectrometer will provide the most flexibility when making measurements, but often times a measurement can be made with one or a handful of wavelength points. This paper will present some guidelines to making this choice accompanied by related application data. Applications will include data related to hydraulic fluid, biofuel production, and polymer process applications. As an example, Hydraulic fluid is a hygroscopic material with specifications for water content. While this can be a simple measurement with a two wavelength photometer in controlled situations, there are instances where a more sophisticated approach would be warranted. If temperature variations or some contamination is possible then a

multiple wavelength photometer would be required. If multiple stream monitoring is required then a full scanning system with multiplexing capability would be indicated. Guided Wave is in the unique position to address all of these hardware needs from a 2 wavelength measurement with a ClearViewTM analyzer to a multiple wavelength photometer measurement with a MultiView TM analyzer to a full scanning multiplexed system with the Guided Wave Model 412 NIR Process Spectrophotometer.

(182) **Determining Out-Of-Spec (OOS) Conditions with Fieldable FTIR and Raman Spectroscopy**

Robert Brush[1], Robert Green[1], Jeremy Linoski[1], Wayne Jalenak[1], Christopher Brown[1]; [1]Ahura Scientific, Inc.

Fieldable spectroscopic platforms based on FTIR or Raman spectroscopy offer an easily deployed, cost-efficient approach to achieve increased quality coverage. Performance attributes are important considerations for ruggedized spectroscopic hardware intended for point-of-need usage. Additionally, predictability of the sampling environment decreases significantly in real world field deployment. Truly field deployable instrumentation must break with traditional measurement protocols to provide intelligent control solutions assuring robust performance and consistent confidence levels. Oxidative degradation, atmospheric infiltration, as well as intentional or unintentional adulteration are all examples of routes through which incoming materials may reach out-of-specification (OOS) status. Overwhelming safety, quality and financial concerns justify an increased degree of incoming materials inspection to determine if process feeds are within required specifications. Examples of OOS issues abound within industrial arenas such as food, coatings, fine chemical and petroleum markets. This presentation will focus upon a broad survey of applications within markets specifically benefited by the ability to deploy portable analytical instrumentation. To further extend and complement the existing embedded analysis algorithms of these FTIR and Raman spectrometers, results derived from the application of prediction and classification models to adaptively acquired spectroscopic data will be presented.

(183) **Applications of a Hendheld FT-IR Spectrometer to the Study of Museum Objects**

Steven Barnett[1], Aniko Bezur[2]; [1]A2 Technologies, [2]The Museum of Fine Arts, Houston

FT-IR spectroscopy has been used for many decades in the art conservation field for a variety of applications. While providing valuable information, these methods have traditionally been limited by the need to remove samples from the artwork. The use of *in-situ* techniques, such as ATR, has alleviated this problem to some extent but difficulties often persist due to the spacial configuration of instruments, which is particularly limiting in the case of large works of art. This paper will present applications of a handheld FT-IR where the spectrometer is brought to the work of art. Specific examples related to photographs, sculptures, and paintings will be presented.

(184) **Studies of Lead(II) Halide-1,10-Phenanthroline Photosensitive Materials by FT-IR**

Dale L. Perry[1], Cecil R. Dybowski[2], Shi Bai[2], David Kragsten[2], Margaret J. Blake[1], Santiago Segarra[1]; [1]Lawrence Berkeley National Laboratory; [2]University of Delaware

Infrared spectroscopic studies of 1:1 and 1:2 complexes of lead(II) bromide and lead(II) iodide with 1,10-phenanthroline are reported. Vibrational assignments are made by comparison to reported spectra of the uncomplexed 1,10-phenanthroline molecule and to other metal ion complexes of 1,10-phenanthroline. Small shifts of the ligand vibrational bands are characteristic of the complexes, and stereochemical aspects of the complexes are discussed. Differences in the infrared spectra as a function of structure are discussed. This work was supported by the Petroleum Research Fund of the American Chemical Society, Grant Number 33633-AC5, the National Science Foundation under Grant CHE-0411790, and the U. S. Department of Energy under Contract Number DE-AC02-05CH11231.

(185) **Detection of Polymorphs in CL-20 using Infrared and Raman Spectroscopy**

Kathleen Alam, Laura Martin, Thomas Massis, Rachel Carlson; [1]Sandia National Laboratories

Hexanitrohexazaisowurtzetane, also known as CL-20, was the 20th explosive material created at China Lake Naval Weapons Center. Because of its desirable performance characteristics, CL-20 is being considered for use in explosive components. One area of concern regarding CL-20 is its polymorphic forms. At ambient pressure, there are four known polymorphs, á,â,ã, and å, with å being the most stable at ambient pressures and temperatures. These polymorphs have different densities and conversion may be possible during long term storage, thus changing its desired properties. Knowing the relative concentration of each polymorph within a mixture will be critical for evaluating the change in performance as a function of polymorph concentration. We have used both infrared and Raman spectroscopy to evaluate the relative concentration of polymorphs in a mixture, focusing on low concentrations of á,â, and ã within bulk å CL-20. Synthetic models were developed for each method and used to predict real mixtures. Results will be presented showing the detection limits of each method. Sandia is a multiprogram laboratory operated by Sandia Corporation, a Lockheed Martin Company, for the United States Department of Energy's National Nuclear Security Administration under Contract DE-AC04-94AL85000.

(186) **Synchrotron Infrared Microspectroscopy of Individual Strands or Cells in Mat Formation of Benthic Algae from Freshwater, Pristine Prairie Source**

Jason Murdock[1], John Reffner[2], David Wetzel[2]; [1]Kansas State University, Biology Division; [2]KSU Microbeam Molecular Spectroscopy Lab

Benthic algae forms on the bottom of pools or streams in a complex mat consisting of chemically different compositions. Nutrient uptake studies have been conducted on large algal cells at the subcellular level with mid infrared Focal Plane Array imaging techniques. Benthic algae is a nuisance in terms of clogging pipes and other water passageways. Its formation is influenced by the nutrients available in a close proximity to the algae surface. In this study, rocks covered with benthic algae were collected from a shallow stream located in a pristine prairie populated only by bison in the Konza Prairie Biological Reserve, of Kansas State University. Algae that are attached to the substrate surface at one end only are longitudinally freely moving and exposed on all sides to the nutrient containing water and the sun. The same type of algae with the underside attached by way of a membrane to the substrate has exposure only on the top surface. One objective of this study was a chemical comparison of the two formations. Another object was to isolate single strands or sub-aggregates within the mat to explore the heterogeneity that exists. Synchrotron infrared microspectroscopy was employed with confocal image masking to achieve localized analysis. In the mats probed, 9-10 um strands of algae were analyzed using a 8 um X 8 um confocal masking. Examples presented include a comparison of a fan shaped object in both the freely moving and surface attached algae found in a close proximity. Chemical compositional differences were revealed. In addition, different parts of individual strands that were analyzed showed distinctly different chemical composition.

(187) **Large Area FT-IR Imaging at High Spatial Resolution - How Differing Levels of Spatial Resolution Can Influence Interpretation**

Frank Weston[1], Jim Steensrud[1], Mustafa Kansiz[1]; [1]Varian, Inc

FT-IR Imaging using a 2-D Focal Plane Array (FPA) has established itself as a mainstream technique. With its unique ability to provide spectral (chemical), and spatial (positional) information, application areas are growing substantially. One application of particular importance and popularity are biological samples, including biomedical samples. The resulting infrared spectra and images acquired represent the total chemical composition of the sample under measure. The most prominent spectral features are those arising from macromolecular components, such as proteins, lipids, carbohydrates and nucleic acids. It is this unique ability, to provide spectral and spatial information in parallel that makes FT-IR FPA imaging a powerful technique in biological analyses. The premise that proceeding the morphological changes (often used as markers for the onset of disease), subtle chemical changes occur, allows for the possibility of using FT-IR for earlier detection of these chemical changes and hence possible earlier disease diagnosis. The ability to detect and locate exactly where these subtle chemical changes are occurring provides biomedical researchers with a powerful analytical tool.

(188) **IR Approaches for Quantitatively Measuring Silanol in Silicones**

Elmer Lipp[1]; [1]Analytical Sciences Dept., Dow Corning Corp.

Silanol (SiOH) groups are important in silicone chemistry because of their reactivity, both desirable and undesirable. We have developed a number of IR approaches for quantitatively measuring silanol levels in a variety of silicone fluids and resins. Each of these methods relies on the ability to control H-bonding, and most also rely on deuteration for either isolating silanol absorbances or measuring the ratio of water isotopes following partial deuteration. Per cent to low ppm levels are achievable with one of the available methods. The methods being used will be described in detail.

(189) **Moisture Migration and Intermolecular Relationships in Carbohydrate Films**

Janiece Hope[1], Allen Muroski[1], Doug Elmore[1], Sean Smith[1], Justin Kruger[1]; [1]Cargill, Inc.

The monitoring of moisture migration and crystallization within carbohydrate films is of importance in a number of commercial applications of carbohydrates, and is a critical issue for many food applications. In understanding the interrelationship of moisture with carbohydrates it is important to understand the rate of moisture migration within a carbohydrate system as well as to develop an understanding of the molecular interactions of carbohydrates within a mixture. Despite the prevalence of water and carbohydrates in food materials, there is very little literature to date in doing analyses of moisture diffusion using vibrational spectroscopy. We present work studying the rate of moisture migration in different sugar coatings materials utilizing IR microspectroscopic imaging techniques as well as FTIR kinetics work with multidimensional data analysis to understand the differences in intermolecular behaviors of the carbohydrate mixtures.

(190) **Nanomaterials: Computational and Chemometrics Methods towards "Nanotoxicology"**

Bakhtiyor Rasulev[1], Danuta Leszczynska[2], Jerzy Leszczynski[1]; [1]CCMSI, Jackson State University; [2]Civil&Environ Engineering, JSU, Jackson

Nanoscale materials find use in a variety of different areas, such as electronic, magnetic and optoelectronic, biomedical, pharmaceutical, cosmetic, energy, environmental, catalytic, and materials applications. Nanomaterials exhibit unique physical/chemical properties and impart enhancements to engineered materials, including better magnetic properties, improved electrical activity, and increased optical properties. Because of the potential of this technology, there has been a worldwide increase in investment in nanotechnology research and development. Use of nanomaterials in various industries is projected to increase dramatically in the future and environmental contamination by these materials is expected. Nanotechnology could lead to serious environmental problems. This is because it is still largely unknown how nanoparticles will impact the environment. Moreover, there is still a substantial need to comprehensively investigate all physicochemical and then biological properties of nanoparticles to predict possible impact to environment. Because of their unusual physical and chemical features, the study of nanoparticles as potential toxic agents requires an interdisciplinary approach, involving multiple aspects ranging from physics and chemistry to biology and medicine. Assuming that the peculiar properties of nanoparticles depends from both intrinsic physicochemical features and unusual size of particle, the complex study, including structural, physicochemical and size effects analyses are required to evaluate the toxicity effect of them. This complex approach can be named as computational nanotoxicology approach, which includes ab initio quantum-mechanical methods, quantitative structure-activity relationship methods, molecular modeling and nanoparticle-protein docking methods with utilization of experimental physicochemical and biological activity/toxicity data. Computational nanotoxicology assuming the extension of the traditional quantitative-structure-activity relationship (QSAR) paradigm to nanoparticles, and in this work we are discussing the possible ways of applying the various computational methods, including QSAR approaches for nanoparticles properties and toxicity study.

(191) **Characterization of Self-Forming Nanovesicles by Vibrational Spectroscopic Techniques**

Reinhard Bruch[1], Rajan Bista[1], Emilie Steinhoff[1], Thomas Huser[2]; [1]University of Nevada, Reno; [2]University of California, Davis

We present the first experimental study of self-forming synthetic nanovesicles, trademarked as QuSomes™, using vibrational spectroscopic techniques namely Near-Infrared (NIR) and laser tweezers Raman spectroscopy. Raman spectra of these new artificial nanovesicles suspended in Phosphate Buffered Saline (PBS) have been obtained by using an inverted confocal laser-tweezers-Raman-microscopy system in the spectral range of 3100 to 500 cm-1. This spectrometer works with an 80 mW diode-pumped solid-state laser, operating at a wavelength of 785 nm in the TEM00 mode. The laser is used both for optical trapping and Raman excitation. Similarly, NIR absorption spectra of these novel nanovesicles have been recorded in the spectral range of 9000-4800 cm-1 by using a new miniaturized micro-mirror spectrometer based on micro-optical-electro-mechanical systems (MOEMS) technology. The two amphiphiles considered in this study, differ in their hydrophobic chain length and contain similar hydrophilic polyethylene glycol (PEG) head groups. Such synthetic PEG coated lipids exist in liquid form at room temperature and spontaneously form liposomes (nanovesicles) upon hydration. In this work, we have focused on the band assignments for the spectra of single QuSomes™ nanovesicle acquired by means of both vibrational spectroscopic techniques. In particular, we have found that the most prominent bands in the studied spectral region of Raman spectra are dominated by vibrational modes arising from C-C and CH2 bonds. Similarly, NIR spectra are primarily assigned as first and second overtone of C-H stretching mode and second overtone of C=O stretching mode. These spectroscopic techniques have proven

to be an excellent tool to establish the fingerprint region revealing the molecular structure and conformation of QuSomes™ nanoparticles. The nanovesicles formed in suspensions confirm high stability and are therefore considered as potential candidate for varieties of future applications including lipid based novel substances and drug delivery systems.

(192) **Metal-Ion Binding Properties of Phosphoserine Immobilized on Magnetic Nanoparticles**

Anselm Omoike; [1]University of Michigan-Flint

O-phospho-L-serine was immobilized on magnetic nanoparticles during the precipitation of the particles and after precipitation of the magnetic nanoparticles. The nanoparticles were characterized by Fourier transform infrared spectroscopy and X-ray photoelectron spectroscopy. The potential applications of the nanoparticles in enrichment of Fe (III), Cu (II) and Zn (II) were examined by batch method at different pH (3.0 to 6.0) and fixed ionic strength of 10 mM. Both FTIR and XPS data confirmed the successful immobilization of phosphoprotein on the magnetic nanoparticles. The metal ion enrichment data indicate that the immobilized nanoparticles show higher affinity for both Fe (III) and Cu (II) and lower affinity for Zn (II).

(193) **Assessment of Accuracy for Non-Invasive Bone Raman Spectroscopy in Mice**

Kathryn A. Dooley[1], Matthew V. Schulmerich[1], Jacqueline H. Cole[1], Jaclynn M. Kreider[2], Steven A. Goldstein[2], Michael D. Morris[1]; [1]Chemistry, U. Michigan; [2]Orthopaedic Surgery, U. Michigan

Bone fragility is associated with changes in composition that are metrics of bone tissue quality. Currently, no *in vivo* techniques are available for assessing the composition contributions to bone quality in animals used for laboratory studies of disease states. We have developed a noninvasive Raman spectroscopic fiber-optic probe to acquire bone spectra through the skin of mice and other small animals; the geometry utilized is illumination in a line and collection in a disk-shaped area. The objective of this study is to investigate the accuracy for measuring bone composition parameters noninvasively in mice with this line/disk probe. The small size of mouse limbs require that great care be taken in positioning the fiber-optic probe to obtain valid results. Because mouse bones are small, the transcutaneously detected bone Raman spectrum from them is less intense than those from larger specimens, for which probe placement is less critical. In addition, probe placement on the small mouse limb can affect the background fluorescence from skin melanin, complicating background subtraction. We discuss the design of fiber-optic probes for noninvasive spectroscopy of small animal limbs, with emphasis both on distributed laser light to avoid thermal damage to the tissue and on strategic placement of collection fibers to maximize bone spectrum recovery. With the line/disk probe, the recovered bone factors and exposed bone spectra did not differ significantly ($p=0.12$), as measured by the carbonate-to-phosphate ratio. Also, the average cross-correlation coefficient between the transcutaneous and exposed bone spectra was 0.96. Preliminary measurements on rat and canine limbs demonstrate that the spectroscopic measurement of bone quality is easily adapted to these larger animals with only minor changes in the placement and spacing of optical fibers.

(194) **Applications of Micro-Raman Spectroscopy for Detection of Cancer and Viruses**

Lori Kamemoto[1,2], Shiv Sharma[1], Anupam Misra[1], Qigui Yu[2], Ningjie Hu[2], Hugh Luk[3], Marc Goodman[3], Pavel Zinin[1]; [1]Hawaii Inst. of Geophysics & Planetology; [2]John A. Burns School of Medicine; [3]Cancer Research Center of Hawaii

We will review data demonstrating that near-Ir laser excited micro-Raman spectroscopy is a powerful analytical tool for detecting critical differences in biological samples, and can be developed in the future as a screening tool for cancer and viruses. Cervical cancer and normal cervical tissues were obtained from human subjects, and were flash-frozen immediately after removal of the surgical specimen. Flash-frozen tissue specimens without any additives were then analyzed with Raman spectroscopy. Assistance in determining the correct areas to be examined were obtained by staining sections for pathological identification, and the presence of staff with expertise in histology. Cervical cancer and normal cervix were analyzed in the presence of a surgeon, histology technician and Raman specialist, to ensure identical spectroscopic conditions and positive identification of the tissue to be examined. Raman spectra of cervical cancer cells show significant intensity differences in comparison to that of the normal epithelial cell spectra. These differences were visibly significant. In another set of experiments, chicken embryo fibroblast cells were infected with ALVAC virus labeled with green fluorescence protein (GFP). Raman spectra of several individual normal uninfected and infected chicken embryo cells were collected under identical spectroscopic conditions. All spectra were observed with a NIR micro-Raman system utilizing a 785 nm laser with 10 mW of laser power. A 60 second integration time and 50 micron slit width was used for all Raman spectra of individual cells. Visual identification of infected cells was made using GFP as marker for the virus infected cells. Raman spectra of virus infected cells showed significant differences in comparison to that of normal cells. New Raman bands at 536, 854, 925 and 1086 cm-1 were observed in the virus infected cells. Apart from the presence of new Raman peaks in the spectra of the infected cells, there are significant differences in the relative intensities of various Raman peaks, which can also be used as analytical tool for detecting icells nfected with ALVAC Virus.

(195) **Atmospheric Pressure Surface Sampling and Ionization**

Gary Van Berkel; [1]Oak Ridge National Laboratory

The success of any analytical measurement is often dictated by the inital sampling process. In analytical mass spectrometry, the success of an experiment requires the ability to form the desired ions of the analyte with high efficiency. This presentation will discuss work in my group to develop approaches that combine together sampling of surfaces and ionization of analytes, both at atmospheric pressure, for analysis by mass spectrometry. Following a brief introduction of this emerging field, sometimes called ambient mass spectrometry, emphasis will be given to our work with liquid microjunction surface sampling probes. The basics of this sampling and ionization approach will be overviewed and applications such as coupling planar separations with mass spectrometry and spot sampling thin tissue sections for drug metabolism and disposition studies will be highlighted.

(196) **The Role of Human Salivary Defensin Peptides in Response to Vaccination**

James Stephenson[1], Michael Gardner[1], Megan Rowland[1], Jonathan Bundy[1]; [1]Research Triangle Institute

Defensins are highly basic cationic peptides that not only play a role the innate and adaptive immune response, but are also important in biomedical based research on HIV-1, cystic fibrosis, Crohn's disease, tumor classification, and have promise in the pharmaceutical field as a new class of antibiotics. Here we present

a parallel assay for the alpha (HNP1-3) and beta (HBD1-2) classes of defensins in saliva that varies in dynamic range from to 1 ng/mL to10 ug/mL. The method utilizes solid phase extraction of saliva samples combined with a peptidomic method to identify and quantitate defensin targets. The approach involves limited saliva sample manipulation and is easily amenable to automation. The saliva samples analyzed are derived from a large cohort study to understand the role of polymorphisms in genes of innate and adaptive immunity in modulating the response to vaccination for two gastrointestinal tract infections: typhoid and cholera. The alpha-defensin levels observed range from 1 to 10 ug/mL and correlate well with known active concentrations for a variety of microorganisms. The concentration range for beta-defensins was between 1-33 ng/mL. This method is easily adapted for use in a clinical immunology setting, and can be modified for other biological matrices. The biological impact of this approach will come from the ability to examine production, secretion, and regulation of defensin peptides in a direct fashion. Statistical correlation of expression levels with response to vaccination, age, and gender will be presented as it pertains to the relevant aspects of innate and adaptive immunity.

(197) **Mass Spectrometry Strategies to Identify Lipid Biomarkers of Disease**

Gavin Reid[1], Todd Lydic[1], Xi Zhang[1], Rheal Towner[2], Julia Busik[1]; [1]Michigan State University; [2]Oklahoma Medical Research Foundation

There is an increasing recognition of the important role that cellular lipids play in the regulation of normal cell function, and of the role of aberrant lipid metabolism in the onset and progression of several diseases, including diabetes, diabetic complications and cancer. However, the enormous complexity of membrane lipid structures that arises from the attachment of fatty acids with different chain lengths and degrees of unsaturation to a glycerol, phosphoglycerol, sphingoid or sterol backbone, as well as the presence of chemically diverse functional headgroups in these molecular species, provides a significant analytical challenge to the development of robust high throughput mass spectrometry based strategies to characterize the global lipid compositions of normal cells or tissues, and to identify and quantify the changes in lipid profiles or modification states that occur as a function of the onset and progression of disease. This presentation will describe results from our recent studies aimed at (i) developing a detailed understanding of the gas-phase fragmentation reactions of protonated or deprotonated precursor ions of various lipid classes, as well as their various ionic-adducts (e.g., Na+, Cl-, CH3OCO2-), and (ii) the development and application of robust, high throughput and sensitive 'shotgun' tandem mass spectrometry (MS/MS) based lipidomics approaches using multiple lipid-class specific precursor ion and neutral loss scan mode experiments in a triple quadrupole mass spectrometer, or multistage (MSn) tandem mass spectrometry in a quadrupole ion trap mass spectrometer, to characterize and quantify the temporal changes in lipid profiles associated with the onset of diabetic retinopathy in a streptozotocin induced rat model, and in the development of hepatocellular carcinoma in a transgenic mouse model.

(198) **Peptide Fragmentation Assisted by Low Temperature Plasma**

Yu Xia[1], Zheng Ouyang[2], R. Graham Cooks[1]; [1]Department of Chemistry, Purdue University; [2]Weldon School of Biomedical Engineering

All experiments were carried out using a Finnigan LTQ (Thermo Electron Corp., San Jose, CA). A T-shape glass tube (OD: 7.8 mm, ID: 4.8 mm) was placed directly in front of the heated capillary of the mass spectrometer. A nano-electrospray (nano-ESI) emitter was inserted into the glass tube in line with the mass spectrometer inlet with a distance of 2 cm. A helium low temperature plasma (LTP) was effected in the T-shape glass tube by applying an ac (30 kHz, 3 kV) to two electrodes attached on the outside wall of the tube while using the glass wall as dielectric barrier for discharge. The helium LTP was turned on while the nano-ESI emitter was inside the plasma region for 2 minutes. After the plasma was turned off, a high voltage (1-2 kV) was applied to the nano-ESI emitter containing peptide solution and the subsequent mass spectrum was recorded. A series of peptides with various sequences and different sizes (5-30 amino acid residues) were studied. Fragments due to amide bond cleavages were generally observed giving rise to a-, b- and y-type of fragments. The fragmentation patterns for all the peptide ions observed after LTP treatment, however, were very different from their ion trap CID data. For example labile modifications such as phosphoric acid groups were preserved for molecular ion species and for the fragment ions which should have the modifications. When the high voltage applied to the nano-ESI emitter was relatively low, the fragmentation could last for more than ten minutes for each two minute plasma treatment. In addition to fragment ions, several adduct ions were also observed with a 63 Da mass increase from the protonated molecular ions, which was possibly due to the addition of HNO3 generated from the LTP. A mechanistic study was carried out on the possible causes of the fragmentation induced by LTP. It was found that the discharge barrier surface for the LTP was not involved in inducing peptide fragmentation, while the surface of nano-ESI emitters played a role. Deionized water, which was stored in nano-ESI emitters and subjected to LTP was analyzed via inductively coupled plasma mass spectrometry (ICPMS). The elemental analysis results showed increase of concentrations for various metals, which were released from the wall surface of the nano-ESI emitter (made from borosilica glass) to the solution during plasma. The same fragmentation pattern to that obtained after plasma treatment was reproduced in the nano-ESI of peptide solution by directly adding high concentration of electrolyte. The fragmentation process was proved to be occurring at atmospheric pressure before charged droplets or ions entered a mass spectrometer. A hypothesis for the ion activation and dissociation was proposed based on the observed results.

(199) **Towards Nanoscale Chemical Imaging: Investigation of Near-Field Optical Processes for Use in Atmospheric Pressure Desorption/Ionization Mass Spectrometry**

Douglas Goeringer[1], Kent Meyer[1], Olga Ovchinnikova[1], Kin Ng[2]; [1]Oak Ridge National Laboratory; [2]California State University Fresno

Prerequisite to creating and using nanomaterials to control molecular level processes is the capability for nanoscale chemical imaging. Although scanning probe microscopy techniques enable the framework of matter to be ascertained at the atomic scale, the associated images inherently provide no information about chemical composition and molecular structure. More recently, near-field scanning optical microscopy (NSOM) imaging has been combined with fluorescence, Raman, and infrared systems to produce spectroscopic information at unprecedented spatial resolution (~100 nm). In NSOM optical spectroscopy, a laser-illuminated, pointed probe produces intensity enhancement in a localized region at the apex and comparable in diameter to the tip (as small as 20 nm). Because the optical near-fields responsible for optical excitation in NSOM spectroscopy also can produce nanoscale surface effects, the tip can presumably function as a near-field, desorption/ionization source for MS chemical imaging at unprecedented nanometer-scale spatial resolution. The modifications that have been made to adapt an atomic force microscope (AFM) for investigation of tip-enhanced, near-field

desorption/ionization MS under atmospheric pressure conditions will be presented, and the results of on-going experiments with the instrument will be described.

(200) **Space Charge Effects and Ion Motion Control in the Orbitrap Mass Analyzer**

Richard H. Perry[1], Gary A. Salazar[1], Robert J. Noll[1], Wolfgang Plass[2], R. Graham Cooks[1]; [1]Purdue University; [2]II.Physikalisches Institut

Mass spectrometry (MS) is a highly regarded analytical technique owing to its speed, high sensitivity and its utility in structurally characterizing a wide range of analytes. Advances in genomics, proteomics, and metabolomics increasingly require the analysis of complex mixtures containing a variety of chemical compounds with concentrations spanning many orders of magnitude. These challenges demand instruments with better performance characteristics including resolution, mass accuracy, dynamic range, and tandem MS capability. Many of these demands were met with the recent introduction of the orbitrap mass analyzer, an ion trap comprised of a spindle-like inner electrode and a barrel-like outer electrode with a DC potential applied between them. Stable ion trajectories involve motion around and along (axial plane) the central electrode. The axial frequencies of the confined ions are determined by differentially amplifying the image current induced on the outer electrode (split at z = 0), followed by fast Fourier transform to yield a frequency (and hence mass-to-charge) spectrum. The orbitrap has high resolving power (150,000) and mass accuracy (less than or equal to 5 ppm), as well as low complexity and cost relative to other high-performance analyzers including FT-ICR. Until recently, few studies have probed the fundamental properties of the orbitrap, which is necessary if its performance is to be improved. In previous work in our laboratory, small mass shifts, thought due to ion-ion interactions, were observed in orbitrap mass spectra. In the current paper, a systematic study of space-charge effects on ion motion and performance characteristics is undertaken. These effects can be mitigated in some cases by applying AC waveforms to the outer electrodes to rephase confined ion populations. Experimental results were obtained using a prototype instrument that has a smaller orbitrap (20 mm diameter) than the commercial instrument (30 mm diameter) and thus space-charge interactions may be stronger. Our own simulations (Ion Trajectory SIMulation software, ITSIM 6.0) suggest that confined ions are nearly harmonic oscillators and provide a model to understand ion-ion interactions and the mechanism of rephasing. Effects of ion number and initial ion positions have been studied. Simulations will be compared with experimental results.

(201) ***In situ* Quantitative Evaluation of Saturation vs. Unsaturation in Biodiesel Production**

Dale LeCaptain[1], David Allan[1], Michael Todd[1], Doug Hasso[1]; [1]Central Michigan University

Solving the growing energy crises will likely require a combination of energy sources to decrease petroleum demand. Biodiesel is made from plant oils either directly or from waste plant and animal oils. A major production issues for using waste streams as the biodiesel production feedstock is effectively controlling the cloud point of the biodiesel. The cloud point is the temperature at which the non-homogenous material starts to solidify or freeze. This solidification is a direct result of the chain length and degree of saturation. Demonstrated here is the application of *in situ* Raman spectroscopy for the determination of saturation level during biodiesel production.

(202) **Raman Spectroscopic Analysis of Warrior Wound Biopsies: What Happens when Good Wounds Go Bad?**

N. J. Crane[1], T. S. Brown[1], J. S. Hawksworth[1], F. A. Gage[2], D. Tadaki[2,3], P. W. Perdue[2], J. R. Dunne[2], J. W. DeNobile[2], E. A. Elster[2,3]; [1]Naval Medical Research Ctr.; [2]Naval Medical Research Ctr.; [3]Uniformed Services Univ. of Health Sci.

Wound healing is the result of complex cellular and molecular signals, ultimately leading to closure of the wound gap and the formation of scar tissue. It is believed that the molecular environment of the wound plays a large role in the fate of the wound. In some unfortunate cases, the clinical outcome is either delayed wound healing or wound dehiscence (the parting of the surgical layers of a wound). One theory of failed wound pathogenesis is inflammation, followed by fibroblast senescence, which preceeds an inability to deposit collagen, finally resulting in poor wound breaking strength. In chronic wounds, this pathogenesis is prompted by a prolonged inflammatory response, while in acute wounds, this pathogenesis is prompted by an exaggerated inflammatory response. As such, much remains to be learned about the structure and composition of the tissue itself during the wound healing process. There is a lot of inter-observer variability in wound assessment and even experienced surgeons sometimes have difficulty predicting whether or not a wound will heal normally. Current methods for wound assessment are clinically based on and include criteria such as the patient's general condition, injury location, perfusion in and around the wound, and the gross appearance of the wound (i.e. is the wound bed granulated or plagued by biofilm). Many of these observations, however, are subjective. We have examined several wound biopsies from patients with wounds that either exhibited normal healing or impaired healing. Decreased collagen and nucleic acid content are demonstrated in wounds with impaired healing. Because Raman spectroscopy can detect molecular changes such as structure and content, it could offer a potential objective diagnostic for assessing the status of wounds.

(203) **Raman Spectroscopy, a New Tool for Early Diagnosis of Osteoarthritis**

Karen A. Esmonde-White[1], Gurjit S. Mandair[2], Farhang Raaii[4], Francis W.L. Esmonde-White[2], Blake J. Roessler[3], Michael D. Morris[2]; [1]University of Michigan, Biomedical Engineering; [2]University of Michigan, Chemistry; [3]Univ. Mich. Medical School, Rheumatology; [4]Wayne State Univ., Orthopedic Surgery

Raman spectroscopy is an invaluable musculoskeletal tissue diagnostic, enabling the identification of bone spectroscopic markers to micro-damage and age-related fragility disorders, such as osteogenesis imperfecta and osteoporosis. In this study, we demonstrate feasibility of adapting some of these Raman methodologies to evaluate changes in joint fluid composition and to identify cartilage-condition markers associated with osteoarthritis (OA). Synovial fluid aspirates taken from forty human patients with various grades of osteoarthritis were deposited directly onto solid substrates. The synovial fluid droplets were allowed to dry prior to examination using a near-infrared Raman microprobe. Using standard univariate and multivariate classification methods, we show that Raman spectra obtained from these dried droplets correlated with joint damage severity as measured by conventional radiographic scoring methods used by clinicians. Our preliminary results provide the first real indication that Raman spectroscopy would be a suitable candidate for the evaluation of joint damage in OA patients. A Raman-based tissue diagnostic is highly appealing as the approach is fast, does not require ionizing radiation, and would enable long-term monitoring of therapeutic interventions. Cartilage or underlying bone tissue (subchondral bone) taken from murine-models of OA was also examined. Raman spectra of subchondral bone acquired from healthy and damaged specimens

indicate that subchondral bone is also affected by OA. Finally, we outline the design of a novel Raman-based arthroscopic probe, which could be used to examine subchondral bone in a clinical environment.

(204) **Development of Raman-Based Techniques for Biomedical Spectroscopy and Imaging**

James Chan[1,2]; [1]Lawrence Livermore National Laboratory; [2]NSF Center for Biophotonics, UC Davis

Raman spectroscopy has experienced a tremendous growth in its application to biological and biomedical research over the past ten years, primarily because it offers attractive capabilities not easily found in standard biological methods. It is one of the few techniques available that can obtain biochemical information from live cells and tissues nondestructively, noninvasively, and without exogenous labels. The advancement of this field requires research that focuses on both developing new Raman-based instrumentation and demonstrating their relevance to biological and biomedical research. Our group has been developing different Raman-based techniques for the spectroscopic analysis and microscopic imaging of different biological samples. A laser trapping Raman spectroscopy (LTRS) technique, which has several advantages over standard Raman techniques, has been developed that is suitable for the chemical analysis of small particles and cells in solution. This talk will include a discussion of the different applications of LTRS that have been pursued in our lab, such as its use for biodetection, cancer detection, cardiovascular research, regenerative medicine, and studying single cell dynamics. In addition, our recent efforts in developing a microfluidic-based LTRS system for cell delivery, analysis, and sorting to achieve a prototype 'Raman-activated cell sorter' will be presented. Our group has also been developing novel coherent anti-Stokes Raman scattering (CARS) microscopy techniques based on time-resolved detection for Raman imaging of cells and tissues. These techniques improve upon the current CARS techniques by simplifying the instrumentation and providing a new method for detecting weak Raman signals above the strong autofluorescence that can be generated in many biological samples. This work was supported, in part, by the Laboratory Directed Research and Development Program at Lawrence Livermore National Laboratory, the National Science Foundation Center for Biophotonics, and the UC Davis Cancer Center. The Center for Biophotonics, an NSF Science and Technology Center, is managed by the University of California, Davis, under Cooperative Agreement No. PHY 0120999. This work was performed under the auspices of the U.S. Department of Energy by Lawrence Livermore National Laboratory under Contract DE-AC52-07NA27344.

(205) **Spatially Offset Raman Spectroscopy for Depth-Sensitive Measurements in Excised Breast Tissues**

Matthew Keller[1], Anita Mahadevan-Jansen[1]; [1]Vanderbilt University

Most women with early stage breast cancer have the option of breast conserving therapy, which involves a lumpectomy for the complete removal of the primary breast lesion with tumor-free margins, followed by radiotherapy. Since the presence of tumor in the excised specimen within 1-2 mm of the surgical margin is strongly correlated with the risk of local tumor recurrence in the breast, there is a need to develop a non-invasive, real-time tool that can evaluate the margin to assure complete removal. Previous results in our lab indicate that Raman spectroscopy can rapidly classify *ex vivo* breast tissues into four histopathological categories with 99% accuracy. Standard Raman probe configurations, however, cannot interrogate tissue to the desired depths for this application. Spatially offset Raman spectroscopy (SORS) has recently been developed to examine strong Raman scatterers such as bone or calcifications through several mm of soft tissue. We have explored the use of this general technique for detecting tumor signatures under various depths of overlying normal tissue, both with phantoms and human breast tissues. Preliminary results indicate that while standard probe configurations cannot interrogate to the desired depth of up to 2mm, spatial offsets of 2 to 3 mm can detect tumor-like signatures under normal, fatty layers of tissue with a relatively short integration time.

(206) **Correlating Cell Biochemistry and Fungal Lifestyle using FTIR, Raman and SERS Spectroscopy**

Kathleen M. Gough[1], Rusty J. Rodriguez[2,3], Regina S. Redman[2], Susan G.W. Kaminskyj[4], Merrill Isenor[1]; [1]Univeristy of Manitoba; [2]University of Washington; [3]US Geological Survey; [4]University of Saskatchewan

Fungi have a major impact on both humans and the environment. Many fungi play a mutualistic role: mycorrhizae support the growth of terrestrial plants by conferring stress tolerance or protecting them against pathogens, while benefiting nutritionally from the plant. We are using synchrotron Fourier transform infrared (sFTIR) spectromicroscopy, Raman and Surface-enhanced Raman scattering (SERS) microscopy to obtain spatially resolved biochemical information about endophytic spores and hyphae. Previous work in our group includes the characterization of hyphae from the saprotrophs Aspergillus nidulans and Neurospora with sFTIR in order to examine biochemical differences between species at hyphal tips and along hyphae in optimal and stressful environments. Raman and Surface-enhanced Raman scattering (SERS) have also been used to examine A. nidulans, grown on commercially available Klarite substrates (www.d3technologies.co.uk). In the present work, we are studying the spores and hyphae of three endophytes, Curvularia protuberata, Fusarium culmorum and Colletotrichum magna, with sFTIR, Raman, and SERS to learn more about their biochemical composition and how it varies between different strains of the same species. C. protuberata confers heat tolerance, but the second strain does not. The two strains of F. culmorum are obtained from marine and non-coastal plants. The first confers salt tolerance; the second does not. C. magna is a plant pathogen but a single gene insertion has produced a mutualistic strain. Questions being addressed include the ways in which metabolic strategies (efficient use of resources) differ for endophytes and saprotrophs, and the effects of growing the endophyte fungi under stressful conditions related to their isolation host plant, compared to congeneric saprophytes. Fungal hyphae are ideal candidates for cell composition analysis at high spatial resolution, permitting us to develop and validate new analytical approaches and to exploit the potential for correlation of results from multiple spectroscopic techniques.

(207) **Chemometric Analysis as a Means to Differentiate Class Evidence**

John Goodpaster; [1]IUPUI

Upon being presented with a questioned and known sample of evidence, the duty of the forensic scientist is to evaluate if the two samples may share a common origin. This can be accomplished by examining class characteristics, or features that can distinguish groups of samples from one another but cannot individualize an item. Hopefully, the probability of two unrelated samples having indistinguishable class characteristics is low. However, the burden is on the forensic scientist to evaluate this risk by demonstrating that the sample type in question is inherently diverse. Furthermore, reliable laboratory techniques must exist that can discern this diversity in both pristine and evidentiary samples. Chemometric techniques are well suited to address these issues and multi-variate approaches have been increasingly used to study data and sample types that are relevant to forensic science. In particular, this talk will discuss the use of multi-variate statistical methods such as

agglomerative hierarchical cluster analysis, principal components analysis and discriminant analysis on various types of data such as GC/MS and UV-visible absorbance spectra. Specific applications to be discussed include the analysis of ink using Pyrolysis GC/MS and differentiation of red hair dyes using UV-visible microspectrophotometry. By combining instrumental and statistical techniques, issues such as the extent to which evidence can be truly differentiated, which analytical techniques are more discriminating, and quantitative associations of questioned and known samples can be addressed.

(208) **Chemometric Analysis of LIBS Data: Identification of Explosives**

Candice Bridge[1], Michael Sigman[1], Martin Richardson[1]; [1]University of Central Florida

A series of organic analytes were examined by LIBS, both as solid substrates and at trace levels as thin films on solid supports. The samples were analyzed in air and argon atmospheres and the intensities of the C (I) (247.88 nm), CN (0,0) (388.27 nm) , C2 (0,0) (516.41 nm) and O (I) (777.25 nm) emissions were examined by principle components analysis (PCA). Spectral ranges incorporating the C (I) (247 – 249 nm), CN (383 – 390 nm), C2 (515 – 517 nm) and O (I) (776 – 778 nm) emission bands were also treated by PCA and the results compared to the individual peak data. The resulting PC vector loadings were analyzed by Euclidean distance cluster analysis to identify groupings and trends that could be related to chemical structure and/or elemental composition of the analytes. Effects of the atmosphere (air versus argon) and the nature of the analyte (bulk solid versus thin film) will be addressed. The PC models were applied to data from a duplicate set of samples that were analyzed by LIBS and the Euclidean distancees to each of the original PC loadings were used to create receiver operating characteristic (ROC) curves. The ROC curves provide a method of assessing the utility of LIBS-PCA for identification of organic analytes. This work emphasizes the analysis of secondary high explosives and related compounds for forensic and security applications. This work was supported under award number W911NF0610446 from the US ARO MURI program on Ultrafast Laser Interaction Processes for LIBS and other Sensing Technologies, award number 2004-IJ-CX-K031 from the Office of Justice Programs, National Institute of Justice, Department of Justice, and by the State of Florida. Points of view expressed in this presentation are those of the authors and do not represent the official position of the sponsoring organizations.

(209) **Comparison of Differential Mobility Spectrometry and Mass Spectrometry for Gas Chromatography and Two-Way Classification of Ignitable Liquids from Fire Debris**

Yao Lu[1], Peter Harrington[1]; [1]Ohio University

The forensic significance of arson analysis accelerates the applications of new technologies in this area. In facing of the recently reported methods of arson analysis, the performance of differential mobility spectrometry (DMS) was quantitatively compared with mass spectrometry (MS) for gas chromatographic detection of ignitable liquids from fire debris on the two-way data with a novel mathematic tool, projected difference resolutions (PDRs). A fuzzy rule building expert system (FuRES) was also applied for the classification of seven kinds of ignitable liquids based on two-way GC-DMS and GC/MS data analysis, respectively. The results show that mass spectra data exhibit more structural information than DMS data, while DMS chromatograms are more elucidative than MS chromatograms for pattern recognition. For the purpose of classification of different types of ignitable liquids, two-way data objects were more effective than integrated chromatograms or spectra.

(210) **Performance Evaluation of a Sensitized Thermal Detector for Infrared Forensic Visualization of Blood Stains on Fabrics using Chemometrics-Driven Simulations**

Heather Brooke[1], Megan Baranowski[1], Jessica N. McCutcheon[1], Anthony R. Trimboli[1], Stephen L. Morgan[1], Michael L. Myrick[1]; [1]University of South Carolina

An infrared camera sensitized to specific spectral regions for the detection of blood at crime scenes is under development in our laboratory. Sensitization is accomplished by depositing onto the camera detector a film of material similar to the analyte to be detected, and/or by using appropriate filter material(s). Our design evaluation process is driven by MatLab® simulations in which the spectral response of the camera to a particular sample is convoluted with the effects of the deposited film and filtering materials. Diffuse reflectance spectra were taken from a variety of textile fabrics, both neat and doped with blood at varying concentrations. The spectral response of the camera system is then employed, in conjunction with measures of discriminating ability based on principal component analysis (PCA) and/or linear discriminant analysis (LDA) to evaluate the performance as instrumental design parameters (film types, thickness, etc.) are adjusted to determine optimal material combinations for the sensitizing film and filter(s). These simulation results are compared with experimental results from an unmodified microbolometer camera to validate the development of this instrument. Preliminary results indicate significant differences between substrates, as well as between neat and blood-stained fabrics.

(211) **Forensic Applications of Multivariate Statistical Methods for Discrimination of Trace Evidence**

Stephen L. Morgan[1]; [1]University of South Carolia

Identification of patterns in data and interpretation of observed differences is a frequent task for the forensic chemist. A fiber examiner might evaluate likelihood of associations between known and questioned fibers with microspectrophotometry. A trace evidence chemist might compare pyrolysis gas chromatograms of a paint chip left on a bicycle at a hit-run incident and chromatograms of paint from suspect vehicles. An arson investigator, in attempting to match headspace gas chromatograms from questioned fire debris with chromatograms of known accelerants, often looks for familiar features to reduce the complexity of the data. One issue of concern with the use of any “new” technique in forensics is that its validity and relevance applied to a particular forensic question may be challenged in court. Admissibility of scientific in the courtroom (1) depends on several factors including whether the scientific technique has been tested in an objective manner, whether it has been subject to peer review and publication, whether the rate of error has been established, whether standards and controls have been maintained, and the degree to which the technique has been generally accepted in the scientific community. Multivariate statistical methods not only can be employed to address the statistical significance of differences in patterns in all the above forensic situations, but also has a well established basis in both theory and practice. In part to address the issue of error rate, forensic scientists have used the term ‘discriminating power’ to refer to a particular techniques ability to discriminate between different evidence samples. However, as discriminating power is often measured, the effect of experimental uncertainty in the analytical chemical data is overlooked. This paper offers a short review of methodologies, along with forensic discrimination applications in which analytical chemical data has been treated with multivariate statistics. The objective of this presentation is to provide analytical chemists and forensic scientists with a basic understanding of these powerful data analysis tools. (1) Daubert vs. Merrill Dow Pharmaceuticals, Inc. (1993) 509 U.S. 579, 113 S. Ct., 2786, 2796.

(212) **Evaluation of Chemometric Approaches for the Analysis of Textile Fibers via Room-Temperature Fluorescence Excitation-Emission Matrices**

Krishna veni Appalaneni[1], Matthew Rex[1], Hector Goicoechea[2], Andres Campiglia[1]; [1]University of Central Florida; [2]Universidad Nacional del Litoral

The discrimination power of multivariate curve resolution-alternating least squares (MCR-ALS) and parallel factor analysis (PARAFAC) are evaluated for the analysis of room-temperature fluorescence excitation emission matrices (RTF-EEM) recorded from textile fibers and their respective extracts. RTF-EEM data formats are directly recorded from non-extracted fibers with the aid of a sample holder specially designed to optimize signal-to-background ratio. We demonstrate that the combination of RTF-EEM spectroscopy to chemometric analysis provides a valuable tool for non-destructive analysis of forensic evidence.

(213) **Novel Hollow Gold Nanospheres: Synthesis, Structure, Plasmon Absorption, SERS, and Photothermal Cancer Therapy**

Jin Zhang[1], Adam Schwartzberg[1], Tammy Olson[1], Chun Li[2]; [1]UC Santa Cruz; [2]UT M. D. Anderson Cancer Center

Metal nanomaterials have attracted considerable attention due to their novel properties and potential applications. Optical properties of metal materials strongly depend on the shape of the nanostructure. It is therefore possible to manipulate the shape to obtain the desired optical properties for specific applications of interest. We have recently synthesized and characterized a new metal nanostructure, namely hollow gold nanpphsere (HGNS), that has unique structural and optical properties. By controlling the wall thickness and diameter of these HGNSs, narrow and tunable absorption in the entire visible to near IR region can be obtained. The narrow absorption band, due to the structural uniformity, results in highly consistent SERS (surface enhanced Raman scattering) results based on single HGNS SERS measurements. In addition, hollow Au-Ag double wall nanosphere have been designed and successfully synthesized that show enhanced SERS activities over HGNSs. SERS offers both molecular specificity and extremely high sensitivity and is an ideal analytical tool for chemical and biological detection and imaging. The metal substrate for SERS is a critical component for high quality SERS measurements. Furthermore, the unique combination of spherical shape, small size (30-50 nm), strong, narrow and tunable plasmon absorption of the HGNSs, make them an ideal system for photothermal imaging and therapy of cancer. Both *in vitro* and *in vivo* studies using carcinoma cancer cells have been successfully demonstrated. In addition, hollow Au-Ag double wall nanosphere have been designed and successfully synthesized that show enhanced SERS activities over HGNSs.

(214) **Two Novel Nanoscale Phenomena**

Ting Guo[1]; [1]University of California, Davis

Two recent discoveries made in the Guo lab in UC Davis will be discussed. The first is nanoscale energy deposition afforded by gold nanoparticles as a result of x-ray absorption. The detection of such deposition is achieved with strand breaks of DNA molecules in solution. A direct application of this new concept is improved x-ray therapy. Other potential applications will be discussed. The second discovery is catalysis by nanomaterials in which nickel nanoparticle catalysts immobilized on single walled carbon nanotubes demonstrated extremely high catalytic activity toward carbon dioxide reforming of methane. Mass spectrometry is used to determine the turnover rates of this and other control catalysts.

(215) **Multilayered Nanospheres as Scattering Probes with Multiple Resonances**

Anil Kodali[1], Rohit Bhargava[1]; [1]University of Illinois

Metal-dielectric nanoprobes of multilayered spherical structure have the potential to improve the sensitivity of detection in imaging modalities based on elastic scattering like optical coherence tomography, light scattering spectroscopy, polarization spectroscopy as well as inelastic scattering processes such as Raman Scattering. They offer stable, reliable signals and are not limited by artifacts like photo bleaching, blinking etc. Further, they possess high optical tunability in their far-field scattering properties with respect to configuration. Geometrical parameters like number of layers, relative layer size and total size of the sphere can be used to design probes with resonances at desired excitation. The types of dielectric and metal used effect the resonance peak position and height. The tunability of resonance peak width with respect to these parameters also provides an opportunity to create several probes with multiplexing capability in visible and NIR excitation range. We present here the effect of varying different parameters of these probes on their far-field properties by using an analytical Mie-based solution. A stable recursive computational formulation is implemented to evaluate electromagnetic scattering. We specifically address an optimization technique to design probes with maximal multiple scattering resonances. The constraints due to feasibility of fabrication on such optimized structures will be examined. Finally we make a comparison of the multilayered structures with other dielectric core-metal shell probes like nanoshells.

(216) **Gold and Silver Nanocrescents with Infrared Plasmonic Properties as Tunable Substrates for Surface Enhanced Infrared Absorption Spectroscopy**

Jennifer Shumaker-Parry[1], Rostislav Bukasov[1]; [1]University of Utah

Controlling the size, shape, and orientation of metal nanoparticles in order to tune and optimize the particles' optical properties for specific applications remains a challenge in the field of plasmonics. Tuning the localized surface plasmon resonance (LSPR) wavelength as well as the localized field enhancements is especially important for spectroscopy applications such as surface enhanced Raman spectroscopy (SERS) and surface enhanced infrared absorption spectroscopy (SEIRA). Although SERS has receive a lot of attention with the engineering of nanoparticle-based substrates, the activity in SEIRA development has been less, most likely due to the lack of tunable substrates for the IR spectral region. We describe the development of gold and silver nanocrescents as tunable substrates for SEIRA studies. We use nanosphere template lithography to fabricate gold and silver crescent-shaped structures which exhibit multiple, polarization-sensitive plasmon resonances that are tunable from the visible through the infrared. Large electromagnetic field enhancements are expected due to the sharpness of the crescent's tips and the ability to bring these sharp tips into close proximity to each other. Using the crescent-shaped structures as substrates, we demonstrate the importance of spectral tunability for maximizing signal enhancements in SEIRA. The nanocrescent area normalized SEIRA signal enhancement increases from 7700 to 46000 with an increase in the extent of overlap of the nanocrescents' LSPR frequency with the frequency of the probed molecular vibration. The broad tunability of the nanocrescents' LSPR properties makes the structures excellent candidates for a range of spectroscopic and sensing applications including SEIRA.

(217) **Tailoring Gold Nanorods for Laser Desorption/Ionization Mass Spectrometry**

Edward Castellana[1], David Russell[1]; [1]Texas A&M University

Nanomaterials offer several unique advantages over traditional platforms for laser desorption/ionization mass spectrometry (LDI-MS) including; simplified sample preparation, relatively uncomplicated low mass spectra (less noise from matrix clusters), and greater flexibility in the sample deposition conditions (e.g., pH, solvents, etc.). Here we exploit the optical properties of gold nanorods to facilitate the LDI of analytes under near-IR laser irradiation. The longitudinal surface plasmon resonance (SPR) absorption band of gold nanorods is dependent on the aspect ratio of the rods. By controlling the aspect ratio one can tune the wavelength of the longitudinal SPR into the near-IR. For a given aspect ratio, analytes adsorbed on the surface of the rods can then be desorbed and ionized under irradiation corresponding to the nanorod's longitudinal SPR absorption wavelength. Another advantage to using nanomaterials is that the surface chemistry is easily controlled through well established methods. Metallic nanorods can be readily functionalized with self-assembled monolayers (SAMs). This gives us the added benefit of tailoring the surface of nanorods for the capture of desired analytes from complex solutions. We are currently designing a biosensor platform whereby analytes are captured by nanorods of various aspect ratios and analyzed by mass spectrometry. By controlling both the aspect ratio and surface chemistry of the nanorods we can screen complex samples in a high-throughput fashion. This has implications in biomarker screening where it is desirable to capture and identify unknown analytes present in low abundances from complex biological fluids.

(218) **Raman Studies of CuInS2Nanoparticles**

Lisa Lau, Rene Rodriguez, Joshua Pak, Dennis Strommen; [1]Idaho State University, Dept. of Chemistry

The next generation of solar cells will likely include multi-junction cells employing absorptive materials which absorb light in a selected region of the solar spectrum. Quantum dots and nanoparticles can be sized-tuned to absorb at different wavelengths and may prove useful for this application. We have made CuInS2 nanoparticles of various sizes and colors to absorb in the blue, yellow and red parts of the spectrum by microwave heating of a single-source precursor molecule. Currently, the best solar cells made from CuInS2 use bulk crystalline CuInS2 in the chalcopyrite phase with a 112 orientation. X-ray diffraction data indicate our nanoparticles are crystalline but the XRD data are inconclusive as to whether the nanoparticles are in the chalcopyrite or Cu-Au phase. Raman spectroscopy has been used to determine the phase of bulk CuInS2 crystalline materials. Here we explore the use of Raman spectroscopy to obtain phase information about CuInS2 nanoparticles.

(219) **Nano-LC/MS/MS for MRM Quantitation of Peptides**

Christine Miller[1], Ning Tang[1], Ben Collins[2], Thomas Lau[2], Stephen Pennington[2]; [1]Agilent Technologies, Inc.; [2]University College Dublin

Multiple-reaction monitoring (MRM) on a triple quadruple (QQQ) mass spectrometer provides superior sensitivity and selectivity for targeted compounds in a complex sample. MRM also offers high precision in quantitation and fast scan speed, which makes it an ideal technology for quantitation of peptides. Nanoflow LC/MS provides high sensitivity and is widely used in peptide analysis, but must be robust and reproducible for routine quantitative applications. Using a microfluidic-based nanoflow LC interfaced to a QQQ mass spectrometer, reproducibility for both retention time and response have been demonstrated. Results will be presented for the quantitation of peptides in both simple and complex matrices and for quantitation of the degree of protein phosphorylation. In addition, software approaches to aid in selection of peptides and product ions and for optimization of MRM parameters will be highlighted.

(220) **A Cocktail of Isotopically Labeled Peptide Standards for MRM Based Quantitation of 45 Human Plasma Proteins**

Michael A. Kuzyk[1], Derek Smith[1], Tyra Cross[1], Juncong Yang[1], Angela Jackson[1], Darryl Hardie[1], N. Leigh Anderson[2], Christoph H. Borchers[1]; [1]University of Victoria, Victoria, BC; [2]Plasma Proteome Institute, Washington DC

Conventional approaches to protein quantitation using mass spectrometry (MS) are plagued by difficulties largely attributable to variable signal intensities between analyses and signal suppression from background sample complexity. Recent quantitative approaches have incorporated stable isotope labels (both chemical and metabolic) and have improved the reproducibility of relative quantitation between samples within a limited dynamic range of quantitation. Triple quadrupole tandem mass spectrometers are capable of sensitively monitoring generation of a fragment ion by collision induced dissociation (CID) from an isolated precursor ion using multiple reaction monitoring (MRM) a tandem MS (MS/MS) scan mode. To date, 45 isotopically labeled peptides standards representing 45 distinct human plasma proteins have been synthesized and reversed phase HPLC purified. These peptides represent unique, tryptic peptides containing no missed cleavages and are reproducibly detectable by LC-MRM analysis of 1 ug of trypsin digested plasma. Amino acid analysis and MALDI-TOF MS purity assessment have determined that all 45 peptides are >81% pure. Calibration curves in trypsin digests of whole, human plasma have been conducted for a peptide mixture of all 45 isotopically labeled peptides. A linear response with an average r^2 >0.99 has been obtained for all 45 peptides over a 6,500-fold concentration range.

(221) **Driving Biological Discovery using Quantitative Mass Spectrometry**

Johns Yates[1]; [1]The Scripps Research Institute

A component to understanding biological processes involves identifying the proteins expressed in cells as well as their modifications and the dynamics of processes. Several major technologies, but especially mass spectrometry, have benefited from large scale genome sequencing of organisms. The sequence data produced by these efforts can be used to interpret mass spectrometry data of proteins and thus enables rapid and large-scale analysis of protein data from experiments. Advances in multi-dimensional separations as well as mass spectrometry have improved the scale of experiments for protein identification. This has improved the analysis of protein complexes, and more complicated protein mixtures. Quantitative mass spectrometry can be used to study biological processes such as development or the effects of gene mutations on pathways. Metabolic labeling of whole organisms can now be readily accomplished using 15N labeled proteins as a food source. The use of this method in combination with Shotgun proteomics was used to study rat brain development (P1 to P45) and Daf2 and Daf16 knockouts (insulin signaling pathway) in C. elegans.

(222) **Quantitative Proteomics using 18O Labeling**

Catherine Fenselau[1]; [1]University of Maryland

The implementation of heavy oxygen atoms as labels for mass spectrometry- based comparative proteomics has both advantages and limitations. Advantages include: A universal strategy; Uniform labeling of all peptides; Water as the only by-product; Capability to mine mutations and modifications; Compatibility with all affinity fractionation methods; Chromatographic co-elution of

labeled pairs; Facilitated interpretation of MSMS spectra; Automatable; Applicable without proprietary kits. Limitations include capacity for multiplexing and the introduction of the label at the peptide level. This latter consideration requires that cells and proteins be manipulated as little as possible, and that fractionation be focused primarily on peptides after they have been labeled and mixed. This talk will discuss two dimensional fractionation of isotopic oxygen peptide pairs by off-gel electrophoresis and reverse phase HPLC, and sources of variability in this strategy for quantitation.

(223) **Differential Proteome Analysis using Targeted Label-Free Workflows**

A. Kettani[1], W. Jabs[1], M. Lubeck[1], M. Behrens[1], D. C. Chamrad[2], K. Marquart[2], M. Blueggei[2], B. Sitek[3], B. Korte[3], S. Link[3], C. Stephan[3], K. Stühler[3], H. E. Meyer[3], C. Baessmann[1]; [1]Bruker Daltonik GmbH; [2]Protagen AG; [3]Medizinisches Proteom-Center

Introduction Comprehensive quantification of specific changes in biological systems in response of a certain treatment or perturbation is one of the most important but also among the most challenging tasks in proteomics. Different kinds of separation techniques, of mass spectrometer types, of identification strategies, and of quantification strategies can be applied for this purpose. We investigate the benefits of a targeted label free LC-MS/MS workflow in comparison to a SDS-PAGE ICPL workflow. The results are derived with the aid of a newly developed bioinformatics platform using a cell culture model. Methods For the label-free approach samples from a biological system in different states are measured multiple times in LC-MS runs without pre-fractionation. A highly stable LC system and a high-resolution mass spectrometer form the basis for a robust assignment of identical peptides across all LC-MS runs. Statistical tests are applied to determine regulated peptides which are put on target lists and measured in several LC-MS/MS runs. All MS/MS spectra are combined for a protein database search followed by calculation of protein regulations. The bioinformatics platform supports MS and MS/MS data from several mass spectrometers types as well as different quantification strategies. We compare quantitative results from the label-free workflow and a workflow using ICPL labeling and SDS-PAGE LC-MS/MS. Results LC conditions are optimized to obtain reproducible retention times of same peptides across 20 runs. For the label free workflow a sensitive ESI Q-TOF mass spectrometer with high resolution is applied to detect as many peaks as possible. Data analysis includes a robust assignment of isotopic peaks in different charge states to the originating peptides, and retention time alignment followed by binning of identical peptides across all LC-MS runs. Statistical tests are applied to determine regulated bins from which target lists are derived. In the current study we use 12 targeted LC-MS/MS runs and combine all measured MS/MS spectra for a single protein data base search. Finally, protein regulations are determined. The resulting accuracies of the protein regulations from the label-free approach are similar to the respective values obtained from the ICPL workflow using the same sample. Further benefits of the label-free approach are lower sample consumption due to unnecessary labeling steps, inclusion of many technical and biological replicates in a study, and the ease of additional targeted LC-MS/MS measurements for validation of a particular protein identification and quantification.

(224) **iMALDI for MS-Based Quantitative Proteomics Intended for Clinical Use**

Christoph Borchers[1]; [1]University of Victoria Genome BC Proteomics Centre

A particular focus of our group is the development of mass spectrometry- based techniques such as Multiple reaction monitoring (MRM) and immuno-MALDI towards their use in clinical proteomics for diagnostics. Although (MRM) assays have been highly used for many years in pharmaceutical companies to quantify small molecules in biological specimens, its applicability towards quantitation of peptides in blood samples has just been demonstrated recently. While useful for biomarker studies and phosphorylation site determination this technique is, however, limited to the detection of high to moderately abundant proteins. In our immuno-MALDI (iMALDI) peptide chip technology, specific peptides produced by proteolytic cleavage of selected protein biomarkers are captured using bead-immobilized antibodies against these specific peptides. Thus, this technique is capable of analyzing low abundant proteins. These affinity-bound target peptides are then analyzed by tandem MS using matrix-assisted laser desorption ionization (MALDI). Additionally, absolute quantitation is achieved with stable-isotope labeled epitope molecules as standards. In each assay, the observed peptide mass and sequence data permit determination of the absolute expression level of the captured peptide, as well as highly-specific confirmation of protein identity. We have already developed an iMALDI assay for EGFR enabling the specific detection of EGFR in biopsy samples.

(225) **Proteomics Approaches for Characterizing Microbial Proteomes**

Nathan VerBerkmoes; [1]Oak Ridge National Lab.

Microbial communities play key roles in the Earth's biogeochemical cycles. Our knowledge of the structure and function of these communities is limited because analyses of microbial physiology and genetics have been largely confined to isolates grown in laboratories. Recent acquisition of genomic data directly from natural samples has begun to reveal the genetic potential of communities and environments. The ability to obtain whole or partial genome sequences from microbial community samples has opened up the door for microbial community proteomics. Microbial community proteomics (metaproteomics) is a key to understanding microbial physiology in mixed communities. We have developed and applied a combined proteogenomic approach using genomics and mass spectrometry-based proteomic methods. The key to this technology is the combination of robust multidimensional nano liquid chromatography with rapid scanning tandem mass spectrometry. The model system for the development of these techniques is a low complexity natural acid mine drainage (AMD) microbial biofilm community previously characterized by cultivation-independent genomic methods. The development of the approach on a model low complexity system has allowed us to extend the approach to more complex microbial communities and environments such as soil, ground water, ocean and the microflora associated with the human gut. Key technological advances are needed to obtain "deep" and "wide" proteome coverage in more diverse systems.

(226) **Gary Martin Hieftje: Four Decades of Innovation and Excellence in Analytical Chemistry**

Gary Horlick[1]; [1]Department of Chemistry, University of Alberta

Gary Hieftje has had, and I might say, continues to have a very distinguished career in analytical chemistry at Indiana University. He started at IU in 1969 after graduating from the University of Illinois where he obtained his PhD degree under the direction of Howard V. Malmstadt. His scientific innovation was clear from the start in his work with Malmstadt on the so-called "drop machine". Their first paper entitled "Unique System for Studying Flame Spectrometric Processes" was published in Analytical Chemistry in 1968 and it changed forever how fundamental studies in atomic spectrometry would be approached. His work at Indiana University continued on with basic studies in atomic emission,

absorption and fluorescence spectrometric analysis involving both flame and ICP sources and the development of new atomic methods of analysis and innovative chemical instrumentation utilizing both optical and mass spectrometric based techniques. Beyond these core areas he has very broad scientific interests including laser applications in chemistry, time-resolved luminescence, near-infrared reflectance analysis, correlation analysis and stochastic processes. Over the years he has made insightful contributions in all of these areas. Because of these broad interests and his excellence and enthusiasm in analytical science many students, postdoctoral fellows and visiting scientists have been attracted to study and train in his laboratories at Indiana University. Outside of Indiana he enjoys lecturing on his research. His dynamic, clear and enthusiastic speaking style as well as his science, have make him a widely sought after speaker at conferences and institutions throughout the world. Finally, many awards have come his way for both his research and teaching. In this presentation a summary will be presented of the "first" four decades of the scientific career of this remarkable scientist and great colleague.

(227) **Analytical Laser Spectroscopy - An Amazing Journey**

Rick Russo; [1]Lawrence Berkeley National Laboratory

Graduate education at Indiana University (IU) under the direction of Professor Gary Hieftje (Heef) opened the door to opportunities in a premier National Laboratory at Berkeley. 3 0+ years ago started an adventure that has provided a rewarding career. A graduate education covering droplet generators to short-pulsed lasers (picosecond at the time) allowed this student to delve into an array of technologies based on the IU core education. Fundamental research addressing laser material interactions spawned applications in chemical analysis, fabrication of materials, a nanowire laser, and ultrasonics. The talk will present an overview of these research efforts, demonstrating that a commitment to and a zeal for science as mentored by Heef has surely provided an amazing journey.

(228) **Near Surface Depth Profile Analysis**

Kim Marshall[1], Charles Maul[1], Diane Goodman[1]; [1]LECO Corporation

Glow Discharge Optical Emission Spectrometry (GD OES) has become an important tool in the arsenal of the analytical spectroscopists. Although glow discharge is often used for bulk analysis, its true power lies in its ability to do compositional depth profiling of layered and coated materials. In recent years it has become apparent that GD-OES can be utilized for the analysis of surface layers of only a few nanometers in thickness. The precision and apparent accuracy with which these ultra-thin layers can be determined is impressive. This is particularly so when the speed of the GD-OES analysis is compared to traditional techniques like Auger Electron Spectroscopy, Secondary Ion Mass Spectrometry or X-ray Photoelectron Spectroscopy. These tradition methodologies require 10's of minutes or even hours for the single analysis that GD-OES can complete in under a minute. For this reason the cost of each analysis using GD OES is greatly reduced. Arguably this makes glow discharge spectrometry particularly well suited as a pre filter for the slower, expensive, and yet more accepted traditional techniques. This presentation will focus on the use of glow discharge as a complementary technique for near surface compositional analysis. It will provide an overview of the "near surface" capabilities of glow discharge and compare and contrast these with the capabilities of other more traditional surface analysis techniques. Comparison data from some of the various techniques will be also be presented.

(229) **Mapping Argon Metastable Atoms in an ICP-MS using Absorption Depletion Imaging**

Paul Farnsworth[1], Nicholas Taylor[1], Haibin Ma[1]; [1]Brigham Young University

Argon metastable atoms play multiple roles in the function of inductively coupled plasma mass spectrometry (ICP-MS). They constitute an easily-ionizable reservoir of argon atoms that is critical in sustaining the plasma. In addition, they have long been suspected of playing a significant role in the ionization of analyte and matrix species through a Penning ionization mechanism. Given their significant fundamental role in ICP-MS, density maps of argon metastable atoms would be valuable aids in explaining the response of the ICP ion source to changes in operating parameters and sample composition. Fluorescence imaging techniques that have been useful in mapping analyte densities in the ICP have not been effective in creating maps of argon metastable atoms. Poor fluorescence quantum yields result in unacceptably low signals from fluorescence measurements. Conventional absorption measurements suffer from a lack of inherent radial resolution. Although radial data can be extracted from absorption measurements by use of Abel inversions or tomographic imaging techniques, neither approach is straightforward. In this presentation we will discuss initial results from an alternative absorption technique that yields radially-resolved information directly. The technique relies on the use of a pulsed laser to bleach the population of argon metastable atoms over a short segment of the absorption path length. The change in absorbance induced by the bleaching laser is proportional to the metastable atom population in the bleached segment. Although experimentally complex, this approach to obtaining radially-resolved maps of argon metastable atom density promises to be a valuable tool for the study of the effects of argon metastable atoms on ICP-MS performance.

(230) **Mechanistic Study of Analyte Excitation and Matrix Effects in Inductively Coupled Plasma-Atomic Emission Spectrometry**

George Chan[1], Gary Hieftje[1]; [1]Indiana University, Dept. of Chemistry

Although inductively coupled plasma-atomic emission spectrometry (ICP-AES) is a widely employed analytical technique for elemental analysis of samples of virtually all kinds, and despite the assertions of many instrument vendors and the belief of many users, matrix effects unfortunately abound in ICP-AES. The presence of matrix effects, without the awareness and subsequent correction by an analyst, will lead to an analytical error. Not surprisingly, a great deal of effort has already been devoted to understanding interelement interferences in ICP-AES. However, the detailed mechanisms that lead to these interferences are not yet fully understood. As a result, the currently available methodologies for overcoming matrix effects (e.g., matrix matching, standard additions, and internal standardization) are not based on a rational understanding of the mechanisms and are usually rather time-consuming. If the interferences are fully characterized in a fundamental way and the inter-relationships among emission-line properties, plasma and matrix characteristics are known, it might then be possible to develop alternative matrix-managing techniques that are based on targeting the root cause of such interferences. Clearly, identifying the origins of matrix interferences in ICP-AES is a complicated business. Because our recent studies suggest strongly that matrix interferences are linked closely with excitation processes in the ICP, determining those mechanisms will receive greatest emphasis. In this presentation, new insights on the inter-relationships between mechanisms of analyte excitation and matrix effect will be described.

(231) **Some Remaining Questions, Challenges and Potential Advances in ICP-OES and ICP-MS**

John Olesik[1], Patrick Gray[1], Josh Dettman[1], Elodie Linard[1], Anthony Lutton[1]; [1]The Ohio State University

Although ICP-OES and ICP-MS are often considered to be mature techniques, many questions and challenges remain. Relative sensitivities are still not predictable enough to use a standard containing one element to measure the concentration of another element by ICP-OES. Excitation mechanisms and the origin of matrix effects are not fully understood. Some experimental evidence suggests that coagulation of droplets in the spray chamber is key to aerosol transport efficiency while some fluid dynamic modeling leads to a conclusion that coagulation has no impact. It is now clear that the transport of ions from an ICP to the MS is not explainable by assuming that neutral gas flow dominates. Some spectral overlaps are not entirely predictable in ICP-MS and can cause errors in instrument reported concentrations. While concentration based detection limits for large volumes of sample are often limited by contamination rather than instrument sensitivity, absolute detection limits are insufficient for applications including high spatial resolution LA-ICP-MS and CE-ICP-MS. A great deal of potentially useful diagnostic information is available from ICP-OES and ICP-MS signals but is not being widely used. Some of the remaining questions and challenges in ICP-OES and ICP-MS will be considered. Approaches to answer some of the remaining questions and to improve the performance of ICP-OES and ICP-MS will be discussed.

(232) **FT-IR Imaging of Anisotropy by Polarized Radiation: A Novel Polymer Characterization Technique**

Heinz W. Siesler[1], Christian Vogel[1]; [1]University of Duisburg-Essen

Over the last decade FT-IR imaging with focal plane array detectors has proved a powerful technique for rapid chemical visualization of samples by a combination of spectroscopic and spatial information. Thus, selected sample areas can be analyzed with reference to the distribution of chemical species by FT-IR transmission or ATR spectroscopy with high lateral resolution (up to 3-4 μm). We have enhanced the potential of FT-IR imaging for the characterization of anisotropic polymer films by the use of polarized radiation. Hence, FT-IR dichroic imaging measurements of polymer films which have been previously subjected to mechanical elongation can provide detailed information on the lateral distribution of anisotropy. The present communication will report for the first time the different chain orientation of the blend components in the phase-separated domains of uniaxially elongated poly(3-hydroxybutyrate)/poly(lactic acid) blend films. Furthermore, the FT-IR dichroism imaging results of the strain-induced II(alpha) - I(beta) phase transition and anisotropy in poly(vinylidene fluoride) as a function of the experimental temperature will be discussed in some detail.

(233) **Application of ATR/FT-IR Hyperspectral Imaging and Chemometrics for Studying the Distribution of Materials Sprayed on Heterogeneous Substrates**

Boiana Budevska; [1]DuPont Crop Protection

Attenuated total reflection (ATR) combined with FT-IR hyperspectral imaging has been successfully used in the past to study heterogeneous samples which are not appropriate for transmission measurements. ATR spectroscopy and imaging are also very useful if only the surface heterogeneity is of interest. In many practical situations, it is important to understand the distribution of materials sprayed on heterogeneous substrates. In this case both the materials of interest and the substrate itself are complex and have heterogeneous distribution. Multivariate analysis methods like multivariate curve resolution (MCR) have been successfully applied to study systems when limited knowledge about the chemical composition is available. We have explored the ability of the recently published chemometric method target PLS (R. N. Feudale, S. D. Brown, "An inverse model for target detection", Chemometrics and Intelligent Laboratory Systems 77,75-84 (2005)) to provide valid information about the distribution of crop protection products applied to plant material. This presentation will describe the experimental details and demonstrate the sensitivity of the analysis.

(234) **Imaging ATR Analysis in Non-Square Configurations**

Ellen Miseo[1], Jim Steensrud[1], Frank Weston[1]; [1]Varian, Inc

Infrared imaging using a focal plane array detector is now a mainstream spectroscopic technique. The method provides both spatial and spectral information on a variety of samples. Traditionally, attenuated total reflectance (ATR) methods have extended the power of infrared spectroscopy to samples that are neither reflective nor thin enough to be examined in transmission. ATR imaging (using an ATR crystal with a spectrochemical imaging system, US Patent #6141100) is a relatively new technique that has the same ease of use and sampling capabilities as ATR does for single point analysis. In addition, ATR imaging provides increased spatial resolution. In a macro accessory spectral and spatial information of a sample with micrometer size domains can be obtained. The commercial implementations of ATR imaging accessories provide a field of view that is rectangular rather than square. When used with an imaging camera that is larger than the field of view of the ATR the image is not illuminated on the edges. By configuring the imaging camera to non-square configurations the issues associated with the poorly illuminated areas can be overcome. This paper will explore these configurations and present data from these experiments.

(235) **Processing Efficiency and Mass Balance via InSb Image Pixel Counting of Incoming Material and Product and By-Products**

David L. Wetzel[1], Elieser Posner[2], Hulya Dogan[1]; [1]Kansas State University; [2]Posner Grain Milling & Handling Consult

The method developed concerns unit operation of physical separation processing in which a desired component of a mixture is concentrates a intermediate product stream from the operation and three other streams, two worthy of reworking and a concentrate of undesirable material, are produced. Using a near infrared InSb focal plane array (FPA) instrument equipped with a liquid crystal tunable filter (LCTF) and a 350 X 256 element InSb camera, diffusely reflected radiation from the sample, illuminated by four infrared lamps, produces an image with nearly 82,000 pixels. The range of operation is 1100-2400nm. Distinction between the endosperm and non-endosperm is readily apparent by means of one of two methods. Selectivity of pixels that are primarily endosperm versus those that are primarily nonendosperm is produced with carefully selected wavelengths. Alternatively, a partial least squares (PLS) statistical procedure is applied to give a multi-wavelength characterization of each of the components. The purest possible endosperm is obtained from first midds stock of the KSU pilot flour mill. The data from 82,000 spectra is pooled before applying the PLS characterization. A similar procedure is used for bran that is free of endosperm. With the two distinctly different multi-wavelength characterizations in the custom generated library, it is possible to assign each pixel in the image to one of the two categories. False colors are used to designate pixels that are predominately of one material or the other. Bimodal histograms represent the populations of endosperm and nonendosperm material. Each pixel in the image is characterized as exclusively one material or the other. Endosperm pixels/total pixel enables calculating the percentage of endosperm in each of the streams. With flow rate date the mass balance is calculated. Examples are

given for a 1BK, 2BK, and first purifier stages of dry milling of wheat.

(236) **Robustness of Histological Recognition in Tissues using Fourier Transform Infrared Spectroscopic Imaging**

Rohith Reddy[1], Rohit Bhargava[1]; [1]University of Illinois at Urbana-Champaign

Fourier transform infrared (FT-IR) spectroscopic imaging is an emerging technique that provides both chemically and spatially resolved information that can be used, for example, to perform automated histological recognition in tissues. The uses of Bayesian and genetic-algorithm-based classifiers have been shown to be effective in histological recognition in tissues, yielding an accuracy of 94% to 99%. However, clinical translation of these results requires that the classifiers be robust to factors such as tissue sample preparation and systematic bias introduced by handling of tissues. This paper examines the dependence of classification accuracy on such factors by using independently procured and processed datasets for analysis and validation. Two-class histological classification (epithelium/stroma) is found to have an accuracy of 92% to 95% even when validation was performed on independent datasets, thus highlighting the robustness of our technique. Determining the number of samples (tissue micro-array cores), patients, and pixels required to build a robust classifier are important questions and are discussed thoroughly. It is shown that a relatively small number of pixels are sufficient to capture information about the entire dataset and a statistical analysis of the intra-person and inter-person variance in spectral metrics (features) is presented to understand and explain these results. Datasets with samples from 40 and 16 different patients was used and the number of patients required to build a robust classifier is found to be relatively small and is dependent on acceptable statistical significance and accuracy. The number of spectral metrics required for classification and the effects of signal to noise ratio on classification are also discussed. The use of genetic-algorithm based classifiers in distinguishing cancer from benign tissue is explored. A classification accuracy of greater than 80% in possible at a pixel level (~6μm x 6μm area) using these methods. The algorithms are trained using a small subset of data and tested extensively on data from the same dataset as well as an independent dataset.

(237) **Determination of the Composition of Counterfeit Drugs by Near Infrared Chemical Imaging**

Marta Lopes[1], Jean-Claude Wolff[2], José Bioucas-Dias[1], Mário Figueiredo[1]; [1]Universidade Técnica de Lisboa; [2]GlaxoSmithKline

Counterfeit drugs pose a significant and fast-growing threat to public health and to the pharmaceutical industry. For an individual patient, treatment with a counterfeit drug is at best ineffective, at worst - lethal. For the pharmaceutical industry the threat is primarily a commercial one, with both reputation and revenues at stake. Near infrared chemical imaging (NIR-CI) is a powerful analytical technique that is being used increasingly in the fight against counterfeit drugs. Capable of simultaneously analyzing a number of tablets, NIR-CI can provide rapid 'genuine/fake' detection. The aim of this work is, not only to distinguish between genuine and counterfeit drugs, but to use regression tools on NIR data in order to identify and quantify the compounds present in the counterfeit tablets. NIR images of 12 counterfeit tablets were acquired with a Spectral Dimensions Sapphire NIR-CI2450 spectrometer (Malvern Instruments, Olney, Maryland, USA). By visual inspection of the mean spectrum of the tablets, in comparison with spectra of compounds/excipients frequently appearing in counterfeit tablets, it was found that these samples include, in addition to the active pharmaceutical ingredient (API), microcrystalline cellulose, starch and talc, in a wide range of concentrations. Tablets of pure compounds/excipients were pressed and their mean spectra acquired. They were used as reference in classical least squares (CLS) regression. API content measurements of the counterfeit tablets were carried out by HPLC for validation purposes. Without any information about the samples composition, NIR/CLS could clearly distinguish between tablets with low and high API content, yielding accurate predictions (especially for tablets with high API concentration). Prediction errors were below 7%. The observed errors may have been introduced by not taking into account all the possible ingredients appearing in small percentages in these tablets. Prediction errors might also be due to non-homogeneity of the tablets. Finally, to minimise errors in predicting the API concentration, and consequently that of the remaining compounds identified, libraries of compounds/excipients (e.g., cheaper substitute compounds) frequently encountered in counterfeit drugs should be built. Last but no least, identification and quantification of components might aid in the classification and the sourcing of counterfeits.

(238) **Vibrational Circular Dichroism: Evolution from Instrument Development to Biopolymer Applications. 35 Years and Growing**

Tim Keiderling; [1]University of Illinois at Chicago

VCD had its roots 35 years ago in initial papers dealing with spectra of small chiral organic molecules in solution, which were followed by a number of efforts to explain the observations by use of various theoretical models. As instrumentation and theory developed, many applications of the technology arose. While early instruments were based on monochromators (dispersive detection), current methods depend mostly on FTIR based instruments. Measurements of small polarization difference spectra characteristic of VCD had difficulties with artifacts, and many potential solutions were proposed. While VCD instruments have not changed drastically in the past decade, they are more stable and routinely available now, due to commercialization. Much of this growth is driven by applications in determining absolute stereochemistry of chiral compounds, facilitated by theoretical spectral computation. Another approach has been to derive more detailed structural information from biopolymer systems, including peptides, proteins and nucleic acids by making use of the combination of enhanced spectral resolution in the vibrational region with chirally sensitive band signs and intensities. Here the chirality of the molecule is not due to configuration (which is normally well-known) but to conformation, the residue-to-residue stereochemical relationships, or secondary structure. Various examples of characteristic VCD of biopolymers will be discussed demonstrating its potential for determining structure and sensing local changes, particularly using the advantages of isotopic substitution and theoretical modelling.

(239) **Chiral Analysis using Vibrational Circular Dichroism (VCD)**

Oliver McConnell[1], Yanan He[1]; [1]Wyeth Research

As many of the Exploratory and Discovery research programs at our company feature compounds with one or more asymmetric centers, chiral separations and determination of absolute stereochemistry are vital analytical activities for success in the drug discovery process. Although determination of absolute stereochemistry by X-ray crystallography is generally viewed as the most reliable technique, it requires "X-ray friendly" crystals, which for some compounds is not trivial to produce. Over the past several years, the chiroptical spectroscopic technique of measured versus calculated vibrational circular dichroism (VCD) has become the most frequently used method in our company for the determination of absolute stereochemistry because it doesn't

require the preparation of crystals, only solubility in CDCl3 or dmso-d6. There are limitations, however, related to the size and conformational mobility of the compounds studied. This presentation will provide examples of compounds that have been successfully analyzed using VCD, where truncation of the (calculated) molecule have facilitated successful analysis, and where VCD has failed to provide a reliable determination of absolute stereochemistry.

(240) **Chiral Vibrational Spectroscopy of Amino Acids, Peptides and Ligands**

Karl James Jalkanen; [1]Curtin University of Technology

The chiral and conformational analysis and understanding for biomolecules is an extemely difficult problem. Only a few techniques offer readily available and quick techniques to determine not only the absolute configuration of a molecule, but also its conformer or conformers. Leu-enkephalin is an example of a small peptide which has three different crystal structures, and has been a heavily studies molecule both experimentally and theoretically. In addition to the complexity of the configuratonal and conformational subspaces of biomolecules, there are the added dimensions of temperature (hence the importance of entropic effects) and environment (polar versus non polar envirorment, pH, ionic strength and finally metal ions). Recently it has been shown the "conformer" and "configuration" of flexible ligands bound to receptor proteins are not even stable minimum on the gas phase isolated state (non polar medium) or even those found in either the crystalline environment or in aqueous solution. The use of chiral vibrational spectroscopy to unravel some of this complexity both theoretically and experimentally will be discussed, along with examples of amino acids, peptides and ligands investigated to date. Finally the future developments/breakthroughs which need to be addressed and made will be discussed and presented.

(241) **Computational Aspects of VCD**

James Cheeseman[1]; [1]Gaussian, Inc.

This talk will focus mainly on the practical aspects of predicting VCD spectra using the ab initio Density Functional Theory (DFT) method of quantum chemistry. An overview of the theory of VCD will be presented from a computational standpoint and the relative accuracies of standard basis sets and DFT functionals in predicting VCD will be discussed. The additional complexity introduced by conformationally flexible molecules will also be discussed. Although VCD has predominately been used for AC determination, it can also be used to differentiate structural isomers and additionally to extract local structural information. Examples of these will be presented.

(242) **Examples of 'Missing' Conformers in VCD Calculations, and Strategies for Finding Them**

Steven Wesolowski[1]; [1]AstraZeneca

Protocols for simulating VCD spectra with quantum mechanical calculations typically rely upon conformational search algorithms to locate relevant minima. While usually sufficient, molecular mechanics conformational searches are not fail-safe. Examples where quantum mechanical minima are "missed" by using molecular mechanics conformational searches are provided with an emphasis on conformers related by inversion modes.

(243) **Streamlining the VCD Computational Workflow from Conformer Selection to Structural Assignment**

Don Pivonka[1], Steve Wesolowski[1]; [1]AstraZeneca

With the current availability of commercial VCD instrumentation, spectral acquisition has, in many cases, been rendered the “simple” aspect of the VCD experiment. In contrast, conformer selection, conformer minimization, spectral calculation, accurate assignment of the conformer distribution, and quantitative comparisons of “calculated” vs. “experimental” spectra, components of the VCD experiment are far from a turn-key processes and requires a high level of computational/physical chemical expertise. At present, there is no single software package, which can perform all of the required computations in a cohesive environment. Without in-house software to facilitate input/output file compatibility between software packages from a variety of vendors, and without a means of automated extraction of energy parameters and associated weighted co-addition of conformer spectra from within a conformer series, the comprehensive assessment of even a low molecular weight, highly rigid, conformer series can become a very time consuming task. In this presentation, an in-house Visual Basic based software approach to automation of the VCD computational challenges will be presented. While density functional theory (DFT) calculations of conformer energies remain “intense” calculations with run times often measured in days as opposed to hours, the present approach to automating the computational process has reduced the “human” input factor from hours to only a few minutes.

(244) **Using Ultrafast Time-Resolved Near IR Spectroscopy to Probe Photocatalytic Reactions on TiO2**

Koichi Iwata[1]; [1]The University of Tokyo

We have been developing a femtosecond time-resolved near-infrared spectrometer that covers the spectral range of 900 to 1500 nm with the time resolution of 200 fs. We apply time-resolved near-infrared spectroscopy, which uses the probe light wavelength longer than visible or ultraviolet spectroscopies, to scattering samples, such as TiO2 powders. Time dependent change in the TiO2 photocatalyst (P-25) induced by the photoirradiation was recorded by the time-resolved near-infrared spectrometer. Broad absorption feature was observed immediately after the photoirradiation. This absorption band has been assigned to the photogenerated electrons. The shape of the absorption band changed within a few hundreds of femtoseconds after the photoirradiation. Time dependence of the carrier signals in TiO2 was measured in three different environments, in vacuum, in water, and in an ionic liquid, bmim[PF6], or 1-butyl-3-methylimidazolium hexafluorophosphate. There was no difference observed, within the experimental uncertainties, between the decay kinetics in vacuum and that in water. Presence of the water molecules on the surface of the TiO2 particles does not affect the carrier dynamics in the particle. The ionic liquid, bmim[PF6], however, affects the carrier dynamics. The carrier signal decayed much faster in the ionic liquid. Time constant for the fastest decay component in the ionic liquid was estimated to be 100 fs or less. The cations and anions of the ionic liquid affect the decay kinetics of charge carriers in the TiO2 particle beyond the dielectric shielding normally expected for the bulk TiO2 crystal.

(245) **Picosecond Time-Resolved Spectroscopic Studies of Phototriggers and Polyhalomethanes**

David Lee Phillips; [1]The University of Hong Kong

Polyhalomethanes are important sources of reactive halogens in the natural environment and it is important to understand their photochemistry in both gas and condensed phase environments. While the gas phase photochemistry has been extensively studied, there is much less corresponding condensed phase work. Here, we report picosecond time-resolved resonance Raman (ps-TR3) experiments done to investigate the photochemistry of polyhalomethanes in aqueous environments. We found that photolysis of polyhalomethanes in the condensed phase leads to fast geminate recombination of the radical fragments to form some high energy isomers that can undergo O-H insertion reactions with water.[1] Efficient phototrigger compounds are needed for the very

fast and localized release of biological stimulants that can be employed for real-time monitoring of physiological responses in biological systems. Here, we report a study of the photorelease reactions of pHP phototriggers in order to better understand the mechanism(s) for the photodeprotection reactions that occur in aqueous environments. Time-resolved resonance Raman (TR3) as well as time-resolved transient absorption (TA) and timer-resolved fluorescence (TRF) spectroscopies were used to study the structure and dynamics of the photophysical and photochemical processes involved in the photodeprotection reactions of interest.[2,3] The ps-TR3 and TA experiments found the triplet decay kinetics are highly solvent and leaving group dependent for the p-hydroxyphenacyl (pHP) phototrigger compounds.[2,3] The TR3 method was used to monitor the product formation dynamics for the first time.[3] Our results indicate the cleavage and product formation occur in a step-wise manner in these compounds and we have elucidated a mechanism for the photorelease mechanisms these compounds. References [1] W. M. Kwok, C. Zhao, Y.-L. Li, X. Guan, and D. L. Phillips, J. Am. Chem. Soc. 126, 3119-3132 (2004). [2] C. Ma, W. M. Kwok, W. S. Chan, P. Zuo, J. T. W. Kan, P. H. Toy and D. L. Phillips, J. Am. Chem. Soc. 127, 1463-1472 (2005). [3] C. Ma, W. M. Kwok, W. S. Chan, J. T. W. Kan, P. H. Toy and D. L. Phillips, J. Am. Chem. Soc. 128, 2558-2570 (2006).

(246) **Excited State Photophysics and Photochemistry Probed by Femtosecond Spectroscopy**

Terry L. Gustafson[1], Jessica E. Donehue[1], Nicole M. Dickson[1], Jin Wang[1], Gotard T. Burdzinski[2], Jacek Kubicki[2], Christopher M. Hadad[1], Matthew S. Platz[1]; [1]Department of Chemistry, The Ohio State University; [2]Adam Mickiewicz University, Poland

We are using fs UV/Vis and fs IR spectroscopy, along with ps fluorescence spectroscopy, to probe the structure and dynamics of photogenerated intermediates in several important classes of molecules: diphenyl polyenes, azides, diazo compounds, and MM quadruply-bonded dinuclear metal complexes. The combination of ultrafast electronic and vibrational spectroscopies provides a comprehensive picture of the important intermediates formed following photoexcitation. In this work we present our most recent investigations, including studies of 2-naphthyl azide, which forms the shortest-lived singlet nitrene currently known, and 9-diazofluorene, where we observe the excited state of the singlet fluorenylidene. We also compare the steady-state and time-resolved fluorescence and absorption spectra of 1,4-diphenyl-1,3-butadiene (DPB) to several structural analogues in various solvents. Steady-state fluorescence spectra and time-resolved fluorescence lifetimes probe directly the influence of solvent on the 1 1Bu state. In contrast, transient absorption spectroscopy has the potential of probing both the 1 1Bu and 2 1Ag states, since it is capable of coupling to higher lying states with 1Ag and 1Bu symmetry, respectively. Among the data, we observe a threshold in the dielectric constant of the solvent above which the transient absorption spectra exhibit biexponential decay dynamics. We attribute the two decay components to the lifetimes of the 1 1Bu and 2 1Ag states. These data provide new information on how specific structural details influence the photochemistry of DPB.

(247) **Time-Resolved IR Measurements in Supercritical Fluids: Probing Alkane and Activation and the Role of the Solvent in Green Chemistry Applications**

Michael W. George[1]; [1]University of Nottingham

Supercritical Fluids (SCFs) are curious hybrids of gases and liquids which offer unique opportunities for probing chemical reactions, particularly since their properties (viscosity, dielectric constant, diffusivity etc.) vary with density which is a strong function of temperature and pressure. Fast time-resolved IR Spectroscopy (TRIR) is a powerful tool for probing the structure and reactivity of excited states. Catalytic C-H Activation by organometallic complexes is seen as a promising approach to using methane as energy resource. C-H Activation. The photochemistry of transition metal complexes that can oxidatively insert into alkane C H bonds holds commercial promise for the functionalization of naturally abundant C1 hydrocarbons such as methane in the fine chemicals industry. Understanding the kinetics and mechanism of these reactions is key to such developments. We have used the combination of ps-TRIR and supercritical fluids to monitor the C-H activation of CH4 and C2H6 and the heavier alkanes in solution at room temperature. Supercritical fluids are often cited as alternative solvents in the area of Green Chemistry. The high concentration of gases such as H2 and N2 that are possible in supercritical fluids is often given as a signification advantage over conventional solvents for industrially relevant reactions such as hydroformylation and hydrogenation and preparative chemistry. We will show using TRIR that reactions of organometallic complexes in scCO2 are more complex and careful consideration of the role of the solvent is required

(248) **Monitoring Transition States c/ 2D-IR**

Charles Harris[1], James Cahoon[1], Karma Sawyer[1], Jacob Schlegel[1]; [1]Univ of California at Berkeley

Time-resolved spectroscopy is a powerful tool for understanding the sequential steps in chemical reactions, yet it typically provides little direct information on transition-state structures. We demonstrate that two-dimensional infrared spectroscopy (2D-IR) can provide this information by tracking the transformation of vibrational modes from a reactant through transition state and product. This makes 2D-IR an ideal technique for the study of fluxional processes, in which the reactant and product are identical. We directly monitored the fluxional rearrangement of Fe(CO)5, a process that was proposed by R. S. Berry nearly 50 years ago. The application of this technique to other fundamental chemical reactions will also be discussed.

(249) **Utilizing Two-Dimensional Infrared Spectroscopy in Pursuing an Understanding of Amyloid Aggregation**

David Strasfeld[1], Sang-Hee Shim[1], Yun Ling[1], Martin Zanni[1]; [1]University of Wisconsin

Proteins that aggregate to form amyloid fibers have been implicated as the cause for pathogenesis in numerous human disease mechanisms. Our current understanding of how these fibers misfold and aggregate is drawn from spectroscopic methods with either poor structural or poor temporal resolution. A complete understanding of amyloid aggregation then requires a spectroscopic method that can resolve protein secondary structure in real time. We have made significant advances towards achieving this goal by developing an automated two-dimensional infrared (2D-IR) spectroscopy. Using a mid-IR pulse shaper, we can take 2D-IR spectra in a fraction of the time previously required, and, consequently, interrogate kinetics previously unavailable to 2D-IR spectroscopy. We have applied our technique to the formation of fibers by the human islet amyloid polypeptide (hIAPP), which has been implicated as a cause of type-II diabetes. In elucidating the aggregation mechanism, we have conducted studies that incorporate labeled peptides, lipid vesicles and truncated peptides. By incorporating isotopically labeled amino acids at predetermined positions in the peptide, we can monitor localized structures during fiber formation. Furthermore, as it is known that cell membranes catalyze fiber formation while serving as a target for the disease mechanism, we have conducted fiber formation experiments in the presence of vesicles. Finally, in order to acquire data that will prove tractable in molecular dynamics simulations, we are studying fragments of the full hIAPP peptide. It is our hope that these

combined studies will lead to a full understanding of how amyloid fibers form and insert into cell membranes.

(250) **Pfizer Pforensics: Intriguing Example Case Studies of Non-Authentic Pharmaceuticals**

Amy Callanan[1]; [1]Pfizer, Inc.

Among the many innovative medicines that Pfizer manufactures are Lipitor, the world's most prescribed, and Viagra, the most frequently counterfeited. Recognizing the threat that counterfeits pose to patient health and safety, we have undertaken an aggressive anti-counterfeiting program, to detect and disrupt major manufacturers and distributors of counterfeit products. A critical part of that process is the testing of suspected medicines at our three labs, in the US, UK and China. To date we have analyzed more than 15,000 samples, some of which required integrating multiple analytical techniques to arrive at a conclusion.

(251) **Various On-Dosage Anti-Counterfeiting Technologies Which Can Facilitate Field and Forensic Authentication**

David Schoneker[1]; [1]Colorcon

Protecting the dosage itself, which is ingested by the patient, should be a critical concern in the hierarchy of counterfeit-resistant technologies. Protection must start with the identification and authentication of the dosage because the distribution process for drugs involves repackaging, which is a vulnerable point for counterfeit product introduction, where the dosage becomes separated from the "protected package". "Salting" authentic products with counterfeit products often occurs during repackaging. Counterfeit-resistant technologies for "protecting the package and supply chain" will be far more effective when the dosage itself is also protected with on-dosage identification and authentication technology. On-dosage identification and authentication technologies can help mitigate the security concern of repackaging and "counterfeit salting". On-dosage technology can ensure that the dosage itself is identifiable, protected and authenticated. Micro-taggant and/or chemical taggant technology is commercially viable today, and ensures pharmaceutical product authenticity at the dosage level. These taggant technologies provide quick, confident, and economical identification and authentication of pharmaceutical solid dosages in the field or in the laboratory. For example, micro-taggant technology provides for information-centric marker placement on each tablet to enable absolute identification and authentication by low cost readers. New colorant technologies can also be used to provide unique colors and images that are recognizable by the patient but difficult to duplicate by the counterfeiter. These technologies can provide easy to use tools for patients, customs agents, pharmacists, and regulators to authenticate oral solid dosage forms throughout the distribution chain. Some of the technologies can be used on the dosage and the package to essentially self-authenticate the product and the package without the need for large databases and controls like those required for RFID and other supply chain control techniques.

(252) **Host-Guest Reactive Desorption Electrospray Ionization Mass Spectrometry (DESI-MS) for the Rapid and Quantitative Authentication of Tamiflu Capsules**

Facundo Fernandez[1], Leonard Nyadong[1], Michael Green[2]; [1]Georgia Institute of Technology; [2]CDC Atlanta

The recent outbreak of avian influenza has increased the demand for antivirals. Tamiflu®, the leading antiviral on the market, has become a target for counterfeiters. Reports of counterfeit Tamiflu have already appeared thus creating an urgent need for rapid and sensitive Tamiflu® authentication tools. Reactive Desorption Electrospray Ionization Mass Spectrometry (DESI-MS) with consecutive reaction monitoring (CRM) is presented as a selective and rapid method to screen Tamiflu capsules with minimal sample preparation. DESI-MS analysis of genuine Tamiflu® gives predominantly the protonated monomer and dimer adducts. Doping the spray solution with crown ethers selectively gives a 1:1 protonated complex. Exploration of the gas-phase stabilities of various oseltamivir-crown ether complexes generated by DESI via breakdown curve experiments was in agreement with binding energies for the complexes computed at the B3LYP-D/6-311++G** level of theory. MS/MS analysis of the different complexes yields the protonated oseltamivir monomer which can be fragmented via MS/MS/MS experiments to give the ion at m/z 225. Monitoring this product ion by reactive DESI CRM MS results in a highly selective tool to screen oseltamivir. The addition of two separate crown ethers with different binding selectivities for oseltamivir to the DESI spray allowed the quantitation of the active ingredient without the need of an internal standard by measuring the ratios of the peak intensities of the two complexes. This ratio was shown to be independent of DESI variables such as spray angle, and spray distance to the sample, which normally affect absolute signal intensities and make quantitation difficult. Validation of this quantitative approach against HPLC showed good agreement. DESI provides the advantage of a substantial increase in sample throughput compared to HPLC. Screening of a set of inexpensive Tamiflu® samples collected over the Internet showed that all samples contained oseltamivir.

(253) **Analysis of Suspected Counterfeit Drugs: Supporting Prosecution and Enforcement**

Anthony Zook; [1]Merck & Co., Inc.

Counterfeit pharmaceutical products continue to be an increasing global threat to public safety. Many governments have responded by increasing efforts in enforcing and prosecuting counterfeit related crimes. The pharmaceutical industry can support these enforcement actions with rapid detection and reporting, demonstrating similarities between multiple counterfeit events, and enforcing of trademark violations. These issues highlight the demand for conclusive laboratory analyses of suspected counterfeit products that provide detection and characterization of counterfeit drugs. The ability to detect counterfeit products and packaging components is critical to protecting patients and supporting enforcement actions against the counterfeiters. Case studies utilizing forensic analyses for the characterization of counterfeit pharmaceutical products will be presented. The talk will also include the global application of that information towards the fight against pharmaceutical counterfeiters.

(254) **Immediate Field Analyses of Suspect Pharmaceutical Materials by Handheld Raman and FTIR: A Prescription for Action**

Christopher D. Brown[1], Robert C. Brush[1]; [1]Ahura Scientific

In this talk we discuss the application of handheld vibrational spectrometers for field analysis of pharmaceutical raw materials and finished goods. The extremely broad capability of Raman and FTIR spectroscopies makes them highly attractive for field inspection and screening. The literature has demonstrated the use of both technologies for such varied applications as ID authentication, screening for counterfeited and diverted pharmaceutical dosages, and detection of contamination in bulk materials destined for food and pharmaceutical use. In most practical field applications the design requirements for analytical technologies are as much a function of intended use and concept of operations as they are the performance of the analytical methods themselves. Drawing on illustrative field examples, we discuss a number of these nuances in deploying such field-screening tools, including decision trees, human factors, and performance characterization.

(255) **GC-MS and GC-IRD Studies on Regioisomeric and Isobaric Phenethylamines Related to 3,4-Methylenedioxymethamphetamine**

C. Randall Clark[1], Jack DeRuiter[1], Tamer Awad[1]; [1]Auburn University

This presentation will describe our continuing efforts to develop methods for the differentiation of regioisomeric and isobaric phenethylamines of importance in forensic drug chemistry. In phenethylamine-type molecules there are a total of five regioisomeric side chains yielding major El fragment ions at m/z 58. The high resolution capabilities of capillary GC coupled with the limited number of compounds (a total of five for the methamphetamines having an unsubstituted aromatic ring) has made the differentiation among these compounds routine in forensic drug laboratories. The ring substitution pattern in methylenedioxy-methamphetamine (MDMA) doubles the number of isomers to ten, the five side chain isomers in which the methylenedioxy-ring is substituted in a 3,4-manner and the five in which the methylenedioxy-ring is substituted in a 2,3-pattern. Many of these potential designer analogues have the strong possibility to be misidentified as 3,4-MDMA based on mass spectrometry. In addition to the ten amines containing the methylenedioxy-group, other substitution patterns have the potential to produce mass spectra with fragments of equivalent mass to those of 3,4-MDMA. For example, the reported stimulant methoxy-methcathinones are uniquely isomeric with the MDMAs having the same MW, elemental composition and expected major fragment ions of equal mass to those of the MDMAs (a total of 15 possible isomers). Additionally isobaric substitution patterns especially those likely to undergo few if any unique/characteristic fragmentations such as methoxy-methyl disubstitution of the aromatic ring (a total of 10 unique ring substitution patterns) are compounds with the potential to produce El mass spectra essentially equivalent to that of 3,4-MDMA. Each methoxy-methyl substitution pattern would produce 5-side chain isomers analogous to methamphetamine with the potential to yield mass spectra equivalent to 3,4-MDMA. As the number of compounds having mass spectral equivalence increases so does the challenge of specific identification via chromatographic resolution and other analytical methods. Regioisomeric and isobaric substances are considered a significant challenge for the analytical techniques used to identify specific substances. This is extremely important when some of these molecules are legally controlled drugs of abuse or controlled precursor substances. This presentation will focus on GC-MS and GC-IRD methods for differentiation among these regioisomeric and isobaric phenethylamines in both derivatized (acylation) and underivatized form.

(256) **Novel Aerosol Diagnostics for Nebulization Systems and High-Temperatures Plasmas**

William Bachalo; [1]Artium Technologies, Inc.

Over the past three decades, we have spent considerable effort in investigating the requirements for detailed characterization of aerosols and coupled these requirements with the evaluation of available physical principles that could be used in acquiring this information. A number of methods have been applied to aerosol characterization including mechanical methods such as compactors that utilize droplet momentum to characterize the aerosol, high-speed imaging, and laser light scattering. Each of these methods have advantages and disadvantages in characterizing sprays and their utility is highly dependent upon the specific information sought in the application at hand. During this presentation, what factors are required in appropriately characterizing an aerosol will be discussed and the relative merits of the available characterization methods will be reviewed. Interaction of these physical methods with the aerosol field and its environment will be addressed. Generally accepted light scattering methods will be described and their characteristics evaluated in terms of the information that is available and the reliability of that information. Separation of the light scattering methods into ensemble and single particle counting approaches will enable a clear discussion of the sampling statistics and characteristics of the reported measurements. How the sampling characteristics affect observation of the character and performance of the aerosol will be emphasized. Emphasis will be placed on the light scattering interferometry technique invented by the author and developed into a single particle counting instrument. This method provides the greatest amount of information which includes the direct measurement of the aerosol droplet size distribution, the simultaneous measurement of the velocity for each droplet, and aerosol number density and volume flux which are parameters equally important to the size distribution. Some examples of sprays and aerosol measurements will be presented to emphasize the importance of measuring these characteristics and of the reliability of the method in acquiring these data. A few leaders in nebulization and high-temperature plasma spectrometry have utilized the cited technology and have developed novel techniques that have been used recently for aerosol and plasma diagnostics to improve elemental and isotopic ratio analysis [1]. In this lecture, we examine the state of art in this area, and link them to prospects in both aerosol diagnostic and chemical analysis.

[1] A. Montaser, Editor, Inductively Coupled Plasma Mass Spectrometry, Wiley, 964 pages, 1998.

(257) **Comparison of Total Sample Consumption Systems for the Analysis of Microsamples through ICP-AES and ICP-MS**

José L. Todolí[1], Jean-Michel Mermet[2]; [1]University of Alicante; [2]Spectroscopy Forever, France

In the last times the application of total sample consumption systems has been considered as one of the best choices to carry out the analysis of very low liquid sample volumes (i.e., microsamples) through ICP-AES and ICP-MS. Total sample consumption systems are devices able to provide analyte plasma transport efficiencies approaching to 100%. The advantages of these devices are, among others, higher sensitivities, shorter wash out times and, in some cases, less severe matrix effects as compared to systems based on the coupling of a micronebulizer to a spray chamber. So far there two main total sample consumption systems have appeared: (i) direct injection nebulizers, e.g., Direct Injection High Efficiency Nebulizer (DIHEN); and, (ii) evaporation chambers such as the so called Torch Integrated Liquid Sample Introduction System (TISIS). In the former case the aerosol generated by the micronebulizer (primary aerosol) is directly introduced into the plasma base. Meanwhile the TISIS consists of a pneumatic micronebulizer adapted to a single pass spray chamber. Because, at low enough liquid flow rates, the totality of the solvent is evaporated, this chamber acts as an evaporation cavity rather than as an dropsize selection device. In the present lecture we will discuss the results obtained in a comparison study in which these two liquid sample introduction systems have been evaluated for the analysis of microsamples both in ICP-AES and ICP-MS. Results corresponding to aerosol characteristics, sensitivity and matrix effects caused by acids will be shown.

(258) **Novel Tool for Quantitation of Plant Genomic DNA**

Ryan Brennan[1,2], Savelas Rabb[2], Marcia Holden[3], Michael Winchester[2], Akbar Montaser[1]; [1]GWU Department of Chemistry; [2]NIST Analytical Chemistry Division; [3]NIST Biochemical Science Division

Agricultural and food products containing transgenic materials are a major health and nutrition concern. Because many such

commodities are imported and exported annually, they are also of great economic and trade interest. European countries require labeling of imported crops and prepared food stuffs that contain greater than 0.9 % transgenic material. Such regulations are important to the United States, which is the world's largest exporter of agricultural commodities and prepared food stuffs. The enforcement of such threshold values has created a demand for the development of a reliable analysis technique and Standard Reference Material (SRM) for transgenic materials. The accurate determination of the amount of DNA isolated from a biological material is not trivial. At the National Institute of Standards and Technology (NIST) in collaboration with The George Washington University, we are working towards developing a methodology that can be used to provide accurate measurements of DNA and nucleic acid mass that are traceable to the SI, with a long term goal of providing a SRM for DNA mass. Currently the ICP-OES approach developed at NIST, referred to as high-performance ICP-OES (HP-ICP-OES), incorporating a ratio-based technique with drift correction, is utilized for the measurement of phosphorus content of acid-digested DNA. The HP-ICPOES measurement of phosphorus provides a highly accurate quantitation for both nucleotide monophosphates and DNA with uncertainties of 0.1 to 0.2 %, however requires a significant sample size, restricting its usefulness for the quantitation of DNA. For this work, a novel tool is proposed for facilitating the direct injection of liquid samples into an ICPOES utilizing a d-DIHEN with a completely automated sampling process reported for the first time. With the previously developed HP-ICPOES method in combination with the d-DIHEN, the solution uptake rate is reduced from 170 µL min-1 to 30 µL min-1, with sample size reduced from 10 mL to 2.4 mL, and sensitivity improved by a factor of 2 on average compared to a glass concentric nebulizer with cyclonic spray chamber arrangement

(259) **Nanoelectrospray and MALDI Combined with Ion Mobility-Mass Spectrometry: Structural Insights from Liquid and Solid Phases**

John A. McLean[1], Sundarapandian Sevugarajan[1], Michal Kliman[1]; [1]Department of Chemistry, Vanderbilt University

Ion mobility spectrometry coupled with mass spectrometry (IM-MS) has demonstrated great potential for the identification, characterization, and quantification of analytes in complex biological samples. Structural details of anhydrous biomolecules can be interpreted by comparing experimentally determined collision cross sections (or apparent molecular surface area) with molecular dynamics simulations consistent with the IM results. By using low electrostatic field separation conditions in the IM drift cell, the separation is directly related to the ratio of the ion charge-to-collision cross section (or apparent surface area), but it is presently poorly understood whether the measured ion structures are influenced by the ion source that is used to produce them (e.g. MALDI versus ESI derived ions). Our present drift tube IM–MS instrument was constructed to use moderate pressure MALDI (2-5 Torr) as the ion source for MALDI-IM-MS experiments. In this report, we describe modification of our MALDI-based IM-MS instrument to also operate with a nano-electrospray (nESI) source for investigations that critically compare molecular structures obtained by using nESI or MALDI. The interface uses a keyhole funnel design similar to the hour-glass funnel described by Smith and coworkers (K. Tang et al., Anal. Chem. 2005, 77, 3330-3339) with a continuous dc-bias and rf fields to focus ions to the center of the funnel. Our keyhole ion funnel is designed in such a way to match the geometry of the IM drift cell and is utilized for high ion transmission efficiency from the atmospheric pressure nESI to the entrance of the IM drift cell and as an ion trap to store ions between IM–MS separations. This interface design can also be readily combined with high pulse repetition rate atmospheric pressure MALDI, which emulates a continuous ion source such as ESI, so that a critical structural comparison of MALDI versus ESI generated ions can be made on the same experimental arrangement. Studies comparing the influence of phase of analyte prior to ionization on the prevailing structure that is obtained will be described.

(260) **Enhancing the Tissue Segmentation Capability of Fast Infrared Spectroscopic Imaging via Chemometric Methods**

Rohit Bhargava[1], Frances Pounder[1], Rohith Reddy[1], Xavier Llora[1]; [1]University of Illinois at Urbana-Champaign

Practical decision-making tasks in a pathology laboratory include recognition of various cells in tissues (histology) and the recognition of disease in specific cell types (pathology). These tasks form the gold standard for determining much of clinical care in cancer and in research. Unfortunately, the manual nature of clinical practice precludes high throughput, introduces high variability in diagnoses and renders decisions of unspecified confidence. Here, we present an integrated chemometric framework to accomplish these human tasks using Fourier transform infrared spectroscopic imaging data. We present a modified Bayesian algorithm for segmentation and discuss its optimization for a multi-class approach. Next, we explicitly examine the effect of data quality on the accuracy of segmentation. An entirely automated, post-processing method to improve data quality by ~10-fold is presented. A predictive model for classification accuracy including data quality and biologic diversity, last, is used to predict classifier performance.

(261) **Kinetic Modeling of Hyperspectral Temporal Images**

Paul Gemperline[1], Patrick Cutler[1], David Haaland[2], Erik Andries[3]; [1]East Carooina University; [2]Sandia National Laboratories; [3]InLight Solutions

In this presentation we report the use of kinetic modeling of temporal hyperspectral fluorescence image data to extract kinetic information and rate constants for reactions of interest to biologists and computer modelers. In traditional kinetic modeling algorithms, the initial concentrations of all species in the postulated model must be known; however, in hyperspectral fluorescence images of biological specimens it is impossible to know the initial concentrations of all species. Two modeling techniques are reported here for systems with unknown initial concentrations: direct non-linear (DNL) fitting and separable least-squares (SLS). In the DNL approach, all parameters including rate constants and initial concentrations are estimated with a non-linear solver. In the separable least-squares approach, the inherently linear parameters (concentrations) and non-linear parameters (rate constants) are separated and solved in succession. The SLS method offers significant improvements in computational speed and robustness compared to the DNL method. These two methods are demonstrated and compared for the resolution of photo-bleaching in multicomponent glass beads and in temporal hyperspectral fluorescence images of fixed transiently transfected A549 cells with IKKalpha proteins tagged with Green Fluorescent Protein (GFP) and MAVS proteins tagged with Yellow Fluorescent Protein (YFP). Due to complexities in cell images and the presence of Poisson noise, successful implementation requires S/N based thresholding, pixel selection, fitting of multiple exponential decays for same colored species, and automatic fitting of temporal baseline offsets.

(262) **Modified Alternating Least-Squares as a Flexible Constraint Engine for multispectral Dermoscopy Image Analysis**

Thomas Hancewicz[1], Jesse Weissman[1]; [1]Unilever R&D

The appearance of human skin is important factor in assessment of health and vitality. Dermatologists and other skin care professionals often wish to measure skin color and appearance to understand the cause of various skin conditions and to monitor treatment efficacy. Measurement of skin color and chromophore content has been performed primarily with reflectance spectophotometers and colorimeters, and is usually reported in a color space. It is advantageous, however, to analyze skin color as being the result of interactions with various chromophores and scattering bodies occurring naturally in the skin. Furthermore, the spatial variations that occur within the tissue are important factors in the appearance of skin and for diagnosis and treatment of many medical conditions. Multispectral dermoscopy (MSD) is a new imaging modality designed to allow mapping of chromophore absorption and light scattering in living skin. The tissue is illuminated with white light and images are captured at wavelengths from 420 nm to 720 nm. The data cubes therefore contain reflectance spectra. Analysis of the data involves separating the spectra into contributions from melanin pigment, hemoglobin in blood, and scattering from cellular and fibrous structures. We have developed a multivariate curve resolution method based on modified alternating least-squares (MALS) that employs flexible constraints that use both hard and soft modeling aspects. This provides an improvement on traditional curve fitting methods for MSD data as a layered skin optics model. Results from different processing techniques and from a variety of body sites and skin pigmentation features will be presented and discussed.

(263) **Advanced Methods Characterizing Spatial Heterogeneity in Chemical Imaging Data Analysis**

Frederick Koehler[1], Kenneth Haber[1], E. Neil Lewis[1]; [1]Malvern Instruments, Inc.

Chemical imaging methods are employed to characterize the spatial-chemical heterogeneity in samples through the production of image contrast related to chemical identity and abundance. Beyond identifying chemical species, their location and amount, chemical imaging methods also characterize the morphology of the chemical domains identified in the sample. These metrics can include the number of domains of each chemical species, their size, and shape parameters such as elongation and circularity and their distribution within the sample. In many types of samples, such as pharmaceutical finished tablets, these measurements are recognized as important in understanding the interaction of chemical and physical properties to product quality and performance. An additional important metric available in chemical imaging analysis is the relative, overall spatial heterogeneity of the chemical species within the sample and the size scale at which this heterogeneity becomes evident. The work to be presented in this paper includes results from the application of a number of novel methods of producing an overall metric characterizing spatial heterogeneity in chemical imaging data analysis.

(264) **InSb Chemical Imaging of Processed Mixtures Analyzed for Ingredient Identity, Concentration and Distribution**

Lauren Brewer[1], David Wetzel[1], Hayes Charles[1]; [1]KSU Microbeam Molecular Spectroscopy Lab

Modern chemical imaging with an InSb near-IR focal plane array has the potential for providing information regarding the identity, quantity, and distribution of every ingredient in a mixture. Using the SapphireTM (Spectral Dimensions/Malvern, Columbia, MD), each pixel (x, y location) in the image has a size determined by elements in the focal plane array detector system and its associated lens used to collect radiation from the specimen. When the granulation of the product is similar to or larger than the image pixel size then each pixel, when chemically identified, can be enumerated in a particular column for that ingredient. From these data the relative amount of each ingredient is determined. This is particularly useful in manufacturing when the processing of raw ingredient materials and their blending into a product results in a mixture of guaranteed specifications. Quantitative analysis via NIR imaging is illustrated with mixtures of ground corn to which various protein supplements have been added. Individual pixel identity of ground corn versus the protein supplement is established by either selective wavelength discrimination or a PLS multiwavelength characterization. The latter is done for pure specimens of each material that is to be blended. In the blend, the identity of each pixel is assigned by application of the PLS or select wavelength discriminating feature. The percent of supplement is calculated by dividing the number of supplement pixels identified by the total number of pixels in the field. The image reveals the heterogeneity or homogeneity of the blend and the absence of a wrong ingredient or foreign material is assured. To illustrate the analytical scheme for use of chemical imaging a series of feed ingredients stocked in the KSU pilot feed mill were characterized by collecting 240,000 spectra in the 1100-2500 nm range of the indium antimonide focal plane array. After mixtures were produced then images were obtained and using the database prepared, each pixel was identified and counted. As blending of a mixture takes place the distribution of the ingredients can be monitored.

(265) **On-Line Attenuated Total Reflectance Fourier Transform Infrared Analysis of an Oligonucleotides Synthesizer Effluent Stream**

Lamar Dewald[1], Mary Beth Seasholtz[1], Randy Pell[1], Wendy Flory[1]; [1]The Dow Chemical Company

The Dow Chemical Company's Oligonucleotides Plant used an oligonucleotides synthesizer to produce market scale quantities of various products for the pharmaceutical industry. An oligonucleotide is a short, single-strand fragment of deoxyribonucleic acid or ribonucleic acid. Synthesis of an oligonucleotide consists of four repeated reactions – deprotect (deblock), coupling, sulfurize (thiolation), and capping reactions – that are cycled, once-per-base, on a prep-scale column until the desired product molecule is produced. This paper discusses how an on-line Attenuated Total Reflectance Fourier Transform Infrared (FTIR) Analyzer was used to study and optimize the operation of the synthesizer. The FTIR was used to follow each reaction and wash step, monitor the reaction for completion, and collect timing information for reactor control and modeling. These measurements were critical to the synthesizer's operation, as the plant experienced a yield loss and had difficulty in product purification if any of the reactions or washes were incomplete. Extensive modeling was required to monitor reactions throughout the column cycles to account for short-lived transition components. As many as 8000 FTIR spectra were collected (one spectrum every 8 seconds) during the different reaction cycles needed for the particular oligonucleotide. The spectra were used to develop the quantitative chemometric methods required to trend 15 components in the synthesizer. Amidites, solvents, coupling reagents, thiolation reagents, deblocking reagents, and intermediates were all monitored in the process. Components that only appeared during the reaction transitions, e.g. reactant-solvent couples, were identified, quantitated and tracked in spite of the lack of pure-component standards. For these transition components, Self Modeling Curve Resolution was used to isolate pure component

spectra even when the spectra were severely overlapped and had low signal-to-noise ratios. These isolated, pure component spectra were then used to develop models and a quantitative method for the transition components. FTIR results were used to optimize the operation of the synthesizer and provided input into the synthesizer's feedback control system.

(267) **Investigations into Steroid Analysis using Surface Assisted Laser Desorption Ionisation Mass Spectrometry**

Georgia Guild[1], Claire Lenehan[1], Stewart Walker[1]; [1]Flinders University

Steroids are routinely analysed by chromatographic methods including gas or liquid chromatography with mass spectrometric identification. Due to the low concentration and varied polarity of steroids, extensive sample preparation is required prior to analysis and as such researchers are continually searching for improved steroid detection techniques. Matrix Assisted Laser Desorption Ionisation (MALDI) mass spectrometry utilises a chemical matrix to absorb and transfer laser energy to promote analyte desorption and ionisation. The benefits of fast analysis times and soft ionisation can result in rapid and easy to interpret mass spectra. However, the inherent ionisation of the chemical matrix can result in a complex chemical background particularly in the low mass to charge (m/z) region of the spectrum. This can be particularly problematic for the analysis of small molecules (<1000 Da) as the analyte peaks can be masked by those of the ionised matrix. While analysis of steroids and other small molecules has been reported utilising MALDI, research has been directed towards the application of various Laser Desorption Ionisation techniques to circumvent the inherent matrix ionisation that occurs during MALDI analyses. The use of a carbon surface to promote Laser Desorption Ionisation is one such method and is the basis for this research. The analysis of a variety of steroids, namely: estrogens, progestogens and corticosteroids, have been successfully detected using this SALDI method. The resulting mass spectra show predominantly sodiated adducts of the steroids with some potassiated adducts detected at higher concentrations and no observable analyte fragmentation. This enables the detection of multiple steroids in a single mass spectrum, with spectra acquired in less than a minute and does not require complex derivatisation or separation of steroid analytes prior to analysis.

(268) **In-Line Mass Spectrometry Application for Control of Critical Drying Points**

John Wasylyk[1], William Bartels[1], Ming Huang[1], Robert Wethman[1], Charles Ray[1]; [1]Bristol-Myers Squibb Co.

At some point during the production of pharmaceutical intermediates, active products, or final formulation, the removal of residual solvents becomes a critical process. Control of solvent removal to below a specified level must be obtained while retaining the desired properties of the product of interest. These properties can include maintaining the correct form or polymorph, a specific hydration level, and/or physical characteristics of the dried material. We have used in-line mass spectrometry during development to understand the key mechanical parameters required to yield quality product. Furthermore, this understanding has led us modify conditions such as vacuum level, temperature, and agitation timing, improving cycle time, and retaining ideal physical characteristics. We will present data from both laboratory and pilot plant studies where mass spectrometry played an integral role in developing and implementing successful drying protocols.

(269) **Approaches to Increase Molecular Selectivity in Porous Silicon Based Laser Desorption/Ionisation Mass Spectrometry**

Rachel Lowe[1], Endre Szili[1], Paul Kirkbride[2], Gary Siuzdak[3], Nicolas Voelcker[1]; [1]Flinders University; [2]Australian Federal Police; [3]The Scripps Research Institute

In recent years, the integration of nanostructured assemblies into analytical devices has lead to unprecedented levels of device miniaturisation, sensitivity and analysis efficiency. One particular analytical technique that has benefited from the integration of nanomaterials is laser desorption/ionisation mass spectrometry (LDI-MS). To date, the most successful nanomaterial in LDI-MS has been porous silicon (pSi). pSi-based LDI-MS was originally termed desorption/ionisation on silicon (DIOS). The development of pSi LDI-MS has allowed surface-based molecular desorption/ionisation without the need for chemical matrices, and opened up the previously inaccessible low mass region for small molecule analysis. This analytical tool is of particular relevance to metabolomics, pharmaceutical development, environmental science and forensic science. In the latter, this technique is invaluable as pSi LDI-MS requires only sub microliter volumes per analysis and therefore is ideally suited to forensically relevant samples because of the small sample volumes often encountered. pSi offers a number of advantages over other nanomaterials, including high UV absorptivity, tuneable pore dimensions and ease of chemical modification. This research examines the relationship between pSi surface fabrication parameters, pore dimensions and LDI-MS of small molecules. In addition, surface chemical modification has been previously shown to passivate the pSi surface from oxidation and in some cases enhance detection capabilities. Here, we investigate the utility of different surface functionalities for the detection of forensically relevant small molecules. The surface functionalisation is also extended to incorporate antibodies, producing a molecular selective platform for benzodiazepine analysis. This research further advances the use of pSi surfaces for LDI-MS of forensically relevant small molecules, particularly their application in illicit drug roadside testing.

(270) **GC-MS and Electron Ionization LC-MS with Supersonic Molecular Beams**

Aviv Amirav[1], Alexander Gordin[1], Marina Poliak[1], Kfir Gil[1], Tal Alon[1], Alexander B. Fialkov[1]; [1]Tel Aviv University

We have combined the benefits of supersonic molecular beam (SMB) interface and its fly-through EI ion source with the Varian 1200 GC-MS and MS-MS, resulting in a new and powerful GC-MS platform with record setting performance including: GC-MS of compounds over 1000 amu: High GC column flow rates lower the elution temperatures and allow much larger molecules to elute. We analyzed a mixture of heavy linear chain hydrocarbons all the way to C84H170, all with dominant molecular ions. GC-MS of thermally labile compounds: The lower elution temperatures greatly enhance the range of labile compounds amenable for analysis such as carbamate pesticides, high explosives, underivatized steroids and polar drugs. Improved S/N: Enhanced molecular ion provides significant enhancement in the detection sensitivity via SIM or RSIM on the molecular ion. Fast GC-MS: Fast GC-MS analysis was achieved through the use of very high column flow rates for fast splitless injections and the high system selectivity due to the combination of enhanced molecular ion and MS-MS. Electron ionization can significantly benefit LC-MS through the provision of automated library identification and elimination of matrix ion suppression effects. We developed a new approach for Electron Ionization LC-MS with SMB named Capillary Separated Vaporization Chamber and Nozzle system (CSVCN). The output of LC was pneumatically vaporized in a GC injector like vaporization chamber and the vaporized sample and solvent were transferred to and expended from a 300 µm

supersonic nozzle into the vacuum system, followed by sample electron ionization while it is vibrationally cold in the SMB. Effective pneumatic spray based sample thermal vaporization was performed at about 2 Atm, while the supersonic expansion was at about 0.1 Bar nozzle backing pressure as needed to suppress cluster formation with the solvent vapor, yet to obtain good vibrational cooling. CSVCN provides a robust EI-LC-MS interface and enables the mounting of the vaporization chamber on a GC thereby having GC-MS and LC-MS in a one system with fast automated interchange between these two modes.

(271) **Fundamental Properties of DC Atmospheric-Pressure Helium Discharges Used in Mass Spectrometry**

Jacob Shelley[1], George Chan[1], Steven Ray[1], Gary Hieftje[1]; [1]Indiana University

Reduced-pressure discharges have long been used in mass spectrometry and atomic emission spectrometry. Because of this widespread use, the fundamental characteristics of such discharges have been extensively studied to improve their utility in chemical analysis. Interestingly, the characteristic current-to-voltage (i-V) curve changes significantly as the pressure is increased. At a convenient pressure limit, the resulting atmospheric-pressure glow discharges (APGDs) initially gained analytical importance with the development of atmospheric-pressure chemical ionization (APCI). APCI, which uses a corona discharge in ambient air, creates reagent ions such as protonated water clusters, which can be used for ionization of gas-phase analytes. More recently, APGDs in helium have been used for molecular mass spectrometry in the form of direct analysis in real-time (DART) and the flowing atmospheric-pressure afterglow (FAPA). These ionization sources have many advantages, including limited fragmentation because of inherent collisional cooling, wide dynamic range due to a high density of reagent ions, and increased ionization efficiency due to high-energy species formed in the discharge. In the present study, several fundamental parameters of three different helium atmospheric-pressure discharges were examined. To achieve comparability the sources were operated in the same discharge cell configuration, consisting of a pin cathode and a plate anode with a hole drilled into the plate. This is the configuration employed in both FAPA and DART. The cell body was made of quartz to permit spatially resolved emission maps of both the discharge and the afterglow to be obtained. Parameters that were examined include OH rotational temperature, electron number density, excitation temperature (derived from the addition of Ar to the discharge), and ionization temperature (using Fe atom/ion emission lines from ferrocene). These spatially resolved features yield important information not only about the fundamental discharge characteristics, such as DART using a corona and FAPA using a glow discharge, but also about proper sample positioning to maximize both ionization and desorption. Finally, a mass spectral comparison of the different discharge modes was performed. Topics of particular importance include matrix effects caused by competitive ionization and thermal stress on the sample.

(272) **A Miniature Mass Spectrometer with a Miniature Rectilinear Ion Trap**

Scott Smith[1], Jeffrey Maas[2], Zheng Ouyang[3], William Chappell[2], Robert Cooks[1]; [1]Dept of Chemistry, Purdue Univ.; [2]Dept of Elec & Comp Eng, Purdue Univ.; [3]Dept of Biomedical Eng, Purdue Univ.

This presentation will describe the design, construction, and evaluation of miniature Rectilinear Ion Traps (RITs) as well as a miniature RIT array in a hand-held mass spectrometer. The RIT is an attractive candidate for miniaturization owing to its simplicity of design, its large trapping capacity, and its proven performance. The geometry of the RIT is also beneficial in terms of an enhanced capability of operating at higher pressures when compared to hyperbolic equivalents owing to a wider pseudopotential well. Previous designs for portable mass spectrometers have incorporated single RITs with critical dimensions (x0 by y0 by z) of 5 x 4 x 50 mm. This presentation will describe the operation of an RIT with dimensions 1.66 x 1.33 x 16.67 mm as well as an array comprised of twelve such RITs. Additionally, a single RIT (x0 = 1.66 mm) with increased trapping capacity (z = 40 mm) will also be described. The benefit of reduced scaling is evident in the lower power consumption of the ion trap owing to the inverse quadratic relationship between RF voltage and the trap dimensions during mass-selective instability scanning. An array and a lengthened RIT are investigated because the trapping capacity scales with trapping volume and hence such geometries may be necessary to compensate for lost sensitivity. Though neither the array nor the lengthened RIT provide full capacity compensation when compared to full-scale RITs, the advantages of low-power operation with reduced sensitivity may be acceptable. Prototype versions of an array fabricated with stereolithography (SLA) have been tested on a bench-top instrument; these arrays performed over the mass range 150-1200 at a drive frequency of 740 kHz and an operating pressure of 15-20 mTorr in air buffer. Typical peak widths of 2-4 Th (full-width at half-maximum) were observed. Advances have been made in the SLA fabrication methodology as well as in the metallization process, which should improve electrode surface smoothness and device performance. Additionally, the new traps will be tested at a drive frequency of 1 MHz in order to provide a deeper pseudopotential well depth for enhanced performance.

(273) **Nanos Gigantum Humeris Insidentes: Approaches for Sensor Development in the 21st Century**

Radislav Potyrailo[1]; [1]GE Global Research

This talk will be focused on two aspects of development of the 21st century chemical and biological sensors – new sensing materials and new transducers. These developments are standing on the shoulders of our scientific giant, Prof. Gary Hieftje, who has developed the foundations of the modern microanalytical instrumentation and sensors. The first part of the talk will critically analyze new opportunities for sensing materials provided from in-depth understanding of materials properties and structure on nanoscale. Several examples from our labs will demonstrate the superb performance (e.g. selectivity, long-term stability, detection limits) of new sensing nanomaterials (e.g. semiconductor nanocrystal/polymer composites, plasmonic nanohole and nanopillar arrays, hierarchical photonic crystal structures). The second part of the talk will detail new prospects in sensing with our recently developed resonant transducers. The attractive capability of these individual transducers to provide selective multianalyte response and to reject interference effects became possible from the analysis of the complex impedance of the transducer response. These transducers are designed as resonant antenna structures of conventional 13.56 MHz passive radio frequency identification (RFID) tags. For chemical and biological sensing antennas are coated with sensitive films. Thus, unlike other approaches of using RFID sensors, where a special sensor should be designed at a much higher cost, these sensors are very cost-effective (<<$1) and can be ubiquitously deployed for a variety of applications.

(274) **Chemistry In-Silica: Sensor Arrays Based on Tailored Xerogel Platforms**

Frank Bright; [1]UB, SUNY

Sol-gel processing chemistry is widely used to create materials that are useful in areas ranging from low-k materials, to thermal insulation, stationary phases in the separation sciences and chemical sensors. Xerogels, nanoporous sol-gel derived materials formed by solvent evaporation at or near ambient conditions, are particularly attractive for chemical sensor applications. Over the

past 15 yrs we have been studying and exploiting xerogels as a means to create tailored platforms for optical sensing applications. The speaker will summarize his research group's efforts in the area of xerogel-based sensor platforms with particular emphasis on the potential of sol-gel-derived xerogels, low-powered light sources, and new detector array schemes to construct chemically responsive sensors and sensor arrays for simultaneous multi-analyte detection. The speaker will also summarize his research group's efforts to develop novel xerogel-based chemical sensors that do not utilize biomolecules as the recognition elements.

(275) **Developing Chemical Instrumentation using Microelectronics Fabrication Tools**

J. Michael Ramsey; [1]University of North Carolina at Chapel Hill

The microelectronics industry has developed a broad range of tools over the past five decades for fabricating intricate devices at the micrometer and nanometer scale. We have spent the last two decades trying to apply these miniaturization concepts to the design of microscale devices (instrumentation) for the elucidation of chemical and biochemical information. The diversity of chemical and biochemical measurement techniques that have been implemented on microchips includes various electrophoretic and chromatographic separations, chemical and enzymatic reactions, noncovalent recognition interactions, sample concentration enhancement, and cellular manipulations. In addition, the types of samples addressed by microchips has been broad in scope, e.g., small ions and molecules, single and double stranded DNA, amino acids, peptides, and proteins. These devices have low cost and small footprints while consuming miniscule quantities of reagents and can rapidly produce precise results. All of these features suggest the possibility to perform chemical and biochemical experimentation on a massive scale at low cost on a bench top, a goal being pursued by many laboratories around the world. More recently we have been investigating the prospects of shrinking channel lateral dimensions by a factor of approximately 1000, i.e., to molecular length scales. The fabrication of nanofluidic channels allows fundamental studies of transport at previously unexplored length scales as well as enabling potentially new capabilities such as the detection and characterization of single molecules. Moreover, we have been trying to shrink the mass spectrometer to pocket portable size while retaining much of its informing power. Recent developments in these areas will be addressed.

(276) **Eye on Ions - Forays with MS for Isotopic and Metallomic Analyses**

David Koppenaal[1], Charles Barinaga[1], George Hager; [1]Pacific Northwest National Laboratory; [2]Indiana University; [3]University of Arizona

Recent group research can be characterized by the clever oronym phrase 'eye on ions'. A number of new mass spectrometry approaches for improved elemental/isotopic and metallomic applications will be described. These include the development and application of focal plane MS detector technology (All the Signal, All the Time) and the more recent development of high-resolution elemental MS (Atomic OrbiTrap) approaches. In the former project we have developed three generations of charge sensitive array detectors, including a large-scale device capable of covering the entire atomic mass spectral range with ~1700 micro-detectors that can be independently accessed with either destructive or non-destructive readouts. The advantage to be gained here is improved isotope ratio determinations for all ions, all the time. The latter project describes recent work coupling an ICP ion source with an Orbitrap MS analyzer, resulting in direct high-resolution measurements of elemental isotopes with R>200,000. Such resolution, if routinely and ruggedly realized, can provide freedom from nearly all polyatomic and atomic isobar in interferences in ICPMS, and can provide immediate dividends in radioananalytical and metallomic analyses.

(277) **Research in the AAA Problems**

Robert Lodder[1]; [1]Spherix Inc.

During a career a scientist will typically work on all kinds of different problems. Some will have a broad impact and some will not. There are three general problems that promise to have such an impact on science as a whole that they have been called AAA problems. 1. Artificial Intelligence 2. Aging 3. Astrobiology Briefly, Artificial Intelligence (AI) is important because we hope to some day soon build machines with human and superhuman intelligence (see Moore's Law and AI) . Once this happens, all problems that can be solved by intelligence will be solved, because we can build more and more machines that will work day and night on the problems until the answers are obtained. Aging is an important problem to solve because eradication of aging and disease will allow humans to live forever. Once humans live forever, they will continue to learn more and more until all problems that can be solved by intelligence are solved. However, once humans live forever we will need more space to reproduce, and human life will have to expand beyond planet Earth. Astrobiology is the study of life in the universe. The tools of astrobiology will eventually be used by the human species to understand and explore the universe, and to expand our existence beyond first our planet and then our solar system. Many of us who worked in some fashion with Professor Gary Hieftje at Indiana University have had the opportunity to work on AAA problems in different ways. 1. in Artificial Intelligence (AI): through work in chemometrics and intelligent field data collection and laboratory systems. Nonparametric methods like BEST and BENDS can now be implemented in detectors through the use of Integrated Sensing and Processing (ISP) techniques. 2. in Aging: through work in age-related diseases like type 2 diabetes, atherosclerosis, stroke and MI. Novel medical devices and new drugs have been developed and commercialized through subsequent work. 3. in Astrobiology: through work in remote sensing, planetary and interstellar hyperspectral imaging. It would have been unfortunate to go through an entire career without ever having the opportunity to work on an AAA problem. Luckily, we did not have to.

(278) **Simultaneous Molecular and Elemental Mass Spectrometry for Comprehensive Elemental Speciation Analysis**

Steven Ray[1], Duane Rogers[1], Gary Hieftje[1]; [1]Indiana University

Modern analytical atomic analyses must often determine the chemical forms or non-covalent complexes associated with an element of interest, as well as the quantity and identity of the atoms constituting a sample. In plasma-source mass spectrometry, elemental speciation is typically determined by hybrid techniques, or by using multiple, separate analyses targeted at the two types of chemical information. In this latter strategy, the complementary nature of the inductively-coupled plasma (ICP) and electrospray ionization (ESI) sources to produce atomic and molecular chemical information, respectively, has been noted by many researchers. A unique time-of-flight mass spectrometer (TOFMS) is described here that is capable of employing both ICP and ESI ionization sources in a simultaneous, tandem fashion. Ions produced by independent ionization sources from a single sample, or the eluent from a single separation, are analyzed by a common TOFMS, providing complete elemental and molecular mass spectral information. The information conventionally collected by multiple analyses is thereby obtained in a single step. The use of TOFMS within this role permits the entire mass range to be observed with high temporal resolution, and without spectral skew error. The coupling of this system with chromatographic separations is

particularly advantageous, as run-to-run variations are eliminated, and unknown or unexpected components within a sample can then be directly identified.

(279) NeSSI Based Calibrated Gas Mixing System for Sensor Development and Calibration

Kent Mann[1], Brian Marquardt[2], Conor Smith[1], Charles Branham[2]; [1]University of Minnesota; [2]University of Washington

A gas mixing system based on the NeSSI (New Sampling/Sensor Initiative) platform has been constructed for sensor development and calibration. The system allows for high precision gas dilution (for example ppm mixtures of oxygen in nitrogen) with mass flow control (MFC) valves. Gas phase samples of volatile organic compounds can also be generated and further diluted. The entire system is computer interfaced through a user-friendly LabView program that allows sensor testing and calibration sequences to run for many days unattended. Applications of the system to vapochromic and oxygen sensor design will be discussed.

(280) Parker and NeSSi: Application of Bus Communications and Analytics in Sample Handling Systems

Mike Cost; [1]Parker Hannifin

The integration of modular sample handling systems and microanalytics provides end users with powerful capabilities. The need to reduce process feedback timing, increase system flexibility, reduce conditioning volumes and minimize system footprint, while maintaining optimum control of key sample handling parameters, necessitates the use of NeSSi based hardware. We will provide an overview of the Parker modular sampling system integrated with common communication protocols for enhanced process analysis capability. The benefits of integrating modularity, measurement and communications into a single system will be discussed. To compliment advances in communications architecture, we will present further advances in top work components for improved fluidics handling. An update on field implemented systems and a review of applications diversity using modular based systems will also be presented.

(281) Combining Analytical Sensors and NeSSI to Improve Process Understanding

Dave Veltkamp[1], Brian Marquardt[1,2]; [1]CPAC, University of Washington (UW); [2]Applied Physica Lab (APL), UW

This talk will focus on the use of a new industrial sampling system hardware architecture to provide fluidic interconnects and analytical sampling points for investigating reaction chemistries carried out in micro- , or small-scale, reactors. The fluidic system features commercially available, standardized, modular surface-moiunt components and substrate fluidic pathways based on the New Sampling/Sensor Initiative (NeSSI) products. These provide sample (reactiants, standards, and/or products) delivery, conditioning, and monitoring fuctionality and when combined with real-time analytical monitoring, provide a versitile system for studying reaction mechanics, kinetics, optimization, and scale-up issues in a compact and rugged platform. We will show that having the ability to control and monitor feed, intermediate, and product steams in a micro-reactor system allows for enhanced research opportunities.

(282) Calibration and Evaluation of Small Fiber Optic Oxygen Sensors with a NeSSI Gas Generation System

Charles W. Branham[1], Conor Smith[2], Kent Mann[2], Brian Marquardt[1]; [1]University of Washington; [2]University of Minnesota

Vapochromic compounds such as platinum double salts react directly to solvent vapors and simple gases by reversibly incorporating these molecules into their loosely packed crystal lattice; this causes the luminescence of the compounds to drastically change in both fluorescence wavelength and intensity. The optical response of a specifically designed compound can be directly related to the identity and concentration of the solvent vapor or gas incorporated. This unique vapo-luminescence behavior has helped to establish these compounds as new sensing elements for fiber optic based sensors. Our current work is focused on developing an optical vapochromic oxygen sensor for both gas phase and dissolved gas applications. There is much interest in developing new oxygen sensors for process analysis because of their extensive use in both oceanic and environment studies. These sensors are very attractive for distributed area and environmental sensing because they are reversible, small, fast, robust and inexpensive. In this seminar, I will focus on the development and calibration of a new platinum vapochromic compound that will be used as both a gas phase oxygen and dissolved oxygen sensor. The experiments were designed to utilize a novel gas handling system, New Sampling/Sensor Initiative (NeSSI), as the primary system for controlling and mixing of calibration and sample gases. I will also present a new surface mounted vapochromic oxygen sensor developed for use on the NeSSI system and a new oxygen fiber optic probe for *in-situ* analysis of dissolved oxygen in various water based applications.

(283) Dynamic Nuclear Polarization for NMR Signal Enhancement

Sandra Garcia[1], Jeff Walton[1], Songi Han[2], Michael J. McCarthy[1]; [1]University of California Davis; [2]University of California Santa Barbara

Nuclear magnetic resonance spectroscopy generally yields spectra with less mass sensitivity than other types of spectroscopy (e.g. NIR, Raman). Methods to enhance the mass sensitivity include reduction of the radio frequency coil size, isotope enrichment and polarization enhancements. Over the last few years we have been investigating the utility of sensitivity enhancement using microcoils and the subsequent development of microscale-NMR based on microfabrication techniques. While we have achieved sufficient sensitivity to measure physical properties, the mass sensitivity of the technique remains lower than desired for many process analytical applications. We have set out to improve this mass sensitivity by combining microcoils with Dynamic Nuclear Polarization (DNP). The nuclear spin of a proton can be hyperpolarized by transferring the much higher polarization from the electron to the nucleus of interest. This process, known as DNP or the Overhauser effect leads to a non-equilibrium nuclear spin polarization, i.e. NMR signal enhancement, of two to three orders of magnitude in solution samples. DNP works by irradiating the unpaired electron of a stable radical with radiation at its microwave resonance frequency. The electron and the nuclear spins are coupled through a motion-mediated relaxation process, thus as the electron spin relaxes, it transfers its polarization to the nearby nucleus. The higher signal obtained through DNP makes it possible to carry out NMR and/or MRI experiments at a much lower magnetic field, e.g. at 0.05 to 1.0 Tesla, as well as at reduced concentrations. Lower magnetic fields result in smaller and lower weight instruments that are easily transported and handled and can be built with NeSSITM compatibility in mind.

(284) New Intrinsically Safe Digital Bus Based Controller Area Network Applicability to Integrated Process Gas Chromatography Sample Handling Systems

Tracy Dye[1], Patrick Lowery[2]; [1]ABB Process Analytics; [2]CIRCOR

Process gas chromatography (GC) samples are typically hydrocarbons that are highly volatile or explosive in nature. These samples must be conditioned, filtered, monitored, and maintained at high temperature by use of a sample handling system (SHS). If any

device in the conditioning system fails, the chemical plant or refinery may have to shut-down a process unit, divert a chemical process, or worst-case, an expensive process analyzer may be damaged. An industry consortium drafted a new CANbus physical layer standard, CiA103, which allows analyzer suppliers and integrators to construct smart SHS using an intrinsically-safe (IS) CAN communication bus interface which is incapable of generating an ignition event. The IS CAN system configurations allow for multi-drop, multi-variable data and system architectures that coupled with standard I/O reduce cost of installation, ease of SHS configuration, and that can withstand highly aggressive environments. The new CAN architecture also allows for multi-variable sensing, control, safety, and process analysis scalability up to a plant-wide or analyzer network using various field bus or Ethernet topologies. This paper focuses on a production ready CANbus enabled process GC analyzer and an IS CANbus enabled SHS showing the system's attributes and benefits when using new IS SHS sensing/control devices throughout its design.

(285) **Ignoring Pharma: Moving Spectroscopy into the Real World**

Fred LaPlant[1]; [1]3M Inc.

Serving the pharmaceutical industry has been the principle concern of instrument manufacturers for the past 30 years. The combination of strict regulatory requirements, favorable profit margins, and highly skilled workforce has enabled implementation of spectroscopic solutions to many pharmaceutical problems. Unfortunately it is rare to have these factors coexist in other industries. Many of the solutions that would be acceptable to pharma would be insupportable elsewhere. This presentation will discuss the issues and opportunities in developing spectroscopic measurements outside of pharma, including application development, financial considerations, and gaining acceptance of spectroscopy in industrial environments.

(286) **Making Do - Weighted Regression Models for use with Less-Than-Perfect Data**

Jeremy Shaver[1]; [1]Eigenvector Research, Inc.

Many on-line process applications must be developed using existing, historical data which was collected while the process under study is "in-control". Under these conditions, a large amount of the available data appears at, or close to, set-point values and only a minority of the data is measured when in transition between set points or in process "excursions" (out-of-control conditions.) Often, however, accurate model predictions are most critical in these excursion and transition periods because they are needed to help bring the process to the desired set point. The data collected during set-point transitions and excursions are even more critical when building inferential models with complex data relationships. With inferential modeling, a relationship between measured data and a property of interest is empirically inferred from the process data and measured property values. Such models are common when spectroscopic instruments are used in on-line monitoring because the relationship between physical properties and measured spectral response can be complex. Unfortunately, inferential models and historical data can be somewhat incompatible because, when a large number of samples in historical data all exhibit a similar value (i.e. over-representation of a given value) with only minor variations, an inferential model may expend undue effort in predicting those over-represented samples to the detriment of minor, but real, deviations of other samples. In this work, we demonstrate a simple, automatic sample-weighting method which helps correct for the over-representation observed in historical data. The effect of sample weighting on self-prediction, cross-validation, and prediction of an independent test set are all noted for the modeling of a polymer end-property using on-line Raman spectroscopy.

(287) **Novel Spectroscopic and Statistical Approaches for Measuring Spatial and Chemical Heterogeneity in 'Sparse' Samples**

Neil Lewis[1], Kenneth Haber[1], Linda Kidder[1], Frederick Koehler[1], Janie Dubois[1]; [1]Malvern Instruments

Many manufactured products including most pharmaceuticals are composite physical mixtures in which the chemical composition, physical properties and spatial arrangement of the individual components all contribute to summary key performance indicators (KPIs). For some finished products this spatial and chemical heterogeneity is a desired or manufactured 'attribute', in others it is the result of contamination or inconsistencies in the initial raw materials, or variability imparted during one of the manufacturing steps. In many cases manufacturing problems arise as a result of these uncontrolled heterogeneities but the origin of the problem can sometimes be manifested at quite low average concentrations, can be localized in one or more areas of a relatively large sample, and/or only measurable at the microscopic level. However, a true understanding of the extent and impact of this chemical heterogeneity is only captured when a sufficient number of individual measurements of the sample are recorded at the appropriate spatial resolution. These types of measurements may be generally thought of as falling into a class of 'sparse' problems in which the information we are trying to access within the sample is either sparsely populated and/or the amount of information that needs to be recorded to adequately describe a particular sample is more optimally addressed with a smaller number of directed measurements rather than the brute force approach of chemical imaging or mapping. We will present data from a measurement approach that is specifically designed to address problems in which either the sample is physically sparse or a conventional spectroscopic mapping approach would produce significant redundancy in the collected data by repeating equivalent measurements over and over again.

(288) **Practical Applications of Raman Spectroscopy in Pharmaceutical API Process Development**

Robert Wethman[1], John Wasylyk[1], Ming-Hsing Huang[1], Jonathon Haulenbeek[1]; [1]Bristol-Myers Squibb

Raman spectroscopy has become a valuable tool to conduct pharmaceutical development. Raman spectroscopy is proving to be a powerful, flexible and efficient technique providing valuable information to support QbD and scale-up studies. The presentation will highlight several examples where raman spectroscopy provided enhancements in processing cycle time, analysis cycle time, and data gathering. Special focus will be given to keys for successful method development and transfer.

(289) **Laser Raman Spectroscopic Technology and Results in Oceanographic Science Applications**

William J Kirkwood[1], Peter G Brewer[1]; [1]Monterey Bay Aquarium Research Institute

Scientists and engineers at the Monterey Bay Aquarium Research Institute (MBARI) in cooperation with Kaiser Optical have successfully developed and deployed two generations of deep ocean laser Raman spectrometer (DORISS 1 & 2) systems, the first such systems ever for deep-ocean field work. Laser Raman spectroscopy allows the non-invasive interrogation of geochemical targets *in-situ*, and the MBARI team has successfully combined these units with remotely operated vehicles for real-time measurements to depths of 4,000 m. Geochemical explorations of the deep ocean have historically relied on samples recovered from surface ships, manned submersibles, and remotely operated

vehicles (ROVs). Historically the samples are processed on the ship or held frozen until shore-based analysis can be performed. During recovery, these samples are exposed to changes in pressure and temperature which may alter their geochemical composition; this problem is particularly acute for methane hydrates, which are unstable at atmospheric T and P. Our first system (DORISS 1) worked, but required significant improvements in reliability for expeditionary use. These challenges were met, again in collaboration with Kaiser engineers, and a far more robust system was developed. This paper will discuss the efforts we have made to increase the sensitivity of our second generation Deep Ocean Raman *in-situ* Spectrometer (DORISS 2) and the lessons learned along the way. This talk describes the engineering approach taken to build these systems, the challenges faced during development, and solutions to these challenges. Also, the talk will illustrate the various steps taken to work in the ocean that make the application challenging but also rewarding. The talk will review the cruise deployments of the completed systems for investigation of sea floor hydrates in Barkley Canyon, and for hot vent sites at Gorda Ridge. Results from these studies will be presented as an example of the performance capabilities of the DORISS 2 instrument and supporting technology for ocean science.

(290) **Process Raman: Challenges and Rewards**

Brian Marquardt[1]; [1]University of Washington

The application of Raman spectroscopy for quantitative analysis of a variety of unique processes using chemometric calibration methods will be described. The ability to accurately quantitate molecules with Raman spectroscopy can potentially open new doors in process analysis by introducing a fast, non-invasive, information rich, high-resolution monitoring technique. The combination of chemometric analysis methods and the high selectivity of Raman spectroscopy to "fingerprint" organic and inorganic compounds can be a very effective combination. The complications related to using Raman in a process stream or environmental application occurs when significant spectral background interference is encountered (both fluorescence and inherent background signals). In this presentation, I will present examples of Raman data collected in a variety of processes such as: fermentations, salmon farming, deep ocean research, polymer production and others will be described with emphasis on background correction and quantitation. Each process presented will be vastly different in both the physical sampling environment and the chemical information extracted. A description of the optical sampling approaches used to obtain reproducible Raman spectra in the presence of strong and variable backgrounds and interferents will also be discussed. These variable background signals lead to major problems when calculating multivariate calibration models and they must be addressed. Fortunately, preprocessing methods such as iterative baseline correction can be applied, prior to analysis, in order to reduce these process/environmental effects on the spectra. Various preprocessing algorithms will be briefly described and demonstrated for the minimization of background interference before Raman calibration. This presentation will be focused on utilizing Raman spectroscopy in conjunction with chemometric analysis methods to non-invasively and continuously monitor analyte concentrations in a variety of processes.

(291) **Combining Calibration Transfer and Preprocessing: What Methods, What Order?**

Charles E. Miller[1], Robert T. Roginski[1], Neal B. Gallagher[1], Barry M. Wise[1]; [1]Eigenvector Research, Inc.

Spectroscopic instrument differences can be mitigated by data preprocessing methods (e.g. baselining, derivitization, multiplicative scatter correction) and standardization methods (e.g. piece-wise direct standardization, orthogonal signal correction, generalized least squares weighting). Each of these methods has strengths and weaknesses in the face of different types of instrument non-idealities. Can these methods be used in combinations that are more effective than single approaches? This talk discussed how combinatiions of techniques can be used. Approaches are tested on 3 NIR data sets with different standardization issues.

(292) **Practical Aspects of PAT Method Transfer in the Pharmaceutical Industry**

Bronwyn Grout[1,2]; [1]Pfizer Inc; [2]School of Pharmacy, University of London

Process Analytical Technology (PAT) is now well established in the pharmaceutical industry and the strategic and functional benefits of PAT implementation have been extensively discussed in both literature and on the conference and seminar circuit. However concern has been raised regarding the resource intensive aspect of PAT method development and subsequent robustness and maintenance. One proposed approach to removing the burden of method development is centralised method development and deployment to multiple locations through PAT method transfer. Though this may relate to any PAT technology, this topic typically revolves around the transfer of spectroscopic techniques with multivariate quantitative methods of analysis. Recent research on such NIR methods (still the primary technology utilised in PAT applications) has demonstrated that method transfer is possible. However the practicalities of method transfer for NIR methods is often not discussed. This presentation discusses the significant challenges of method transfer in the pharmaceutical Industry. The cultural and educational challenges of 'high tech' chemometrics verses traditional analytical test method transfers will be covered along with validation considerations, and common quality organisation concerns and regulatory considerations. Instrument and sample related issues will also be discussed such as challenges in determining appropriate transfer samples, instrument robustness and method transfer associated with new product introduction and product transfers. Additionally the alternatives to method transfer, such as mechanisms for rapid revalidation, harmonised technologies and suppliers and less resource heavy non-quantitative methods will be compared.

(293) **Universal Quantitative Standards for the Transfer of Assays of Actives in Intact Tablets using Reflection NIR Spectroscopy**

Nathaporn Hongsrisuk[1], Roger Jee[1], Tony Moffat[1]; [1]The School of Pharmacy, University of London

The aim of this study was to transfer active assays created on one NIR instrument to another using universal quantitative standards. Reflectance near-infrared (NIR) spectra of 116 Sterwint ® 500 mg paracetamol intact tablets (29 batches, 76.5 to 91.6% m/m active, nominal diameter 12.9 mm) were measured on three different FOSS NIRSystems instruments. Reference values for the active were measured according to the BP 2008. Instruments: A, XDS Masterlab spectrometer; B, XDS spectrometer fitted with a Rapid Content Analyser (RCA) and C, 6500 monochromater fitted with a RCA. The following transfer standards were used; avicel PH101, benzoic acid, methylparaben, paracetamol, sucrose, mean sample spectrum (38 paracetamol tablets), mean paracetamol tablets (other brands) and a set of six different pharmaceutical tablets. Two containers, 12 mm diameter vial and a 50 mm diameter cell were used to measure the powders. Spectra of tablets measured on instrument B and C were corrected using the difference spectrum of the transfer standard measured on A and B or C respectively. These corrected spectra were then used to predict the paracetamol content using a model developed on A. A three factor PLSR calibration

model (1100-2498 nm) using SNV + 1st derivative spectra on instrument A gave an RMSEP of 0.57% m/m. Direct transfer of spectra from instrument B gave RMSEP = 0.81% m/m and pt-test = 0.00 (paired Student's t-test between predicted values and reference values). Corrected spectra gave better results, e.g. a set of tablets (0.58% m/m, 0.23), mean sample spectrum (0.56% m/m, 0.23) and sucrose in vial (0.58% m/m, 0.08). Transfers between different instrument types (A and C) were less successful using direct transfer (0.97% m/m, 0.00). However, corrected spectra extremely facilitated the transfer; a set of tablets (0.52% m/m, 0.62), methylparaben in vial (0.52% m/m, 0.92), and mean sample spectrum (0.52% m/m, 0.55). Mean sample spectrum and a set of tablets gave best transfer models. These results support that transfer standard needs to closely match the sample both chemically and physically. Additionally, model selection was also an important aspect, e.g. increasing the level of smoothing during spectral pre-treatment generally improved transfer.

(294) **NIR Determination of Crystallization Solvent Composition: Method Development and Transfer from Lab to Pilot Plant**

Charles Goss[1], Seán Sisk[2], Bob Cooley[1], Bobby Glover[1], Rahn McKeown[1], Tom Lovelace[1], Brian Crump[1], Darryl Ertl[1]; [1]GlaxoSmithKline, RTP, NC, USA; [2]GlaxoSmithKline, R&D Lab, Cork, Ireland

The production and performance of pharmaceutical medications can depend strongly on the physical properties of the active pharmaceutical ingredient (API), which follow directly from the crystallization and isolation conditions used during API manufacture. Crystallization of an API is a complex process that can be influenced by many factors such as solvent composition, API concentration, seeding, temperature, agitation, etc. Obtaining a reproducible crystallization process requires that the critical parameters be identified and appropriately controlled. This talk will describe the development of a near infrared (NIR) spectroscopy method for online measurement of important API crystallization solvent composition parameters and its transfer from lab to Pilot Plant.

(295) **Augmented Classical Least Squares Methods for Improved Calibration Transfer and Maintenance**

David Haaland[1], David Melgaard[1], Christine Wehlburg[2], Robert Guenard[3], Randy Pell[4]; [1]Sandia National Laboratories; [2]MITRE Corporation; [3]Merck & Company; [4]The Dow Chemical Company

Multivariate spectral calibrations, (generally Partial Least Squares [PLS] or Principal Component Regression [PCR]) are finding increased use in industrial settings, especially in the areas of quality control, process monitoring and pharmaceutical analyses. However, there are a number of barriers to their greater wide-spread use such as the difficulty of maintaining calibrations on a drifting spectrometer and transferring calibrations between spectrometers. Time consuming recalibration is one solution to this problem, but it is generally too expensive to implement in practice. Piece-wise direct standardization (PDS) employing one or more calibration standards measured on a drifting spectrometer or on each spectrometer to be used in analysis has become the industry standard for solving these calibration maintenance and transfer problems. However, we find that new algorithmic approaches can be more readily implemented and achieve improved calibration maintenance and transfer performance. The new approaches are the augmented classical least squares (ACLS) and CLS/PLS hybrid algorithms. These algorithms can be updated directly during prediction without the need for recalibration or without the necessity to explicitly determine a transfer function. The ACLS algorithm will be explained and its improved performance relative to PDS methods will be demonstrated for both calibration maintenance and calibration transfer using a system of dilute aqueous solutions and mixtures of organic liquids. Not only are the prediction abilities on the test samples improved with these alternative algorithms when transferring or maintaining calibrations, but the ability to detect outlier samples is also improved. Sandia is a multi-program laboratory operated by Sandia Corporation, a Lockheed Martin Company, for the United States Department of Energy under Contract DE-ACO4-94AL85000. Sandia is a multi-program laboratory operated by Sandia Corporation, a Lockheed Martin Company, for the United States Department of Energy under Contract DE-ACO4-94AL85000.

(296) **Examples of NIR Calibration Transfer across Identical and Different Hardware Platforms**

Michael Surgeary[1], Ronald Rubinovitz, Ph.D[1]; [1]Buchi Corporation

Calibration transfer is a critical element of Near-Infrared (NIR)applications. Many manufacturers who use NIR for raw material identification and quantification of components in materials have the need to utilize multiple NIR spectrophotometers throughout their facilities. It is essential to be able to develop calibrations using spectra generated on one NIR spectrophotometer and then transfer the calibrations to other NIR spectrophotometers at different locations. Some manufacturers may need to replace outdated NIR spectrophotometers but still maintain the functioning calibrations that are in use. Since no analytical instrument can be considered exactly equivalent, careful consideration must be exercised when transferring NIR calibrations. This presentation will demonstrate that it is possible to successfully transfer NIR calibrations. Specific examples will be used to present a methodology for effective NIR calibration transfer for both identical and similar hardware platforms. Calibrations transferred to other NIR spectrophotometers must demonstrate the same performance and capabilities across all instrumentation. To achieve this, there must be consideration for the type of instrumentation involved in the transfer, software tools available, calibration development, mathematical transformations, and model optimization. The criteria for evaluating successful calibration transfers will also be discussed.

(297) **Development of a Multiplex Spectrometer for Doubly-Resonant SFG Spectroscopy**

Taka-aki Ishibashi[1], Toshiki Maeda[1]; [1]Hiroshima University

Vibrational SFG is now widely used for investigating molecular structures of interface species. This is because the method permits the interface specific observation of vibrational spectra. Usually vibrational SFG spectroscopy is performed under electronically non-resonant conditions. However, vibrational SFG under electronically resonant conditions, that is vibrationally-electronically doubly resonant SFG (DR-SFG), enhances the sensitivity and selectivity. The signal enhancement due to electronically-resonant effect improves the sensitivity of SFG. The enhancement is expected only for species that have electronic absorption at the SFG frequency. Therefore, DR-SFG offers a kind of molecular selectivity to SFG. By measuring UV/VIS probe frequency dependence of vibrational SFG band intensity, we can obtain an electronic spectrum of interface species for each vibrational band. The DR-SFG excitation profiles thus obtained are useful to investigate mixed mono-layers, where several chemical species co-exist and give us complex vibrational spectra, because we can sort out vibrational bands guided by corresponding electronic spectra. DR-SFG also allows us to detect the chirality of thin films. To fully exploit the advantages of DR-SFG, it is desirable that the wavelength of the UV/VIS probe is variable as widely as possible. We have developed an SFG spectrometer designed for DR-SFG spectroscopy. The apparatus employs a

multiplex detection method and has a wide tunability of the UV/VIS probe wavelength (235-390, 400, 420-795 nm). In the conference, we will introduce the spectrometer and present some of results that represent features of DR-SFG.

(298) **Modeling of Plasmas, Plasma-Solid and Laser-Solid Interaction**

Annemie Bogaerts[1]; [1]University of Antwerp

In this talk, an overview will be given of different modeling activities going on in our research group, in the field of plasmas (for analytical and technological applications), laser ablation, and plasma-solid interaction. Plasmas are not only used in analytical spectrochemistry, but also in a growing number of technological, biomedical and environmental applications. To improve these applications, a good insight in the plasma behavior is desirable. We try to obtain this by numerical simulations. There exist several approaches to model plasmas, with their advantages and disadvantages. We make use of fluid, Monte Carlo (MC), particle-in-cell – Monte Carlo (PIC-MC) and hybrid models. In this presentation, several examples will be given of these plasma modeling activities, to illustrate the capabilities and limitations of the various modeling approaches. The following topics will presented: • Fluid modeling for describing detailed plasma chemistry, leading to nanoparticle formation in plasmas; • Fluid modeling for describing dielectric barrier discharges (DBDs), used for instance as microplasmas in analytical spectrometry; • PIC-MC modeling for describing magnetron discharges; • Hybrid MC-fluid modeling for describing glow discharges (used in analytical spectrochemistry). Beside modeling the plasma itself, it is also interesting to simulate the plasma-solid interaction, for applications such as thin film deposition and surface etching. For this purpose, we apply molecular dynamics (MD) simulations. The capabilities and limitations of MD simulations will be illustrated for the case of plasma deposition of thin films. Next to the plasma-solid interaction, we also study the interaction of a laser with a solid material, i.e., laser ablation, for the purpose of sample introduction into an ICP. The laser-solid interaction leads to heating, melting and vaporization of the solid material. This is described with a heat conduction equation. A vapor plume is formed, which expands into a background gas (or in vacuum). This is described with Navier-Stokes equations. Moreover, because the vapor plume is at high temperature, a plasma will be formed, and the laser will interact with the plasma, yielding laser absorption. This means that only a certain fraction of the laser light will actually reach the solid surface, i.e., called “plasma shielding”. Finally, the laser ablated material will be transported from the laser ablation cell, through a transport tube, into the ICP. By using fluid dynamics equations, we can calculate the gas flow and particle transport, and make predictions on optimal cell designs.

(299) **Analysis of Bismuth in Pharmaceuticals**

Brent Ferguson[1], Rebekah Kimbrough[1], Marina Koether[1]; [1]Kennesaw State University

Bismuth, a chemical element, is found in an organometallic complex used for the relief of upset stomachs. The formulation of the drug ranges from liquids to tablets to caplets with varying amounts of bismuth. Both, a literature search for the biochemical mechanism of the effect as well as a chemical analysis of the bismuth composition in the variety of preparations were conducted. The analysis began with the dissolution and release of the bismuth from the complex and ended with the determination of bismuth in the prepared solutions by Flame Atomic Absorption Spectroscopy. To determine concentration, standard curves were prepared. To ensure recovery and reproducibility, standards were spiked into the samples. Thus, a number of drugs containing bismuth were analyzed to ensure that the quantity listed on the product was the quantity found.

(300) **Thermoelectrically Cooled Cryocell Assisted LA-ICP-MS and Liquid ICP-MS Analysis of Metals in Kidney and Liver Samples from Beached Porpoise**

Matthew Horton[1], Aldemaro Romero[2], Roger Buchanan[2], Robyn Hannigan[3]; [1]CETAC Technologies; [2]Arkansas State Univ., Dept. of Bio. Sci.; [3]Arkansas State Univ. Dept. of Env. Sci

The aim of this investigation is the determination of element concentrations and profiles in the inner organs of a beached harbor porpoise (Phocaena phocaena) carcass stranded off the coast of Cape Cod, MA, in 2003. Eleven elements were detected and measured in liver and kidney samples. A thermoelectrically cooled sub-zero laser ablation sample cell was devised for the analysis of porpoise liver and kidney tissues. The temperature controlled cooling cell has a user programmable operational range between 0 and -30oC. The cooling cell was used here to preserve the integrity of the sample during ablation and to evaluate the affect of sub-zero temperatures on reproducibility. Metal ion concentrations in samples were determined using LA-ICP-MS. Frozen tissue samples were ablated using a CETAC LSX-213 Laser Ablation System, operating at 213 nm. Ablated samples were carried by a Helium carrier stream into the argon plasma of a PerkinElmer Elan 9000 ICP-MS system. During laser ablation tissues were maintained at room temperature or cooled to subzero temperatures (-10 to -30 oC) in the laser ablation cold cell to monitor the effect of sample temperature on ablation efficiency. Results from laser ablation analyses were compared to ICP-MS analyses of tissue samples digested with ultrapure nitric acid. Metals in the digested samples were measured and detected using optimized ICP-MS conditions. Of the metals analyzed (V, Cr, Cu, Zn, Se, Ag, Cd, Hg, Pb, U, Tl) elevated levels of Hg (~100 ppm) and Cd (~80 ppm) were found in the liver and kidney respectively. Results from laser ablation ICP-MS analysis were - depending on the metal -comparable within 2-10% RSD to liquid digestion based ICP-MS values. Precision in LA-ICP-MS was dramatically improved for analyses of tissues cooled below sub-zero temperatures compared to room temperature analyses.

(301) **Distribution of Cd, Zn, Se and Fe in Prostate Cancer Specimens**

Todor Todorov[1], Alan Koenig[1], Andre Kajdacsy-Balla[4], Andrey Sarafanov[2], Marion Gray[3], Jose Centeno[2]; [1]US Geological Survey; [2]Armed Forces Institute of Pathology; [3]James Cook University, Australia; [4]University of Illinois - Chicago

Prostate cancer is a major health issue worldwide. It is the most frequently diagnosed male cancer and the second leading cause of cancer death in men after lung cancer. Since environmental factors are modifiable, they have important implications for the prevention and progression of prostate cancer. Four trace elements, Cd, Se, Zn and Fe, have been highlighted in the literature as important to prostate cancer. Research has found a distinct biological antagonistic effect between Zn and Cd in the human prostate gland. Zn is beneficial for normal prostate function and show decreased levels in prostate cancer patients. On the other hand, Cd, a toxic element, is elevated in patients with prostate cancer. Studies have shown that men with higher levels of blood Se have a decreased chance of developing prostate cancer. Iron is an essential element, but high levels have been associated with increased cancer cell invasion. Although prostate cancer is widely studied, its trace element etiology is unknown. In this paper we describe laser ablation inductively coupled plasma mass spectrometry (LA-ICP-MS) as a tool to investigate the distributions of Cd, Se, Zn and Fe in cancerous and non-cancerous prostate cells. For this study we used prostate tissues from the Cooperative Prostate Cancer Tissue

Resource bank. The tissue slices were prepared using a cryogenic tissue slicer, and elemental analysis was accomplished in a laser ablation cryocell. Calibration was performed with frozen liver paste certified for Zn, Cd, Fe and Se levels. In the presentation, we will discuss the laser ablation parameters and performance using the developed cryocell. Elemental concentration maps were generated for each of the elements of interest and were compared to adjacent H and E (hemotoxalin and eosin) stained sections. The information obtained in this study provides a better understanding of the mechanism of trace elements in prostate carcinogenesis by determining whether abnormal levels of toxic metals occur in cancer cells or in the surrounding stroma and normal-appearing glands.

(302) **Calibration-Free LIBS Analysis of Space Resolved Spectra from a Cu-Fe-Mn-Ni Alloy Plasma**

Gabriele Cristoforetti[1], José Antonio Aguilera[2], Carlos Aragon[2], Elisabetta Tognoni[1]; [1]CNR-IPCF, Italy; [2]Universidad Publica de Navarra, Spain

A plasma was induced in air by irradiating the surface of a Cu-Fe-Mn-Ni alloy target with a Nd:YAG laser pulse. Space resolved spectra from a plasma slice, parallel to the target surface, were collected and sent to an imaging spectrometer coupled to an intensified CCD. A deconvolution algorithm was applied to the acquired spectra providing the radial profiles of local emissivity in the plasma. A space integrated spectrum was also acquired for comparison purpose. The Calibration Free - LIBS algorithm was applied to the local emissivity spectra, so that the relative abundance of the minor components Fe, Mn and Ni in the different plasma regions was calculated; for aim of comparison, the same procedure was used for the analysis of the space integrated spectrum. The plasma temperature was evaluated by using Saha-Boltzmann plots; the electron density was measured from the Stark shift of the 538.34 nm Fe I line. The use of local emissivity spectra, rather than that of integrated spectra, leads to a satisfactory agreement between CF-LIBS results and nominal concentration values, especially in the central region of the plasma. From these preliminary measurements, space resolved spectra appear to be more suited for quantitative analysis via CF-LIBS than space integrated spectra.

(303) **Cryo-Cell Innovations for Biological Tissue Analysis by Laser Ablation ICP-MS**

Steven Hughes[1], Joseph Brady[1], Robert Fry[1]; [1]Spectr-LAse

In a pathology or toxicology lab, cryostatically prepared thin-sections of frozen biological tissue are typically viewed under a microscope with back illumination. With laser ablation, this normally doesn't work because thin sections of these tissues normally don't yield sufficient ICP or ICP-MS sensitivity. Tissue sections for laser ablation are typically cut thicker, to allow increased ablation rates, enhance sensitivity, and prevent the laser from ablating through to the underlying support substrate. The thicker "cut" normally would not permit a back illumination scenario, due to opacity, and so a top side illumination is typically used instead. However, this does not facilitate the visual contrast possible with back side illumination of a cryostatically prepared thin section, to examine and correlate pathology with laser ablation data. This paper will explore possibilities and design considerations in using back illumination for laser ablation analysis of cryostatically prepared thin sections. Several options will be presented to avoid the laser cutting through the thin section and ablating the underlying substrate, while still effecting the desired analytical sensitivity. A novel cryo-cell design will be presented which facilitates back illumination with frozen thin sections and yields the desired sensitivity.

(304) **Second Order Nonlinear Optical Imaging of Chiral Crystals (SONICC)**

Garth Simp; [1]Purdue University

The major cost in terms of time and expense in protein structure determination by x-ray crystallography often rests in the identification of conditions for generating diffraction-quality protein crystals. In this work, the unique selection rules of second harmonic generation (SHG) microscopy were found to enable sensitive and selective imaging of protein microcrystals with negligible contributions from solvated proteins or amorphous protein aggregates. The ratio of the forward-to-backward detected SHG provides a measure of the particle size, suggesting detection limits down to crystallites ~100 nm in diameter under low magnification (10x). These detection limits already exceed commercially available methods by approximately 6 orders of magnitude, with significant room for improvement (e.g., using higher incident peak powers and higher magnification). As such, a million-fold greater number of conditions for protein crystallization can be screened with the same quantity of initial protein. In studies of microcrystallites of green fluorescent protein (GFP) prepared in 500 pL droplets prepared in crystallization micro-arrays designed in-house, the SHG intensities rivaled those of fluorescence but with superb selectivity for crystalline regions. GFP in amorphous aggregates and in solution produced substantial background fluorescence, but no detectable SHG. In addition to being sensitive and highly selective, second order nonlinear optical imaging of chiral crystals (SONICC) is directly compatibility with virtually all common protein crystallization platforms.

(305) **Investigations of Thermotropic Phase Behavior of Newly Developed Synthetic PEGylated Lipids using Raman Spectro-Microscopy**

Rajan Bista[1], Reinhard Bruch[1], Aaron Covington[1,2]; [1]Department of Physics, University of Nevada, Reno; [2]Nevada Terawatt Facility, Reno, Nevada

In this study, a temperature-induced Raman spectro-microscopic technique has been utilized to detect and analyze the phase behaviors of two newly developed synthetic PEGylated lipids trademarked as QuSomes™, which spontaneously form liposomes upon hydration in contrast to conventional lipids. The amphiphiles considered in this study differ in their hydrophobic hydrocarbon chain length and contain different units of polyethylene glycol (PEG) hydrophilic head groups. Raman spectra of these new artificial lipids have been recorded in the spectral range of 3100-500 cm-1 by using a Raman microscope system in conjunction with a temperature-controlled sample holder. The gel to liquid phase transitions of the sample lipids, composed of pure 1,2-dimyristoyl-rac-glycerol-3-dodecaethylene glycol (GDM-12) and 1,2-distearoyl-rac-glycerol-3-triicosaethylene glycol (GDS-23) have been revealed by plotting peak intensity ratios in the C-H stretching region as a function of temperature. From this study, we have found that the main phase transitions occur at a temperature of approximately 5.2 oC and 21.2 oC for pure GDM-12 and GDS-23, respectively. Furthermore, the lipid GDS-23 also shows a post phase transition temperature at 33.6 oC. To verify our results, differential scanning calorimetry (DSC) experiments have been conducted and the results are found to be in an excellent agreement with Raman scattering data. This important information may find application in various studies including the development of lipid based novel substances and drug delivery systems.

(306) **Chemometrics to Handle and Resolve Time Resolved Spectroscopic Data**

Cyril Ruckebusch[1], Lionel Blanchet[1,2], Ludovic Duponchel[1], Jean-Pierre Huvenne[1]; [1]LASIR CNRS USTLille; [2]Universitat de Barcelona

Time-resolved spectroscopy (transient UV-visible, IR and Raman) is widely used to follow the evolution of photo-induced processes at different time-scales, from femtosecond to millisecond. It is expected to reveal the existence of intermediate species, to probe their photodynamic and to provide characteristic structural or molecular information. However, in transient absorption experiments, the data are not easy to interpret. On the one hand, transient spectra are difference spectra with severely overlapping positive and negative contributions. On the other hand, when ultrafast spectro-kinetic data are considered, deconvolution of the apparatus function, deviation from the ideal bilinear model or structured errors should be considered… Data pre-treatment, data analysis and resolution are thus required in order to recover useful chemical information when unknown or complex photoreactions are studied. As we aim to demonstrate in this presentation, the application of data-driven chemometric methods should not be overlooked when dealing with time resolved spectra. Soft-modeling methods provide an answer to some of the usual requirements for unraveling the intermediate and kinetics of the process studied. The most important is the need for global (multivariate) data analysis, with as few assumptions as possible but still allowing very flexible implementation. Flexibility is required in order to handle the structure of time-resolved spectroscopic data and the complexity of the studied photochemical systems. In particular, multivariate curve resolution – alternating least squares under constraints (MCR-ALS) is a very powerful alternative to global analysis and model targeting. Specific constraints such as kinetic constraints can be implemented in the hybrid Hard-Soft-Modeling version of the algorithm. This will be illustrated on fast FTIR monitoring of (bio)chemical photoinduced systems. We will show that it enables to circumvent rank-deficiency in difference spectroscopy. Besides, additional information (e.g., chemical knowledge, apparatus function) or additional "species" (e.g., stationary absorption spectrum) can be introduced in the resolution of more challenging ultrafast spectroscopic data. This will be illustrated on more challenging femtosecond UV-visible and IR data sets. We will also investigate the error structure and point out error sources in pump-probe experiment.

(307) **Use of Harmonized Data Standards to Simplify use of Chemometric Methods for Online Analysis**

Steve Best; [1]Coblentz

For many years chemometric techniques have been applied to process analysis to help move more testing out of the lab and on to the process line itself. Unfortunately adoption has been hindered due to the lack of a standard approach to data communication and storage meaning that the promise of 'plug and play' analyzers with resultant efficiencies has not been fulfilled. Typically each implementation of an analyzer has required custom software and expensive expertise to enable the analyzer to be effective and reliable. This paper will explain a two fold approach to increasing the effectiveness of this technology. Firstly ensuring that all the data required to develop and maintain multivariate models is standardized and centralized. Coupling format conversion software prevalent in the desktop spectroscopy field with the new data management capabilities of modern LIMS systems can provide a platform optimized for the linking of analyzer data streams and reference data from offline techniques. Secondly providing the means to control multiple vendors' instruments centrally through standard protocol. Using standard instrument interfaces analyzers can be 'wrappered' to present a common control set. This removes the need to have specialist software knowledge on an instrument by instrument basis. These standards can allow actual spectral data can be exposed to the historian or LIMS system should a process deviate from specified norms. This ensures that raw data is available to correct the model to cope with new variations – for instance a variation in the quality of raw feed.

(308) **Estimation of Myoglobin Oxygen Saturation from Spectra of Cardiac Tissue using Multivariate Curve Resolution**

Francis W.L. Esmonde-White[1], Lorilee S. L. Arakaki[2], Kenneth A. Schenkman[2], Wayne A. Ciesielski[2], David H. Burns[1]; [1]McGill University; [2]University of Washington

A method for adaptive modeling of spectra from tissue for myoglobin oxygen saturation was developed. The multivariate curve resolution (MCR) technique was compared with a classical least squares method for estimation of myoglobin oxygen saturation in simulated and biological cardiac tissue. Tissue simulations with fixed and variable hemoglobin concentrations were examined to compare the performance of the techniques under different conditions. Myoglobin saturation estimates using MCR with variable hemoglobin composition were shown to decrease estimation error by 75% compared to least squares estimates. The range of myoglobin saturation required for MCR to function was examined. Results show that the spectral data set must include myoglobin saturation values that vary from at least 85% to 100% for myoglobin oxygen saturation calibration using MCR. Myoglobin oxygen saturation endpoints in 9 guinea pig hearts were estimated from spectra using MCR and classical least squares. Results showed saturation estimates using MCR to be better than estimates using classical least squares. Endpoints at the 100% level were estimated to be 89 +/- 4% using MCR as compared to 199 +/- 54 % using classical least squares. MCR provides a means for practical measurements in clinical settings.

(309) **Sensor Fusion of IR, NIR, and Raman Spectroscopic Data for Polymorph Quantitation of an Agrochemical Compound**

Jalice Manso[1], Steven Brown[2], Boiana Budevska[1]; [1]DuPont - Crop Protection; [2]University of Delaware

Vibrational spectroscopic techniques have been successfully employed to qualitatively and quantitatively study different crystal forms of an organic molecule, also known as polymorphs. In the present investigation a Rapid Content Analyzer (RCA) Near Infrared (NIR), a Fourier Transform Infrared (FTIR) with a Horizontal Attenuated Total Reflectance (HATR) accessory, and a portable Raman system were used. These non-destructive and quick methods that require no sample preparation were selected because X-Ray Powder Diffraction (XRPD) provides limited information to determine amount of one polymorph of Compound X in a binary polymorphic mixture. Compound X is a molecule of interest in the agrochemical business. Partial Least Squares (PLS) regression models were built for each spectroscopic technique and compared against each other before and after data processing. The robustness of the models was determined by comparing the Root Mean Square Error of Cross Validation (RMSECV), the Root Mean Square Error of Prediction (RMSEP), and the number of latent variables (lvs) required by the model. The NIR data provided the better predictive model after data processing. HATR and Raman were comparatively poor performers. Furthermore, an exploration of data fusion to determine if model robustness can be improved by combining the three spectral data sets of a sample, as suggested by Liu Y. and Brown S. D. (Anal Bioanal Chem, 2004, 380: 445-452). Data fusion has been employed for a wide range of applications it has not been applied to polymorphs in a mixture for quantitative analysis. Low-level fusion, mid-level fusion, and high-

level fusion PLS model were constructed and compared against each other and against the values obtained for NIR.

(310) **Simultaneous Spectrophotometric Determination of Albendazole and Praziquantel using Two Different Mathematical Spectrophotometric Approaches**

Maria Toral[1], César Soto[2], David Contreras[2], Juanita Freer[2], Sandra Orellana[1]; [1]Universidad de Chile; [2]Universidad de Concepción

Helminthiases and Bilharziasis are common parasitic diseases of great economical and public health importance. Since the anthelmintic spectra of most drugs used for treatment is limited, combinations of more than one ingredient are required to control mixed helminthic infections effectively. Due to this it is very important the development of new methods for the simultaneous determination of these drugs. The mixture of Praziquantel (PZQ) and Albendazol (ABZ) in mass ratio of (1:10) is used for the treatment of these diseases. The present work analyses two mathematical approaches for simultaneous determination of ABZ and PZQ. The different calibration methods utilised were: second derivative spectrophotometry (SDS) and regression of partial least squares (PLS). For SDS the selected experimental conditions and analytic parameters were the following. PZQ: lanalitic = 224nm, LOD =3.35 x10-8 molL-1 , LOQ = 1.12x10-7 molL-1 ABZ: lanalitic = 327 nm, LOD =1.32x10-7 molL-1 , LOQ =4.41x10-7 molL-1 Both drugs were measured by zero-crossing method. For PLS calibration were used 54 samples. The data were mean-centred and smoothed by the mobile mean (25 variables) and first derivative (5variables). The principal components number were chosen by cross validation, these were 2 for PZQ and 5 for ABZ. The LOD and LOQ were determined by subrrogate signal variable method, these were: PZQ: LOD =1.37 x10-6 molL-1 , LOQ = 4.56x10-6 molL-1 ABZ: LOD =2.02x10-6 molL-1 , LOQ = 6.73x10-6 molL-1 Both mathematical approaches were used in synthetic samples of mixtures of these drugs, including the pharmaceutical proportion (1:10, PZQ:ABZ), the recovery percentages for both went near to 100%. These methods are being applied quantification of both drugs in pharmaceutical formulations. ACKNOWLEDGMENT We are grateful to the FONDECYT for financial support, Project Nº1070605.

(311) **Simultaneous Glycoproteomic Strategies Utilizing Ion Mobility-Mass Spectrometry: New Insights from Structural Separations**

Larissa S. Fenn[1], John A. McLean[1]; [1]Vanderbilt University

Proteomic studies using mass spectrometry (MS) based techniques have demonstrated enormous potential in life sciences research. However, technological challenges remain in the rapid and accurate characterization of peptide and protein post-translational modifications (PTMs, e.g. phosphorylation, glycosylation, etc.). It is essential to characterize PTMs because variations from their normal abundance and changes in PTM patterns can be indicative of specific disease states. For example, protein glycosylation patterns have been associated with diseases including prostate and ovarian cancer, Alzheimer's, HIV/AIDS, and diabetes. However, the characterization of protein glycosylation is particularly challenging by MS-methodologies because of the intricate branching of carbohydrates and the large number of potentially isobaric glycan positional isomers. Typically, glycosylation studies are performed in two-steps: (i) characterization of the protein (i.e. proteomics), and (ii) characterization of the carbohydrates (i.e. glycomics). Unfortunately, this separates the glycomics information from that of the positional context of the carbohydrate on the protein (viz. glycoproteomics). In this report, we describe recent progress in performing simultaneous glycoproteomics by using ion mobility-mass spectrometry (IM-MS) separation strategies. Ion mobility-MS provides rapid (us-ms) two-dimensional separations on the basis of analyte structure and m/z in the IM and MS dimensions, respectively. Simultaneous glycomics and proteomics can be performed because carbohydrates and peptides of similar mass preferentially adopt different gas-phase structures, i.e. carbohydrates are generally more compact compared to peptides. To evaluate IM-MS separations in a simultaneous glycoproteomics approach, standard glycoproteins were digested with trypsin or pronase and subsequently with PNGase F to produce peptides and N-linked glycans in the reaction mixture. These were then analyzed using both a uniform-field IM-TOFMS constructed at Vanderbilt (in collaboration with Ionwerks, Houston, TX) and a traveling-wave IM-MS instrument (Synapt, Waters, Manchester, UK). For both instruments, MALDI and ESI are compared, as well as operation in both positive ion and negative ion modes. O-linked glycans were obtained through chemical deglycosylation of standard glycoproteins and then structurally characterized by the same means. Furthermore, ion mobility shift reagents are also evaluated to further differentiate particular glycan species on the basis of selective-chemical tagging to alter analyte structure (e.g. to differentiate between N- and O-linked glycans).

(312) **Phosphoproteomic Mapping with Two-Dimensional Structural Separations by Ion Mobility-Mass Spectrometry**

Randi L. Gant[1], Thomas J Kerr[1], John A. McLean[1]; [1]Vanderbilt University

Protein post-translational modification (e.g. phosphorylation, glycosylation, etc.) is typically sub-stoichiometric and can occur at femtomolar or lower levels. Thus, mass spectrometry (MS) based approaches have are widely used for PTM mapping studies owing to the high sensitivity, selectivity, and throughput such techniques afford. Although great advances have been made in proteomics, phosphoproteomic mapping remains a significant challenge, in particular because of the temporal heterogeneity of phosphorylation (e.g. point in the cell cycle, etc) and the potential for elimination of phosphoric acid in sample preparation and analysis. To facilitate high throughput and accurate phosphoproteomic mapping, we have developed strategies using rapid (us-ms) two-dimensional (2D) gas-phase separations on the basis of ion mobility-mass spectrometry (IM-MS), which provides analyte separations on the basis of both apparent surface area (i.e. ion-neutral collision cross-section) and mass-to-charge (m/z), respectively. Importantly, for a given charge-state, different classes of biomolecules exhibit characteristic correlations in collision cross section vs. m/z based on their relative gas-phase packing efficiencies (nucleotides > carbohydrates > peptides > lipids). We have developed IM-MS strategies whereby phosphopeptides are selectively derivatized with high density tags based on lanthanide chelating agents. Thus, phosphopeptides are selectively shifted to regions of IM-MS space that are not predicted to contain signals. This affords high confidence level phosphopeptide assignments in PTM mapping, which can subsequently be sequenced in a data dependent manner by tandem MS. In this report, we present results obtained using two types of IM-MS instrumentation, namely a uniform field MALDI/ESI-IM-MS and a traveling-wave MALDI/ESI-IM-MS (Synapt, Waters Corporation, Manchester, UK). Proof-of-concept experiments for relative quantitation in phosphoproteomic mapping is provided for a series of model pSer and pThr peptides, which are subsequently applied in the phosphoproteomic mapping of the protein APPL-1. APPL-1 is a membrane-bound adaptor protein whose function is not currently known, but it is thought to recruit kinases AKT2 and PIK3 in the cell signaling pathways responsible for cell migration.

(313) **Top-Down Sequence Analysis of Antibody Fragments by an Ion-Mobility Time-of-Flight Mass Spectrometer**

Asish Chakraborty[1], Weibin Chen[1], Carola Dame[2], John Gebler[1]; [1]Waters Corporation; [2]Slotervaart Hospital/The Netherlands

Top- or middle-down MS methodology directly fragments intact proteins or their components to obtain information for protein characterization. However, direct fragmentation of large proteins and their components tends to generate many different types of fragment ions, making the spectra interpretation and sequence deduction very difficult. The hybrid ion mobility/time-of-flight mass spectrometer possesses a unique ion-mobility separation (IMS) function and is capable of separating fragment ions by size, shape, and charge prior to mass spectrometric detection. In this presentation, we have demonstrated the utility of IMS separation coupling with CID in the top-down sequencing of antibody fragments for the characterization of a recombinant IgG1 monoclonal antibody. During these studies, intact antibodies were cleaved into 3 fragments using a limited proteolysis method with endoproteinase Lys-C followed by reduction with DTT to produce the light chain (LC), Fc half (Fc/2) fragment and F determinant (Fd). These fragments were separated on an ACQUITY BEH 300, C4, 1.7 µm column using reversed-phase UPLC in-line with a quadrupole ion-mobility/time-of-flight mass spectrometer. The fragmentation was done with a number of selected charge states. Fragments coming out the collision cell were subsequently transferred into the ion-mobility cell for ion separation based on the charges, sizes and masses prior to time-of-flight mass measurement. Spectral information that contains fragment ions of similar charge states were then generated from the drift scope by selecting different regions of m/z vs. drift time plots. This ion-mobility separation and post data processing lead to the simplification of fragmentation data, thus revealing low intensity peaks that would have been masked by high mass signals in a spectrum where no mobility separation is used. The post-fragmentation IMS separation thus allowed a segment of antibody sequence to be easily deduced.This technique has the potential to be used in identifying unknowns and sites of post-translational modifications associated with an antibody.

(314) **Determination of Protein Conformational Changes by an Ion-Mobility TOF MS**

Asish Chakraborty[1], Weibin Chen[1], John Gebler[1]; [1]Waters Corporation

The function of protein-based drugs strongly depends on 3D structures, and conformational changes generally result in the loss of drug potency and the alternation of the pharmacological properties of the product. Thus, physicochemical characterizations on the higher-order structures of protein drugs are very important to drug development. Conventional NMR and X-ray methods can elucidate protein geometries but are slow, generally require large quantities of pure protein, and thus unsuitable for direct analysis of real biological matrixes. Optical spectroscopy and circular dichroism provide information about a particular structural or functional feature of a protein and are generally not sensitive enough to detect the subtle conformational changes caused by small alterations in the protein structure. ESI MS has been widely adopted for the study of proteins. Coupled with a TOF analyzer, it not only enables accurate mass measurement of intact proteins, but also provides information on the number of charges and the charge state distributions of protein ions. However, MS methods are generally insensitive to 3D structures of proteins and protein complexes. Here we present a novel ion-mobility mass spectrometer that uses a combination of ion-mobility spectrometry (IMS) and ESI MS to resolve and identify protein conformations in the gas phase that cannot be assessed by MS alone. IMS separates gas-phase ions with different collisional cross sections and/or charge states. When subjected to IMS separation, a tightly folded protein conformer with a smaller cross section would travel faster in an IMS cell and be separated from a less folded conformer of the same protein. Similarly, protein ions from same conformer but with different charge states may also be separated, with the more highly charged species having a shorter mobility time. This presentation shows the utility of a commercial ion-mobility mass spectrometer for probing the conformational structures using a model protein, cytochrome c. Our results show that the ion-mobility spectrometry is capable of resolving the population of coexisting conformational states of cytochrome c and revealing the conformational changes induced by acid or organic solvent addition, and can be used to quickly probe the conformations or conformational changes of therapeutic proteins in drug formulations.

(315) **Preparation and Characterisation of Solvatomorphs of Rifampicin**

Sushma Gupta[1], Deepika Thakur[1], Poonam Arora[1]; [1]University Institue of Pharmaceutical Sciences

Solvatomorphs are unit cells differ in their elemental composition through the inclusion of one or molecules of solvent in stoichimetric or non-stoichiometric ways. Some stable solvatomorphs require vigorous conditions for desolvation before melting, while others loose solvent of crystallization under much milder conditions and are converted to amorphous form after desolvation. The detection many solvatomorphic forms with characterization and selection of the desired one are very important in pharmaceutical research and development.The study emphasized on the preparation and characterization of Solvatomorphs of Rifampicin, an anti tuberculosis drug. Recrystallisation of drug from various solvents (recommended by ICH guidelines) lead to eight solvatomorphs which resulted desolvation peak in DSC (60-70oC) with corresponding weight loss in TGA is approx. 8.6%, 8% , 9.5%, 8% and 7% for Form I (benzene), Form II (THF), form III (ethylacetate), Form IV (butan-2-one) and Form VI (acetone) suggesting 1:1 rifampicin:solvent. XPRD studies revealed an amorphous halo in the range 10-300C was supported by Scanning Electron Microscopy for Form I, form II, form VI, form VIII was with no specific crystal shape. Semi crystalline nature of Form IV and Form V at 14.0770C (990 counts), 14.351 (1620 counts have shown drusy habit, botryoidal habit. However, Form III and form VII are more crystalline appeared as bladed habit and striated habit with 2*f*á value 14.263 (3600 counts) and 7.9340 (1869 counts) respectively. The main differences in the peak corresponding to the amide and carbonyl group were observed by FTIR spectroscopy. Further distinction was done by enthalpy of solution shows exothermic behavior in decreases order. The solubility results are in agreement with the XRD and heat of solution. The study concluded that Form VIII obtained from THF:propionic acid (90:10) was shown to be highly amorphous having no melting endotherm and decomposition exotherm which was supported by the presence of complete amorphous halo accompanied by highest value of enthalpy of solution -36.851 kJ/mol. This form is most soluble having maximum dissolution rate.

(316) **Simple and Rapid Spectrophotometric Method for the Determination of Erythromycin Esters in Pharmaceutical Formulations**

Priti Mehta[1], A. K. Shukla[2]; [1]Institute of Pharmacy; [2]Suvic Pharmaceutical Laboratory

Erythromycin is a macrolide, most commonly used antibiotic in number of common infections. Various esters of erythromycin have been prepared in an attempt to improve stability and facilitate absorption. Erythromycin and its derivatives are available in a

wide variety of oral, topical and parental products. Microbiological assay is the official method for the estimation of Erythromycin esters as per United State Pharmacopoeia and Indian Pharmacopoeia. It has variety of disadvantages including lengthy incubation period, lack of the sensitivity towards the antibiotics etc. In British Pharmacopoeia, HPLC method is given for the estimation of Erythromycin ester derivatives using methanol and acetonitrile. Terespolsky has reported instability of Erythromycin ester derivatives in methanol and acetonitrile. Number of other methods were also reported which include either extraction with organic solvents or have lengthy sample preparation with elevated temperature. The purpose of this work is to develop a simple, selective and rapid method for the determination of erythromycin ester derivatives in their pure form and in Pharmaceutical formulations. Esters of Erythromycin found to react with o-nitro benzaldehyde in presence of Acetic acid-hydrochloric acid mixture to form a colored product having useful absorption band at 486nm. Different variables affecting the color development were studied and optimized. The method was used to determine 10-50 mcg/ml Erythromycin in final measured solution. The simplicity of the method permits rapid analysis and it is suitable for routine control. In order to establish the validity of proposed procedure, commercially available Pharmaceutical formulations were analyzed. The reliability of the method was estimated by parallel determination against the reported method.

(317) **A Multivariate Model Free Approach for Pharmaceutical Tablet Content Uniformity Analysis via NIR**

Yang Liu[1], Sonja Sekulic[1]; [1]Pfizer Global Research and Development

The current prevailing NIR tablet content uniformity analysis method requires a predictive multivariate model, such as a partial least square (PLS) model, to provide the Active Pharmaceutical Ingredient (API) concentration information. The PLS model is in general dependent on the formulation, tablet shape/size and NIR instrumentation and typically involves a large amount of development and validation effort. In the early process development stages of a drug product, to construct a quantitative model is often impractical because the constant modification of the formulation, process parameters and product appearance invalidate the quantitative model. In this presentation, a multivariate model free approach for pharmaceutical tablet content analysis is developed. This approach focuses on the individual batch trend analysis and does not require a pre-established predictive model. The algorithm uses specific preprocessing to isolate the active information into one latent variable. Therefore, the outliers and steady state of the process can be effectively identified. Combined with a minimum number of HPLC tests, intensive stratified tablet core testing can be achieved quantitatively. The results from a real drug product process will be presented. The HPLC/NIR model free equivalency was established based on 17 batches at R&D and ICH scale data on two types of NIR instruments and different drug loadings. A fast response and significantly reduced HPLC testing were achieved for the process development. This approach is inherently instrument independent and robust to batch-to-batch variation. It can also be applied to other spectroscopic data such as Raman spectroscopy, where a calibration model is also generally needed.

(318) **Online PAT Monitoring for Parenteral Process Understanding and Design Space Mapping**

Yang Liu[1], Robert Leasure[2], Fred Carroll[1], Mark Berry[1], Richard Ferraina[1], Joanne Lukaszewicz[1]; [1]Pfizer Global Research and Development; [2]Pfizer Global Manufacturing

Compounding is a critical unit operation for parenteral oral solution products. In this presentation, online spectroscopic PAT tools were used to provide real time dissolution information to gain process understanding of the design space and to facilitate process scale up. The focus is on the PAT implementation and the gaining of process understanding. Two PAT online dissolution monitoring applications for a real drug product compounding process implemented in the manufacturing setting will be presented. The first application is to use a UV probe to monitor the dissolution of two preservatives under a designed process parameter matrix. The online data were used to map the response surface of the design space and to gain process understanding. The second application is to use a NIR probe to monitor the Active Pharmaceutical Ingredient (API) dissolution. The large scale and a lab scale results were compared. The data were used to estimate the dissolution completion time and to evaluate the risk of incomplete dissolution for the given process parameters.

(319) **Development of an IN-Line API Concentration Determination for Control of Crystallization and Metastable Zone Evaluation**

Ming Huang[1], Robert Wethman[1], Daniel Hsieh[1], John Wasylyk[1]; [1]Bristol-Myers Squibb

The active pharmaceutical ingredient (API) under study crystallizes as a mixture of different solid forms; therefore controlled crystallization procedures are critical to ensure that the desired form and particle size distribution are always produced. In addition, determination of the metastable zone is critical in establishing an appropriate crystallization protocol. A controlled crystallization was achieved by promptly seeding at the optimal temperature and concentration of the API followed by controlled temperature ramps to room temperature to complete the crystallization process. An in-line Raman spectroscopy method was developed to monitor the concentration during the crystallization. The in-line Raman method provided the operators with the instantaneous information about the API concentration and allowed them to make the necessary adjustments quickly to meet the target concentration. The same Raman method was also used in conjunction with a Lasentec FBRM probe and a RC-1 reaction calorimeter to determine the width of metastable zone to help establish the optimal seeding concentration. Method development, construction of a chemometrics model, and determination of the metastable zone will be discussed.

(320) **Pharmaceutical Hydrate Transformation Kinetics: Effects of Polymer Excipients**

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In the production of drug products, it is essential for pharmaceutical companies to have only one crystalline form of the active pharmaceutical ingredient in a tablet. Frequently the active pharmaceutical ingredient is of the anhydrous form due to the improved solubility and bioavailability of that crystal form. However, the anhydrous crystal can transform to the hydrate crystal in the presence of water, which can be a problem during the production of drug tablets in unit operations such at wet granulation. The addition of polymeric excipients can modify or inhibit this anhydrous to hydrate transformation process. The transformation of the model compound caffeine was studied using Raman spectroscopy. In-line Raman measurements were collected of caffeine slurries in the presence of different polymer excipients. A calibration model was used to quantify the amounts of anhydrate and hydrate caffeine, and kinetic profiles of the caffeine transformation were constructed. Results show that cross-linked polyacrylic acid (PAA) was the most effective at inhibiting the transformation. PAA was able to affect both the nucleation and the crystal growth rate of the caffeine hydrate. These results were confirmed using optical microscopy.

(321) **Evaluation of the Impact of Container Interference for Bulk Material Authentication using a Handheld Raman Spectrometer**

Jeremy Linoski[1], Robert Green[1], Robert Brush[1], Wayne Jalenak[1], Christopher Brown[1]; [1]Ahura Scientific, Inc.

Recent instrumental advances have lead to commercial availability of several portable spectroscopic technologies, including handheld near-Infrared, mid-Infrared, and Raman. While laboratory vibrational spectroscopy has been a popular choice for raw material identification, widespread applicability of portable systems for material authentication has only recently been highlighted. Applicable sampling approaches are an important practical consideration when evaluating technologies for field (i.e. warehouses) raw material authentication. For example, mid-Infrared spectroscopy requires that a sample be first removed from its packaging in a clean environment to prevent possible contamination then subsequently prepared in a suitable form for analysis. Raman and near-Infrared (NIR) do not suffer from this difficulty as it is possible to analyze solids through packaging materials. Raman, as opposed to NIR, offers the additional capability to directly measure liquids in their containers. Ulmshneider, et. al. demonstrated that the presence of packaging can have a marked impact on features present in NIR spectra; however, they also concluded selective identification methods for packaged solids can be developed when appropriate chemometric data treatments are used. The authors failed to discuss the long-term difficulties encountered using NIR when either packaging thickness or type (polyethylene vs. polypropylene, etc.) are changed by the raw material supplier. Compton's early work using Raman to examine packaged goods demonstrated that spectroscopic contribution due to packaging was nearly negligible for the materials studied. In the present study, we expand upon these results and evaluate method robustness to changes in container packaging. To accomplish this, methods for several common solid and liquid raw materials were developed using a single reference spectrum collected on neat samples. The methods were then challenged by measuring the materials under different packaging arrangements including clear and amber glass, and single, double, and triple bagged samples. R.L. Green, C.D. Brown, "Raw Material Authentication Using a Handheld Raman Spectrometer", Pharmaceutical Technology, March 2008. M. Ulmschneider, E. Pénigault, "Direct Identification of Key Intermediates in Containers Using Fourier-Transform Near-Infrared Spectroscopy Through the Protective Polyethylene Primary Packaging", Analusis, 2000, 28, 136-140. D.A. Compton, S.V. Compton, "Examination of Packaged Consumer Goods by Using FT-Raman Spectrometry", Applied Spectroscopy, 1991, 45, 1587-1589.

(322) **Replacement Method Development for Hazard Solvents using Method in Korean Pharmaceutical Codex**

Kyung-Yoal Yoo[1], Dal-Hwan Kim[2], Ryoon-Kyung Lee[1], Seung-Hwan Kim[1], Jin-Hee Nam[1], Soon-Han Kim[1]; [1]Dageu Regional Korea Food & Drug Administration; [2]Korea Food & Drug Administration

The Korean Pharmaceutical Codex is published in 1983. As speedy development of new drugs and improvement of science and technology, the need of revision of drug specification through the ICH guidelines and discussion between regulatory agency and drug industry for the safer and efficient drugs is getting higher. It is a world-wide trend that they gradually don't use hazardous reagents to human health and environment, especially, in developed countries. Objective of this research was to replace the hazard solvents using method in Korea pharmaceutical codex. In case of identification using TLC, we established the methods replacing those hazardous reagents with the solvents subject to class 2 or 3 in ICH solvent guide line. We also found that the testing methods in codex cannot be employed to real samples because of their poor performance. We finally performed inter-laboratory validation of newly established methods, insuring the reliability of them. Therefore, this study indicated that these new methods are expected to be utilized for preparing revised version of Korean pharmaceutical codex.

(323) **Application of LC-MSn in Conjunction with Mechanism-Based Stress Studies for the Elucidation of Drug Impurity Structure**

Rosario Fico[1], Min Li[1], Mingxiang Lin[1], Abu Rustum[1]; [1]Schering-Plough Corporation

Through a case study, the use of LC-MSn technique in conjunction with a mechanism-based stress study is shown to be a very effective way in the rapid elucidation of unknown drug impurities. In this case, the drug substance sample was first analyzed using LC-MSn through which the unknown species was found to be a valeryl-containing, isomeric impurity of the active pharmaceutical ingredient (API), betamethasone 17-valerate, based on its molecular ion and major fragments. Since a substantial knowledge regarding a large number of isomeric impurities of betamethasone has been accumulated in the literature as well as in our laboratory, a hydrolytic stress study (forced degradation) of the isolated unknown species was then designed and carried out accordingly in order to remove the valeryl group from the unknown species. During the stress study, a betamethasone isomer was generated as expected. However, a new unknown species isomeric to betamethasone 17-valerate was also formed unexpectedly. By comparing the UV spectra and more importantly MSn fragmentation patterns of the two newly formed species with those of betamethasone, dexamethasone, betamethasone 17-valerate, and betamethasone 21-valerate, these two unknown species generated in the stress study were identified as dexamethasone and dexamethasone 21-valerate, respectively. Based on the plausible reaction mechanism of the forced degradation, the original impurity present in betamethasone 17-valerate drug substance was then identified as dexamethasone 17-valerate; the structure assignment was later confirmed by various 1D and 2D NMR experiments. The efficient conversion from dexamethasone 17-valerate to dexamethasone 21-valerate was also observed during a 2D NMR acquisition of the isolated dexamethasone 17-valerate sample.

(324) **Effects of Formulation and Processing Changes on a NIR PLS Model for Determining Tablet Hardness**

Melissa Mrozek-Morrison[1], Thomas Lang[1], Wencan Chen[1], Angela Olsofsky[1], Charles Yang[1]; [1]Amgen, Inc.

The hardness of a pharmaceutical tablet can directly impact drug product quality attributes such as disintegration time and dissolution, as well as the integrity of the tablet upon packaging and shipping. Conventional methods for measuring tablet hardness are destructive in nature, and require offline testing of a small subset of samples as representative of the entire batch. Near-Infrared spectroscopy offers an attractive alternative for determining tablet hardness in a non-destructive manner, with the added potential for on-line or in-line measurement. However, the sensitivity of multivariate NIR models to chemical and physical sample properties unrelated to hardness can limit the general use of such methods in early formulation development, where variations in the formulation composition and processing frequently occur. A multivariate NIR method was developed for determining the hardness of a pharmaceutical tablet formulation. Tablets were prepared using a range of compression forces (2 to 20 kN), resulting in hardness values of 0.6 to 6.0 kp as measured by conventional crushing tests. Diffuse reflectance NIR spectra were collected for each tablet, and a multivariate calibration model was

developed relating the NIR spectra to the tablet hardness value using partial least squares (PLS) regression. The root mean square error of prediction (RMSEP) was 0.19 kp. Tablet formulation and processing changes such as wet granulation versus direct compression and varying drug load were evaluated for their effects on the NIR model.

(325) **Characterization of Protein Modifications using Liquid Chromatography and Data Independent Acquisition Tandem Mass Spectrometry**

Hongwei Xie[1], Martin Gilar[1], John C. Gebler[1]; [1]Waters Corporation, Milford, MA

Modifications such as deamidation and oxidation are common in recombinant protein products and have the potential to affect the stability, safety and activity of therapeutic protein drugs. Effective control and monitoring these variations require a sensitive and reproducible strategy to identify and quantify such product and process related modifications. We have applied an online Ultra Performance Liquid Chromatography –Data Independent Acquisition Tandem Mass Spectrometry (UPLC-MSE) approach to map digests of a monoclonal antibody. Tryptic digests of the antibody were separated on a 2.1x150mm, 1.7im C18 Acquity PST column, then, eluted and fragmented in a QTOF instrument. Data were acquired in a parallel data independent acquisition mode (MSE). Modified peptides at sub-stoichiometric abundances were successfully characterized. Modification type, sites and stoichiometry were achieved using this approach. More than 6 asparagine(N) deamination sites and 2 methionine(M) oxidation sites were identified from heavy chain; Two N deamination sites and one M oxidation M site were identified from light chain of the antibody. The stoichiometry of these modifications was determined. For better understanding and charactering these modifications, we are working on identification and resolution of aspartic acid and isoaspartic acid isoforms resulted from identified N deamidations, and distinguishing in-source oxidation from the true M oxidation in the antibody chains using synthetic peptides with same modifications as we identified.

(326) **Surface Enhanced Raman Spectroscopy for the detection of Chemical Agent Surrogates**

Baolong Bai[1], Gary Rayson[1]; [1]New Mexico State University

Following the terrorist attacks on September 11, 2001, there has been an heightened need for monitoring for materials for the presence of chemical agents. Such detection systems must be capable of responding to very low concentrations of materials and be able to identify targeted chemical species within relatively complex samples. One class of spectroscopic techniques for accomplishing this task is surface enhanced Raman scattering. Recent investigations within our laboratory have been directed toward the utilization of an ultra short pulse, high peak power laser (>2 MW) for the collection of enhanced Raman spectra of chemical agent surrogates adsorbed onto aggregated colloidal silver. .Design advantages of this configuration and resulting SERS detection characteristics will be described and its utility in anti-terrorist applications will be discussed.

(327) **Photobleaching Behavior in Raman Spectroscopy**

Richard Spragg[1], Robert Alexander[1], Nancy Kawai[2]; [1]PerkinElmer LAS UK; [2]PerkinElmer LAS USA

Raman spectra often include an unwanted broad background of uncertain origin, generally referred to as fluorescence. When this is very large the associated noise makes measuring the Raman spectrum difficult or even impossible, and when it is smaller it interferes with accurate measurement. In many cases the background can be reduced by photobleaching, exposing the sample to the laser for some time before recording the spectrum. We have used Principal Components Analysis (PCA) to investigate photobleaching in a range of materials. The Raman signal is constant in spectra recorded after different exposure times while the background intensity is varying. PCA of the mean-centered data therefore shows only the background signal. Although most of the background variation is associated with a single factor there can be one or more additional factors. These are not simply associated with noise as the scores on them vary systematically with exposure time. Commonly there is a minor factor associated with a rapid initial change in the background that is qualitatively different from the larger subsequent change. This behavior will be illustrated for several different materials. Alternative approaches to separating the Raman and background signals will be compared with simple subtraction or baseline correction routines. Strategies for time-efficient data collection will be discussed.

(328) **Confocal Raman Microscopy of the Interfacial Region of Liquid Chromatographic Stationary Phase Materials**

Jennifer L. Gasser-Ramirez[1], Joel M. Harris[1]; [1]Department of Chemistry, University of Utah

Considerable research has been directed toward investigating the relationship between organic modifiers and the structure of reversed-phase liquid chromatographic (RPLC) stationary phases. Organic modifier retention in the stationary phase has previously been determined by non-linear chromatography measurements. Solvatochromic, fluorescent, and spin probe molecules have also been used to characterize the polarity and heterogeneity of the resulting modified interfacial environment. Confocal Raman microscopy allows the *in situ* examination of the interior environment of chromatographic stationary phase particles, without the use of probe molecules. The accumulation of organic modifiers at the solid/liquid interface can be quantified and the interactions of the modifier with the stationary phase layer can be determined. Specifically in this work, we have investigated the interactions of acetonitrile with C18 functionalized particles using confocal Raman microscopy, which enables the sampling of small volumes (~1fL) within individual 10 μm particles. Bare chromatographic silica was also studied in order to resolve the interactions of acetonitrile with residual surface silanols. The nitrile stretching frequency of acetonitrile depends sensitively on its local microenvironment. The populations of solution-phase and interfacial acetonitrile are thus spectroscopically distinguishable. The results show that the nitrile stretch scattering from acetonitrile within a single RPLC chromatographic particle is composed of three different spectroscopic contributions, namely silica associated acetonitrile, C18 layer associated acetonitrile, and acetonitrile in the bulk solution. Data are presented quantifying excess acetonitrile at the stationary phase interface. Confocal Raman microscopy was also applied to measure the accumulation of the ion interaction reagent, cetyl pyridinium chloride, at the interface of a C18 RPLC stationary phase particle. This accumulation was found to be very sensitive to the solution ionic strength, which points out the significance of repulsive interactions within the double layer.

(329) **Micro-Cavity Resonator: A Novel Method for Improving the Raman Signal without SERS from Sub-Micron Size Materials**

Anupam Misra[1], Shiv Sharma[1], Lori Kamemoto[1,2], Pavel Zinin[1], Qigui Yu[2], Ningjie Hu[2]; [1]University of Hawaii, HIGP/SOEST; [2]Hawaii AIDS Clinical Res. Program, UH

Surface enhanced Raman Spectroscopy (SERS) has been shown in the past by various researchers to detect Raman spectra of chemicals in very small concentrations. However applicability of SERS technique utilizing colloidal nano particles has been severely

limited in the analytical laboratory because of several reasons. SERS spectra usually contain extra spectral features which are also not reproducible over time. Presence of hot spots and limited life time of the colloidal solution adds extra difficulty in using SERS for analytical purpose. In this presentation, we will describe a novel method for improving the Raman signal obtained from very small samples (of the order of pico-grams) without using surface enhanced Raman spectroscopy (SERS) technique. A new method of "micro-cavity resonator" uses various mechanisms which collectively improves the total Raman signal from the sample. A micro-cavity substrates helps in exciting the sample with multiple reflections of incident laser beam, as well as that of the Rayleigh scattered photons from the system. The cavity also effectively holds more volume of the sample in comparison to flat surfaces providing some signals enhancement due to volume effect. And, further signal enhancement is achieved when the shape of the cavity is controlled to reflect back the Raman photons scattered in the forward direction back in the observing microscope objective of the micro-Raman system. Some of the important advantages of the micro-cavity technique are (1) enhanced Raman signals are highly reproducible, (2) they contain no extra spectral feature, (3) entire Raman spectra is enhanced, (4) substrates shows very long life time. In this presentation we will show data showing enhancement of entire Raman spectra of various chemicals in very low concentration (e.g. 10-5 molar Rhodamine 6G) and describe simple and effective ways of making micro-cavity substrates with uniform shapes and sizes. Applicability of technique to obtain Raman spectra from biological samples which have very low Raman cross-section will be discussed. Apart from its applicability to Raman spectroscopy, the technique is equally applicable to other analytical optical spectroscopic techniques which involve interaction of photons with substance under investigation.

(330) **Surface Enhanced Raman (SERS) Nanoparticle Reagent Delivery Device for *in-situ* Sample Analysis**

Thomas Tague[1], Sergey Shilov[1], Marco Leona[2]; [1]Bruker Optics; [2]Metropolitan Museum of Art

SERS can be used to conduct Raman spectroscopy studies of analytes such as natural and synthetic dyes, pharmaceutical compounds, and other organic substances that are too fluorescent, or are present in concentrations too minute to yield usable Raman spectra. Previously, much effort has been given to developing substrates that would be suitable for enhancing the Raman signal with limited success. The sample had to make excellent contact with the surface to yield any improvement in the Raman signal or be dissolved and deposited directly. These substrates are impractical for solid samples of interest that are small (less than 1mm). The identification of dyes is generally conducted by extraction followed by HPLC analysis. This requires a sizable sample (5 millimeter of threads from a textile, for instance) and makes it impossible to approach paintings and drawings, where samples larger than 100 μm cannot be removed. It is frequently not possible to have large sample quantities in forensic or unknown contaminate particle investigations. The use of a novel micro-deposition device for the delivery of silver nanoparticles onto microscopic samples to develop SERS into a molecular microscopy technique has been explored. Pre-aggregated colloids (obtained by pre-mixing Ag colloid and an aggregating agent) can now be successfully deposited using a novel SERS reagent delivery device very precisely and reproducibly, where the resultant drop size is 20 microns in diameter. The drop dries very quickly allowing for the micro-Raman analysis in seconds. The delivery device is aligned to the microscope objective for accurate delivery. The drops can be delivered singly or in rapid sequence. Positive results for highly fluorescent molecules never previously characterized with SERS have been obtained, such as alizarin, berberine purpurin, laccaic acid, and many others.

(331) **High-Performance Liquid Chromatographic Determination of Bile Acids using Micellar Phase-Transfer Catalysis and Fluorescence Detection**

Suh-Jen Jane Tsai[1], Win-Ya Lee[1], Yu-Sheng Chung[1], Pei-Yin Hsieh[1]; [1]Dept. of Applied Chemistry, Providence Univ.

Bile acids, being the final products of cholesterol metabolism in the liver, are of vital importance for tracing the distribution of cholesterol in tissue. Abnormalities in cholesterol biosynthesis or metabolism are often shown in the variation of concentrations and the proportion of various bile acids in different tissues. Thus, some hepatobiliary diseases can be diagnosed. However, the determination of bile acids in the tissues has been an important challenge. In this work, bile acids including ursodeoxycholic acid (UDCA), hydodeoxycholic acid (HDCA), cholic acid (CA), chenodeoxycholic acid (CDCA), deoxycholic acid (DCA), and lithocholic acid (LCA) have been determined by HPLC with fluorescence detection. Bile acids were transferred to the micellar phase with tetrakis(decyl) ammonium bromide (TDeABr). TDeABr was employed as the ion-pair reagent. Inside the micelle, bile acids reacted with 4-bromomethyl-7-methoxycoumarin (BrMMC) and the fluorescence intensity of bile acids derivatives at 410 nm was measured with the excitation wavelength, 320 nm. The experimental conditions including reaction temperature, reaction time, effects of sodium carbonate, acetone, pH and the concentration of TDeABr and BrMMC have been optimized. The optimized eluent ratio for the gradient elution was as following: acetonitrile: methanol: water (v/v/v) = 30:50:20 for the elution time up to 25 min. while the corresponding eluent ratio was 21:70:9 for the elution time from 25 to 45 min. The separation was performed with the elution rate of 1.0 ml min-1. Analytical characteristics such as dynamic range, linearity for the calibration curves, reproducibility, and detection limit have been evaluated under the optimized experimental conditions. Results demonstrated that the proposed method was applicable for the determination of trace bile acids in bovine and pork livers.

(332) **On-Board Pneumatic Valves for Multiplexed Applications in Microfluidic Devices**

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On-board, pneumatically actuated valves in a self-contained fluidic cartridge enables rapid, low dead volume delivery of multiple fluid streams for multiplexed molecular- or immunoassays in which successive reagent additions or washes are required to perform the assay. On-board valves produced using a laminate fabrication process offer a cost effective way to perform these various steps as well as providing a simple and low-dead volume interface to integrated reagent reservoirs. This permits the entire assay to be contained in a single disposable device, suitable for point-of-care or field portable applications. An important consideration for incorporation of these valves into a commercially viable device is their reproducible manufacture and robust performance under application conditions. In this paper we demonstrate the repeatable performance and optimal operating conditions of these valves in a device containing eight channels and eight valve diameters.

(333) **Electrophoretic Capture: A New Approach to Separations**

Michelle Meighan[1], Michael Keebaugh[1], Stacy Kenyon[1], Alicia Quihuis[1], Mark Hayes[1]; [1]Arizona State University

The ability to employ molecular diagnostics will enable personalized medicine through both individual risk assessment for disease and by facilitating distinct therapeutic treatment for each

individual. We introduce fundamental developments that can lead biochemical analysis by dynamically capturing specific species in an array format from a complex mixture without molecular recognition elements, which combines the high-resolution capabilities of capillary electrophoresis with the advantages of array-based technologies. The device exploits differential transport near the capillary entrance by employing a large contraction ratio and setting flow and field gradients opposite one another. Initial experiments investigate the interface where potential is initiated near a channel by examining the fundamental parameters of flow dynamics, applied potential, and electrophoretic mobility. Preliminary results indicate the successful entrapment of particles and ionic species in solution. Using a 75mm i.d. capillary that was 13 cm in length, positively-charged methyl violet dye (MW: 393.9) was isolated from a solution of 5mM aspartic acid buffer (pH 2.8) containing various neutral dyes of similar molecular weights.

(334) **Pre-Concentration and Determination of Polycyclic Aromatic Hydrocarbons (PAHs) on Centrifugal Microfluidic Discs**

Josiane P. Lafleur[1], Andrien A. Rackov[1], Scott McAuley[1], Eric D. Salin[1]; [1]McGill University

Polycyclic Aromatic Hydrocarbons (PAHs) are widespread by-products of incomplete combustion. They have been present in our environment long before our industrial era due to natural causes such as forest fires and volcanic eruptions. However, their concentrations have increased dramatically over the past centuries as a result of the burning of fossil fuels. Our water resources get contaminated through atmospheric deposition, runoffs from contaminated areas as well as sporadic events such as oil spills. Many PAHs are toxic to aquatic life and several have carcinogenic properties and are listed by the US Environmental Protection Agency (EPA) as priority pollutants. Great variations in PAHs concentrations are observed in the environment and pre-concentration is often required to detect the low levels present in some ground waters. We will present a novel solid phase-extraction device on a centrifugal microfluidic disc for the rapid pre-concentration and determination of PAHs in water. Both *in-situ* fluorescence spectroscopy and direct absorption spectrophotometry will be contrasted and compared for the detection of a test compound, fluorescein and results for the PAH anthracene will be presented. One of the main advantages of this device is that only a simple motor is needed to induce liquid flow, making simultaneous on-site extraction and measurement of multiple samples potentially easy while minimizing sample losses and contamination.

(335) **Purification of Pharmaceutical Candidates From Biological Fluids by Countercurrent Chromatography.**

Jill Hochlowski[1], Jeff Pan[1], Philip Searle[1], Tom Nemcek[1], Dave Blanchard[1], Dave Dingle[1], Steve Spanton[1]; [1]Abbott Laboratories

Countercurrent Chromatography has a 25-year history of application in the natural products field where the complex mixtures produced by microbial sources are directly amenable to this liquid-liquid purification technique. Higher order biological systems in drug discovery ADME studies – such as serum, bile, etc - present a similar purification challenge. In these studies one is looking to separate and identify small quantities of biologically active components within a sea of compound complexity. Further, since the most data intensive analytical technique for small molecule drug candidate analysis is NMR spectroscopy, the requisite of separation results require a high degree of purity of final compound. Abbott Laboratories has deployed a high throughput analytical countercurrent chromatography system with hyphenated analytical detectors, and studied the applicability of this instrumentation in purifying pharmaceutical candidates, and metabolites thereof, from mammalian biological hosts.

(336) **Measuring Dissociation Constants of Mono-Hydroxy Polycyclic Aromatic Hydrocarbons via Capillary Zone Electrophoresis**

Gaston Knobel[1], Andres D. Campiglia[1]; [1]University of Central Florida

Capillary electrophoresis (CE) is emerging as a valuable tool to determine the ionization constants of a wide variety of compounds. Its main advantages include high sensitivity, selectivity and low sample consumption. The work presented here compares the pKa values of six biomarkers of polycyclic aromatic hydrocarbons (PAH) to those obtained via ultraviolet spectroscopy. These include 1-hydroxynaphthalene, 2-hydroxynaphthalene, 9-hydroxyphenanthrene, 2-hydroxyfluorene, 1-hydroxypyrene and 3-hydroxybenzo[a]pyrene. Urine analysis of monohydroxy-PAH (OH-PAH) has long been recognized as an accurate assessment of human exposure to PAH. Generally formed during incomplete combustion of organic matter, PAH are ubiquitous environmental pollutants whose toxicity largely depends on their metabolic fate. The pKa values presented here provide a better understanding of the migration characteristics of OH-PAH and establish the foundation for a single method of PAH and OH-PAH analysis in urine samples.

(337) **Synthesis, Characterization, and Liquid-Liquid Electrochemistry of a New Class of Chiral Hydrophobic Room Temperature Ionic Liquids**

Julie B. Rollins[1], John C. Conboy[1]; [1]University of Utah

Room temperature ionic liquids (RTILs) are receiving a growing amount of attention in many areas of chemistry including organic synthesis, catalysis, electrochemistry, and separations. Hydrophobic RTILs have been shown to replace volatile organic solvents in liquid-liquid extractions, and chiral RTILs have successfully been used to separate enantiomers in gas chromatography. By combining these two properties, hydrophobicity and chirality, liquid-liquid extractions that are enantiomerically selective may be achieved. A new class of chiral hydrophobic RTILs based on a quaternary ammonium cation and bis(perfluoroalkylsulfonyl)imide anion has been synthesized. The physical properties: density, viscosity, water content, conductivity, and electrochemical stability have all been studied. These RTILs are capable of serving as chiral electrolytes that form a polarizable window at the interface between two immiscible electrolyte solutions (ITIES). The chiral cation of this new class of chiral hydrophobic RTILs may facilitate enantiomeric transfer across the ITIES. These studies open a new area of liquid-liquid electrochemistry that investigates the transfer thermodynamics of chiral molecules across an organic/aqueous interface.

(338) **The Effect of Temperature Gradients in Solvating Gas Chromatography**

Jordan Smith[1], Nicole Taylor[1], John-David McElderry[1]; [1]Brigham Young University

Solvating gas chromatography (SGC) is a high-speed version of supercritical fluid chromatography where the pressure restrictor at the column outlet is removed. This causes large density gradients and limits the number of range of compounds that can be analyzed with SGC. On-column laser-induced fluorescence was used to monitor the progress of analytes through the column. High efficiency is observed in isothermal separations, but the retention times can be excessive for less volatile compounds because the mobile phase loses its solvating properties as it moves along the column. Applying temperature gradients along the column decreases separation times and maintains a constant linear velocity

of the analytes. We will report on the effect of temperature gradients on efficiency and speed of separation in SGC.

(339) **Development and Validation of Method for Simultaneous Quantification of Different Marker by Reverse Phase HPLC and HPTLC in Sida Species**

Vaibhav Shinde[1], Kamlesh Dhalwal[1], Kakasaheb Mahadik[1]; [1]Poona College of Pharmacy, Bharati Vidyapeeth Univ

Abstract Quantification of bioactive principles through modern analytical tools is essential for establishing the authenticity and creditability of prescription and usage of herbal drugs. In the present study, simultaneous quantification of vasicine and vasicinone by reverse phase HPLC (RP-HPLC) and HPTLC methods were developed. In the RP-HPLC method, the drugs were resolved using a mobile phase of acetonitrile–0.1M phosphate buffer–glacial acetic acid (15:85:1, v/v/v) with pH adjusted to 4.0 using phosphoric acid on a C18-ODS-Hypersil (5 microm, 250 mm x 4.6 mm) column in isocratic mode. The retention time of vasicine and vasicinone was 5 and 8.7 min, respectively. In the HPTLC method, the chromatograms were developed using a mobile phase of ethyl acetate: methanol: ammonia (8:2: 0.2, v/v) on precoated plate of silica gel 60 F254 and quantified by densitometric absorbance mode at 300 nm. Validations of the methods were done to demonstrate its selectivity, linearity, precision and accuracy as recommended in the ICH guidelines. Excellent linear behaviors over the investigated concentration ranges were observed with the values of R2 higher than 0.998 for both the analytes. Recovery values of 99.16-101.89%, percentage relative standard deviation

(340) **Validation of HPLC Method for Simultaneous Determination of Gallic Acid and Ellagic Acid in Herbal Extract and Formulations**

Kamlesh Dhalwal[1], Vaibhav Shinde[1], Kakasaheb Mahadik[1]; [1]Poona College of Pharmacy

Quantification of bioactive principles through modern analytical tools is essential for establishing the authenticity and creditability of prescription and usage of herbal drugs. Phyllanthus amarus and Syzygium cumini are two most widely used Rasayana drug in India. In this paper, we present a method for the simultaneous determination of gallic acid and ellagic acid by reversed-phase high-performance liquid chromatography (HPLC) using ultraviolet detector at 280 nm and involving isocratic elution. Validation of the method was done to demonstrate its selectivity, linearity, precision and accuracy. Excellent linear behaviors over the investigated concentration ranges were observed with the values of R2 higher than 0.998 for both the analytes. The recoveries, measured at three levels for gallic acid and ellagic acid, varied from 97 % to 102 %. The method was simple, sensitive, rapid and reproducible for the estimation of gallic acid and ellagic acid. In order to ensure the quality of the Phyllanthus amarus and Syzygium cumini, we can apply this validated method for determination as well as to evaluate the quality of herbal extracts and formulations. Key words: Phyllanthus amarus, Syzygium cumini, Quantification, Validation, HPLC.

(341) **Analysis of Trans-Fatty Acids by Gas Chromatography/ Infrared Spectroscopy (GC/IR)**

Katsunori Ishii[1], Aya Harada[2], Kouichi Toda[2], Kunio Awazu[1]; [1]Graduate School of Engineering, Osaka Univ.; [2]Technofleet Inc.

In recent years, it has been suggested that risks of heart disease, suppression of the immune system, carcinogenesis raise by consuming the trans fatty acids in large quantities. Fabrication and sale of the products including trans fatty acids already have been regulated in many Western countries. In Japan, the research for regulation of trans fatty acids has been finally started. Early establishment of the analytical methods to measure trans fatty acids is essential because we can confirm the safety of foods by revealing the content of trans fatty acids. To intake trans fatty acids in moderation leads to the prevention of related diseases. Objective of this study is to develop the accurate and quantitative analyze method for trans fatty acids research. We have developed the gas chromatography/ infrared spectroscopy (GC/IR) system and analyzed several kinds of trans fatty acids and products including them using GC/IR.

(342) **Quantification of Pantoprazole by High Performance Liquid Chromatography in Human Plasma**

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A sensitive and selective HPLC method with UV detection (287 nm) was developed and validated for quantitation of pantoprazole, proton-pump inhibitor, in human plasma. Following a single-step protein precipitation extraction with acetonitrile (3 mL), the analyte and internal standard (omeprazole) were separated using mobile phase of Ammonium acetate buffer(6.5pH, 0.01M) / Methanol / Acetonitrile (30:40:30 v/v, pH* 7.20) on reverse phase Phenomenex C18 column. The lower limit of quantitation was 100 ng/mL, with a relative standard deviation of less than 4%. A linear range of 100–5000 ng/mL was established. This HPLC method was validated with between-batch and within-batch precision of 1.2–3.1% and 0.8–2.3%, respectively. This validated method is sensitive and repeatable enough to be used in pharmacokinetic studies.

(343) **Development of a Centrifugal Microfluidic System for Rapid On-Site Analysis of Environmentally Important Species**

Angela LaCroix-Fralish[1,2], Jennifer Clare[1], Cameron Skinner[1], Eric Salin[2]; [1]Concordia University; [2]McGill University

Micro-total analysis systems (ìTAS) have enabled the miniaturization and simplification of environmental contaminant detection methods. Reduced reagent and sample consumption, speed of analysis, and field portability are only a few of the advantages ìTAS systems provide. Centrifugal microfluidics have the added advantages of using centrifugal force for moving liquids, thereby avoiding solvent and filtration problems encountered with electroosmotic flow typically used in ìTAS manifolds. These properties suggest that centrifugal ìTAS systems may offer many advantages as analysis platforms for the on-site analyses of a variety of important environmental pollutants. A model instrument has been developed and characterized for rapid, classical spectrochemical reactions. The system is designed for the determination of nitrite, nitrate and hexavalent chromium, three common pollutants. The system uses a single disc that requires a total of 200ìl of analyte using a centrifugal disc that filters a single water sample before splitting it into three aloquots, which are then mixed with coupling reagents, and detected on-disc with a pathlength of 1.02 mm. Using a multi-wavelength technique for the precise determination of the reference signal, the detection limits for these three systems are 9, 33, and 7 µg/l for N-NO2-, N-NO3-, and Cr6+ respectively. A comparison between this technique and several conventional techniques highlights the strengths and limitations of the system.

(344) **A Powerful New Structural Information Tool for Complex Mixtures and Polymers; Chromatography Hyphenated with Solvent Removal to FTIR**

Tom Kearney[1], William W. Carson[1], Sidney Bourne[1]; [1]Spectra Analysis, Inc.

Full-spectrum mid-infrared FTIR is a powerful technique for determining structural and compositional information. Historically

FTIR has been limited to pure compounds, or the major components of a mixture. GC, gradient and isocratic LC and GPC can separate complex mixtures, and when coupled with the DiscovIR-GC™ or the IR100 Award Winning DiscovIR-LC™ FTIR detection system continuously produces solid phase FTIR spectra of the separated constituents. The LC and GPC versions use a new solvent removal technology embedded in the fully automated Hyphen™ interface module, which produces an aerosol stream of sample particles. The sample is deposited as a continuous solid-phase spiral track on a cryogenic ZnSe disk in a vacuum chamber. As the spiral track is created, it rotates through the focus of an internal FTIR microscope producing a complete library-searchable solid-phase spectrum every 0.6 seconds. Typically GC produces low nanogram to high pictogram sensitivity and LC produces low microgram to high nanogram sensitivity while preserving chromatographic resolution. (Sigma = 0.8 seconds with polystyrene.) The Hyphen system is compatible with all GPC and LC solvents and most volatile buffers. The disk can store a day's to a week's chromatography before being cleaned. The combination of chromatography with FTIR detection allows library identification or functional group characterization of the constituents. Functional group variations across polymer distributions are readily determined. Many pilot scale up and production problems are solved by comparison of good and bad samples or starting materials with reaction products and byproducts. Deformulation solves many failure analysis problems and allows understanding how others have solved similar problems.

(345) **Combining Chromatography, Spectroscopy and Chemometrics to Solve Real-World Analytical Problems**

Thomas Hancewicz[1], Dane Drutis[1]; [1]Unilever R&D

One of the key actives used in over-the-counter skin care products if all trans-retinol. The principle challenge in delivery of active retinol is the molecule's stability in formulated product. Convenient and accurate measurement is a key tool to the full investigation of the role of formulation in effecting product stability. This talk will describe our efforts to apply chemometrics to support this research. The principal formulation work requires methods that are sensitive, reproducible and suitable for high throughput screening. The most obvious approach to characterizing retinol stability in complex formulations is standard HPLC chromatographic analysis with UV-Vis diode array detection (DAD). UV-Vis without chromatography is faster, but less accurate -- analysis is often tedious and in this case insufficiently sensitive, relying on the existence of unique absorption wavelengths for the product and its degradation products. Our approach to this problem is to combine these analytical techniques with self-modeling curve resolution chemometrics. We will show: 1) the analysis of HPLC-DAD analysis is faster and more accurate and 2) UV-Vis spectroscopy becomes a viable method for routine high throughput screening of retinol stability samples.

(346) **Chromatographic Alignment for Improved Multivariate Analysis**

Scott Ramos[1], Brian Rohrback[2]; [1]Infometrix, Inc.

In the petrochemical industry, a significant portion of analytical work is done by chromatography, and much of that is by high resolution GC of very complex mixtures. The critical nature of these samples demands precise interpretation of separated components. Yet, even with the more sophisticated retention time control in modern instruments, retention times still vary, and analysts must spend precious company time manually verifying peak assignments. Recent developments of alignment algorithms have been very successful in mitigating the effects of retention time variability. Ideally, the aligned profiles no longer require manual review, thus saving the companies time and money. The bonus is that multivariate analysis is also more reliable because the fluctuating peak positions in the samples in a data set become a minor, rather than major, source of variability. Case studies from the petroleum industry will be presented to illustrate the issue and its resolution.

(347) **Chemometrical Experimental Design-Based Optimization Studies in Capillary Electrophoresis Applications**

Frank Gomez, Ruthy Montes, Grady Hanrahan; [1]California State University, Los Angeles; [2]California Lutheran University

The use of chemometric response surface methodology (RSM) in several capillary electrophoresis (CE) studies is described. Here, we use RSM in one, the estimation of affinity constants between receptors and ligands in flow through partial filling affinity CE (ACE) and competitive binding partial filling affinity capillary electrophoresis (CBPFACE) and, two, in the optimization of reaction in an enzymatic reaction using electrophoretically mediated microanalysis (EMMA). Also described is the first detailed examination of flow injection-CE (FI-CE) active parameters and their interactions via RSM. In each case, the adequacy of the determined models was validated by experimental runs with the predicted model solutions. The use of chemometrics in CE has significantly reduced the number of experiments and time required in optimization experimental protocols. This presentation will demonstrate the usefulness in employing RSM to specific CE applications thereby proving the utility of chemometrics design in experimental optimization.

(348) **Application of Experimental Design and Artificial Neural Networks in Modern Separation Studies**

Grady Hanrahan[1], Ruth Montes[2], Joseph Rower[1], Toni Riveros[2], Frank A. Gomez[2]; [1]California Lutheran University; [2]California State University, Los Angeles

With the advent of modern separation methods comes the need for advanced experimental design and optimization techniques to aid in achieving optimal separation conditions. The combination of experimental design and artificial neural networks (ANNs) has recently been shown to be a powerful tool in such efforts. This talk will concentrate on studies using a factorial design/ANN combined approach in optimizing conditions in capillary electrophoresis (CE). More specifically, its use in maximizing conversion of NAD to NADH using the enzyme G6PDH. Results will show the usefulness of such an approach for efficient prediction of optimal experimental conditions. Future studies utilizing this approach will also be discussed.

(349) **Experimental Design, Optimization and Pattern Recognition in Chromatography: Applications and Perspectives**

Stephen L. Morgan[1], Sparkle T. Ellison[1], Pakritsadang Kaewsuya[1]; [1]University of South Carolina

Selected past and present applications of chemometrics in chromatography (experimental design and optimization, as well as multivariate statistics) will be presented in this talk. Early applications of empirical optimization methods in chromatography were originally based on two concepts: formulation of chromatographic response functions to measure the quality of multicomponent separations, and systematic mapping and modeling of chromatographic performance as a function of its experimental variables. Empirical models, derived from planned experimentation, that relate chromatographic retention and experimental variables in both gas and liquid chromatography (e.g., stationary and mobile phase choices, temperature, pH, solvent composition) have been extensively used to optimize chromatographic separations. On the other hand, early applications

of pattern recognition to chromatography involved manual selection of peaks to form pattern vectors. Selection of chromatographic variables from higher dimensional data (e.g., chromatography coupled to spectroscopy or mass spectrometry) remains a challenge, particularly in terms of peak alignment. Reasonable approaches to format chromatographic data for pattern recognition and to capture relevant information from the chromatogram are now available. Applications of multivariate statistics to chromatography will be shown for monitoring quality control, calibration, and discrimination of analytical samples from one another.

(350) **Multivariate versus Univariate Optimization of Separation Conditions in Micellar Electrokinetic Chromatography**

Carlos Garcia[1], Jessica Felhofer[1], Grady Hanrahan[2]; [1]UT San Antonio; [2]California Lutheran University

We used a chromatographic response function (CRF) that included an output for each of two performance parameters (resolution and analysis time) to optimize the separation of five bisphenols by micellar electrokinetic chromatography (MEKC) using multivariate response surface methodology (RSM). To validate the real utility of this approach, we have also compared the efficiency of the proposed optimization method with a traditional univariate analysis. For both methods, the selected variables of the analysis were: buffer concentration, pH, amount of organic solvent, and concentration of surfactant. The predictive nature of a validated response surface design allowed for the elucidation of a strong interactive effect and resulted in a more labor efficient optimization when compared to the univariate approach.

(351) **Utilization of Chemical Imaging during Formulation Design – Identification of Critical Quality Attributes**

Hung Tian[1], Hitesh Chokshi[1]; [1]Roche

The physical and chemical characterization data derived from simultaneous spectroscopic and imaging studies have demonstrated potential to advance our insight and understanding of the complexities of a solid dosage form. This presentation will illustrate the utilization of near infrared chemical imaging (NIR-CI) in identification of critical quality attributes (CQA) in Phase I and II clinical formulation design and optimization leading to market formulation. The early identification of the CQA assures efficient and objective formulation and process optimizations. Furthermore, it sets scientific foundation for the implementation of the Quality-by-Design (QbD) principle throughout a formulation development life-cycle. In this presentation, three case studies will be discussed in details 1. NIR-CI were utilized in determination of critical physical quality attributes (CPQA) of Compound X and excipients to guide formulation design and establish a correlation of the CPQA with human exposure. The NIR images also guided in development of a bio-relevant dissolution method. The study suggested that a uniform and intimate mixing of the Compound X and a key excipient be critical for the co-dissolution which likely led to the optimal bioavailability in human 2. Hyperspectral NIR imaging was utilized as the primary tool to investigate the changes in *in-vitro* dissolution behavior as a function of the characteristics of the film coating on a tablet dosage form. Statistical distributions of components in the images of the tablet coating were studied based upon quantitative shape analyses of their chemical domains. NIR-CI provided a quick and reliable characterization of difference in the tablet film coatings attributed to the scales of coating operations, which resulted in substantial changes in the *in-vitro* dissolution behavior of the final dosage form. 3. *In vivo* animal study indicated that bioavailability of the selected model drug was strongly influenced by its polymorphic forms. The anhydrate was the desired polymorph, and the presence of the monohydrate was shown to lower the bioavailability in animals. NIR spectroscopy and NIR-CI were used to determine potential polymorphic transformation of the drug in the tablets during manufacturing and storage. A PLS model was developed to determine the monohydrate content in the tablet stability samples.

(352) **Quantitative Measures of Spatial Resolution for Chemical Imaging of Pharmaceuticals**

John Kauffman[1], Sean Gilliam[1], R. Scott Martin[2]; [1]FDA Div. of Pharmaceutical Analysis; [2]Saint Louis University

Microfluidic methods have been used to construct resolution targets composed of thick, non-opaque, light scattering polymeric materials on silicon substrates. Chemical images of these devices exhibit lower spatial resolution than that measured with metal-on-glass resolution targets, and this behavior is attributed to lateral photon diffusion resulting from subsurface scattering. Photon diffusion is expected to occur when pharmaceutical materials are examined with chemical imaging technology. The resolution targets described in this presentation have been used to develop quantitative measures of the spatial resolution that is achievable when pharmaceutical materials are imaged. Quantitative measures of resolution are based on best fit model functions that provide estimates of the impulse response extracted from bar targets that are thick and non-opaque, and scatter light. We will discuss the relative merits of two different measures of spatial resolution, as well as the influence of factors such as signal-to-noise ratio, numerical aperture and excitation penetration depth on resolution.

(353) **NIR Chemical Imaging for Enhanced Understanding of Blending Processes**

Carl Anderson[1], Ma Hua[1], Zhenqi Shi[1]; [1]Duquesne University

The role of near-infrared (NIR) chemical imaging for understanding the blending process in secondary pharmaceutical manufacturing will be demonstrated. Applications to this single unit operation span key topics such as quality by design (QbD), design space, and process analytical technology (PAT). While imaging is not currently a common tool for online analysis in secondary pharmaceutical manufacturing, it plays a key role in facilitating the understanding necessary for many subsequent applications. Specifically, it is a critical technology for understanding and monitoring the blending of pharmaceutical powders. The data for this work comes from a series of experiments wherein off-line NIR images of the contents of a blend were collected over time. Images from each time-point include the top, bottom, and two cross-sections of the blend, providing detailed information about the distribution of constituents through the blend container. Analysis of the data provides insight to blend behavior, develops an understanding of optimum locations for blend sensors, and suggests importance of detecting all constituent concentrations for determining the end point of blending.

(354) **Terahertz Pulsed Imaging as a Process Analytical Tool for Tablet Film Coatings**

Philip Taday[1]; [1]TeraView Limited

Pharmaceutical companies coat tablets to improve the physicochemical properties of simple compressed tablets for cosmetic or therapeutic purposes. The coatings can control the release of the active pharmaceutical ingredient (API) tablet coatings ensure bioavailability, minimise harmful effects and the waste of the drug by delivering it at the specific site and at the optimum level. These functions may be compromised if a coating is non-uniform or has defects. These parameters have been difficult to assess with most optical spectroscopic methods. Technological advances now allow us to access the terahertz region of the electromagnetic spectrum (0.1 to 3 THz) which can be to non-destructively analyse the coating. Terahertz pulsed imaging

provides a quick and non destructive 3D mapping technique for determining the composition and integrity of intact chemical materials and coatings. TPI yields unique information for product formulation, product quality, and root cause analysis of multi-layered products and laminates. Recently, the FDA and other groups have demonstrated the potential of TPI indicate the dissolution performance of commercial products. This paper reviews the application of TPI to coating thickness analysis. We will look at the critical attributes of coatings and how they affect the tablet's performance.

(355) **Chemical and Morphological Imaging of Pharmaceutical Products: Measuring the Impact of Process Conditions on Finished Tablets**

Janie Dubois[1], Lisa J. Makein[1], Linda H. Kidder[1], Maurizio Valleri[2], E. Neil Lewis[1]; [1]Malvern Instruments; [2]Menarini Pharmaceuticals

Pharmaceutical solid dosage forms are convenient to manufacture, distribute and administer but are structurally complex and can have unpredictable behavior. Variability introduced during the manufacturing phase can have a significant, and unintended, impact on the final quality and performance of the product. It is therefore essential that any potential process changes be evaluated and controlled to maintain the quality of the product. The current push within the pharmaceutical industry to achieve Quality by Design goes even further than evaluating the end result of process changes. It is hoped that with a clear understanding of Critical Quality Attributes (CQA), changes in certain manufacturing processes can be offset through controlled changes of other parameters. Near infrared chemical and morphological imaging can be used to investigate the impact of changes to a manufacturing process and, more importantly, provide enhanced product understanding that promotes identification of CQAs. In this study, tablets from a wet granulation process, a direct compression process and a direct compression process that additionally uses micronized active pharmaceutical ingredients (API) were compared. Data were collected over 12.5 x10.2 mm and 40 x 32 mm image areas using a SyNIRgi chemical imaging system in the spectral range 1200-2400 nm. Most of the tablets were imaged intact, although several were also shaved to expose the interior surface. Chemical and morphological analyses of the distribution of components were performed using ISys 5.0. Results will show that NIR chemical imaging was able to distinguish between the same product manufactured using different processes. These products would have been indistinguishable using either HPLC or a conventional optical spectroscopic technique. In particular, we will show that in this formulation, the use of direct compression instead of wet granulation caused regions of increased heterogeneity of the API distribution on the tablet surface.

(356) **The Use of Chemical Imaging to Support the Mapping of a Product Design Space**

Stepehen Hammond[1]; [1]Pfizer Inc

The fundamental aspect of a "design space" for solid oral dosage forms, is the understanding of performance of a product related to the critical material properties of ingredients and how they form the matrix of the product. The measurement and understanding of the material attributes that are critical to quality, and how they change the product performance. A key premise to this strategy is that you have the required tools to explore and understand the critical attributes of the product and the process from which it comes. Chemical imaging tools have been developed that enable us to gather information about solid pharmaceutical products at the matrix level. It is possible to generate chemical maps of the solid matrix and relate the structure to the product performance. This presentation will: •Describe the tools that are available for understanding the solid dosage forms. •Provide examples of the tools being used to understand a product and the process used for manufacture, in terms of the critical to quality attributes of the ingredients and the effect they have on the solid dosage matrix and product performance.

(357) **Investigation on the Mechanisms Underlying the Signal Improvement Observed in the Double Pulse Laser Ablation**

Gabriele Cristoforetti[1], Stefano Legnaioli[1], Vincenzo Palleschi[1], Elisabetta Tognoni[1]; [1]Institute for Chemical Physical Processes, CNR

The ablation of materials obtained by focussing a laser pulse on their surface (Single Pulse ablation) is often used as sampling procedure for chemical analysis purposes, e.g. in LIBS technique. Recently, a variation of such approach, making use of two laser pulses (Double Pulse ablation) separated by a suitable temporal delay, was introduced since it leads to a substantial enhancement of the signal. The causes of such improvement are investigated by analysing the time- and spectral-resolved plasma emission and the craters morphology obtained in SP and in DP configurations at different air pressures. The calculation of plasma thermodynamic parameters shows that the emission enhancement is just to a minor extent originated by variations of plasma temperature, but it is rather produced by a marked increase of the atomized mass present in the plume. An increase of mass removal from the target is also found by the morphological analysis of craters. It is observed that the plasma mass and the craters dimensions in DP ablation are similar to those found in SP at reduced air pressure; the increasing of the air pressure up to the atmospheric value results in a progressive lowering of the plasma emission and of the crater depth. Results suggest a complex picture where the air pressure drives the laser shielding effect, which in turn affects the relevance of melt displacement, melt expulsion, and phase explosion mechanisms. It is suggested that the enhancement observed in the DP configuration is mainly due to the air rarefaction produced by the first laser pulse, which causes a less effective shielding of the second laser pulse. The hypothesis agrees with the faster expansion of the plumes and the shock waves observed in the DP ablation by shadowgraphic imaging. It is also suggested that phase explosion occurs in DP laser ablation while in SP ablation at atmospheric pressure it is inhibited. At the opposite, melt splashing seems to be much more efficient in the latter case that in the former one. Such results could also explain the observed correlation between the ablated atomized mass enhancement and the matrix thermal diffusivity in metal targets.

(358) **Experimental and Theoretical Studies of the Dynamics of the Laser Induced Plasma and the Associated Particle Generation Process**

Sy-Bor Wen[1]; [1]Texas A&M University

From experimental studies, microscale laser ablation shows a general trend under different laser energy level in a background gas with an atmospheric pressure. Vaporized material expands rapidly into a background gas once it is generated from the target. The rapid expansion can compress the background gas and then forms a highly expanding shockwave in the background gas. The laser energy conversion ratio can be estimated from the trajectory of the shockwave measured from shadowgraph images. This rapid expansion stops within few microseconds after the laser pulse. The temperature of the vapor plume is more than ~10,000 K at the end of the expansion. The high temperature vapor plume induces a strong spectral emission and a consequent energy transport from the vapor plume to the background gas. The size and shape of vaporized material changes due to this radiative cooling process. A vortex ring in the vaporize material region is often observed during

this stage when the laser energy is >~10mJ. The presence of vortex ring pushed the vaporized material further away from the target and forms a mushroom-shaped distribution of the vaporized material in the background gas. Once the temperature of the vapor plume is less than the boiling temperature, condensation starts in the vaporized material region and forms nanoparticles. A second vortex ring can also be observed in the condensed vapor plume under appropriate laser energy and background conditions. This vortex ring changes not only the shape of the condensed vapor plume but also the cooling rate and then the particle size distribution in the condensed vapor plume. Based on the experimental results, simplified plasma dynamic model for each stages (expansion, cooling and condition) is proposed, which can predict trend of evolution of the vaporized material (laser induced plasma). Appropriate characterization of the dynamics and the subsequent cooling rate of the vaporized material generated after a laser ablation through the theoretical analysis terms about to be important to determine the emission and condensation of the vaporized material along with the appropriate ablation conditions for laser ICP-MS and LIBS.

(359) **Discrimination of Complex Chemical Substances with Laser Induced Breakdown Spectroscopy**

Jong Yoo[1], Richard E. Russo[1], Xianglei Mao[2], JeeBum Lee[3], Sungho Jeong[4]; [1]Applied Spectra, Inc; [2]Lawrence Berkeley National Laboratory; [3]Chonnam National University Medical Schl; [4]Gwangju Institute of Science and Technology

LIBS is a powerful technique for the rapid chemical analysis. By analyzing the elemental spectral signatures with chemometric algorithms, molecular compounds with similar components (but different chemical formulae) can be determined. Within a multitude of organic and inorganic samples, even compositionally similar materials were discriminated using principal component analysis (PCA). Our approach also enables categorizing the human skin malignancy. In the latter case, LIBS and Raman spectra were acquired in parallel to improve the discriminating capabilities.

(360) **Overview of Standoff Laser Induced Breakdown Spectroscopy Progress at U.S. Army Research Laboratory**

Frank De Lucia[1], Jennifer Gottfried[1], Chase Munson[1], Andzrej Miziolek[1]; [1]U.S. Army Research Laboratory

For several years now, the U.S. Army Research Laboratory has been involved in using Laser Induced Breakdown Spectroscopy as a potential detection method for hazardous materials. There are several characteristics of LIBS that make it an attractive detector system for U.S. Army applications – can obtain data in real time, does not require any sample preparation, and the instrumentation can be configured for field use. One such configuration allows collection of spectra at standoff distances. Several standoff LIBS systems have been tested in laboratory conditions up to 50 meters in order to detect hazardous materials. Spectra were also collected from a variety of confusant samples. In order to discriminate between the hazardous material of interest and confusant samples, chemometric methods such as Principal Components Analysis and Partial Least Squares Discriminant Analysis are utilized.

(361) **LIBS Analysis and Imaging of Very Low Mass Lodading of Metals Delivered on Surfaces**

Jose Almirall[1], Cleon Barnett[1], Erica Cahoon[1], Monica Joshi[1]; [1]Florida International University

Sub-nanogram quantities of metals delivered onto surfaces were detected by multiple-shot LIBS experiments. Microdrop printing devices delivering as low as ~ 0.1 nanoliters of multi-element standard solutions with a precision of better than +/- 1% were used to develop a calibration strategy for the quantitative determination of metals delivered onto surfaces. Absolute mass quantities in the sub-nanogram range were detected by a less than a 20 laser desorption-LIBS experiment. Quantitative analysis of multi-element standards was possible using this technique. Chemical imaging of surfaces using LIBS will also be presented. The capabilities of delivering microdrops onto surfaces opens the possibilities of calibration strategies such as standard addition for the quantitative analysis of materials at very low mass loadings.

(362) **Double-Pulse LIBS Signal Enhancement Correlated to Nanoparticle Size Distributions**

Andrew Effenberger[1], Steven Buckley[2,3]; [1]Dept. of Chemistry, Univ. California, San Diego; [2]Dept of MAE, Univ. California, San Diego; [3]Photon Machines, Inc.

The signal enhancement from dual-pulse LIBS is investigated by correlating the nanoparticle production from the ablation of brass and the Boltzmann temperature in the ablation plasma. Several dual-pulse and single-pulse experiments were completed. In the dual pulse experiments a pre-ablative plasma 0.5 - 1 mm above the surface was created from a laser pulse parallel to surface target and an ablative plasma was created from focusing a laser pulse directly onto the target surface and intersecting the volume in the pre-ablative plasma. The timing between the two pulses and the power of the pre-ablative pulse were varied. Seven different emission lines from copper and zinc were integrated and averaged from four 100 shot spectra accumulations. Particle size distributions were measured using a scanning mobility particle sizer (SMPS) for each condition. Dramatic increases in mass ablation and variations in the particle size distribution were noted as a function of inter-pulse delay in the double-pulse experiments compared with the single-pulse experiments. These increases, along with the change in the Boltzmann temperature of the plasma, are correlated with signal enhancement of both Cu and Zn lines in double-pulse LIBS of brass. In general, the predicted theoretical increase in LIBS signal based on Boltzmann temperatures alone is not sufficient to explain the increased double-pulse signal enhancement; the combination of temperature and increased nanoparticle mass appear to work in tandem to provide enhanced signal. Continuing work related to nanoparticle size distribution from single- and double-pulse LIBS will be discussed.

(363) **Towards Multicomponent Nanoparticle-Based Catalysts for Solar Hydrogen Generation from Water**

Frank Osterloh[1], Owen Compton[1], F. Andrew Frame[1], Elizabeth Carroll[1], Michael Sarahan[1], Cory Mullet[1], Shirley Chiang[1], Nigel Browning[1], Delmar Larsen[1]; [1]UC Davis

The efficient generation of chemical fuels using abundant solar energy is of great economic and ecological interest. We present a modular strategy to build photochemical water splitting catalysts by linkage CdSe, KCa2Nb3O10, K4Nb6O17 nanosheets and Pt and IrO2 nanoparticles. The structures are supported by direct covalent bonds or by -aminoalkylsilanes. Upon UV or visible irradiation all composites are active for photocatalytic hydrogen evolution from water, with the activity depending on the nature of the linkers and on the components. Femtosecond absorption spectroscopy and electrochemistry were used to probe charge generation and transport in these structures and across the nanoparticle-solution interfaces. The nanostructures were also characterized with electron microscopy, and visible and fluorescence spectroscopy.

(364) **Direct Monitoring the Bond Strength of CO at Au@Pt Core-Shell Nano-Particle Electrodes by *in-situ* Electrochemical Surface-Enhanced Raman Spectroscopy**

Yan Xia Chen[1], Pu Zhang[1], Jun Cai[1], Shao Xiong Liu[1], Jian Feng Li[2], An Wang[2], Ping Ping Fang[2], Xiao BIng Lian[2], Bin Ren[2], Zhong Qun Tian[2]; [1]aHefei National Laboratory for Physical Sciences a; [2]State Key Laboratory of Physical Chemist

We monitored the real time change of Pt-C (in Pt-CO) peak frequency and band intensity with COad coverage on Au core - Pt shell nanoparticle electrode surfaces by electrochemical *in-situ* surface-enhanced Raman spectroscopy (SERS) combined with a thin layer flow cell. A decrease/increase in the Pt-C (C-O) vibrational frequency with the increasing in COad coverage is observed, reveals the decreasing CO adsorption energy with increase in COad coverage. With increase in the potential the peak frequencies of Pt-C (C-O) decrease (increase) respectively. The correlation of Pt-C)C-O)bonding behavior and the electrocatalytic activity of COad oxidation will be discussed.

(365) **Soft X-Ray Spectroscopy of Thin Film Solar Cells – Towards an Understanding of the Chemical and Electronic Structure of Interfaces**

Clemens Heske; [1]UNLV

The macroscopic properties of thin film electronic devices depend on many parameters, some of which cannot be easily controlled. In particular, the properties of interfaces between different layers of the device are difficult to assess. First, interfaces are composed of two "surfaces", and even surfaces at solid-vacuum interfaces are very different from the bulk. Second, interfaces have a life of their own: many of their characteristics are developed only during the interface formation process , which often takes place at elevated temperatures in non-ideal environments and involves chemical and electronic modifications on the nanoscale. In this talk, I will use one specific example [the CdS/Cu(In,Ga)(S,Se)2 interface in high-efficiency thin film solar cells], to show how (a) interface properties depend on the interface formation process itself, (b) interfaces play an important role for the performance of thin film devices, (c) soft x-ray spectroscopy is uniquely suited to unravel some of the secrets of such interfaces, and (d) how this nanoscale knowledge can then be used to improve the performance of thin-film devices on a macroscopic scale.

(366) **Surface Bottom-Up Synthesis of Redox Molecular Wires and Their Electron Transfer Behavior**

Hiroshi Nishihara[1]; [1]The University of Tokyo

"Redox polymers" in which redox species are connected to form a polymer chain, especially in the mixed valence state, are one of the representative electron-conducting substances. In most of the previous studies of redox polymers, polymer chains are randomly distributed in the film. We have recently developed a facile interfacial bottom-up method to fabricate redox polymer chain of bis(terpyridine) metal complex oligomers and polymers with the desired number of redox complex units combined with conjugated linkers and with a designed hetero-metal sequence at the surface. Films of linear and branched oligomer wires of $Fe(tpy)_2$ (tpy = 2,2':6',2"-terpyridine) were constructed on a gold electrode surface by the interfacial stepwise coordination method employing a surface-anchoring ligand, $(tpy\text{-}C_6H_4N{=}NC_6H_4\text{-}S)_2$ (L_1), two bridging ligands, 1,4-C6H4(tpy)2 (L_2) and $1,3,5\text{-}C_6H_3(C{\equiv}C\text{-}tpy)_3$ (L_3), and metal ions. The quantitative complexation of the ligands and Fe^{II} ions was monitored by electrochemical measurements in linear oligomers of L_2 up to eight complexation cycles and in branched oligomers of L_3 up to four cycles. STM observation of branched oligomers at low surface coverage showed an even distribution of nanodots having uniform size and shape, suggesting the quantitative formation of dendritic structures. The electron transport mechanism and kinetics for the redox reaction of the films of linear and branched oligomer wires were analyzed by potential step chronoamperometry. The unique i-t behavior, obtained similarly in all conditions indicates that electron conduction occurs not by diffusional motion but by successive electron hopping between neighboring redox sites within a molecular wire. This is the first observation of redox conduction in a single molecular wire in redox polymer films. The analysis provided the electron transfer rate constant between the electrode and the nearest redox complex moiety, k_1 (s^{-1}), as well as that between intra-wire neighboring redox complex moieties, k_2 ($cm^2mol^{-1}s^{-1}$). We also fabricated photo-electron conversion system with porphyrin-terminated molecular wires on an ITO surface synthesized using stepwise metal-terpyridine complexation reactions. The efficiency and the electrode potential significantly depended on the metal center of the bis(terpyridine) complex unit in the molecular wire.

(367) **Electron Transfer through a Self-Assembled Monolayer of Thiol-End-Functionalized Porphyrins and Metalloporphyrins**

Lu Xiaoquan[1]; [1]Northwest Normal University,P.R.China

The monolayers of several thiol-end-functionalized porphyrins (abbreviated as H2TPPO(CH2)nSH, where n=3,4,6,9,10 and 12) and metalloporphyrins were self-assembled on gold surfaces and investigated by cyclic voltammetry(CV), electrochemical impedance spectroscopy(EIS) and scanning electrochemical microscopy(SECM) and the intention was to study the effect of electron transfer with the alkyl chain length and the insertion of metallic ions of self-assembled SAMs. The CV peaks of the Fe(CN)63-/4- couple were used to identify the efficiency of electron transfer through the different alkyl chain length of self-assembled monolayer(SAM). The results suggested that H2TPPO(CH2)nSH and MTPPO(CH2)3SH could form high-quality SAMs on gold surfaces. The SAMs blocked electron transfer from the gold electrode to solution. When the surface coverage enhanced gradually with the increased length of the thiol-end-link spacer(alkyl group), the electron transfer ability of the SAM decreased because of the increased insulator properities of the alkyl chain. The unique structure of porphyrin moiety as a large terminal group had a great influence on the electron transfer with the increased alkyl chain length. From the area occupied by each molecule and the cross-sectional area of tetraphenyl-porphyrin on the surface of electrode, the area S of mono-porphyrin, the distance of S–S, the tilt-angle values and the size and separation of pinholes of saturated porphyrin SAMs on the surface of gold electrode were estimated. With the insertion of metallic ions, the electron transfer ability of the SAM of MTPPO(CH2)3SH increased compared to that of the SAM of H2TPPO(CH2)3SH, which can be understood in two different ways: (1) the insertion of metallic ions resulted in the distortion of porphyrin molecules and the molecular structure of MTPPO(CH2)3SH played an important role in electron transfer through the SAM and (2) the insertion of metallic ions and the electron tunneling probability through the monolayer.

(368) **Metal Nanoparticles Stabilized by Metal-Carbon Covalent Bonds**

Shaowei Chen[1]; [1]University of California, Santa Cruz

Monolayer-protected nanoparticles represent a unique class of functional nanomaterials with the chemical and physical properties that differ vastly from those of their bulk materials and molecular species. Previously, the particles are typically stabilized by mercapto-derivatives by taking advantage of the strong chemical affinity of thiols to transition-metal surfaces. More recently, we and others have demonstrated that other chemical linkages might be exploited to stabilize and functionalize metal nanoparticles. Specifically, metal-carbon single-bond linkages have been used to

stabilize gold, platinum, palladium, and titanium nanoparticles by using diazonium derivatives as the precursors. Because of the strong metal-carbon covalent linkages and low interfacial contact resistance, the particle materials exhibited unique conductivity properties. For instance, when the particles were stabilized by biphenyl moieties, metallic temperature dependence of the ensemble conductivity was observed within the temperature range of 100 to 300 K, whereas with the introduction of a saturated (alkyl) spacer, at low temperatures the particle ensembles exhibited semiconducting characters and at high temperatures, became metal-like. The transition temperature was around 200 K. This was accounted for by the Mott's metal-insulator transition model. Additionally, when freshly prepared ruthenium nanoparticles are exposed to diazo derivatives, nitrogen is released and the resulting carbene fragment binds strongly to the ruthenium surface forming ruthenium-carbene pi bonds. The particle materials properties can be further manipulated by the olefin metathesis reactions of these carbene-stabilized nanoparticles with vinyl-terminated derivatives, where multiple and versatile functional moieties can be incorporated onto individual nanoparticles.

(369) **Latest Results on High Resolution IMS-MS**

Michael Bowers[1], Paul Kemper[1], Nicholas Dupuis[1]; [1]UC Santa Barbara

We are in the process of final testing of a high resolution ion mobility cell coupled to both quadrapole and TOF mass spectrometers. The 2 meter cell operates at nominally 15 torr with a room temperature resolution of 100 to 120. The cell is temperature variable from 100 to 450K. Both nano ESI and LDI/MALDI ion sources are available. Examples from both sources will be given. Emphasis will be on peptide/protein systems. Preliminary work indicates that many new features are observed even in well studied systems like bradykinin(+1, +2 and +3 charge states) and its aggregate states. Equally interesting data has been obtained on a number of protein systems. These data present major theoretical challenges which we are addressing.

(370) **Characterization of an 800 kDa eIF3 Protein Complex: Effects of CID and Solvent Disruption using Ion Mobility MS**

Julie Leary, Matthew Schenauer, Armann Andaya, Raluca Stefanescu; [1]University of California Davis

eIF3 is an important initiation factor, comprised of 13 different protein subunits, which partners with mRNA and the 40S ribosome during protein translation. We have analyzed the intact complex, whose mass approaches 800 kDa, using ESI-ion mobility mass spectrometry. Nanospray conditions are optimized to obtain the accurate mass of the intact complex, while CID and solvent disruption of the complex is used to probe the individual protein subunits. Collisional cross sections (CCS) are measured for the subunits that dissociate from the intact complex by both solvent disruption and CID. Definite trends are observed and while one single conformation appears to predominate for the solvent disrupted subunits, multiple conformers are observed for those produced by CID. Modeling data using trajectory method shows good correlation with the experimental data.

(371) **Investigation of Alternate-Construction and Variable Duty Cycle Gating Waveforms for Digitally-Multiplexed Atmospheric Pressure Drift Tube Ion Mobility Spectrometry**

Facundo Fernandez[1], Mark Kwasnik[1]; [1]School of Chemistry and Biochemistry. Georgia Tech

One of the shortcomings of atmospheric pressure drift tube ion mobility spectrometry (AP-DTIMS) is its intrinsically low duty cycle caused by the rapid pulsing of the ion gate (400-25µs) followed by a comparatively long drift time (50-100ms) which translates into a loss of sensitivity. Multiplexing approaches via Hadamard and Fourier-type gating techniques have been reported in the literature for increasing the sensitivity of AP-DTIMS. Here, we report an expansion of the Hadamard multiplexing approach which encompasses arbitrary binary ion injection waveforms with user-selectable duty cycles ranging from 1 to 50%. This approach enables variation of the dynamic range in a continuous manner, preventing detector saturation and space charge effects. A custom built AP-DTIM spectrometer fabricated with resistive glass and a Faraday plate detector was used for all experiments. Maximum-length pseudorandom sequences and arbitrary sequences with duty cycles ranging from 1 to 50% were applied to a push-pull home built circuit driving a Bradbury-Nielsen ion gate. The effect of arbitrary sequences of different lengths (n=255 to n=4096) and different gate widths (400 to 25µs) on signal-to-noise ratio will be presented. Preliminary data indicates that, for a 255 element sequence, signal-to-noise ratio gains of approximately 2.6, 3.0 and 3.3 could be achieved for sequences with duty cycles of 10, 30 and 50% respectively. For a 4096 element sequence, signal-to-noise ratio gains of approximately 5.1, 6.3, 4.1, and 2.4 were observed for sequences with duty cycles of 1, 2, 5 and 10% respectively. It was noted that a sampling of arbitrary sequences of identical duty cycles produced not only different signal-to-noise ratios but also different baseline structures. Evenly spaced sequences were also tested to investigate the interactions between successively injected ion packets. However, these sequences produced a marked deterioration in the signal-to-noise ratio gain. Experiments performed with simplex-type maximum-length 255 and 2048 element pseudorandom sequences produced a signal to noise ratio gain of 6.5 (7.9 theoretical) and 7.7 (22.6) respectively.

(372) **A Novel Ion Mobility Device: Overtone Mobility Spectrometry (OMS) and Potential Applications**

Stephen Valentine[1], Ruwan Kurulugama[2], David Clemmer[2]; [1]Predictive Physiology and Medicine, Inc.; [2]Indiana University

A new ion mobility spectrometry (IMS) instrument providing increased resolving power when compared with traditional IMS separations is described. The device consists of sequential mobility regions separated by ion gates. Unlike traditional IMS separations requiring an initial pulse of ions to initiate the mobility measurement, the new technique utilizes a continuous ion beam and the frequency-dependent application of a retarding field to each of the ion gating regions. For measurements, a number of mobility regions is grouped together dictating the number of distinct electric fields utilized during an experiment. This number is termed the phase of the system and can vary from 2 to theoretically any larger number (limited by measurement practicality). As an example, if 2 regions are utilized (a 2-phase system), 2 electric field settings are applied to the drift tube. The first introduces a retarding field at the end of each of the 2 regions and the second introduces a retarding field between each of the 2 regions. By applying the 2 fields in a frequency-dependent manner, a mobility filter is created. That is, ions of a specific mobility (regional drift time = 1/f) that can move from one mobility region to the next without encountering the retarding field are selected for detection. The frequency can be scanned to create a mobility spectrum consisting of ion intensity as a function of applied frequency. Studies have revealed two very important features of the new separation technique. First, harmonics of the fundamental separation frequency can be used to improve the resolving power for ions of similar mobilities with some loss in sensitivity. Second, the resolving power is directly proportional to the overall number of mobility separation regions (effectively, drift tube length) as opposed to the square root of the drift region distance found in traditional IMS techniques. Here we

present examples of improved resolution of specific ions having similar mobilities. Additionally, mobility modeling results are presented to describe the separation process. Finally, potential applications as well as limitations of the technique are discussed.

(373) **To Cyclize or Not Cyclize - What is a Peptide Fragment to DO?**

Nicolas Polfer[1]; [1]University of Florida

Introduction Peptide tandem mass spectrometry is the cornerstone of protein identification in proteomics. Recently, however, it has been shown that "b" ions can engage in re-arrangement processes that result in cyclic structures [1]. If these cyclic structures subsequently open up at a different bond than where they were initially formed, the resulting fragment ions no longer reflect the original amino acid sequence. The prevalence of such unwanted reactions appears to be much more important than previously acknowledged, with ~40% unidentified product ions in typical peptide collision-induced dissociation (CID) spectra. In a recent infrared (IR) spectroscopy study on CID products of the pentapeptide Leu-enkephalin we have shown that a mixture of linear and cyclic structures are formed both for "b4" and "a4" product ions [2]. Here, we propose to systematically characterize CID products using infrared (IR) spectroscopy and gas-phase H/D exchange, to establish trends for the cyclization chemistry. Method The IR spectroscopy experiments were conducted at the FOM institute 'Rijnhuizen" (the Netherlands) using a Fourier transform mass spectrometer and irradiating the CID products with the free electron laser for infrared experiments (FELIX). The H/D exchange experiments were performed at the University of Florida, using a Fourier transform mass spectrometer. The CID fragments were subjected to CH3OD (10-8 Torr) for different periods of time to study their exchange kinetics. Preliminary data It will be shown that the complementary information from both of these structural techniques gives insights into the prevalent reaction processes. Our preliminary data on gas-phase H/D exchange for some of the b fragments show striking bimodal distributions in the case of the larger bn fragments, where n>=4. These results are compatible with a mixture of chemical structures, since these would be expected to have different proton affinities, resulting in different H/D exchange kinetics. We have confirmed the chemical structures formed by IR spectroscopy, using FELIX, as the spectra display diagnostic vibrations, such as the CO stretch of the oxazolone ring structure and the C=O-H+ bending mode of the cyclic structure. A detailed interpretation of these IR spectra is carried out with density-functional theory (DFT) calculations, and will be presented. [1] Harrison, et al. JACS 2006, 128, 10364-10365. [2] Polfer, et al. JACS 2007, 129, 5887-5897.

(374) **Fundamental and Applied Investigations into Glow Discharges**

G.M. Hieftje[1], G. Gamez[1], M.R. Webb[1], G. Chan[1], C. Engelhard[1], S.J. Ray[1]; [1]Indiana University

Glow discharges have been popular for use in elemental analysis for over 40 years. In its most popular configuration, the Grimm lamp, it is capable of analyzing both conductive and non-conductive solids directly, and of providing depth resolution on the nm scale. In other modes of operation, and over a range of pressures, the glow discharge can also provide both atomic and molecular information, often in a switched or modulated fashion. Despite this popularity and versatility, the fundamental features of the analytical glow discharge are still not fully characterized. Basic investigations by Laqua and others helped to understand the cathodic sputtering that yields free atoms and ions necessary for analysis; other work, largely by physicists, also provided important information. However, the first fully integrated model of the conventional glow discharge was produced by Annemie Bogaerts, recipient of this year's Lester Strock Award. This important new model incorporates all the processes that occur in the glow, and enables prediction of spatially resolved densities of plasma and sample species, temperatures, and emission features. Of course, every model requires validation in order to be accepted. The first part of this presentation will detail methods and results for characterization of a planar-cathode glow discharge. Electron features of the source were obtained by Thomson scattering, while cathode surface temperatures were estimated from the melting point of materials inserted into the cathode material. Abel-inverted emission patterns yielded radially resolved concentrations of excited-state species. These results will be compared to those predicted by the Bogaerts model. In a second study, the fundamental features of an atmospheric-pressure glow discharge were determined. It was found that gas-kinetic temperatures and electron number densities are greatly elevated at atmospheric pressure, compared to the reduced-pressure glow or even to a chemical flame. As a result, both ionization and vaporization interferences are lowered, while signal-to-background ratios approach those expected of a much higher-power source, such as the inductively coupled plasma.

(375) **Driving Laser Ablation Fundamentals to Applications**

Rick Russo[1], Xianglei Mao[1], Sy-Bor Wen[1,2], Dayana Gonzalez-Oropeza[1], Jhanis Gonzalez[1]; [1]Lawrence Berkeley National Laboratory; [2]Texas A&M University

The underlying mechanisms of laser ablation continue to elude our interpretation. Numerous models have been compared to experiment measurements as a means of predicting performance. Successful overlaps exist for some cases, but to date there is no unifying theory to describe this explosive process. The challenge remains after several decades to find such solutions as laser ablation is utilized in numerous applications, specifically for direct solid sample chemical analysis. Improvements in applications cannot rely strictly on empirical pursuit. The two dominant analytical measurement technologies based on laser ablation are LIBS (laser induced breakdown spectroscopy) and laser ablation sampling into an ICP-MS. A need to provide smaller spatial measurement scales for nanotechnology, with improved sensitivity for detecting smaller quantities of mass, will require enhanced efficiency of converting ablated sample into an appropriate form (atoms, ions, aerosols) for analysis. The talk will describe both fundamental and experimental studies related to plasma generation and particle formation for LIBS and ICP-MS applications, respectively.

(376) **Laser Induced Plasmas: Prediction of Plasma Composition**

Igor Gornushkin[1,2]; [1]University of Florida, Gainesville, FL, USA; [2]BAM, Germany, USA

So-called calibration-free methods become popular in laser induced breakdown spectroscopy (LIBS). These methods conveniently differ from the conventional, calibration-based ones by significant reduction in experimental work (no calibration) due to extensive data treatment, plasma modeling and computation. The focus of this work is on the post-breakdown plasma model [1]. The model is used to solve the inverse initial value problem, that is to determine the plasma composition from the measured plasma spectrum. This is realized through the Monte Carlo procedure where the initial plasma parameters are iterated until a good agreement is achieved between the calculated and experimental spectra. Calculations are performed for the aluminum plasma adiabatically expanding into vacuum. The results are compared to those obtained with the other calibration-free method based on the Boltzmann plot approach [2]. 1. I.B. Gornushkin, S.V. Shabanov, N. Omenetto, J.D. Winefordner, J. Appl. Physics 100 (2006)

073304. 2. A. Ciucci, M. Corsi, V. Palleschi, S. Rastelli, A. Salvetti, E. Tognoni, Appl. Spectrosc. 53 (1999) 960-964

(377) **Aerosol Flow Dynamics and Transport Systems in Laser Ablation Inductively Coupled Plasma Mass Spectrometry**

Detlef Gunther[1], Joachim Koch[1], Jorge Pisonero[2], Markus Waelle[1], Rolf Dietiker[1], Matthias Fricker[1], Robert Kovacs[1], Bodo Hattendorf[1]; [1]ETH Zurich, Laboratory of Inorganic Chemistry, CH-; [2]Department of Physics, University of Ovi

Laser ablation inductively coupled plasma mass spectrometry is becoming an advanced analytical technique for direct elemental analysis in solids. Especially precision and accuracy in trace element analysis and isotope ratio determinations have been significantly improved using UV-ns and UV-fs lasers for sampling. These improvements are mainly based on the fact that many of the well-known drawbacks of this technique (particle size distribution, elemental fractionation, quantification, transport efficiency, vaporization efficiency) have been studied in great detail by different research groups. Transport systems have been developed since the beginning of coupling laser ablation to AAS, ICP-OES and ICP-MS and it has been realized that all ablation cells work for aerosol transport. However, different strategies have been reported which allow manipulating the signal shape obtained during analysis (i.e. signal to noise ratio). More recently, sampling position independent aerosol transport has been recognized as one of the important features, especially when analyzing large samples. Within the last years aerosol extraction and transport efficiency has been studied and the results indicate that the aerosol transport in LA-ICP-MS is in the order of 65 – 90 % depending on the laser used for ablation and the ablation gas environment. In addition, visualization of the aerosol expansion of ns and fs laser ablation in argon and helium has contributed to a better understanding of the aerosol dynamics during initial expansion and transport, which assists the optimization of the ablation cell design. However, most of the research on the aerosol transport has been carried out experimentally, which is time consuming and partially inefficient due to required construction of a new cell. Bogaerts et al. have shown that computer simulations can be successfully used to describe the trajectories of particles during their flight from the ablation to the ICP through the entire transport system. The agreement between simulations and experiments is most convincing and may be considered a milestone towards an a-priori design of new transport systems, because various interactive parameters can be optimized virtually. This presentation will highlight the past, present and future of aerosol transport system designs in laser ablation and their current capabilities. Some examples for optimizing gas flow dynamics and geometry of the transfer system will be shown and discussed in terms of their respective applicability. Furthermore, new experimental results and computer simulations will be compared. Autrique, D., Bogaerts, A, Lindner, H., Garcia, C.C., Niemax, K., Spectrochim Acta 63B (2008) 257-270 Bleiner, D., Bogaerts, A., Belloni, F, Nassisi V, j. Applied Physics, 101 (2007) Bleiner, D., Bogaerts, A., J. Anal Atom. Spectrom. 21 (2006) 1161-1174

(378) **RF and Pulsed Glow Discharges, and Crater Formation in glow Discharges**

Volker Hoffmann[1]; [1]IFW Dresden

In the last years the main research in the field of analytical glow discharges was directed to radio-frequency (rf)[1] and pulsed discharges[2]. In both operational modes there are no static electrical conditions, because voltage and current change permanently. In the case of rf discharges one cycle corresponds to about 100 ns and pulsed discharges are generated in the µs and ms range. The time dependence of the analytical signals and adequate gating of the detection opens the way to vary the experimental parameters to large extent in order to get more information, like spatial resolved analysis in 3 dimensions[3] or speciation analysis evaluating prepeak, plateau and afterpeak[4]. However, the optimisation of the experimental setup becomes only possible with a deep understanding of the ongoing processes. This includes as well as the source and instrument geometry as the discharge parameters. The simple trial and error method e.g. to get flat craters varying pressure and voltage in the dc mode will not work in finite time. Therefore, much effort was done and is going on in the cooperation between experimenters and the modelling group from Annemie Bogaerts in Antwerp to understand and optimise the analytical glow discharge techniques[e.g. 5]. References [1] J. Pisonero, J. M. Costa-Fernández, R. Pereiro, N. Bordel, and A. Sanz-Medel, Radiofrequency glow-discharge devices for direct solid analysis, Anal Bioanal Chem 379 (2004) 17-29. [2] W. W. Harrison, C. Yang, and E. Oxley, Pulsed Glow Discharge - Temporal Resolution in Analytical Spectroscopy, Anal. Chem. 73 (2001) 480A-487A. [3] M. R. Webb, V. Hoffmann, and G. M. Hieftje, Surface elemental mapping using glow discharge—optical emission spectrometry , Spectrochim. Acta Part B 61 (2006) 1279-1284. [4] C. L. Lewis, M. A. Moser, D. E. Dale Jr., W. Hang, D. C. Hassel, F. L. King, and V. Majidi, Time-Gated Pulsed Glow Discharge: Real-Time Chemical Speciation at the Elemental, Structural, and Molecular Level for Gas Chromatography Time-of-Flight Mass Spectrometry, Anal Chem 75 (2003) 1983-1996. [5] A. Bogaerts, L. Wilken, V. Hoffmann, R. Gijbels, and K. Wetzig, Comparision of Modeling Calculations with Experimental Results for Rf Glow Discharge Optical Emission Spectrometry, Spectrochim. Acta Part B 57 (2002) 109-119.

(379) **Molecular Emission in Compositional Depth Profiling using GD-OES**

Arne Bengtson; [1]Swerea KIMAB

GD-OES is an established technique for rapid compositional depth profile analysis (CDP) of a variety of surface films and coatings, including polymer-based materials. However, in several applications molecular emission appear in addition to the atomic spectra, resulting in analytical errors due to spectral overlap. The nature of molecular emission spectra is described, and previous work on molecular emission in glow discharges is briefly reviewed. Work from sputtering of polymers and other materials with a large content of light elements in a Grimm type source are reviewed. Substantial emission has been observed from several light diatomic molecules (CO, CH, OH, NH, C2). For comparison, results from an investigation of molecular emission spectra from mixed gases in a Grimm type glow discharge are presented. An important observation is the observation of spectra from molecular species not present in the original plasma gas, indicating dissociation and subsequent recombination processes. Experimental work on depth profiling of polymer coatings and thin films are presented. The results confirm that molecular emission gives rise to apparent depth profiles of elements not present in the sample. The possibilities to make adequate corrections for such molecular emission in CDP are discussed.

(380) **Determining Blend Content Uniformity during Manufacturing using NIR in a High Shear Mixer**

Edita Botonjic-Sehic[1], Glenys Foster Roberts[1], Krishna Venkatesh[1], Richard Lienhart[1]; [1]Barr Laboratories, Inc.

The understanding and control of drug manufacturing is quickly becoming of great interest to the pharmaceutical industry. Monitoring of the process can be accomplished by using tools that can be applied within a PAT framework. The additional data generated by this monitoring contributes to the understanding of the process. While, when PAT is applied to the quality by design (QbD) concept, one can generate a holistic approach to the design,

development and implementation of drug manufacturing, this is not always possible when applying PAT concepts to an existing commercial product as is the case at Barr Laboratories. While QbD may not have been applied during the initial development of the process, a wealth of knowledge exists around the critical parameters, which affect the outcome of the manufacturing process. This knowledge has been derived from the successful manufacture of many batches over a period of years and has also been generated as a result of experimentation conducted in order to improve process performance and to better understand critical process parameters. At Barr, we have also taken a risk management approach to the PAT project, built on solid scientific principals which, when integrated into production systems, can provide real-time information aiding in the understanding and control of a consistent drug production process. This PAT system utilizes multivariate statistics and statistical analysis (MVA) to determine relationships among any given measured parameter of the process. The system used at Barr Laboratories to determine blend content uniformity in a high shear mixer is described herein and shows how such a system can be a roadmap to a successful process analytical approach.

(381) **Implementation of Control Systems for a Fluid Bed Processor**

Brian Zacour[1], Michael Moore[1], Steven Short[1], Zhenqi Shi[1], Robert Cogdill[1], James Drennen[1], Carl Anderson[1]; [1]Duquesne University Center for Pharmaceutical Tech

Recent regulatory initiatives offer the advantage of operational flexibility in the pharmaceutical manufacturing industry. Process control models are the foundation for establishing a design space, as well as enabling process monitoring and control. The objective of this work was to develop a process control model for a lab scale fluid bed processor (FBP) using PAT measurements and real-time data management. The critical finished product characteristics from the process were identified. Subsequently, experimental designs were employed to identify the variables that have the greatest impact on the final product characteristics. Process models were then calculated to predict the process response based upon critical variables. Control models were deployed and implemented via control systems and a communication network. This system received information from the FBD controls, internal sensors in the FBD, and a near-infrared (NIR) sensor, and used this information to set the processing parameters at each step in the process. The net result was fully automated control of the process from dry powder blending, through granulation, and drying.

(382) **Multivariate Re-calibration Utilizing QbD Approach to Monitor Blend Uniformity**

Dongsheng Bu[1], Saeed Hashemi[2]; [1]CAMO Software Inc; [2]Wyeth Pharmaceuticals

Quality by design (QbD) means developing manufacturing processes that produce high-quality product based on understanding of the parameters critical to process quality. The objective of this study was to develop and validate quantitative methods for process monitoring using near-infrared (NIR) spectroscopy for real-time monitoring of blend uniformity of active and hydroxypropyl methyl cellulose (HPMC). Eighteen different formulated blends were prepared based on a design of experiment (DOE). Fifteen samples were used for the calibration models and the remaining three samples were used for the external validation set. The NIR methods, including DOE and partial least square (PLS) analysis, showed promising results in the pilot study for the determination of blend homogeneity in product formulations. As the applications moved from blend process understanding in research to the process monitoring and further to manufacturing, it was required to validate the developed NIR analytical methodology for the larger scale blenders.

(383) **Implementation of QbD/PAT in Pharmaceutical Development and Manufacturing - Some Theoretical and Practical Aspects**

Jun Huang[1], Rina Chokshi[1]; [1]Wyeth

Some current principles and tools of QbD/PAT in pharmaceutical development and manufacturing will be reviewed and discussed. The presentation will share views and experience on how QbD/PAT, the science and risk-based approaches, can be integrated into pharmaceutical product and process development systematically. Case studies will be given, touching upon QbD/PAT elements such as risk assessment, process analyzers, chemometrics, design space and real time release, etc.

(384) **PAT in the Pharmaceutical Industry; Looking Forward**

Patrick Rameas[1]; [1]GlaxoSmithKline

Slow to adopt change and fear of regulation, the pharmaceutical industry is behind other industries in utilizing process analytical technologies. Since the release of the FDA's PAT guidance document in September, 2004, the pharmaceutical industry has embraced PAT. Even with varying implementation approaches, pharmaceutical companies are starting to realize the benefits of PAT. Benefits seen include reduced batch failures, less production downtime, decreased root cause investigation time, increased throughput, process and product knowledge. This presentation will discuss some of the various ways PAT is currently being applied linking with risk management and quality by design initiatives. Then, a detailed look at the near future will be shown outlining the current trends and hot topics. Finally, a longer term look toward the future will be offered.

(385) **The Use of Process Analytical Technology (PAT) Tools in Biofuels Production**

Jose Menezes[1], Pedro Felizardo[1], Maria Joana Neiva-Correia[1]; [1]Technical University of Lisbon

Biofuels are produced in a sequence of large batch operations involving multiple phases, a bio/chemical reaction and several separation/purification steps. The final product must comply with multiple quality specifications despite the variability in the raw-materials and the complexity in the unit operations used in their processing. Overall biofuels production are prone to PAT implementations the same way a pharmaceutical process does. Even more so if one examines process economics and its associated logistics. The final product cost structure shows that there is a strong case in favour of using PAT throughout (1) raw-mats qualification, (2) production process monitoring and process supervision, and (3) end-product multiparametric release. The logistics associated with the production of large quantities of a commodity type of product by batch operations, with strict quality specifications, increases the need to reduce end-product variability as well to to use fast multiparametric quality control / lot release methods. Here we report on the use of PAT tools on the above context for industrial processes. We conclude showing that PAT tools are cable of mapping raw-materials, finger-printing process trajectories and calibrating for the most important quality specifications, both as individual chemical and physical attributes or as combined quality attributes, overall providing more a consistent and economically sound process.

(386) **UV Resonance Raman Discovery of Gibbs Free Enrgy Landscape for Protein Alpha Helix Folding**

Sanford Asher[1], Alexander Mikhonin[1], Edward Gooding[1], Lu Ma[1], Bhavya Sharma[1], Sergei Bykov[1], Zeeshan Ahmed[1], Nataliya Myshakina[1]; [1]University of Pittsburgh

We developed a powerful method to follow the evolution of secondary structure in the amide peptide bonds of peptides and proteins. UV Raman excitation into these ~200 nm electronic transitions results in the enhancement of the amide vibrations of the peptide backbone. In our most recent studies we reassigned the amide III region and found a particular band (the amide III_3 band) which reports selectively on the Ramachandran Ψ angle and the state of peptide bond hydrogen bonding. We demonstrate that this band is Raman scattered independently by each peptide bond with insignificant coupling between peptide bonds. We also show that isotope editing of a peptide bond (by replacing the C_α - H with C_α - D) allows us to determine the frequency of an individual peptide bond within a peptide or protein which gives us its Ψ angle. Consideration of the Boltzmann equilibria allows us to determine the Ψ angle energy landscape which connects secondary structure conformations. The Ψ angle coordinate is the most important reaction coordinate required to enable the understanding of the mechanism(s) of protein folding.

(387) **Raman and Raman Optical Activity Studies of Biomecular Structure and Behaviour**

Ewan Blanch; [1]University of Manchester

This is an exciting time for vibrational spectroscopies in biological research as they are applicable to most samples under a wide range of conditions and are highly sensitive to structural information. Raman spectroscopy and Raman optical activity (ROA), which measures a small difference in Raman scattering from chiral molecules in right- and left-circularly polarized light [1,2], are two particularly powerful vibrational techniques for studying both proteins and ribonucleic acids (RNA). Raman and ROA provide complementary information about structure, with Raman spectra containing many bands from side chains (in proteins) or bases (in RNA) that are sensitive to their local environments while the main ROA bands originate in secondary and tertiary structure. Chemometrics and bioinformatics can greatly increase the information content of Raman and ROA spectra. In this presentation the principles behind ROA spectroscopy of biomolecules will be introduced before recent examples from our laboratory of the application of Raman and ROA spectroscopies are presented. i) Structural characterizations of ribosomal and virus-associated RNAs [3]. ii) 2D correlation Raman and ROA analyses of unfolding transitions in both proteins and RNA. Moving window and autocorrelation analyses allow us to more accurately interrogate the complexity of conformational transitions underlying pH- and thermally-induced unfolding as well as the misfolding of proteins/polypeptides into amyloid fibrils (the basis of diseases such as Alzheimer's and Type II diabetes). iii) Structural studies on glycosylaminoglycans which are an important class of carbohydrate-peptide polymers found in animal tissues. iv) The Biological Raman Database, a new bioinformatics resource for analysis of protein Raman and ROA spectra. [1] L. D. Barron, Molecular Light Scattering and Optical Activity, 2nd Edn. (2004), Cambridge University Press: Cambridge. [2] L. A. Nafie, Annu. Rev. Phys. Chem. 48 (1997) 357-386. [3] A. J. Hobro, M. Rouhi, E. W. Blanch and G.L. Conn, Nuc. Acids Res. 35 (2007) 1169-1177. [4] L. Ashton, L.D. Barron, B. Czarnik-Matusewicz, L. Hecht, J. Hyde and E.W. Blanch, Mol. Phys. 104 (2006) 1429-1445.

(388) **Deep Subsurface Raman Spectroscopy of Biological Tissue and Pharmaceutical Products**

Pavel Matousek[1]; [1]Rutherford Appleton Laboratory

A number of analytical applications require spectroscopic characterisation of deep layers in diffusely scattering media with high chemical specificity. Examples include disease diagnosis of bone and cancer and the quality control of pharmaceutical products. Conventional vibrational spectroscopy techniques that have required degree of chemical specificity and sensitivity can only access shallow layers in these samples. The presentation will discuss recently developed methods, Spatially Offset and Transmission Raman spectroscopy, for deep non-invasive probing of biological tissue and other turbid media. Several examples from biomedical, security and pharmaceutical application areas will be given.

(389) **Rapid Characterisation of Biological Systems using SERS and Machine Learning**

Roy Goodacre[1], Roger Jarvis[1], Iqbal Shadi[1], Ketan Patel[1], Yun Xu[1], Mike Anderson[1]; [1]University of Manchester

Recently surface enhanced Raman scattering (SERS) has been shown to be a very important analysis method for generating biochemical information from biological systems. Investigations in to the application of SERS for the characterisation and identification of bacteria have accelerated since the first reports were published within the last few years, where we showed [1] that SERS was reproducible enough to allow the identification of bacteria to the sub-species level; and see [2]. Our more recent work on the comparison of extracellular and intracellular SERS will be reported in this presentation, and we shall demonstrate that SERS can be used to make rapid measurements from low numbers of bacteria in just a few seconds. The SERS spectra that we generate from bacterial cells are information rich and so multivariate data analysis methods are needed to aid in the spectral interpretation and also assess the reproducibility of the SERS substrate. Therefore the development of machine learning for the analysis of the SERS spectra will also be detailed and how this allows one to unequivocally identify a pathogen, or quantify the level of some determinand. Finally, we shall detail a novel production method for thin metal films and illustrate the physical characterisation and SERS potential for this. [1] Jarvis, R.M. & Goodacre, R. (2004) Rapid discrimination of bacteria using surface enhanced Raman spectroscopy. Analytical Chemistry 76, 40-47. [2] Jarvis, R.M. & Goodacre, R. (2008) Characterisation and identification of bacteria using SERS. Chemical Society Reviews 37, in press.

(390) **Combining SERS and SEIRA on the Same Substrate**

Naomi Halas; [1]Rice University

Recent advances in our ability to design and fabricate metallic nanostructures with precise electromagnetic properties has the potential to revolutionize surface enhanced spectroscopies such as Surface enhanced Raman spectroscopy (SERS). For example, the strong local fields supported by surface plasmons in metal nanostructures can be designed to enhance SERS at a specific pump laser wavelength. Electromagnetic resonances and large field enhancements can also be extended into the mid infrared region of the spectrum, to provide high performance substrates for surface enhanced infrared absorption spectroscopy (SEIRA). We have recently shown that SERS and SEIRA enhancements can both be combined on the same plasmonic substrate. This ultimately opens up new opportunities for the ultrasensitive detection and identification of molecular unknowns.

(391) **Surface Enhanced Raman Spectroscopy using Gold Colloidal Nanoparticles for Measurement of Signaling Molecules Used by Quorum Sensing Bacteria**

Jasmine Ervin[1], William Pearman[1], S. Michael Angel[1], Alan Decho[2]; [1]Dept. of Chemistry and Biochemistry; [2]Dept. of Environmental Health Science

Bacteria communicate with each other using signaling molecules, autoinducers (AI), in order to coordinate their behavior. This communication is essential for many biological processes ranging from biofilm formation to bacterial virulence in human and plant pathogens. Investigating how these molecules respond to different environmental stresses *in-situ* may help us to develop methods to control their activities. We have found that Raman Spectroscopy is a spectroscopic method capable of *in-situ* measurements for one class of AI's, N-acyl homoserine lactones (AHLs). Raman spectra of several different AHLs with acyl chain lengths from 4 to 12 carbons were collected for the first. Majority of the spectra share similar characteristics. However, direct discrimination of several AHLs was achieved based on spectral differences in the Raman spectra of the molecules. Based on these results, this method shows great potential for quantitative and qualitative monitoring of AI molecules in environments containing quorum sensing bacteria, as their natural surroundings are changed.

(392) **Tunable Fiber Optic Imaging Bundles for SERS Chemical Imaging Below the Diffraction Limit**

John Kiser[1], Mikella Hankus[1]; [1]University of Maryland Baltimore County

Chemical imaging not only provides structural and spatial information about a sample but also chemical information about the sample. Raman spectroscopy can be a powerful transduction mechanism for chemical imaging due to the narrow vibrational bandwidths and unique spectral fingerprints. Unfortunately, Raman cross-sections are extremely weak (~10-30 cm-2), often necessitating long exposure times, making dynamic chemical imaging impractical. By utilizing a Raman enhancement technique such as SERS, the effective scattering cross-sections are increased making practical imaging times feasible. Various scanning techniques such as NSOM have been utilized in conjunction with SERS for chemical imaging, the point scanning associated with NSOM makes dynamic imaging difficult as well. This paper will discuss the fabrication, characterization, and demonstration of a novel SERS substrate and instrumental system for non-scanning SERS chemical imaging with sub-diffraction limited spatial resolution. These substrates are fabricated by chemically etching a polished fiber optic imaging bundle consisting of 30,000 individual, hexagonally packed, 4-μm diameter elements. The chemical etching process creates uniform cladding spikes onto which a SERS active metal is vacuum deposited, forming the SERS active surface. By varying the size of the silver islands deposited on the cladding peaks active surface plasmons can be tuned to various excitation frequencies. This fabrication procedure creates uniform SERS surfaces, < 3 % RSD, which is important uniform image generation. The tunability of these substrates as well the imaging capability have been characterized via plasmon absorption as well as SERS images of patterned Raman scatteres. In addition to the less than 280-nm spatial resolution capable from these bundles when employed in a conventional imaging format, this paper will also discuss the ability to increase the resolution significantly by a mechanical dithering of the fiber probe.

(393) **Multivariate Curve Resolution: A General Approach for Extracting Real Information from Analytical Data**

Thomas Hancewicz[1], Dane Drutis[1], Jesse Weissman[1]; [1]Unilever R&D

Multivariate curve resolution (MCR) has emerged as the chemometrics method of choice for analyzing many types of different and varied analytical data. It is common to find Raman, FTIR, NIR, NMR, UV-VIS, MS, Fluorescence, and many forms of hyphenated HPLC data being analyzed by MCR or related chemometric methodology. The reason for this is that MCR when implemented correctly can speed up complex analyses and provide additional information that might otherwise have gone unnoticed. This talk will give an overview of MCR methodology and an introduction to the many kinds of data that can be effectively analyzed using such methodology. We will give a brief review of MCR and sample applications in Raman, FTIR, NMR, MS, and DAD-HPLC. The methodology will be discussed in terms of quality of analysis and the ability of MCR to provide improved information relative to more traditional methods of analysis.

(394) **Nonlinear Classification in Spectroscopic Imaging by Means of Kernel Principal Component Analysis Applied to Analyses of Bacterial Contaminations**

Frank Vogt[1], Robert Luttrell[1], Eduard Duranty[1]; [1]University of Tennessee, Dept of Chemistry

Spectroscopic imaging acquires a large number of spectra from different sample locations and thus provides insights into heterogeneous distribution of analytes. Typically, spectroscopic techniques are supported by chemometrics for quantification of target analytes as well as for qualitative discrimination of materials or sample conditions (e.g. growing conditions or healthy/diseased). A prominent approach to visualize the distribution of spectroscopic information is Multivariate Image Analysis (MIA) which performs a PCA and then encodes three user selected score images in red, green and blue. Different spectral signatures show up in different colors. Spectroscopic imaging is especially well suited for applications in bioanalytical chemistry when samples often are heterogeneous. One application discussed here is the classification of E. coli contaminations and the assessment of its spatial extend. However, when classifying biological materials three main challenges are encountered: (1) Often there are more compounds found in the samples than possibly can be incorporated into a calibration. (2) Measurement conditions are ill-defined and thus the spectral data have a low reproducibility. (3) Most biological samples consist of the same groups of compounds (lipids, amides, carbohydrates, RNA/DNA etc.) and thus have very similar spectroscopic properties. The first two challenges have a detrimental impact on conventional, linear chemometric methods; the third requires novel approaches to discriminate samples of very similar chemical compositions. This presentation reports on the use of Kernel Principal Component Analysis (KPCA) for material classification that is superior to MIA. KPCA is a non-linear expansion of PCA and is better adapted to extract nonlinear relations in the spectroscopic data. Due to this non-linearity, KPCA can derive parsimonious models with enough degrees of freedom to adequately describe or classify the different components. One drawback has to be handled in a data preprocessing step: At one point in the algorithm, KPCA has to decompose the 'large covariance matrix', which has dimensions number of spectra by number of spectra. In spectroscopic imaging, this covariance matrix can contain gigabytes of data. To make computations feasible in reasonable amounts of time, a wavelet compression has been incorporated.

(395) **Application of Excitation Emission Matrix Fluorescence to Monitor Flavonoid Aggregation**

Renee JiJi[1], John Simpson[2], Dan Zerjav[1]; [1]University of Missouri

Recently, a family of naturally occurring polyphenols, known as flavonoids, have become a subject of great interest due to their many apparent health benefits including their anti-oxidant properties and anti-amyloidogenic properties. Of particular interest to the Alzheimer's community is the ability of selected flavonoids to reduce the toxicity of the beta-amyloid peptide *in vitro*. Although flavonoids have great therapeutic potential, their behavior in aqueous environments can be unpredictable, primarily due to the potential formation of concentration dependent aggregates as well as pH dependent hydrolysis products. Before flavonoids based therapies can be introduced, a better understanding of their complex behavior of flavonoids is needed. The flavonoid quercetin is a potent anti-amyloidogenic compound. Therefore, we have characterized a series of aqueous quercetin solutions which varied in both pH and concentration, using excitation-emission matrix (EEM) fluorescence. The data was analyzed using parallel factor analysis (PARAFAC), with preliminary results indicating distinct concentration dependent fluorophores, suggesting aggregates are present at low micro-molar concentrations.

(396) **Multivariate Prediction of Fuel Quality Parameters: Developing a Robust Capability for the US Navy**

Kevin Johnson[1], Jeffrey Cramer[1], Mark Hammond[1], Robert Morris[1], Susan Rose-Pehrsson[1]; [1]US Naval Research Lab

Acceptance and adoption of chemometric methods in fuel quality parameter prediction from compositional analysis (e.g. NIR spectroscopy) has been slow, despite a relatively large number of literature reports indicating the feasibility of such an approach. Part of the reason for this reluctance is due to the relative complexity of PLS and other regression techniques, which leads to difficulty in providing accurate prediction intervals similar to those obtained with legacy ASTM methods currently in use for fuel quality parameter prediction. Additionally, owing to the chemical complexity of the samples themselves and to the nature of the refining process, it is often difficult to obtain representative calibration sample sets. This can lead to a lack of robustness in model predictions for subsequent "high leverage" unknown fuel samples. The presented work depicts application of outlier detection strategies as well as strategies for calculation of useful prediction error estimates for assessment of several common fuel quality parameters in actual Navy fuel samples. In particular, the capability of the mean-squared error of calibration to accurately estimate component sources of variance in a regression model as a function of calibration set construction is modeled and discussed. Methods to provide accurate prediction intervals with the less-ideal calibration sets often encountered in this application are developed and these methods are incorporated into a prototype real-time near-infrared fuel analyzer and initial results are presented.

(397) **Chemometric Resolution of Fully Overlapped Capillary Electrophoresis Bands: Quantitation of Carbamazepine in Human Serum in the Presence of Several Interferences**

Héctor Goicoechea[1], Luciana Vera Candioti[1], Maria Julia Culzoni[1], Alejandro Olivieri[2]; [1]LADAQ, Universidad Nacional del Litoral; [2]IQUIR, Universidad Nacional de Rosario

Drug monitoring in serum samples was performed using second-order data generated by capillary electrophoresis-diode array detection, processed with a suitable chemometric strategy. Carbamazepine could be accurately quantitated in the presence of its main metabolite (carbamazepine epoxide), other therapeutic drugs (lamotrigine, phenobarbital, phenytoin, phenylephrine, ibuprofen, acetaminophen, theophylline, caffeine, salicylic acid), and additional serum endogenous components. The analytical strategy consisted of the following steps: a) serum sample clean-up to remove matrix interferences, b) data pre-processing, in order to reduce the background and to correct for electrophoretic time shifts, and c) resolution of fully overlapped capillary electrophoretic peaks (corresponding to carbamazepine, its metabolite, lamotrigine and unexpected serum components) by the well-known algorithm multivariate curve resolution - alternating least squares, which extracts quantitative information that can be uniquely ascribed to the analyte of interest. Mean recoveries were 102.6 % (s = 7.7) for binary samples, and 94.8 % (s = 13.5) for spiked serum samples, while CV(%) = 4.0 was computed for five replicates, indicative of the acceptable accuracy and precision of the proposed method.

(398) **Multivariate Analysis of Chemical Data using Genetic Algorithms**

Barry Lavine[1], Nikhil Mirjankar[1], Kadambari Nuguru[1], Mehul Vora[1]; [1]Department of Chemistry, Oklahoma State University

A genetic algorithm for pattern recognition analysis of multivariate chemical data has been developed. The pattern recognition GA selects features that optimize the separation of the classes in a plot of the two or three largest principal components of the data. Because the largest principal components capture the bulk of the variance in the data, the features identified by the pattern recognition GA primarily convey information about differences between the classes in a data set. This approach to feature selection and classification has several advantages. First, it avoids overly complicated solutions that do not perform as well on prediction sets because of overfitting. Second a chemist is allowed to perform pattern recognition on data at a higher level, e.g., detection of outliers, identification of major clustering trends and incorrectly assigned samples in the training set, recognition of unusual data structures including the asymmetric case, and correlation of class membership information with external property variables. Third, chance or spurious classification, which is always of concern when using any variable selection technique, is not a problem because of the stringent criteria imposed on feature selection by the pattern recognition GA. A current project involving the use of the pattern recognition GA will be discussed. Oligonucleotide microarray data consisting of 44,928 gene expressions from 100 individuals with each individual assigned to one of two classes: reoccurrence or no reoccurrence of prostrate cancer 60 months after surgery was analyzed using the pattern recognition GA. Genes that could correctly classify every sample as to the reoccurrence of prostrate cancer were identified and discriminants developed from them have been validated.

(399) **PARAFAC-SIMCA of Five-Way Fluorescence Data for the Classification of Estuarine Water**

Gregory Hall[1], Jonathan Kenny[2]; [1]U.S. Coast Guard Academy; [2]Tufts University

Fluorescence measurement of environmental samples is a unique opportunity to generate truly multi-way data ideal for analysis by methods such as Parallel Factor Analysis (PARAFAC). Time Resolved Excitation Emission Matrices (TREEM) ordered by location is five-way data. TREEM of surface water from three different ports in the United States, (Baltimore, Boston, and Sturgeon Bay) were analyzed by PARAFAC to determine the significant contributing fluorescent factors from Dissolved Organic Matter (DOM). The scores of these factors were used to classify new samples from each port utilizing a Soft Independent Model of Class Analogy (SIMCA) model showing outstanding specificity. These results will be compared to PARAFC-SIMCA of subsets of the TREEM, specifically Excitation Emission Matrices (EEM) and Wavelength Time Matrices (WTM). This application shows the

potential of multi-way data to elucidate time and location trends of oceanographic and environmental data.

(400) **Frontiers of 2D Correlation Spectroscopy**

Isao Noda; [1]The Procter & Gamble Company

Two-dimensional (2D) correlation spectroscopy has become a popular and versatile tool in the last two decades for the analysis of various spectral data. Spectral variations induced by a dynamic or static perturbation applied to a sample are systematically examined by a simple cross correlation method. The result is displayed in the form of a graphical 2D map defined by two independent spectral axes. Because of the fundamental simplicity of the technique, 2D correlation can be applied to a great number of analytical problems using different spectroscopic probes, experimental conditions, and sample systems. Some of the noteworthy recent trends in 2D correlation spectroscopy include the combined use of classical multivariate techniques with correlation technique, experimental design specifically designed for 2D spectroscopy, advanced manipulation and refinement of 2D spectra to extract more information, and extension of the technique to the field outside of conventional optical spectroscopy. Specific examples based on biomolecules and polymers are used to demonstrate the advantages of these new developments in 2D correlation spectroscopy.

(401) **The use of Two-Dimensional Correlation Spectroscopy to Study Centrosomal Proteins and Protein Interactions**

Belinda Pastrana[1,2]; [1]University of Puerto Rico; [2]Center for Protein Research

Post-translational modification and calcium binding are key pre-requisites for centrosome duplication and separation. These processes are regulated in healthy tissues and are defective in disease states such as cancer. Abnormalities, such as amplified and multipleb centrosomes, are often observed in human breast, colorectal, and other cancers. Centrin is an EF-hand protein that plays both structural and regulatory roles in the centrosome. Three isoforms have been identified in humans two of which are presented in this work: human centrin 1 (Hcen1) and human centrin 2 (Hcen2). The spectral region of 1700 – 1530 cm^{-1} was studied to determine the order of events during the thermal perturbation. For Hcen1 the order of events throughout the thermal perturbation is detailed as the following: alpha-helix followed by beta-sheets then glutamate and finally beta-turns while for Hcen2 the order of events for the entire temperature range is then following: 3_{10}-helix followed by aggregation then β-turns, arginine and finally loops. A higher thermal stability was observed for Hcen1 than for Hcen2 and a pre-transition at 1.7 – 4.8 ˚C and the onset of the transition temperature was also observed for Hcen1 at 80.5 – 84 ˚C. Unlike Hcen1, Hcen2 was observed to aggregate at the temperature range of 43 – 58 ˚C. Therefore, we were able to establish differences in stability, conformation and dynamics between these closely related calcium binding proteins. Furthermore, this calcium-binding protein interacts at low calcium levels with a novel 1242-amino acid protein known as Sfi1, which contains up to 23 centrin-binding sites. Coupled biophysical, structural, and dynamic analyses of the centrin/Sfi1 complex are essential to the understanding of its biological function. Using an interdisciplinary approach we have determined the conformational changes involved in the centrin-$Sfi1p_{21}$ complex formation by FT-IR spectroscopy, two dimensional correlation spectroscopy and isothermal titration calorimetry. The binding was exothermic and the thermodynamic data for Hcen1-$Sfi1p_{21}$ was the following: N 1.33 ± 0.0165, Ka 1.59 $x10^7$ ± 2.48 $x10^6$ M, ΔH -1.72 $x10^4$ ± 301.1 kcal/mol and ΔS -23.8 kcal/mol. We have also established the relative stability of these proteins by differential scanning calorimetry. Our experiments address key questions underlying the molecular basis of this complex interaction.

(402) **Applications of 2D-COS in VCD Spectroscopy: Protein Fibrillation Dynamics In Insulin**

Laurence A Nafie[1,2], Shengli Ma[1], Rina K Dukor[2], Teresa B Freedman[1]; [1]Syracuse University; [2]BioTools, Inc.

Vibrational circular dichroism (VCD) is the difference in the infrared (IR) absorbance of a chiral sample for left versus right circularly polarized radiation. We have applied two-dimensional correlation spectroscopy (2D-COS) to IR and VCD spectroscopy in a number of areas, including the pH dependence of L-alanine, the simplest chiral amino acid. The results of these latter studies were presented at the 2D-COS meeting in Wisconsin in August 2005, and published among the papers from the conference proceedings.1 Recently, we have extended these studies by recording the time dependence of IR and VCD spectra of lysozyme and insulin under conditions of low pH and heating that induce the formation of fibrils.2 We found that the VCD intensity of certain bands grows dramatically with fibrillation while the IR spectra only shift in intensity distribution as a function of frequency, thus demonstrating a unusual sensitivity of VCD to protein fibrillation. We have constructed 2-COS VCD and IR plots of insulin fibril formation that enhances the information obtained directly from the 1D corresponding spectra. In this presentation, we will describe these 2D-COS protein fibrillation spectra and discuss the interpretation of the results. 1"Two Dimensional Vibrational Circular Dichroism Correlation Spectroscopy: pH Induced Spectral Changes in L-Alanine", by Shengli Ma, T.B. Freedman, X. Cao and L.A. Nafie, Journal of Molecular Structure ,799, 226-238, (2006). 2 Vibrational Circular Dichroism Shows Unusual Sensitivity to Protein Fibril Formation and Development in Solution" by Shengli Ma, Xiaolin Cao, Mimi Mak, Adeola Sadik, Christoph Walkner, Teresa B. Freedman, Igor Lednev, Rina K. Dukor and Laurence A. Nafie, J. Am. Chem. Soc. 129, 12364-12365 (2007).

(403) **Perturbation-Correlation Moving-Window 2D Correlation Spectroscopy and Its Applications to a Series of Vibrational Spectra**

Yukihiro Ozaki[1], Shigeaki Morita[2], Isao Noda[3]; [1]Kwansei Gakuin Univerisity; [2]Nagoya University; [3]Procter & Gamble Co.

We have developed a novel method in 2D correlation spectroscopy named perturbation-correlation moving-window 2D (PCMW2D) correlation spectroscopy. [1] This method provides synchronous and asynchronous 2D correlation spectra spread on a plane between spectral variable axis and perturbation variable axis from a series of spectra collected under a certain perturbation change, e.g., temperature-dependent spectra, time-resolved spectra, etc. Thus, information of complicated spectral variation along the perturbation direction can be visualized in the 2D spectra. For example, in the case of temperature-dependent infrared spectra, synchronous and asynchronous PCMW2D correlation spectra are plotted in the plane between wavenumber and temperature axes. Not only intensity changes but also band position shifts are visualized in the PCMW2D correlation spectra. [3] Several works concerned with the PCMW2D correlation spectroscopy will be introduced. Temperature-dependent infrared spectra of polymer solids (poly(vinyl alcohol) [1-2], cellulose [4-6], etc.), thermogravimetric-infrared spectra of bio-degradable polymers (poly(3-hydroxybutyrate) [7], etc.) and time-resolved infrared spectra of water sorption process into biocompatible polymers (poly(2-methoxyethyl acrylate) [8], etc.) were analyzed by the PCMW2D correlation spectroscopy. References: [1] Applied Spectroscopy, 60, 398-406, (2006). [2] Journal of Molecular Structure, in press (doi:10.1016/j.molstruc.2007.12.004). [3] Journal of Molecular Structure, 799, 16-22, (2006). [4] Applied Spectroscopy, 60, 611-618, (2006). [5] Biomacromolecules, 7, 3164-3170, (2006). [6] Biomacromolecules, 8, 2969-2975, (2007). [7] Applied

Spectroscopy, 61, 755-764, (2007). [8] Applied Spectroscopy, 61, 867-872, (2007).

(404) **Dynamic FT-IR Spectroscopy using Continuous Scan Dual Channel Acquisition**

Sergey Shilov[1], Michael Joerger[1]; [1]Bruker Optics

A new data acquisition technique was proposed for acquiring dynamic FT-IR spectra from systems subjected to periodical perturbation. Dual channel analog-to-digital (AD) converter is used for this purpose. First channel of AD converter records signal from the detector of FT-IR spectrometer while instrument is in continuous scan mode. Second AD channel records periodical stress applied to the sample. Two 3D data arrays are generated after the several scans of the spectrometer: 1) Set of double modulated interferograms 2) Set of time-resolved stress. Proposed demodulation algorithm allows to demodulate interferograms and extract the signals that change in-phase and out-of-phase with periodical stress. Application of this technique to studies of polymers under the periodical mechanical stress will be discussed in detail.

(405) **The Physics of Femto- and Nanosecond Laser-Generated Aerosols in ICP-MS**

Roland Hergenröder; [1]Institute for Analytical Sciences

The detailed explanation of the particle distribution function in a laser generated aerosol under ICP-ablation conditions is necessary for different reasons: It has been shown that precision, accuracy and the correct use of matrix-matched standards is strongly influenced by the aerosol. Improvements can only be achieved if laser ablation conditions are better controlled and closer adapted to the analytical task and the capabilities of currently used inductively-coupled plasmas. A deeper theoretical and experimental insight into the relevant mechanisms and their relation to the applied lasers seems to be a pre-condition for any improvement in this direction. A model for generation of small particles from laser ablation products under helium or argon atmosphere is proposed and compared with experimental findings. The conditions employed in the model correspond to a typical LA-ICP-MS measurement. It is shown that small particles with a size up to 100 nm can be produced by gas-to-particle conversion with a subsequent coarsening due to particle coalescence. The two mechanisms can be separated in a physical meaningful way and modeled independently. The particle distribution function is calculated for different background gases. The calculations demonstrate that the small particle fraction of the total particle distribution is not significantly influenced by a change of background gases. It is shown how these particles contribute to the total particle distribution. The discussion illuminates under which conditions small particles, which have been found favorable for the analytical performance of an ICP, are predominantly produced. Qualitatively, the mechanism allows understanding the size dependent chemical composition of the particles. The differences in ns- and fs-laser ablation are discussed. The calculations are compared with different ablation experiments and good agreement is found.

(406) **Do Laser-Based Analytical Methods Really Go Nano?**

Christopher Latkoczy[1,2], Ralf Kaegi[2], Detlef Guenther[1]; [1]ETH Zurich, D-CHAB; [2]Eawag, SWW

Over the last years tremendous efforts have been carried out to push the spatial resolution capabilities of laser ablation inductively coupled plasma mass spectrometry or laser-induced breakdown-based analytical methods towards the nanometer range. Advances not just at the detection part with enhanced spectrometers available but also at the sampling process itself using lasers with shorter pulse durations made it possible to reach such limits. Nevertheless, the understanding of fundamental processes at such size scales gained much more importance to further control and to explain the various phenomena involved in the different ablation and excitation processes. New approaches to simultaneous monitor a mass spectrum and an emission spectrum can both provide detailed information on laser-induced plasma and, therefore, might shed light on some of the fundamental processes involved. We will discuss such ongoing studies, talk about current expectations and limitations and present selected instrumental approaches to e.g. determine nanometer sized colloid particles in aqueous systems or aerosol particles in ambient air.

(407) **Current and Future Directions of Laser Ablation ICP-MS at the US Geological Survey: Application Based Investigations and Reference Materials Development**

Alan Koenig[1]; [1]United States Geological Survey

While significant work has already been established for the utility of Laser Ablation ICP-MS (LA-ICP-MS) in geological sciences and a variety of other fields, the technique has struggled with widespread acceptance as a quantitative tool. The US Geological Survey LA-ICP-MS Facility has been involved in quantitative applications of LA-ICP-MS for mineral and geological systems for over 15 years. The development of quantitative trace element methods for a variety of mineral, geological and environmental samples has required detailed methods development and validation as well as production of new calibration reference materials. We present an overview of current applications, new reference materials, new developments in quantitative trace element mapping and future directions. Detailed validation of LA-ICP-MS methods for trace element mapping is presented in this paper. While qualitative ICP-MS response maps have been presented for a variety of materials using laser ablation, improper or incomplete correction of raw response signal maps for variations in ablation yield is a potential source of error and possible incorrect interpretation on the spatial distribution of trace elements. Differences in ablation yields across different density and composition biological materials that result in incorrect raw intensity distribution maps relative to corrected concentration maps are presented. Mainstream acceptance of LA-ICP-MS into routine labs has been hampered by both the lack of reference materials and quantitative validation for a range of materials. While the advancement of shorter wavelength (sub 200 nm) and shorter pulse duration (femtosecond) lasers has demonstrated a decreased dependence on matrix matched reference materials, such reference materials are still critical for most applications. The USGS Reference Materials Program has expanded the number of materials suitable for calibration of LA-ICP-MS analyses. New calibration materials for bone, teeth, shell, wood and mineral materials have been produced and are in production. Additionally, the new USGS GS-Series of synthetic basaltic glasses have greatly expanded the number of well characterized glasses that are suitable for geological materials analyses. An overview of remaining challenges and new results for quantification with a variety of laser technologies will be presented.

(408) **Femtosecond and Nanosecond Laser Ablation–Time-of–Flight Based Inductively Coupled Plasma Mass Spectrometry.**

Jhanis Gonzalez[1], Dayana Oropeza[1], Xianglei Mao[1], Richard Russo[1]; [1]L. Berkeley National Lab

In this study, three sample introduction approaches (liquid nebulization, nanosecond and femtosecond pulsed laser ablation) into a Time of Flight based-ICP-MS were evaluated on the basis of signals intensities and ratios of selected element/isotopes, differences from the bulk composition, reproducibility (RSD), and stability in time (TRSD).

(409) **The Forensic Analysis of Gel Ink Pens by Laser Ablation Inductively Coupled Plasma Mass Spectrometry (LA-ICP-MS)**

Benjamin Naes[1], Yaribey Rodriguez[1], Tatiana Trejos[1], Jose Almirall[1]; [1]Florida International University

The analysis of questioned documents in forensic science is often overshadowed by more exposed forms of forensic analyses (i.e. DNA evidence, ballistics) in mainstream media. Nevertheless, document related crimes, such as forged checks, stock and tax fraud, altered wills, and counterfeiting represent one of the most prevalent forms of crime committed in society today. Deciphering whether a document is authentic or fraudulent can often become a complicated task requiring years of experience and familiarity with many types of physical and chemical analyses. Many of the chemical based methods used by document examiners (i.e. TLC) rely on pattern recognition in reference to known sources of origin and typically provide qualitative results at best. In addition, the destructiveness of these techniques is considered a drawback and thus must be considered in forensic cases. Therefore, a method to analyze questioned documents that is nondestructive (or virtually nondestructive), is reproducible, provides representative sampling, and lastly provides quantitative information is highly sought after in the forensic community. The research presented will propose an analytical method that upholds each of those characteristics in order to determine the trace elemental content of inks of differing origins. More specifically, a method involving laser ablation inductively coupled plasma mass spectrometry (LA-ICP-MS) for the analysis of gel inks on paper, and a subsection on the analysis of paper itself, will be presented and evaluated. Since gel inks have grown in popularity over the past few years and provided that currently there are no analytical methods capable of differentiating these types of inks, the analytical approach addressed will be novel for the chosen sample of interest and hence strengthen the field of forensic document analyses. Quantitative results by LA-ICP-MS were obtained utilizing self-created matrix-matched gel ink standards; in this research a MicroFab Technologies, Inc. Jetlab®4 inkjet printer (Dallas, TX) was used to create matrix-matched standards consisting of varying concentrations of the elements of interest in this study. The developed standards were then used to check the analytical approach in terms of accuracy and precision. Finally, these standards were used to characterize and differentiate a sample set of gel ink pens (of differing manufacturers and production dates) in terms of their respective trace elemental profiles.

(410) **Mainstream Laser Ablation and Technology Innovations**

Steven Hughes[1], Joseph W. Brady[1], Robert Fry[1]; [1]Spectra-LAse

The benefits of laser ablation ICP and ICP-MS are well known, but the instrumentation has previously been cost prohibitive for the vast majority of laboratories analyzing solid samples. There have been many improvements since the early work in th 1980's. Long standing technical issues, such as optical instability, poor camera image quality, valve fouling (and failure), window condensation, lack of an auto-sampler, lack of interchangeable optics to facilitate a large spot option (for remediation of sample heterogeneity), lack of adequate post processing software, lack of adequate user applications support, and the lack of suitable calibration standards have (collectively) combined (with price barriers) to limit the application of laser ablation to a surprisingly small percentage of those laboratories which actually analyze solid samples. Laser ablation has not yet become a “mainstream” analytical method. High voltage spark, x-ray, and fusion and/or acid digestion for nebulizer based ICP and ICP/MS analysis statistically comprise the mainstay of most laboratories. This presentation will introduce “mainstream” laser ablation and discuss a variety of long-overdue LA innovations, including auto-samplers, multiple optical improvements, a large spot option, bulk analysis, no-foul valving, integrated post processing software, and a customer applications support laboratory (CASL) with secondary calibration standard development services.

(411) **Advances in Sum-Frquency Spectroscopy Technique**

Y. Ron Shen[1]; [1]University of California at Berkeley

Sum-frequency vibrational spectroscopy (SFVS) has been proven to be a most powerful and versatile tool for surface studies. It is the only technique that can be used to obtain surface vibrational spectra of liquids, polymers and buried interfaces. It is unique in its ability to probe surface molecular orientations and monitor *in situ* surface reactions and the associated dynamics. However, improvement of the technique is still needed in order to make it more powerful and useful. We discuss here a few recent advances in this respect. One important advance is in the development of phase-sensitive(PS)-SFVS. The surface response in SFVS is the surface nonlinear susceptibility , which is a complex quantity. Conventional SFVS allows only spectroscopic measurement of , but not its phase. Using spectral interferometric schemes, one can now measure both and , providing complete spectral information on a surface or interface. Such a measurement permits better resolution of the spectral features and, in the case of a continuum of resonances, more correct presentation of the resonant spectrum. In usual arrangement of SFVS, only the IR input is tunable over vibrational resonances. If the visible (or uv) input is also tunable over electronic resonances, then doubly resonant or 2D surface spectroscopy becomes possible. It has the advantages of having not only much higher sensitivity, but also better selectivity in identifying and quantifying coupling between electronic and vibrational transitions. With ultrashort laser pulses, it also permits determination of the associated coupling dynamics. It is often stated that SFVS is only surface-specific and applicable to interfaces between media with inversion symmetry. Generally, however, SFVS is also applicable to surfaces or interfaces of bulks without inversion symmetry. This is because an interface is likely to have structural symmetry different from that of the bulk, and choosing proper beam geometry and input/output polarization combinations allows us to suppress the bulk contribution to SFVS, making surface spectral features discernible. Illustrating examples will be presented in the talk. This work was supported by U.S. Department of Energy and National Science Foundation through WaterCAMPWS.

(412) **Air-Aqueous Interfaces Studied using Vibrational Sum Frequency Spectroscopy**

Heather Allen[1]; [1]The Ohio State University

Vibrational broad bandwidth and scanning sum frequency generation spectroscopy is used to understand the structure of liquid surfaces. The structure and orientation of lipids, water, inclusive of the dangling OH, and salts, are probed. The air-aqueous interface preferentially orients surface adsorbed molecular and ionic species. Details of the sum frequency instrumentation, broad bandwidth and scanning, will be discussed as well as selected air-aqueous interfacial systems.

(413) **Sum Frequency Generation Imaging Microscopy of Self Assembled Monolayer Patterns**

Steven Baldelli[1], Katherine Cimatu[1]; [1]University of Houston

Vibrational spectroscopic imaging is demonstrated for a variety of organic functionalized patterned surfaces. The images from sum frequency generation imaging microscopy (SFGIM) are analyzed using 3 different contrast mechanisms in the interpretation of the transition from bright to dark regions-of-interest (ROI). For this experiment, microcontact printing was used to spatially control the surface monolayers by using a patterned stamp and by varying the

terminal functional group of the backfilling solutions. Analysis, by the three different methods, suggested that there was significant mixing between the stamped and backfilled regions which influenced the contrast in the images at the resonant peaks. In addition, the interference between the resonant peaks and non-resonant background also had an effect on the resulting image appearance.

(414) **Precise Structural Analysis of Interfaces and Materials by Nonlinear Optical Stokes Ellipsometry**

Garth Simpson; [1]Purdue University

The sensitivity of second harmonic generation (SHG) and sum-frequency generation (SFG) to molecular orientation yields exquisite insights into local structure at interfaces. As the scope of NLO investigations expands into microscopy measurements, so too has grown the need for faster and more precise methods of acquiring and analyzing polarization-dependent NLO measurements of complex systems. One new approach will be described, in which complete nonlinear optical ellipsometry can be performed in just a few ms, yielding the complex-valued elements of the nonlinear polarizability tensor to 2-3 significant figures. Nonlinear optical Stokes ellipsometry (NOSE) requires no moving parts and is directly compatible with common microscopy platforms. Fundamentals and applications of fast, precise polarization analysis by NOSE will be described.

(415) **Study of Interfacial Molecule using Novel Non-linear Electronic Spectroscopy**

Pratik Sen[1], Shoichi Yamaguchi[1], Tahei Tahara[1]; [1]Molecular spectroscopy Lab., RIKEN, Japan

Interface plays very important roles in many fields, ranging from industrial chemistry to molecular biology. The static and dynamic properties of molecules at interfaces have been attracting a lot of attention in last decade. In spite of its importance, our knowledge about molecular science at an interface is very limited compared with our understanding about molecules in bulk solution. Recently our group developed a new 2nd order nonlinear spectroscopy called electronic sum frequency generation (ESFG) technique. It allows us to obtain electronic spectra of interfacial molecules discriminatively from bulk. The advanced version of the ESFG technique, with heterodyne detection capability, can be used for the determination of the absolute orientation of a molecule at an interface. Another improvement was done to the ESFG technique by introducing the femtosecond time resolution to the ESFG signal to investigate ultrafast dynamics of molecules at liquid interfaces. We show that these new spectroscopic techniques have many unique applications.

(416) **Label-Free Detection of Drug-Biological Membrane Interaction**

Trang T. Nguyen[1], John C. Conboy[1]; [1]University of Utah

Drug-membrane interactions play a crucial role in the pharmacology and activity of drugs. In addition, the partitioning of drugs into cellular membranes controls bioavailability. The detection of drug interactions with the membrane has been obtained using several techniques such as UV-Vis absorbance spectroscopy, fluorescence, IR, Raman and NMR. These techniques are well characterized and generally possess equivalent sensitivities when examining drug interactions with solution phase vesicles. However, these techniques also associate with several limitations. UV-Vis absorbance spectroscopy and NMR are not suitable to measure the association of drugs to single lipid membrane. In fluorescence techniques, an extrinsic fluorescent tag must be covalently linked to the drug molecule for detection except for the case that some drugs are inherently fluorescent. This modification may perturb the membrane-drug interaction, as the fluorescent labeled drug could have a different lipophilicity, charge and size compared to the native drug. Vibrational methods, IR and Raman, suffer from spectral congestion and the inability to selectively isolate the resonances of the drug molecule from the surrounding lipid matrix. In this study, we report the use of Ultraviolet-Visible Sum Frequency Generation (UV-Vis SFG) as a label-free technique to detect the interactions between drugs and biological membranes. Several important classes of known membrane associated drugs were examined by UV-Vis SFG; these include antibiotics (tetracycline and azithromycine), anesthetics (tetracaine), and non-steroidal anti-inflammatory drugs (ibuprofen). The kinetics and equilibrium binding affinities of the drugs associated into lipid membranes were obtained. The results showed that UV-Vis SFG is a powerful and novel technique to directly measure the adsorption of such small molecules onto a single biological membrane without an intrinsic fluorescent label.

(417) **Metabolomics by Ion Mobility Mass Spectrometry**

Herbert Hill[1]; [1]Washington St. University

Here we report on the use of ion mobility mass spectrometry (IMMS) for monitoring metabolite changes caused by dietary stresses over time in lymph from rats. Ion mobility is a rapid gas phase separation technique and when coupled with a mass spectrometer enables rapid evaluations of metabolomes. Major advantages of IMMS include a rapid separation step with high-resolution prior to the mass spectrometer and that compounds from the same class fall on a trend line in the IMMS contour plots. An important aspect in investigating the metabolome is to exam shifts caused by stresses such as toxins, nutritional, or diseases. For this study, we investigated the change in metabolite profile between dietary stressed rats. Lymph samples from rats were taken before feeding the rats a bolus of Ensure and in hour intervals for six hours after feeding. The metabolites were extracted using methylene chloride, evaporated to dryness and brought back in methanol. Each sample was analyzed by electrospray ionization-AP IMS/TOF MS in both positive and negative ion detection modes. Metabolite ions in the spectra consist of [M+H]+, [M+Na]+, [M+Cl]-, and [M-H]-. Preliminary metabolite identification was conducted based on m/z values of ions detected and/or mobility-mass data of standards that were analyzed by the AP IMS/TOF MS. In negative mode, an average of 276 metabolite ions and 100 isomers were detected in each sample. An average of 428 metabolite ions and 220 isomers were detected in positive ion detection mode. Approximately 90 peaks were found to be common in each sample between positive and negative mode detection. Principal components analysis (PCA) and partial least squares discriminant analysis (PLS-DA) of the ~90 common peaks were used to visualize changes in metabolite profiles as the result of feeding. The maximum deviation was determined from these runs to be ± 0.25 (Da) for m/z, ± 0.02 cm2/(V*s) for K0, and ± 20 (%) for intensity.

(418) **Emerging Directions for the Structural Analysis of complex Biological Samples using Ion Mobility-Mass Spectrometry**

John McLean[1]; [1]Vanderbilt University

Following the paradigm of the human genome project, much of current systems biology research entails characterizing, quantifying, and cataloging the biomolecular inventory of a sample at specific dimensions of space (e.g. cellular, tissue, or organism level) and time (e.g. point in the life cycle, healthy vs. diseased state). One of the grand challenges in systems biology research is the development of new measurement strategies that incorporate simultaneous "omics" data acquisition and that provide both spatial and temporal information. Ion mobility-mass spectrometry (IM-MS) techniques have demonstrated great potential for characterizing complex biological samples, primarily because

different molecular classes (e.g. peptides, carbohydrates, oligonucleotides, lipids, etc.) adopt structures in conformation space (correlation of collision cross section vs. m/z), which is predictable based on prevailing intramolecular folding forces. Although the preponderance of IM-MS studies have focused on protein and peptide ion separations, this report describes recent efforts to define the conformation space in which different classes of biomolecules are found in support of simultaneous metabolomic, proteomic, lipidomic, and glycomic studies. Furthermore, molecular dynamics simulations are used to interpret why specific types of molecules adopt specific structural motifs. For example, structural differences for carbohydrates and glycans are observed in a predictable manner for different isobaric positional and structural isomers. Analogously, isobaric lipids of different class (e.g. sphingolipids and glycerophospholipids) adopt distinct structural differences owing to the degree of coordination with alkali metals in competition with intramolecular hydrogen bonding forces. Based on these studies, we describe how the general position of signals in conformation space can yield information about which biomolecular class a particular signal belongs, and within a biomolecular class, what additional information can be interpreted from experimental results by using molecular models. The limitations of such interpretation are also addressed, in particular for conjugate or hybrid species, for which chemically-selective derivatization may be used to move specific analytes to regions of conformation space not predicted to contain signals. These approaches are demonstrated in new applications for retaining spatial analyte distributions by imaging MALDI-IM-MS as well as characterizing the temporal metabolic response cell populations to chemical stimulants by combining microfluidic platforms with nESI-IM-MS.

(419) **Snapshots of Gas-Phase Separated Complex Polymers for Rapidly Distinguishing Changes in Molecular Makeup**

Sarah Trimpin[1], David Clemmer[2]; [1]Wayne State University; [2]Indiana University

The synthesis of increasingly complex polymers has created daunting, sometimes insurmountable problems for their chemical analysis. The importance is magnified by use in, for example, medical applications and consumer products. Ion mobility spectrometry time-of-flight mass spectrometry (IMS-MS) is sensitive to minor changes in chemical composition and is especially powerful in providing images of separated complex polymer compositions. Blends, differing by as little as the structural differences of isomers, end-groups, or repeat-units, and copolymers, can be separated in the gas-phase producing unique images corresponding to shape, molecular size, and abundance visualizing minute changes. Bulk energy-manipulation further increases the richness of the dataset by altering shapes or inducing fragmentation of all ions thereby increasing separation or fragment yield. This methodology is unique in its flexibility, sensitivity, resolving power, and speed in analyzing these complex materials indicating utility for characterization, quality and regulatory requirements.

(420) **Ion Mobility-Mass Spectrometry Studies of Factors that Influence Structure(s) of Gas-Phase Peptide Ions: The Effects of Multiple Charge-Carrying Sites**

David H. Russell; [1]Texas A&M University

Ion mobility-mass spectrometry (IM-MS) has evolved as a versatile and sensitive probe of gas-phase ion structure(s) for a wide range of compounds of importance to areas ranging from materials science to chemical-biology. IM-MS can be combined with MALDI and ESI so experiments can be carried on a wide range of sample molecular weights and mass-to-charge ratios. In this talk we will focus on the effects of intra-molecular interactions, charge location, and charge state (presence of multiple charges) on the structure of the gas-phase ions. Collision cross-sections for singly charged Ac-(AAKAA)nY-NH2 (n = 3-7) and Ac-Y(AEAAKA)nF-NH2 (n = 2-5) peptide ions were measured by using ion mobility-mass spectrometry (IM-MS). The [M + H]+ ions of the AAKAA series are composed primarily of partial helices, whereas the [M + H]+ ions of AEAAKA series are composed primarily of charge-solvated globules. Derivatization of the polar side chains (K and/or E) or the N- or C-terminus has a significant effect on the structures of the ions. We will show that the helix/globule preference is the result of strong intra-molecular interaction, i.e., charge-solvation. The effects of charge-site and the presence of multiple charges on the structure(s) of gas-phase ions will be demonstrated by results of studies on the peptide gramicidin A (a pi-helix conformation) and the effects of multiples charges will be demonstrated by results of studies on the peptide melittin.

(421) **New Technologies for Standoff Detection of Explosives at Tens of Meters**

M. Bonner Denton[1], Roger P. Sperline[1], Wit T. Wisniewski[1], David A. Jones[2], Christopher A. Gresham[2]; [1]University of Arizona; [2]Sandia National Laboratories

For some time ion mobility spectrometry has been used for detecting chemical warfare agents and explosives. However, the current generation of commercial instruments are limited to the detection of particles of explosives, often sampled by “swipe” or walk through “puffer” portals. Several new technologies are being employed for implementing an instrument capable of detecting vapor from explosives at distances approaching twenty meters and more. A new generation of instrumentation employing improved ionization geometries, new gaiting technologies and advanced differential detectors will be described. Compression gaiting provides increased resolution, while the use of custom capacitive transimpedance differential amplifiers provides vastly improved sensitivity and increased immunity to environmental electrical interference. Each of these improvements will be described and how their combination can provide an instrument capable of both improved resolution and greatly enhanced sensitivity. Current capabilities will be presented along with a discussion of even more advanced concepts that promise to provide further improvements in sensitivity.

(422) **Design and Implementation of an Efficient and Automated Acoustically Levitated Drop Reactor for Studying Reaction Kinetics**

Christopher Field[1], Zakiah Pierre[1], Alexander Scheeline[1]; [1]University of Illinois Urbana-Champaign

We present the details necessary for building an efficient acoustic drop levitator with reduced electrical power consumption and greater drop stability compared to previous designs. The system is optimized so that the levitated drop may be used as a chemical reactor. By introducing a temperature, pressure, and relative humidity sensor for feedback control of a linear actuator for adjusting resonator length, we have built a completely automated system capable of continuous levitation for extended periods of time. The result is a system capable of portable operation and interfacing with a variety of detection instrumentations for in stillo (in drop) measurements. Initial results of simple reaction kinetic experiments carried out in a levitated drop are presented.

(423) **Investigation of Photobleaching and Saturation of Single Molecules by Fluorophore Recrossing Events**

Sean Burrows[1], Randall Reif[1], Dimitri Pappas[1]; [1]Texas Tech University

A method for the investigation of photobleaching and saturation of single molecules by fluorophore recrossing events in a laser beam is described. The diffraction limited probe volumes encountered in single molecule detection produce high excitation irradiance, which can decrease available signal. Single molecules of several dyes were detected and the data was used to extract interpeak times above a defined threshold value. The interpeak times revealed the number of fluorophore recrossing events. The number of molecules detected that were within 2 ms of each other were considered a molecular recrosssing for this work. Calcein, fluorescein and R-phycoerythrin were analyzed and the saturation irradiance and photobleaching effects were determined as a function of irradiance. This approach is simple and it serves as a method of optimizing experimental conditions for single molecule detection (SMD).

(424) **FT-IR and Quantum Cascade Laser Based Trace Gas Sensors**

Christina Young[1], Claire Gmachl[2], Boris Mizaikoff[1,3]; [1]Georgia Institute of Technology; [2]MIRTHE, Princeton University; [3]University of Ulm

Mid-infrared absorption spectroscopy based on FT-IR devices or quantum cascade laser (QCL) light sources offers a viable solution to the present demand for molecularly selective and sensitive real-time chemical gas sensors. While FT-IR based sensors provide access to a wide range of molecular fingerprints within the entire mid-infrared regime of the electromagnetic spectrum with response times of several minute, such sensors are usually rather bulky and of limited applicability for portable hand-held devices. Here, QCLs offer an alternative light source emitting in a narrow yet tunable frequency band selected to overlap with molecular absorption features of interest, thereby providing enhanced sensitivity while maintaining the molecular selectivity. In the work presented here, different types of gas sensors will be discussed including (i) FT-IR based hollow waveguide gas sensors to simultaneously detect ppb-level benzene, toluene, and xylenes during laboratory and field deployment, (ii) widely tunable external cavity coupled quantum cascade lasers in combination with hollow waveguide gas sensing modules and multivariate data evalutation for multianalyte detection of ethyl chloride, dichloromethane, and trichloromethane at low ppb detection limits [1], and (iii) the detection of carbon dioxide utilizing QCL based reflectance measurements with the potential of selectively quantifying carbon dioxide concentrations in human blood or tissues in a non-invasive measurement. [1] Young, C., Kim, S.-S., Luzinova, Y., Weida, M., Arnone, D., Takeuchi, E., Day, T., and Mizaikoff, B. "External Cavity Widely Tunable Quantum Cascade Laser Based Hollow Waveguide Gas Sensors for Multianalyte Detection", Sensors

(425) **Streamlining Protein-Drug Research and Formulation with Vibrational Spectroscopy**

Rina Dukor[1], Laurence Nafie[2,1]; [1]BioTools, Inc.; [2]Syracuse University

As the genome is decoded for its protein content in the present era of proteomics, there is a growing need for techniques that can rapidly and effectively translate the isolation of new proteins into accurate structural information. As more proteins are discovered it is becoming clear that only a small fraction are amenable to analysis by the traditional methods of x-ray diffraction or NMR. Many of these proteins are membrane proteins or glycoproteins that do not readily, or may not ever, be crystallized. These advances in protein discovery have led to the development of new biotechnology drugs. The characterization of proteins is required at all stages of development – from R&D to formulation to manufacturing. Although detailed structure is required for developing new drug targets, an average conformation, a fold, or even a conformational change is sufficient for the development of biopharmaceuticals. No other technique is better poised to address this need than vibrational spectroscopy. Vibrational spectroscopy is not new to protein structural studies but it has been plagued by 'common knowledge' that such studies require high protein concentrations; long collection times and possibly use of deuterated water. Although there is truth to some of these claims – the advantages outweigh them. The vibrational spectroscopy of proteins , FT-IR, VCD, Raman and ROA , allows comparison in all types of formulations – liquids, gels, sprays and solids allowing analysis of API's in solution, injectable, or formulated tablets. It is fast, inexpensive and provides detailed information on the type of fold or family, secondary structure and tertiary structure. There is no limit on the size or type of protein – antibody, hormones, factors, glycoproteins and membrane proteins – all can be analyzed by vibrational spectroscopy. Recently, VCD has been used to measure protein secondary structure in the presence of excipients such mannose and glycine, where the excipients have no VCD interference in the amide I region. Furtermore, VCD exhibits an increased sensitivity to fibril formation and can be used to follow the long-term growth and maturation of protein fibrils. In this presentation, we will discuss advances in vibrational spectroscopy as applied to structural studies of proteins.

(426) **Prediction of Complex Bioprocess Operation Variables by On-Line Acquisition of Different Spectroscopic and Spectrometric Methods**

Karl Bayer; [1]Univ. Natural Res.& Applied Life Sciences Vienna

Due to the large impact of recombinant proteins to different areas of human life the improvement of product yield and quality are the key areas of bioprocess research and development. Although bioprocessing emerged from chemical processing the performance of prediction and control regimes of bioprocesses is still far from standards established in chemical industries. In order to increase the level of bioprocess operation improved understanding of the biological system in use and advanced tools for monitoring and analysis of cell physiology are required. Hence, the progress of research is largely impaired by the complexity of the cell factories and deficiencies in process monitoring and control due to a lack of targeted on-line sensors. Although, in recent years a broad spectrum of bioanalytical methods, e.g. transcriptomics, proteomics came up for the quantification of highly specific biochemical variables their acquisition is off line, tedious, time and cost consuming. Therefore chemometric methods are used to set up correlations between highly relevant off-line process variables and on-line signals of different analytical devices. Key variables, such as the amount of biomass, plasmid copy number and content of recombinant protein were predicted by application of artificial neural networks using off gas analysis and alkaline consumption rate data sets. Further improvement of bioprocess monitoring is gained by the extension of the spectrum of on-line signals and identification of metabolic significant off-line data reflecting specific features, e.g. stress response. Therefore, additional on-line devices comprising dielectric, NIR and multi-wave fluorescence spectroscopy and proton mass transfer mass spectrometry were coupled to the bioreactor delivering more than 250 different on-line signals triggered by different biochemical compounds. In order to improve the on-line prediction of physiologically relevant data the acquisition of corresponding transcriptome and proteome data was intensified as well. This set up enables the extraction of previously unavailable information in real time leading to the acceleration of

the development process by targeted process design and fulfilling the requirements of PAT as well.

(427) **Hybrid Analytical Approaches: Simultaneous Physical and Chemical Characterization as a Tool for Pharmaceutical Quality by Design**

Neil Lewis[1], Kenneth Haber[1], Frederick Koehler[1], Janie Dubois[1], Linda Kidder[1]; [1]Malvern Instruments

As the sophistication of dosage forms increases to include drug delivery devices, drug cocktails, biopharmaceuticals etc., the number of possible failure modes, and their complexity is likely to increase, and their root cause more difficult to unravel. As a result, the need to identify the critical to quality attributes (CQAs) is becoming increasingly important for ensuring product quality. In order to fully characterize the relevant CQAs, it is now accepted that it is desirable to measure both the physical and chemical properties of the finished drug products and to develop an understanding of how their interaction ultimately impacts product quality and performance. In most cases measuring the chemical and physical properties of materials is accomplished by separate analytical methods but there is an increasing recognition that novel analytical (hybrid) instrumentation that measures both these properties simultaneously is extremely valuable. In principle, these approaches enable characterization of structure/function relationships, and provide insight into how these relate to product performance. As a result, the value of these hybrid approaches is beginning to gather momentum in the pharmaceutical and other industries particularly as the complexity of finished products continues to increase, and the mechanisms that drive performance become less well understood. We will present data derived from new hybrid analytical technologies that combine and correlate molecular spectroscopic data with morphological information to derive improved measurement efficiency and new insight into complex manufactured products. In addition, extensions to standard multivariate data analysis methods that attempt to correlate chemical, physical and morphological heterogeneity to determine their impact on product performance will be discussed.

(428) **Implementation of Multiplexed FT-NIR Technology as a PAT Tool to Improve Antibody Manufacture by Mammalian Cell Culture**

Linda M. Harvey[1], Payal Roy Choudhury[1], Ronan D. O'Kennedy[2], Brian McNeil[1]; [1]Strathclyde Fermentation Centre, Glasgow, UK; [2]GSK Biopharm CEDD, Beckenham, UK

The bioprocessing industry has gone through a period of rapid change in recent years, with changes in product spectrum, strains, production scale and , of increasing importance, regulations governing production and quality of the products generated. The latter being of particular relevance in antibody manufacture where glycosylation and folding of the resultant proteins are specific issues and product qulaity and reproducibility are key to the success of the industry. This paper will discuss the application of Process Analytical Technology (PAT), in this case a multiplexed FT-NIR system with 6 optical channels, to improve antibody manufacture from a mammalian cell culture (CHO). The aim is to develop a process understanding throughout the product life cycle by using PAT tools to identify critical to qualtiy (CtQ) factors. The PAT tool was implemented during Early Development of the process i.e. at a unit operation identified as being one which contributed the greatest variability and consequently greatest process risk. The paper will discuss the selection route followed to identify an appropriate PAT tool, the application of the technique to the process, problems encountered in developing models which are fit for purpose and how the problems were dealt with or solved. The CHO cell Case Study will show how this technology generated real time mulitanalyte information from multiple bioreactors.

(429) **PAT in Biologics Manufacturing**

Jose Menezes; [1]Technical University of Lisbon

The potential of Process Analytical Technology (PAT) in biomanufacturing is far from properly exploited mainly due to: insufficient use of intrinsically multiparametric monitoring tools (e.g., NIR), disregard or ineffective use of available information (e.g., data on historical batches and raw-material lots), lack of a process/plant wide perspective for the proposed PAT strategy. Here we describe how information obtained with several at-line and on-line PAT monitoring tools on different process steps of bioprocesses can be used in a consolidated way and in a process perspective to better understand and control (both feed-forward and feed-back) the industrial production of complex biomolecules.

(430) **New Sensing Concepts for Process Analytical Technology**

Radislav Potyrailo[1]; [1]GE Global Research

This lecture will critically analyze the remaining unmet needs for in-line monitoring instrumentation in pharmaceutical and other industries and will present several examples from our laboratories on the development of innovative sensors with previously unavailable capabilities.

(431) **Raman Spectroscopy of Extremophiles: The Exomars Mission**

Howell GM Edwards[1], Ian J Scowen[1], Michael D Hargreaves[1], Ian Hutchinson[2], Richard Ingley[2]; [1]University of Bradford; [2]Brunel University

The survival strategies of extremophilic organisms in terrestrially stressed locations and habitats are critically dependent upon the production of protective chemicals in response to desiccation, low wavelength radiation insolation, temperature and the availability of nutrients [1]. The adaptation of life to these harsh prevailing conditions involves the control of substratal geology; the interaction between rock and the organisms critical and the biological modification of the geological matrix plays a very significant role in the overall survival strategy [2,3]. The identification of these biological and biogeological chemical molecular species in the geological record is necessary for the recognition of the presence of extinct or extant life in terrestrial and extraterrestrial scenarios. Raman spectroscopic techniques have been identified as valuable instrumentation for the detection of life extraterrestrially because of the use of non-destructive laser-based excitation of organic and inorganic molecules with a high discriminatory power. The interactions effected between biological organisms and their environments are detectable through the molecular entities produced at the interfaces, for which the vibrational “fingerprints” are unique. A very important attribute of Raman spectroscopy is lack of sample preparation required in order to interrogate the specimen; this has been a major factor in the proposal for the adoption of Raman instrumentation on robotic landers and rovers for plantary exploration, particularly the forthcoming ESA ExoMars mission [4]. In this paper, the merits of using Raman spectroscopy for the recognition of key molecular biosignatures from several terrestrial extremophile specimens will be illustrated. The data and specimens used in this presentation have been acquired from the Arctic and Antarctic cold deserts, a meteorite crator and from a hot desert saltpan evaporate locations. Data from a flight CCD Raman system will also be demonstrated , from which it will be possible to assess the advantages of Raman spectroscopic techniques for the detection of biosignatures in real geological and simulated specimens. References [1]Cockell CS, Knowland JR., Biol. Revs., 74, 311 – 345, 1999. [2]Wynn-Williams DD , Edwards HGM , Planetary Space Sci., 48, 1065-1075, 2000 [3]Wynn-Williams DD, Edwards HGM , Icarus, 144,

486-503, 2000 [4]Jorge-Villar SE, Edwards HGM, Anal & Bioanal. Chem., 217, 100-113, 2006

(432) **A Combined Raman-LIBS Spectrometer for the Exomars Mission**

Fernando Rull[1]; [1]Unidad Asociada UVA-CSIC al CAB

ExoMars (planned launch 2013) is the first flagship mission of the Aurora programme of the European Space Agency (ESA). The main mission's scientific objectives are: To search for signs of past and present life on Mars; To characterise the water/geochemical environment as a function of depth in the shallow subsurface; To study the surface environment and identify hazards to future human missions; To investigate the planet's subsurface and deep interior to better understand its evolution and habitability. These objectives will be achieved using a suite of scientific instruments placed in a Rover able to move over some kilometres (Pasteur payload) and in a Lander (Humbodlt payload). Among the instruments placed in the Rover, the combined Raman-LIBS spectrometer is considered essential for the mission's scientific objectives. This instrument will perform *in-situ* mineralogical and geochemical analysis. Also it will support the search for possible signs of past and present life through identification of possible biosignatures and biomediated minerals. The Raman-LIBS will operate at the Martian surface linked to a robotic arm using both Raman and LIBS techniques and inside the Rover analysing only with Raman the cores obtained by a drill attached to the Rover and capable to obtain samples up to 2 meters of depth. In this work the potential of the combined Raman and LIBS techniques in particular when used at the same spot are discussed together with a general description of the instrument. Also preliminary results obtained with a prototype developed by TNO (Netherlands) under an ESA contract will be presented and discussed.

(433) **Sulfates on Mars: Study of Two Structural Polymorphs of MgSO4•H2O by Raman, IR, XRD, and Humidity Buffer Experiments**

Alian Wang[1], John Freeman[1]; [1]Washington University

Recent mission results from Mars, both orbital and landed, have reinforced the importance of sulfates at the surface of Mars as indicators of past geologic environments and as potential hosts for water. Their potential as a near-surface reservoir for water makes this group of minerals extremely important for understanding Mars' hydrological history. In particular, it is important to understand the exact mineralogy (type of cations and crystallinity), degree of hydration, concentrations, form of deposits, and how to accurately determine these minerals and deposits on the surface of Mars. Monohydrate Mg-sulfate (MgSO4• H2O) was identified on Mars based on NIR reflectance spectra obtained by OMEGA instrument on the Mars Express and CRISM instrument on the MRO. In laboratory, we found there exist two structural polymorphs of MgSO4•H2O (as HH-monohydrate and LH-monohydrate). They have distinct XRD, Raman, and IR spectra, and have different formation pathways and stability fields. We found that HH-monohydrate (i.e. natural-kieserite-like phase) only forms at mid to high relative humidity: either directly crystallized from aqueous solution at high temperature (hydrothermal process); or slowly converted from LH-monohydrate at mid-high relative humidities. The HH-monohydrate was never observed as the final dehydration product of Mg-sulfates of higher hydration degrees (epsomite, hexahydrite, or starkeyite). On the other hand, LH-monohydrate is observed as the end phase of dehydration process of Mg-sulfates with higher degrees of hydration, i.e. epsomite, hexahydrite, and amorphous Mg-sulfate, and especially at relatively lower temperatures. Both polymorphs are stable at low relative humidity. This study provides important clues to gain understanding on the origin of Martian kieserite.

(434) **Applications of Time-Resolved Remote Raman and Laser-Induced Native Fluorescence (LINF) Spectroscopy in Astrobiology**

Shiv Sharma[1]; [1]Hawaii Institute of Geophys., UH

We have developed a combined time-resolved (TR) telescopic Raman and LINF spectrograph with 532 nm pulsed laser excitation and a gated CCD detector. We have used this system for identifying minerals, organic and biological materials to 120 m radial distance. We have measured both time-resolved Raman and LINF spectra at distances in the range 10-120 m of a variety of materials, including (i) water andCO2-ices, gas hydrates, hydrous sulphates, carbonates, biogenic carbonates, and silicate minerals; (ii) organic materials such a naphthalene, anthracene, amino acids, and (iii) biological materials containing phytopigments, e.g., chlorophylls, and carotenes. A comparison of Raman spectra of calcite crystal and that of chicken eggshell show that the CaCO33 in the chicken eggshell is arranged in a calcite structure. The strong LINF band in the spectrum of the calcite crystal has lifetime longer than 1 micro-s, whereas the lifetime of LINF bands of the eggshell are in 10's of nano-sec (ns). The time-resolved Raman spectra of tomato and poinsettia (Euphorbia pulcherrimum) green leaves show resonance Raman features of carotenes. The time-resolved remote LINF spectrum of ruby crystals, and LINF spectra of tomato and poinsettia green leaves yield information that the LINF lifetime of ruby lines is much longer (in milliseconds (ms)) as compared with the fluorescence lifetime of the tomato and the poinsettia leaves (in 10s of ns). These results show that it will be possible to discriminate between inorganic, organic and biogenic materials on the basis of LINF lifetimes even with 8 nano-sec laser pulses and gated detection. Potential applications of the combined time-resolved remote Raman and LINF instrument in astrobiology will be discussed.

(435) **Application of Non-Destructive Raman Spectroscopic Identification of Organic Minerals and Selected Biomarkers in Astrobiological Areas**

Jan Jehlicka[1], Howell Edwards[2], Petr Vitek[1]; [1]Charles University in Prague, Geochemistry; [2]University of Bradford, Chem and Forens

Several geological features found on the surface of Mars by planetary rovers suggest that a possible extinct biosphere could exist based on similar sources of energy as occurred on Earth. For this reason, analytical instrumental protocols for the detection of biomarkers in suitable geological matrices unequivocally and non-destructively have to be elaborated for future unmanned missions. Here we present Raman spectral characterization of several examples of organic compounds which have been recorded using 785 nm or 514 nm excitation - higher n-alkanes, polycyclic aromatic hydrocarbons, salts of organic acids, pure crystalline terpenes as well as oxygen and sulphur-containing organic compounds and carotenoids. Experimental mixtures of â-carotene and usnic acid in mineral matrices were investigated as well.

(436) **The Potential of Raman Spectroscopy for the Analysis of Diagenetically Transformed Carotenoids**

Craig Marshall[1], Alison Olcott[2]; [1]The University of Sydney; [2]University of Kansas

Microbial life, if extinct or extant on Mars, would produce biomolecules that might be preserved and detectable in Martian rocks. Both NASA and ESA are considering the importance of miniaturized Raman spectrometers for future robotic exploration missions to Mars as part of the analytical instrumentation suite on planetary landers for life detection. Therefore, it is crucial to construct a database of biosignatures of Earth microbial life, to facilitate the detection of biosignatures on Mars (and possibly beyond). Much work has been focused on carotenoids biosynthesized from extant extremophile microbes as biological

compounds of interest for life detection. However no work has been performed on assessing the potential of Raman spectroscopic detection of residual diagenetically altered carotenoids from extinct microbes. The aim of this work is to ascertain the potential of Raman spectroscopy for the analysis of fossil equivalent or diagenetically altered carotenoids. Several hundred natural carotenoids have been described that are distinguished by the number of conjugated bonds in the polyene chain and different cyclic and linear end-groups. There is a large variety of functionalities in various positions such as keto, aldehyde, ester, hydroxy, methoxy, and glycoside groups. Many of the functionalized carotenoids extracted from living organisms and recent sediments have been used to obtain information about biological origins, evolution, and ecology. During diagenesis the carbon-carbon double bonds are reduced to carbon-carbon single bonds in the main polyene chain. In addition, the functional groups are eliminated. For example, during diagenesis β-carotene and lycopene are transformed too much less specific-fossil hydrocarbons such as β-carotane and lycopane. Raman spectra were collected on β-carotene, lycopene, β-carotane and lycopane standards. The difference between the spectra of the natural carotenoid and the diagenetically transformed carotenoid was the lack of the ν(C=C) in-phase stretching mode. Individual Tasmanite microfossils (250 Ma) were assessed for their potential to preserve carotenoids within the resistant cyst-wall biopolymer. This has potential for geobiological studies to elucidate taxonomic affinities of individual enigmatic microfossils as well as astrobiological applications for diagenetically altered biomolecules.

(437) **Raman and Raman/Sem Spectroscopic Studies of Terrestrial Materials of Relevance to Mars**

Elizabeth Carter[1], Craig Marshall[1], Peter Lay[1], Michael Hargreaves[2], Howell Edwards[2]; [1]The University of Sydney; [2]University of Bradford

The quest to understand early and modern life in extreme environments tackles some of the most profound questions of humankind. Areas of intense controversy within the scientific literature include: the origins of the first forms of life in the solar system, their distribution, and the evolution of the earliest forms of life on Earth. This controversy stems from a lack of consensus on the validity of various analytical techniques for establishing the origins of organic material found in extraplanetary and Earth rocks. A major aim of this international collaborative project is to develop a robust methodology using a range of spectroscopic techniques to establish whether ancient organic materials are abiological or are microbial fossils and their relationships to extant biota at the genus level. The suite of analytical techniques used, or to be used, for analysis include: Raman spectroscopy, integrated Raman/SEM, FTIR microspectroscopy and X-ray microspectroscopy. These techniques will be used to probe potential biomarker compounds of both early Earth history and astrobiological significance. In recent years Raman spectrometers have been integrated with a number of alternate technologies with one example being scanning electron microscopy (SEM). These integrated systems enable multiple analyses of the same sample region, under the same conditions, in a single instrument. The structural and chemical analyser (SCA) is the interface which unites the SEM and Raman spectrometer to allow morphological, elemental, chemical, physical, and electronic analysis. This presentation will briefly discuss the methodology developed to investigate samples using the integrated Raman/SEM system. This will be followed by results collected from terrestrial materials of relevance to Mars, including extremophile/geological substrate interactions. Acknowledgements: This research was supported under the Australian Research Council's Linkage International (LX0776464) and Linkage Infrastructure, Equipment and Facilities (LE0560680) funding schemes. The views expressed herein are those of the authors and are not necessarily those of the Australian Research Council.

(438) **Deep UV Raman Investigations of Biological and Meteroitic Samples**

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Here we report on the great capabilities of deep UV Raman experiments. Most chemicals have strong absorption bands in the deep UV and therefore exhibit resonance Raman enhancement of characteristic Raman bands coupled to the deep UV absorption band. In addition to the resonance enhancement, another major advantage of deep UV Raman spectroscopy is that no fluorescence interference exists when excitation is provided at wavelengths below 250 nm. Furthermore the Raman cross section itself is dependent on the excitation wavelength to the inverse fourth power resulting in higher Raman intensity with shorter wavelength laser excitation leading to a reduction in acquisition time. The experiments presented within this study convincingly demonstrate the great capabilities of deep UV Raman spectroscopy. In doing so a bacterial identification with UV-resonance Raman spectroscopy was performed with a recognition rate of nearly 99 % on strain level. Thereby Raman signals from macromolecules like DNA/RNA or proteins can be selectively enhanced by means of UV resonance Raman spectroscopy. The selective enhancement of the cellular DNA/RNA content allows for a correlation with the GC value and therefore for a genotaxonomic classification of bacteria. Furthermore this contribution reports on a deep UV Raman spectroscopical characterisation of the interaction of antibacterial drugs with bacterial cells. Raman spectroscopy has been recognized in the last few years also as a possible and extremely promising method for *in situ* planetary analysis like e.g. the search for signs of extinct and/or extant life on Mars. The search for extant life needs to look for traces of Sugars, Phospholipids, Amino acids, Nucleotides (ATP / ADP), the search for extinct life on the other hand requires to look for organic residuals of biological origin like fossils or related geochemical and mineralogical bio-signatures. Here we report on deep UV micro Raman experiments to investigate extraterrestrial material (meteroites) without disturbing fluorescence and with very convincing S/N ratios. The overall advantages of UV resonance Raman spectroscopy in terms of sensitivity and selectivity are demonstrated and discussed. Finally the application of this new technique for a UV Raman instrument for envisaged astrobiological focused space missions is suggested.

(439) **Photonic Bandgap Fiber Enabled Raman Detection of Nitrogen Gas**

Peter Codella[1], Rui Chen[1], Renato Guida[1], Anis Zribi[1], Alexey Vert[1], Radislav Potyrailo[1], Marko Baller[2]; [1]GE Global Research, Niskayuna; [2]GE Global Research, Munich

Photonic bandgap fibers provide an excellent means of concentrating light energy in a very small volume. These fibers are designed with a hollow core surrounded by a silica honeycomb structure. The structure of the fiber is carefully designed so as to propagate a relatively narrow band of wavelengths with very little attenuation. One particular commercial fiber with a core diameter of 4.9 microns offers losses of only 0.7 dB/m for wavelengths between 530 and 590 nm. The useful band pass extends from about 510 to 610 nm with an attenuation of about 1dB/m at the limits. If the 514 nm line of an Argon Ion laser is used for excitation, the entire Raman spectrum, up to just above 3,000 cm-1, will be contained within the transmission band of the fiber. Nitrogen, for example exhibits strong Raman scattering but the concentration is so low in the gas phase as to make detection difficult without a multi-pass arrangement. Using the microscope capability provided

with most modern Raman systems, it is fairly easy to couple a photonic bandgap fiber to a Raman instrument. The standard 10X objective provides adequate coupling and thereby enables both the light launch into the fiber and collection of Raman scattering exiting the fiber. The microscope stage provides a mechanism for aligning the fiber and maximizing Raman scattering. On our instrument, alignment is required to about 1 micron. The resulting spectra of nitrogen gas at ambient temperature and pressure exhibits an enhancement of about several thousand over that attainable with the objective in air. The enhancement is great enough to see the rotation-vibration lines surrounding the center band. Similar results were observed for oxygen but the enhancement wasn't measured. The design and fabrication of a flow-though cell to hold and align the fiber end allowed calibration of instrument response from 10's of parts per million to pure nitrogen. The enhancement was also found to be a function of fiber length, internal fiber pressure, and laser power. While the observed enhancement makes measurements in the ppm range, problems with reproducibility have limited usefulness.

(440) ***In vitro* Diagnostics using Encapsulated, SERS-Active Nanoscale Taggants**

Richard Freeman, Michael Natan; [1]Oxonica Materials, Inc.

Oxonica has developed a novel, patented nanoparticulate optical quantitation label based on surface enhanced Raman scattering (SERS).1 The particles are built upon a 60-nm diameter Au core, and include a layer of one of a group of organic molecules (the "reporter"), and a 30-nm thick silica (glass) coating. The spectrum of each SERS tag is the Raman signal from the adsorbed reporter. By using different reporters, a large number of spectrally unique tags can be prepared. The glass coating renders the particles exceptionally robust to changes in pH, temperature, and ionic strength, and yet enables subsequent chemical and/or biochemical functionalization. Moreover, because the particles are excited and detected in the near-IR, they are perfectly suited for use in complex, dirty matrices or materials that would confound results from traditional optical labels (e.g. fluorophores). These particles form the basis of a commercial enterprise. In Oxonica Diagnostics, Nanoplex™ Biotags are being developed for use in clinical diagnostics applications, with an emphasis on point-of-use/point-of-care tests. One assay format is called Nanoplex™ Direct.2 In this rapid test, immuno-functionalized magnetic particles and Nanoplex Biotags are pre-loaded in a tube. A small volume of sample is introduced (typically with zero sample prep), and the mixture is incubated. The magnetic particles are then pulled to a location, and the SERS spectrum is measured without any wash steps. This assay platform is amenable to multiplexing, and has been demonstrated to give good accuracy and precision from serum. Nanoplex™ Direct allows no-wash, sensitive DNA detection as well. All measurements are carried out with a toaster-sized (or smaller) reader. Accordingly, this measurement platform has the potential to span point-of-use and high-throughput applications. Another assay format is called Nanoplex™ Rapid, and is based on lateral flow immunoassays (LFI).3 Here, substitution of the SERS-active particles for those used in current commercial devices allows detection limits to be lowered by 100-fold. 1. (a) Faraday Discussions 2006, 132, 321-328; (b) Nanotech Briefs 2007, 4, 7-8. 2. Nanomedicine 2007, 2, 725-734. 3. Advanced Materials 2007, 19, 3100-3108.

(441) **SERS Platforms: The Next Generation of Ultra-Sensitive and High Throughput Detection Solutions**

Caterina Netti[1], Graeme McNay[1], Karen McCarney[1], Alastair Ricketts[1], Ewen Smith[1], Robert Stokes[2], Karen Faulds[2], Duncan Graham[2]; [1]D3 Technologies Ltd; [2]University of Strathclyde

This talk will illustrate how the combination of customised enhanced surfaces, chemistry and instrumentation is rapidly pushing SERS technology towards its next "evolutionary" phase. Sensitivity and specificity are fundamental requirements for many modern application platforms together with speed, user-friendliness and high-throughput capability. Bespoke SERS-based technology solutions which meet these requirements for specific applications in molecular diagnostics and other OEM applications will be shown. In the last few years the main problems that prevented SERS from being a robust and reliable technique have been solved. One of the main problems has been the poor reproducibility. The causes can be identified in the lack of reproducibility of the enhancing surfaces or hot spots, i.e. substrate or colloidal suspension, and in the lack of control of the surface chemistry required to ensure good analyte to substrate attachment. Methods which effectively overcome these problems will be described. Turning reliable engineering of enhancing surfaces and effective chemistry into a total technology solution to a specific problem requires instrumentation able to collect Raman scattering efficiently from the substrate of choice and translate it into an unambiguous quantitative or qualitative result. Examples of SERS solutions based on specific combinations of colloidal suspensions or engineered substrates, effective chemistry/biology, and appropriate instrumentation will be described. These will include solutions for molecular diagnostics and high throughput applications.

(442) **Signal Enhancement in Near Field Raman Spectroscopy**

Richard Bormett, Matthew Bloomfield, Ken Williams

Abstract not available.

(443) **Surface-Enhanced Raman Substrate Comparison**

Jason Guicheteau[1], Steven Christesen[1], Augustus Fountain, III[1], Darren Emge[1]; [1]USA RDECOM ECBC

Surface-enhanced Raman Spectroscopy (SERS) has been shown to be an effective technique for increasing the detection sensitivity in chemical and biological detection applications. SERS has demonstrated a distinct advantage over normal Raman with enhancements of the normal Raman signal typically greater than 104. However this advantage in sensitivity comes with a caveat, in that controlling the spectroscopic reproducibility and enhancement activity of metal nanostructured substrates can be difficult. We will present a survey and subsequent data analysis performed on six nanostructured substrates designed for SERS which include silver & gold colloids, silver nanorods, gold nanoshells, and commercially manufactured gold nanostructures.

(444) **A Single Nucleotide Polymorphism Screening Method Based on Surface-Enhanced Raman Scattering**

Mustafa Culha[1], Omer Faruk Karatas[1], Omer Aydin[1], Mehmet Kahraman[1], Omer Faruk Bayrak[1]; [1]Yeditepe University

There are millions of single nucleotide polymorphisms (SNPs) in human genome, which are critically important for identification of complex genetic diseases and pharmokinetic research. Among the current screening techniques, only microarray technology offers high-throughput screening capability. However, it is possible to increase the number of SNPs to screen even more on a microarry chip by changing the detection technique from fluorescence to Raman scattering. Surface-enhanced Raman scattering (SERS) is plasmonic technique and its enhancement mechanism is mostly result of the localized surface plasmons on the surface of the nanostructured noble metals such as gold and silver. SERS provides detailed chemical information about the molecular structure in the vicinity of nanostructured noble metal surfaces with very narrow bandwidths (naturally less than 1 nm) compared to fluorescence bandwidths allowing multiplexing feature. Therefore, multiple SERS spectra can be combined without significant overlap of the bands. This allows the reduction of the number of spots on the array chip, and more SNPs can be screened on the same given area of fluorescence-based microarray. In this study, we developed a SERS based SNP screening assay. Raman active dyes and ss-DNA probes specific for known SNPs are chemically attached to gold nanoparticles. The PCR amplified gene regions possessing SNPs are immobilized in the denatured form on poly-L/D-Lysine coated glass surface. The prepared SERS probes are hybridized with the immobilized gene regions having SNPs. Finally; the surface is treated with colloidal silver nanoparticles for additional SERS enhancement. From the acquired SERS spectra, a number of possible SNPs can be identified. Considering enormous number of SNPs present on the human genome, this method can allow to screen more SNPs on a smaller surface in a short time. This will help to cut the cost and time for the screening SNPs.

(444b) **Quantitative SERS of Anionic and Cationic Species using Off-the-Shelf Colloid**

S. E. J. Bell, E. Lozano-Diz, A. C. Dennis

Abstract not available.

(445) **Molecular Plasmonics: Single Molecule SERS, Exploring the Plasmonic Periodic Table, and Plasmon Microscopy**

Richard P. Van Duyne[1]; [1]Northwestern University

During the last few years, there has been an explosion of interest and activity in the field of plasmonics. The goal is to control and manipulate light on the nanometer length scale using the properties of the collective electronic excitations in noble metal films or nanoparticles, known colloquially as surface plasmons. An improved understanding of the interactions between adsorbed molecules and plasmonic nanostructures (i.e., molecular plasmonics) is having a significant impact in many areas of plasmonics research including surface-enhanced Raman spectroscopy (SERS),1 new materials, optical microscopy, localized surface plasmon resonance (LSPR) spectroscopy for chemical and biological sensing,2 and nanolithography. This lecture will cover recent developments from the Van Group in three areas: single molecule surface enhanced Raman spectroscopy (SMSERS);3 the plasmonic properties of copper4 and aluminum;5 and (3) the development of single nanoparticle LSPR spectroscopy spatially correlated with high resolution transmission electron microscopy (HRTEM)3 and atomic force microscopy (AFM).6 These studies have enabled fundamental new insights into the electromagnetic (EM) field enhancement mechanism underlying both SER and LSPR spectroscopy. References [1] "Surface-Enhanced Raman Spectroscopy," P. Stiles, J. Dieringer, N. C. Shah, and R. P. Van Duyne, Ann. Rev. Anal. Chem., 1, 601-626 (2008) [2] "Biosensing with plasmonic nanosensors," J. N. Anker, W. P. Hall, O. Lyandres, J. Zhao, N. C. Shah, and R. P. Van Duyne, Nature Materials, 7, 442-453, (2008) [3] "Controlled Plasmonic Nanostructures for Surface Enhanced Spectroscopy and Sensing," J. P. Camden, J. Dieringer, J. Zhao, N. C. Shah, and R. P. Van Duyne, Acc. Chem. Res., 41, ASAP July 17 (2008) [4] "Plasmonic Properties of Copper Nanoparticles Fabricated by Nanosphere Lithography," G. H. Chan, J. Zhao, E. M. Hicks, G. C. Schatz, and R. P. Van Duyne, Nano Letters, 7, 1947-1952 (2007). [5]"Localized Surface Plasmon Resonance Spectroscopy of Triangular Aluminum Nanoparticles," G. H. Chan, J. Zhao, G. C. Schatz, and R. P. Van Duyne, J. Phys. Chem. C., in press (2008) [6]"Investigating Tip-Nanoparticle Interactions in Spatially Correlated Total Internal Reflection Plasmon Spectroscopy and Atomic Force Microscopy" R. L. Stiles, K. A. Willets, J. M. Roden, L. J. Sherry, and R. P. Van Duyne, J. Phys. Chem. C., 112, 11696-11701 (2008)

(446) **Nonlinear Vibrational Spectroscopy for the Analysis of Biological Membranes**

John Conboy[1]; [1]University of Utah

A central issue in molecular biology is the movement of lipid across the cellular membrane. The translocation of lipids is involved in cell apoptosis, the viral infection of living cells, the functioning of antibiotics, antiseptics and drugs, and the regulation and growth of cells. There have been a number of studies attempting to find the putative proteins responsive for lipid transbilayer movement in eukaryotic cells. This has led to a large number of speculative statements about the mechanism of transbilayer movement of lipids in cellular systems. Several groups have speculated that protein mediated process are the main mechanism by which transbilayer migration of lipid occurs. The possibility also exists that the translocation of glycerophospholipids lipids in membranes is not governed completely by active protein transport, but rather by membrane defects, or heterogeneities which can be induce by cholesterol, other lipids, fatty acids, and proteins which perturbed the otherwise uniform landscape of a pure lipid bilayer. We have developed a novel analytical approached using a sum-frequency vibrational spectroscopy (SFVS) to selectively probe the asymmetry in a planar supported lipid bilayer. This new method allows for the detection of lipid flip-flop without the need for a fluorescent or spin-labeled lipid to observe the translocation of lipid species. Planar supported lipid bilayers are used as models for studying the transbilayer movement of lipids and exploring the effect of lipid composition, headgroup and fatty acid chemical structure, on the rate and thermodynamics of lipid transbilayer migration.

(447) **Chemically Modified Electrodes for Rapid On-Line Separation and ICP-MS Analysis of Cesium**

Scott Lehn[1], Kate L. Ziegelgruber[1], Shane M. Peper[1], Douglas C. Duckworth[1]; [1]Pacific Northwest National Laboratory

The practice of chemically modifying electrodes to produce element or molecule specific electrochemical responses for sensors is an active area for chemical research. In the present studies, one such method for Cs specific surface modifications is used in conjuction with electrochemically-modulated separations and on-line inductively coupled plasma mass spectrometric detection, circumventing challenges in trace detection via the measurement of electrolytic processes. This approach proves to be a simple means to simplify and enhance detection for cesium and leverages a the broad chemistries available from sensors research that could readily

be extended to additional elements. The results of optimizing these physically modified electrodes for analytical benchmarks such as selectivity, signal enhancement, electrode capacity, and temporal response will be presented.

(448) **Signal Enhancement in DRC-ICP-MS by Collisional Focussing**

Julian Tyson[1], Maura Mahar[1], Kenneth Neubauer[2], Dennis Yates[2]; [1]University of Massachusetts, Amherst; [2]PerkinElmer Life and Analytical Sciences

The signal enhancement that occurs for some analytes when the paths of the ions through the dynamic reaction cell is modified by collisions with a bath gas, known by several names including "collisional focusing," "ion focusing," and "collisional damping," is caused by the collapse of the ion trajectories toward the center of the reaction cell. Elements included in this study were Al, As, Ba, Be, Cd, Co, Mn, Na, Pb, Se, Sr and V, which were measured at m/z = 27, 75, 138, 9, 114, 59, 55, 23, 208, 82, 88 and 51, respectively. Gold was measured in synthetic geological samples at m/z = 197. The cell gases were methane and oxygen at flow rates: 0.1, 0.3, 0.5, 0.8 and 1.0 ml min-1. The mass filter is controlled by varying the "q" and "a" parameters, which are proportional to the RF and DC voltages on the poles in the reaction cell, respectively. RPq values were varied over the range of 0.05 to 0.9 in increments of 0.05, and RPa values were varied from 0.0 to 0.20 in increments of 0.005. Signal enhancement was observed for a large number of analytes across the mass range in the presence of both methane and oxygen reaction cell gases. Optimal signal enhancement was observed for moderate gas flow rates (0.45-0.5 ml min-1) and moderate RPq values (0.45 or 0.50). All measured signal intensities decreased as RPa values increased; therefore, RPa was set to 0.0 for all sample analyses. Relatively light elements (i.e. elements with m/z ≤ ~23) were scattered in the presence of methane and oxygen, resulting in a significant decrease in signal intensity. Two elements (As and V) reacted with the cell gas, resulting in a signal increase at a mass to charge ratio different than that of the original analyte. The sensitivity for Au increased by 5-times with oxygen as the cell gas, though this was only reflected in a corresponding decrease in the limit of detection for pure standards; for rock digest matrix the limit of detection improvement was not as much.

(449) **Development of Laser Ablation-Inductively Coupled Plasma-Atomic Emission Spectrometry (LA-ICP-AES) Prototype for Monitoring Vitrification of Hanford Radioactive Waste**

Jinesh Jain[1], Aruna Arakali[1], Thomas Lane[1], Douglas Perkins[1], Cary Seidel[2], Larry Lockrem[2]; [1]Hanford Tank Waste Treatment Plant; [2]222-S Laboratory

The Hanford Tank Waste Treatment and Immobilization Plant (WTP) project has developed an integrated prototype system (Hotcell LA with Glovebox ICP-AES). The development was a joint effort between Bechtel National Inc., Washington Group International - URS Corporation, CHG, and Horiba Jobin Yvon. The configuration incorporates shielding and ALARA principles for handling highly radioactive samples. The radioactive materials confinement sections of the LA-ICP-AES, that is, the plasma torch assembly and LA sample stage, are installed in a glove box and hot cell, respectively. The two sections are connected for sample transfer via interface tubing. All components have been installed in the hot cell facility of the 222-S laboratory for completing method demonstration on high level radioactive-waste (HLW) sludge samples. The prototype was based on method development done at U.S. Department of Energy national laboratories (Pacific Northwest National Laboratory (PNNL) and Savannah River National Laboratory (SRNL)) using the LA technique for introducing ablated particles from a simulant glass coupon into an ICP-AES spectrometer. The LA method successfully demonstrated ruggedness and comparability with the time-consuming wet chemistry ICP-AES method. The development of an alternate LA technique was triggered by the need to support the turn-around-time for batch transfers to the High-Level Waste (HLW) melters. WTP design uses a "batch" process to treat, separate, and vitrify the tank waste material received as "feed" from tank farm transfers. At various steps in the process, samples will be taken and analyzed in an on-site laboratory that is under construction in the WTP complex. The correct and timely execution of the analysis of these samples is critical to monitoring WTP processes and necessary to document the qualification of the glass product for disposal. The testing of the LA prototype is an example of implementation of technological advances in sample analysis. The prototype was tested in the factory using NIST 610 and WTP simulant glass coupons prior to shipment. The results of ablated HLW glass coupons along with factory and site acceptance test runs including installation challenges will be discussed. Acknowledgement This work was supported by the US Department of Energy contract # DE-AC27-01RV14136DDE-AC27-01RV14136E-AC27-01RV14136

(450) **Detection Limits Based on Poisson Statistics in ICP-MS**

Martin Tanner[1], Arturo Gomez-Tuena[1]; [1]UNAM Mexico, Centro de Geociencias, Queretaro

Mass spectrometry per se is a counting technique and Poisson statistics is to be used to describe the mayor part of blank measurement uncertainty. This fact is often neglected in publications describing detection capabilities in ICP-MS. Normal distribution can be applied for sufficiently high numbers of acquired counts but in many cases this requirement is not fulfilled and pure Poisson statistics is to be used. Since Poisson statistics deals with distributions of discrete values, mathematical descriptions for detection limits cannot be expressed in closed formulas. Early publications dealing with Poisson statistics in analytical chemistry therefore gave tables, graphs or 'working expressions' to evaluate critical levels and detection limits for distinct blank signal ranges. Such working expressions may be useful if detection criteria need to be calculated by hand. By using modern computer based calculation power large data sets can be evaluated applying exact Poisson statistics. IUPAC recommends for low blank levels in mass spectrometry to use Poisson statistics to evaluate detection capabilities of measurements but no detailed procedure is given. The literature on that topic stems mainly from the field of radioactivity measurements and neglects specific terminologies and technical aspects of ICP-MS. A new methodology is therefore applied to ICP-MS data and evaluated. The new detection limit evaluation methodology ideally fulfills the following criteria: (a) No more distinction between normal distribution and Poisson statistics. (b) Meaningful detection capability statements for blank levels as low as zero counts. (c) Calculations independent from chosen analysis parameters like dwell time. (d) Poisson based calculations must, for high count numbers, coincide with results from the normal distributions model. The methodology follows the IUPAC recommendations in terminology and detection limits are based on the general approach of statistical hypothesis testing. The new methodology is evaluated and discussed on real ICP-MS data. The presentation includes a realistic discussion about the importance of low instrumentation blank levels and the eventual gain in acquiring shorter transient signals.

(451) **Electrophoretically Mediated Microanalysis of Alcohol Dehydrogenase Kinetics and Inhibition**

Rachel Henken[1], Li Yang[1], S. Douglas Gilman[1]; [1]Louisiana State University

The enzymatic activity and inhibition of yeast alcohol dehydrogenase (ADH) was explored using electrophoretically mediated microanalysis (EMMA). The conversion of the fluorogenic substrate NAD+ to NADH by ADH were observed on-column using capillary electrophoresis with laser-induced fluorescence detection with excitation at 350 nm and emission at 450 nm. The reproducibility of this method was analyzed and the Michaelis-Menten kinetic constant (Km) was determined for both the NAD+ and ethanol substrates. Reversible inhibition of ADH by the competitive inhibitor, borate, and the non-competitive inhibitor, bismuth were observed. Irreversible inhibition was studied using N-ethylmaleimide inhibitor of ADH. The Ki values for these inhibitors were determined from the EMMA electropherograms and confirmed with microplate fluorescence assays. This method was developed using a commercial CE using LIF detection for the study of NAD+ dependent enzymes.

(452) **Correlative Spectromicroscopy and Conventional Microscopy for Exploring Fungal Metabolism**

Merrill Isenor[1], Susan Kaminskyj[2], Merrill Isenor[1], Konstantin Jilkine[1], Catherine Liao[1], Margaret Rak[3], Kathleen Gough[1]; [1]University of Manitoba; [2]University of Saskatchewan; [3]European Synchrotron Radiation Facility

Fungi are morphologically simple organisms whose effects range from substantially beneficial to highly detrimental. While metabolically similar to animals, fungi have more tractable genomic and growth characteristics. This very similarity has made them an emerging threat for human health, especially for immune-compromised patients. Anti-fungal drugs can be toxic and/or expensive; cure rates are low and seldom last more than a few months. Fungal relationships with plants are similarly two-edged. Fungal symbionts support plant growth and can recycle nutrients. Fungal-plant root interactions (mycorrhizae) are associated with 95% of plant species and may play key roles in survival. However, fungal plant pathogens are the most important threat to the global food supply. Cell function is related to cell composition. Fungal cells, called hyphae, are cylindrical (3-10 ìm wide and up to 100's of ìm long); growth occurs only at cell tips. Fungal cell ultrastructure, composition, and function can change substantially within a few micrometers. Better understanding of spatially-resolved fungal biochemical composition and its relation to growth environment is essential if we are to exploit or control their activities. We have established concordance between morphological data from visible light and electron microscopy with complementary biochemical images obtained with Surface Enhanced Raman Spectroscopy (SERS), synchrotron FTIR (sFTIR) and synchrotron X-ray fluorescence (XRF). Samples are grown on pristine, inert substrates compatible with multiple techniques; they are preserved without chemicals, and examined at defined sites. Cell walls, which protect hyphae and interface between the cytoplasm and its environment, respond to growth variations and contain key components not found in human or animal cells. The biochemical effects of cell-wall targeting drug treatments have not been well-documented due to technique-related limitations. Substantial biochemical changes are seen in hyphal walls before there are major morphological effects. sFTIR and SERS spectra reveal changes during spore formation and germination (key stages for fungal survival and proliferation), and different resource utilization by saprotrophs, which recycle biomass, versus endophytes, which have symbiotic relations with living plants. We will present these results and discuss the sample preparation and substrate choices that are key to success in these correlative techniques.

(453) **Excited State Electric Dipole Moment of Some Benzene Derivatives through Solvatochromic Shifts**

Neeraja Rani Gaddipati[1], Narasimha Ayachit[1]; [1]SDM College of Engg & Tech., Dharwad, India

The determination of excited state electric dipole moment through solvatochromic shifts is one of the easiest approaches to understand the molecular structure in the excited state. These studies have gained importance due to their application in photo science, especially if they are of biological importance. In view of this the excited state electric dipole moments of some benzene derivatives are determined and reported here. The fluorescence shifts have been used and the results found seems to be more consistent in comparison with the one calculated through absorption shifts. The results presented are also discussed. A qualitative estimate of the orientation of the dipole moments in ground and excited state are also presented and discussed. Of the several methods proposed, the one proposed from N.H.Ayachit[1], N.H.Ayachit et al [2] and N.H.Ayachit & G.Neeraja Rani[3] is used in view of the several advantages it has. References: 1. N.H.Ayachit, Chemical Physics Letters 164, 272(1989). 2. N.H.Ayachit, D.K.Deshpande, M.A. Shashidhar & K. Suryanarayana Rao, Spectrochimica Acta, 42A, 585, 1405(1986). 3. N.H.Ayachit & G.Neeraja Rani, Physics and Chemistry of Liquids, 45, 41(2007).

(454) **Analysis of Complex Samples using a Portable Multi-Wavelength Light Emitting Diode (LED) Fluorescence Spectrometer**

Bai Baolong[1], Dean Anderson[2], Gary Rayson[1]; [1]New Mexico State University; [2]USDA-ARS, JER

Spectroscopic analysis of chemically complex samples often requires an increase n the dimensionality of the measured response surface. This often involves the measurement of emitted light intensities as functions of both wavelengths of excitation and emission resulting in the generation of an excitation-emission matrix (EEM) for each sample. Unfortunately, the complexity of instrumentation for selective illumination of samples with narrow wavelength band-widths of excitation radiation typically limits the application of such measurements from the analysis of in-field samples. This has recently been addressed by the use of a collection of light emitting diodes (LEDs) as excitation sources with varied wavelengths for the generation of EEMs. Although these sources emit relatively broad wavelength bands, analysis of the resulting multi-dimensi0ona spectral signatures using multivariate techniques (e.g., PCA and PARAFAC) enables the direct analysis of complex samples. Application of this technique to agriculturally important samples will be described and the implication of these results for in-field determinations will be discussed.

(455) **Fluorescence Quenching of Polycyclic Aromatic Hydrocarbons near Gold Nanoparticles**

Huiyong Wang[1], Korina Calimag[1], Andres Campiglia[1]; [1]University of Central Florida, Chemistry Department

The research presented here studies the quenching effect of gold nanoparticles (Au NPs) of variable sizes on the room-temperature fluorescence of five polycyclic aromatic hydrocarbons (PAHs). We have applied the Stern-Volmer equation to calculate the fluorescence quenching constants of acenaphthene, anthracene, pyrene, benzo[a]pyrene and indeno[1,2,3-cd]pyrene. Their values and the quenching efficiencies of Au NPs are size and surface area dependent. The magnitudes of the Stern-Volmer constants varied from ~ 1011 M-1 (5nm Au NPs) to ~ 1013 M-1 (40nm Au NPs). Similarly, the rates of quenching efficiencies vary with the particle

size and colloid concentration. Our kinetic studies reveal a double-exponential quenching process with potential use in the improvement of PAHs analysis.

(456) **Single-Molecule Spectroscopic Study of HIV-1 Viral Rev-RRE Interactions**

Hui Wang[1], Yu-Shan Yeh[1], Matthew Daugherty[2], Alan Frankel[2], Paul Barbara[1]; [1]The University of Texas at Austin; [2]University of California, San Francisco

Rev is an important regulatory protein of the HIV-1 virus that promotes the nuclear export of unspliced and partially spliced viral mRNAs. Rev binds to a highly structured portion of the HIV viral RNA, the Rev Responsive Element (RRE) with high specificity and affinity, forming a highly ordered oligomeric ribonucleoprotein complex that directs the transport of intron-containing viral RNA from the nucleus to the cytoplasm before splicing is completed. In addition to the high affinity binding at stem-loop IIB region of RRE, up to over 10 additional Rev molecules also bind cooperatively onto discrete binding sites on RRE through both RNA-protein and protein-protein interactions. Understanding the essential role of Rev-RRE interactions in the course of HIV viral infection and replication has been hampered by the lack of detailed information about the oligomeric ribonucleoprotein complex structures and the kinetics of oligomeric Rev assembly on RRE. Here we have developed a single-molecule fluorescence imaging approach to systematically investigate the oligomeric binding of Alexa 647-labeled Rev on individual Cy3-labeled 234-nt RRE molecules. By correlating single-molecule Fluorescence resonance energy transfer (FRET) results with two-color gel electrophoretic mobility shift assays (EMSA), we can monitor the kinetics of each step in the Rev oligomerization pathway and unravel the corresponding protein-RNA stoichiometries of each transient intermediate binding state. This approach also provides a unique way to map out the discrete Rev binding sites on RRE and probe the secondary structure change of RRE upon Rev binding at the single-molecular level.

(457) **Interaction of 4-Amino Benzoic Acid (PABA) with Ionic and Nonionic Micelles by Fluorescense**

Seema Acharya[1], Rekha Soni[1]; [1]J.N.V. University

The interaction of 4-Amino benzoic acid (PABA) having pharmaceutical and medicinal properties with the normal micelles of ionic and nonionic surfactants, viz., CTAB, MTAB, CPC, DBSS, DSSS, SLS, TX-100, Tween-20 and Tween-80 has been studied by absorption and fluorescence spectroscopy. Experimental results show the evidence of complex formation of the compound PABA with the micelles in the excited state. The interaction of PABA with nonionic micelles is more compared to that with ionic micelles. The quenching of fluorescence of PABA by cetyl pyridinium chloride (CPC) was observed and analysed. The solubilization action has been determined by theoretically calculated spectral parameters like empirical fluorescence coefficient, quantum yield, molar extinction coefficient and Stokes' shift. The fluorescence properties as well as the theoretically calculated spectral data have been used to characterize the microheteroenvironment of the micelles in terms of their polarity, probe solubilization site and critical micelle concentration (CMC). We have briefly discussed the importance of surfactants and biological system models as well as the use of micelles in pharmacy as an important tool that finds numerous applications. Key words: Fluorescence, PABA, micellar solubilization, quantum yield.

(458) **Chemiluminescence and Fluorescence Signal Variations Due to Water Quality**

Maricar Tarun, Stephane Mabic; [1]Millipore Corp

Chemiluminescence and fluorescence techniques are widely used in analytical chemistry and biological sciences. They are selective, sensitive, and offer wide dynamic range compared to other spectroscopic techniques. However, these advantages could be compromised if the reagents used, including the solvents, are not of suitable purity. Dissolved organic compounds in water for instance, could interfere with chemiluminescence and fluorescence signals. Also, proliferation of bacteria in water releases enzymes, like alkaline phosphatase (AP), which could interfere with AP-catalyzed immunoassays. This work illustrates the importance of using freshly produced ultrapure water for luminescence-based experiments. Fluorescence signal intensities of cyanine-labeled antibody solutions were compared when it was made up in buffer prepared using different types of water. Fluorescence signals were also compared in the detection of Hsp70 in rat liver lysate wherein different types of water was used in the experimental protocol. Cy3 and Cy5 signals were higher when freshly delivered ultrapure water was used. Chemiluminescence signal intensities were also compared for AP and horseradish peroxidase (HRP) catalyzed reactions. Freshly delivered ultrapure water with an ultrafilter as a final purifier gave the lowest chemilumuniscent background signals, which leads to better sensitivity. This was confirmed in the detection of Hsp 70 in rat liver lysate using HRP-mediated chemiluminescence, where signal intensities were higher when freshly produced ultrapure water was used.

(459) **Solid-Surface Room-Temperature Fluorescence Determination of Biomarkers on Solid-Phase Extraction Membranes**

Korina Jesusa Calimag[1], Andres Campiglia[1]; [1]University of Central Florida

We present an analytical evaluation of solid-surface room-temperature fluorescence spectroscopy for the determination of metabolites of polycyclic aromatic hydrocarbons (PAH) on commercially available solid-phase extraction membranes. Solid-phase extraction of six biomarkers; 1-naphthol, 2-naphthol, 1-hydroxypyrene, 2-hydroxyfluorene, 3-hydroxybenzo[a]pyrene and 9-hydroxyphenanthrene were carried out with C18 extraction membranes via an optimized procedure that minimizes metabolite loss. PAH metabolites are directly determined on the surface of the extraction membrane via fluorescence spectroscopy with the aid of a solid sample holder specifically designed for the purpose at hand. The analytical figures of merit of this two-step procedure provide a solid foundation to pursue this approach as a valuable tool for routine analysis of numerous samples.

(460) **Fabrication of Porous Cladding Materials for Remote Sensing with Crossed-Fiber Sensor Arrays using Microsphere Templating**

Paul Henning[1], Veronica Rigo[1], Peter Geissinger[1]; [1]University of Wisconsin - Milwaukee

Optical fiber sensing allows for remote spectroscopic measurements to be carried out in harsh environments. The entire fiber length may be used for sensing by locating sensor molecules outside of the fiber core; light propagating in the core interacts with the sensor molecules through evanescent fields, which may also capture the sensor-molecule fluorescence and guide it to the detector. Large sensor arrays can be built, with the location of a particular sensor determined by the arrival time of the corresponding fluorescence pulse at the fiber end with respect to the exciting laser pulse. Thus, many different parameters may be monitored simultaneously. Adjacent sensor regions must be spaced

meters apart along a single fiber because the spatial resolution is constrained by the sensor fluorescence lifetimes. Forming an orthogonal junction with an additional fiber, with the second fiber capturing through evanescent fields, the sensor fluorescence pulses, allows for greatly reducing the spacing between adjacent regions. Small displacements, however, between the fibers can result in large signal changes due to the exponential decay of evanescent fields away from the fiber core/cladding interface. Thus, hydrogel resins are unsuitable for sensing in aqueous environments as polymer swelling causes separation of the junction, resulting in weak, inconsistent signals. Here, microsphere templating was used to create pores in a poly(ethylene) glycol (PEG) based polymer that allow analyte passage to the evanescent region where sensing occurs. Covalent attachment of the fluorosensors minimizes leeching. The structures of these porous junctions were characterized with SEM imaging. Fluorescence measurements show a relatively low response time and improved consistency for replicate measurements. Also, different pH sensing schemes were demonstrated using a variety of fluorophores including fluorescein.

(461) **Data Analysis Tools for Determining Single Molecule Binding Affinities using Total Internal Reflection Fluorescence Microscopy**

Eric Peterson[1], Josh Wayment[1], Moussa Barhoum[1], Karl-Heinz Gericke[2], Joel Harris[1]; [1]University of Utah Chemistry Department; [2]Technische Universität Braunschweig

Automated image analysis tools have been developed to investigate biological molecule binding affinities and kinetics between surface-bound ligands and fluorescence-labeled solution-phase proteins using total internal reflection fluorescence (TIRF) microscopy. Videos of these single-molecule binding events (typically consisting of 300 binding sites monitored over 2000 video frames) contain large amounts of information and thus present data analysis challenges that make automated data-handling tools necessary. Binding events between fluorescence-labeled protein and surface-bound ligands are observed by monitoring the light\\dark state of the fixed binding site; in the unbound state the ligand site is dark, while in the bound state the labeled protein is within the evanescent illumination field and fluoresces brightly. By monitoring the bright and dark states of a binding site over thousands of video frames, the average time bound and time unbound can be measured and used to determine the binding kinetics and the affinity constant of the protein-ligand interaction. This methodology has been used to determine picomolar binding affinities for complexes such as biotin-streptavidin, biotin-antibiotin, and syntaxin complex-snaptobrevin. The data analysis algorithms, developed in the MATLAB® software environment, can locate binding sites, correlate these sites across multiple videos or video frames, collect the on\\off state at each site, and fit the on\\off state information to extract affinity constants and kinetics. We employ a Gaussian function fitting algorithm to locate sites by extracting position information from Gaussian point spread functions (PSF) fit to the experimental single-molecule fluorescence intensity spots with a reproducibility of 90 nm. We have also developed a novel least squares searching algorithm that locates sites more rapidly by finding local minima in a calculation of the sum of the squares the differences between pixel intensities in an ideal PSF and a normalized region around each pixel in the image. Once located, site positions can be correlated between videos or frames to select persistent sites and exclude non-specific interactions with the surface. Binding constants can be extracted from the transient on\\off behavior using autocorrelation or a survival time histogram.

(462) **Intracellular Delivery and Localization of Luminescent Conjugated Polymer Nanoparticles**

Kenneth Christensen[1], Prakash Kandel[1], Lawrence Fernando[1], Jason McNeill[1]; [1]Clemson University

A new class of fluorescent nanoparticles based on 20-70 nm diameter particles of conjugated polymers has been developed. These conjugated polymer nanoparticles are significantly brighter (10-1000X) than the standard organic fluorophores and fluorescent solid-state nanoparticles (i.e. quantum dots), making them attractive reagents as imaging probes in cells. Efficient delivery and targeting of these nanoparticles to cells is key to their broad application in biomedicine and biotechnology. Various biochemical methods (cationic lipids, immunoliposomes, cell penetrating proteins) and physical methods (electroporation, microinjection, scrape loading) have been used to facilitate cellular uptake. We have measured the efficiency of uptake of conjugated polymer nanoparticles in Chinese Hamster Ovary (CHO-K1) cells and a murine macrophage-like cell line (J774.A1). We have also determined the cellular localization of the conjugated polymer nanoparticles delivered by these biochemical and physical methods using immunofluorescence microscopy. These studies give insight to the mechanism of cellular uptake of nanoparticles and their long-term stability and fate in these tissue culture models.

(463) **Studies of the Fluorescence Excitation Spectroscopy of Phytoplankton at the Single Organism Level**

Laura S. Hill[1], Luisa T.M. Profeta[1], Evelyn Lawrenz[1], Tammi L. Richardson[1], Benjamin S. Twinning[1], Christopher J. Hintz[1], Timothy J. Shaw[1], Michael L. Myrick[1]; [1]University of South Carolina

Phytoplankton chlorophyll fluorescence from optical trap setups has been reported in the literature previously. The optical trap utilizes a single laser beam to hold the phytoplankton in place, while an excitation beam enters the setup, causing chlorophyll fluorescence. During this study, an optical trap was assembled using an inverted microscope, and modified to allow for multiple continuous wavelengths to excite the phytoplankton sample. We report excitation and emission for two species of phytoplankton. Additionally this study will examine excitation and emission differences found between individual phytoplankton within a species.

(464) **Quantification of Affinity and Kinetics of Membrane Associated Proteins by Ratiometric Imaging and Flow Cytometry**

Kenneth Christensen[1], Barbara Bull[1], Thomas Caldwell[1]; [1]Clemson University

Quantitative measurements of affinity and kinetic constants are critical to a mechanistic understanding of protein-protein interactions. *In vitro* measurements of affinities generally utilize purified proteins; however, membrane associated proteins are usually difficult to express and purify. Hence, we have developed methods for quantifying affinities of membrane associated protein-protein interactions using intact cells. We have measured equilibrium binding affinities of cell-surface receptors with its exogenous binding protein and receptor-receptor interactions within the membrane using ratiometric imaging, fluorescence resonance energy transfer imaging and flow cytometry. These measurements provide a basis for developing a general method useful for biochemical studies and high throughput screening applications.

(465) **Detection of Reactive Oxygen Species in Cells using a Fluorescent Probe– Application and Limitation**

Kazunari Kondo[1], Sayaka Ohta[1], Reiko Teshima[1]; [1]National Institute of Health Sciences

Reactive oxygen species (ROS) are harmful to living organisms. Intake of unsaturated fatty acids cause to form free radicals and lipid peroxides, resulting in cell damage. On the other hand, a small amount of ROS including superoxide and nitric oxide are considered to be necessary for biological systems. Nitric oxide plays an important role in endothelial cells and neuronal cells. A wide variety of fluorescent probes for detection of ROS is commercially available such as 3'-(p-aminophenyl) fluorescein (APF), 3'-(p-hydroxyphenyl) fluorescein (HPF), dichlorodihydrofluorescein diacetate (H2DCFDA) and 4,5-diaminofluorescein (DAF-2). DAF-2 (DAF-FM) is believed to be specific for the detection of nitric oxide. However, we have to struggle with the specificity of fluorescent probes. Fluorescent probes based on the fluorescein structure often give nonspecific fluorescence in cells after the probes react with some enzyme, not with nitric oxide or ROS. We have recently found that a conjugated triene fatty acid induced nitric oxide production in neuronal cell line PC12 using DAF fluorescent probe. Other biological studies, however, do not support nitric oxide production in the cells. Thus, we tested a wide variety of fluorescent probes for the detection of nitric oxide and other ROS to clarify whether the ROS production in the cells was specific or not. Two newly developed fluorescent probes, Spy-LHP for detecting lipid peroxidation and BESSo for detecting superoxide anion radicals, were tested. We will discuss application and limitation of the fluorescence probes for the detection of ROS at the meeting.

(466) **Oxytetracycline Determination by Derivative Spectrophotometry Based in the Formation of Ionic-Pair with Crystal Violet and its Spectroscopy Verification.**

Maria Ines Toral[1], Sandra Orellana[1]; [1]University of Chile

For the oxytetracycline (OTC) that is an antibiotic commonly used in the salmon industry, in this work, is proposed a method for its determination, which is selective, simple and does not require of sophisticate instrumental. This determination is based on the electrostatic interaction between OTC and a cationic dye, crystal violet (CV) to form an ionic-pair (CV-OTC) that is separate by means of extraction liquid-liquid. The absorption spectra of the ionic-pair organic extracts CV-OTC and CV were registered against air in the UV-visible range. For the optimization of the formation CV-OTC in chloroform medium ammonia pH 9.0±0.2 and OTC $8.0x10^{-7}$ mol/L, an exponential experimental design was carried out, being obtained: concentration CV $1.5x10^{-5}$ mol/L; time extraction 4 min and a volume of extracting of 6 mL. The ionic-pair confirmation was carried out by means of 1HNMR and IR being obtained significant chemical shifts in the signals associated to the ionic-pair CV-OTC compared with the signals of the CV. The ionic-pair formation was also verified by calculations of times of relaxation (T1) by means of 1HNMR; being obtained a decrease of T1 in the signals corresponds to the hydrogens of the aromatic rings and to the CH_3 groups of the ionic-pair. The quantification of CV-OTC was carried out by second derivative spectrophotometry, with a smoothing and scale factor of 10,000, using the zero crossing of the CV, so that the whole absorption can be attributed to the ionic-pair. The instrumental analytic parameters of the method are: λanalytical: 380.0 nm, Limit of detection: $1.71x10^{-8}$mol/L, Limit of quantification: $5.71x10^{-8}$ mol/L, Range of determination: $5.71x10^{-8}$-$3.0x10^{-5}$ mol/L, calibration graph equation: DU = $1.40x10^{6}$xC (mol/L) + 0.0071 R: 0.995. The recoveries in synthetic samples were 98 ± 2 %. The interfering study, established that interference doesn't exist on the ionic-pair analytical signal. The OTC extraction and clean up from salmon muscle was realized with the method [1] modified. To the methanolic extract the ionic-pair method was applied. The recoveries in these samples were between 70 and 90%. Acknowledgement: FONDECYT Project 1070605, CONICYT Doctoral Scholarship. 1. - A .L. Cinquina et al. J. Chromatogr. A, 987 (2003) 227-233.

(467) **Development of Accurate, Real Time and Sensitive Optical Oxygen Sensors for Hydrocarbon Environments**

Mahmoud Shahriari[1], Mike Morris[2]; [1]Ocean Optics Corp.; [2]Spectrecology

This paper presents the development of a novel optical oxygen sensor system utilizing high performance coatings as optical/chemical transducer. The coating material is a sol gel coating hosting oxygen sensitive luminophores and is compatible with hydrocarbon vapors and liquids. The Ocean Optics oxygen sensor has a response time of less than 1 second in gas, a wide dynamic range up to 3 atmospheres of oxygen partial pressure and low detection limit down to ppb dissolved oxygen. The high performance of sensor coatings enables monitoring oxygen and dissolved oxygen in adverse environments such as organic solvents, fuels and aromatic hydrocarbons. The sensor is currently adapted to routine laboratory tests. In this paper we will present data on the sensor performance in different settings where oxygen is monitored using a phase fluorometer as excitation light and detection system and a fiber optic bifurcated bundle as waveguide for transmitting excitation and emission. We also report data showing the sensor performance in gas and liquids particularly in hydrocarbon environments

(468) **Fluorescence Lifetime Global Analysis using a Multiple-Frequency Frequency Domain Fluorometer**

Karen Steege[1], James Mattheis[1], Adam Gilmore[1]; [1]Horiba Jobin Yvon

Applications of a novel method in frequency domain fluorescence lifetime measurements are discussed. The MF2 multiple frequency fluorometer measures the phase and modulation of a fluorescence signal at up to eight frequencies simultaneously. The ability to measure multiple frequencies simultaneously enables the measurement of fluorescence lifetimes over time scales of chemical kinetics. Analysis of fluorescence lifetimes over global parameters such as time (kinetics), temperature, concentration, and local solvent environment make the MF2 capable of measuring the affect of these parameters on the lifetime of a fluorophore. The Universalizer(c) global fitting software tool is utilized for the global analysis of fluorescence lifetimes. Conventional methods such as single-frequency frequency domain lifetime measurements and time-correlated single photon counting do not enable the measurement of lifetimes in such short acquisition times as the MF2 mutliple frequency fluorometer.

(469) **TCSPC Fluorescence Lifetime Microscope System in the Deep UV-Visible and NIR (240nm - 1700nm**

Lin Chandler; [1]Horiba Jobin Yvon, Inc.

Time-resolved fluorescence microscopy is the ultimate tool for investigating dynamic events in cellular/sub-cellular structures and nanomaterials. Applications previously have been limited to wavelengths in the visible region (370-850nm) because microscope optics does not transmit in the deep UV. This paper describes a filter-based confocal system (the DynaMyc™) to measure fluorescence lifetimes and intensity directly under the microscope in the wavelength range of 240–1700 nm for the first time. The system features time-correlated single photon counting (TCSPC) for sensitive and rapid acquisition of luminescence lifetimes from 100ps to 100us. An Olympus BX51 microscope was modified to

transmit light for both excitation and emission down to 240nm in the deep UV. To maintain maximum light throughput, both the excitation light source and the detector are directly coupled to the microscope. Excitations are fast pulsed solid state LEDs or laser diodes. The detectors are the fast response TBX detector for UV-VIS (240-850nm) and the Hamamatsu H10330 NIR PMT for NIR (950-1700nm). This system can be used for mapping of fluorescence lifetimes and intensity with variable spatial resolution (>1um) with an automated stage. This paper will present fluorescence lifetime measurement from a single protein crystal with a diameter of of 70 um, and lifetime mapping obtained from a stained mouse kidney section. The preliminary data for NIR lifetimes measured from NIR quantum dots will also be presented. The potential application for detection of intrinsic fluorescence, such as tryptophan, from single proteins and the deep tissue imaging in the NIR will be discussed.

(470) **CO2 Laser Induced Far-Infrared Fluorescence from Bio-Materials**

Raphael Moon[1], Boris Gelmont[2], Ashish Tripathi[3]; [1]US Army, ECBC, AMSRD-ECB-RT-DL; [2]University of Virginia; [3]Science Applicaitons International Corp

We investigate a novel approach to detecting and identifying bacteria and toxins based upon the premise that the deoxyribonucleic acid (DNA) in bacteria and viruses, and possibly the proteins in toxins will radiate millimeter wave (MMW) energy upon the absorption of infrared (IR) radiation. The proposed hypothesis assumes that IR excitation results in Fermi resonance of molecular vibrations in the DNA phosphate-sugar backbone. The Fermi resonance may result in a low frequency (about half the frequency of excitation radiation) emissive radiation from DNA. To validate this hypothesis an extensive theoretical analysis was undertaken. The theoretical computational modeling included estimation of IR absorption bands of DNA molecular components such as deoxyadenosine 5'-monophosphate (dAMP), of deoxycytidine 5'-monophosphate (dCMP), deoxyguanosine 5'-monophosphate (dGMP), deoxythymidine 5'-monophosphate (dTMP), adenosine, guanosine, cytosine and thymine. For each of the absorption bands in the 9.6 to 10.6 μm wavelength range, a probability of Fermi resonance occurrence was estimated. A tunable CO2 laser was used as the infrared (IR) excitation source. The tunable CO2 laser is capable of emitting IR radiation in 9.6 to 10.6 μm wavelength range. Emission spectra were acquired with a Fourier Transform Infrared (FTIR) spectrometer. The presence of emission spectra in the 20 micron wavelength region indicates a possibility of emission spectra in the MMW region due to Fermi resonance.

(471) **Identification of Micro Particles from Bio-Pharmaceutical Manufacture Process using Multiple Micro-Spectroscopes**

Wen Jing[1], Xiaolin Cao[1], Gary Li[1], Zai-qing Wen[1]; [1]Amgen Inc

Micro particle characterization plays an important role in conducting incident investigations for clinical and commercial manufacturing in Amgen. Most incidents are related to unknown particulates found in products or during the manufacturing processes. These particulates could be particles formed by protein aggregation, or foreign particles introduced by raw materials and facilities. To identify these particles in a solid state, multi-spectroscopic technologies are applied. Fourier Transform Infrared (FTIR) micro-spectroscopy is often used to identify the chemical structure of a particle. Sometimes, FTIR and Raman micro-spectroscopy are combined to determine a particle that is a mixture. Energy Dispersive Spectroscopy (EDS) is also applied to obtain the atomic composition of a particle to support the FTIR and Raman analysis, or to identify an inorganic particle. Scanning Electron Microscopy (SEM) and optical microscopy are used to examine the morphology, size, and/or color of a particle. The analytical results help the investigating team to find the root cause, and evaluate its impact on manufacturing equipments and processes, as well as quality control of raw materials. Examples of these investigations will be presented in this poster.

(472) **Differentiation of Paper and Adhesives in Labels by Fourier Transform Infrared Spectroscopy and Linear Discriminant Analysis**

Deidre Krupp[1], Christopher Detloff[1], Mary Carrabba[1], Mark Witkowski[2]; [1]Southern Oregon University; [2]FDA Forensic Chemistry Center

Diverted pharmaceuticals are in most cases authentic products which may have been repackaged and/or relabeled and funneled into illicit and unregulated distribution channels. Because the products are authentic, a chemical analysis of the individual dosage forms in the packaging cannot be used to determine if a product has been diverted or not. Accordingly, diverted pharmaceuticals are much more difficult for authorities to recognize and investigate. One way to differentiate diverted from authentic products is to examine the product label and packaging. In some cases counterfeit labels on the packaging may provide key evidence and point towards product diversion. Spectroscopic techniques can provide a great deal of information about papers and adhesives. In combination with statistical analyses, such techniques can be used to determine compositional characteristics and to separate similar items into distinct classes. To determine if adhesive labels could be distinguished in this manner, attenuated total reflectance Fourier transform infrared (ATR FT-IR) spectra were collected for the paper and adhesive sides of 42 samples. These spectra were then classified by linear discriminant analysis. For the paper side, spectra grouped according to their intended use (ink-jet, typewriter ink, multi-use, laser), with typewriter, multi-use, and laser classes in close proximity to one another. Adhesive spectra classified very distinctly according to the label's manufacturer. Therefore, ATR FT-IR spectra from both sides of an unknown label can potentially be used in combination to identify it by brand and end-use. These spectra may also provide a means by which to distinguish between authentic and counterfeit pharmaceutical labels and to make associations between labels encountered in seemingly unrelated diverted pharmaceutical investigations.

(473) **Determining the Sensitivity of our Biological Fluorescent Hyperspectral Images**

Howland Jones[1], David Haaland[1], Michael Sinclair[1], Bryan Carson[1]; [1]Sandia National Laboratories

We have designed and developed two hyperspectral fluorescent microscopes for imaging biological samples at Sandia. The first hyperspectral microscope surveys large area samples such as DNA microarrays and biofilms on water treatment membranes. The second instrument is a confocal hyperspectral microscope that generates 3D images of live biological cells, bacteria, and plant related materials. One of the main advantages of using hyperspectral imaging is that it allows us to separate many overlapping fluorophores and create interpretable quantitative images, making it an excellent biological research tool. To analyze the hyperspectral image data generated from these microscopes, we use fast and efficient Multivariate Curve Resolution (MCR) algorithms to extract pure-component spectra and the associated quantitative concentrations. 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 the emitting species present in an image that are above the noise. In this presentation, I will demonstrate methods to quantify the sensitivity and detection limits of our MCR results. Our

methodology to accomplish this task requires a detailed analysis of the instrumental noise sources in our images. Simulation data sets can then be created by varying other factors that influence the sensitivity of our measurement, such as the number of fluorophores, the amount of spectral and spatial overlap, and the relative intensity of the spectrally overlapped fluorophores. These simulation data sets will allow us to understand the sensitivity of each component in a given image based upon the MCR analysis of the hyperspectral image. I will also compare the hyperspectral image results to those that would have been obtained from the sample imaged with a 3-color filter-based commercial flourescence microscope. Finally, I will discuss methods to estimate the statistical significance of the concentration estimates for spectral components resulting from these analyses. *Sandia is a multi-program laboratory operated by Sandia Corporation, a Lockheed Martin Company, for the United States Department of Energy under Contract DE-ACO4-94AL85000. A portion of this work was supported by the Microscale Immune Studies Laboratory Grand Challenge LDRD.

(475) **Chemiluminescent Radicals in HN3/H2/O2 Flames**

R. Sausa[1], M. Grams*[1]; [1]US Army Research Laboratory

Chemiluminescence originates from electronically excited species and provides a simple and useful diagnostic for flame and combustion processes. In this abstract, we report a spectroscopic, imaging, and modeling study of a near stochiometric H2/O2 flame doped with hydrazoic acid (HN3) at low pressure. HN3 is a compound whose detailed chemistry is important in understanding the combustion and decomposition of high-nitrogen, energetic materials used in propellants and in air bags of automobiles. We identify species OH(A), NO(A), and NH(A) by their prompt emission centered at 308, 226, and 336 nm, respectively, and analyze their emission spectra. A Boltzmann, rotational distribution analysis of the spectra yields a temperature of 1300 +/- 100K in the post flame region. This value agrees well with those we obtain with a fine wire thermocouple and OH laser-induced fluorescence. We record the species' concentration profiles with a filtered intensified charge-coupled device throughout the flame, and compare them to those we calculate with the PREMIX flame code. The flame code uses a chemical mechanism that contains over 140 reaction and 35 species, which we obtain from a critical literature review. Rate and sensitivity analyses reveal key reactions for producing and consuming the excited species. We will present these reactions, along with their rates, at the meeting. *NRC/ARL Postdoctoral Research Associate

(476) **Super-Resolution and Raman Chemical Imaging: From Multiple Low Resolution Images to a High Resolution Image**

Duponchel Ludovic[1], Ruckebusch Cyril[1], Milanfar Peyman[2], Huvenne Jean-Pierre[1]; [1]University of Lille-LASIR Lab-France; [2]University of California-MDSP Lab-USA

For many imaging applications, obtaining high resolution images (HR) is a key step. An HR image, with its high pixel density, can present many details about the observed object. We have then a better vision of the reality and therefore better interpretations and knowledge. Since the 1970s, many imaging systems have been developed with different detector configurations as for example the well known charge-coupled device sensor (CCD). Such detectors have rapidly reached their limits of resolution, as people have sought more and more detailed images. The first way to increase the resolution of the devices was an instrumental one, whereby we have reduced the pixel size of the detectors. It was also possible to increase the chip size. The 1980s saw the beginnings of a growing area of signal processing called super-resolution. Super-resolution is defined by the use of image processing algorithms in order to overcome the limitations of optical systems. The main advantage of such signal processing approach is that it costs less and the existing imaging systems can be still used. Moreover, due to physical limits it is sometimes the only way to increase resolution since no alternative instrumental setup may be available. The main idea of super-resolution is the fusion of several low-resolution images (LR) of the same object to obtain one higher-resolution image. Raman spectroscopic imaging is a powerful technique for visualizing the distribution of chemical compounds. With such far-field imaging spectroscopy, the resolution limit is first and foremost dictated by the photon wavelength due to diffraction limit. For classical mapping procedures using visible photon for Raman scattering, 1 micron resolution images are usually considered optimal. Nevertheless this resolution limit is a real constraint, considering imaging spectroscopy of micron-sized samples such as in biology or chemistry. New chemometrics methods are now of great interest to overcome this drawback, while keeping our far-field Raman instruments. The aim of the presented work is to show that fusing several 1 micron resolution images of the same sample acquired with sub-micron shifts can produce a HR image and in a certain way a better resolution in order to explore sub-micronic details.

(477) **Resolution of Raman Spatial Artifacts using Optical Pre-Processing**

Michael Pelletier; [1]Pfizer

Spatial information about the sample in a spectroscopic measurement that is encoded in the angle of incidence of light reaching the detector is lost when the photons are absorbed by the detector. Optical pre-processing can preserve selected portions of this information. The preserved information can be used to resolve confounding effects including spherical aberration on Raman depth profiling and out-of-focus artifacts in Raman mapping. This information can also be used to determine Raman spectra from multiple sample depths or multiple scattering geometries using a single acquisition from the detector. Optical pre-processing hardware added to a commercial Raman instrument, along with custom software, will be described that enable these new spectroscopic imaging capabilities. Known examples of artifacts in the Raman analysis of polymer laminates will be demonstrated and resolved using optical pre-processing.

(478) **Getting the Most from the Microscope in Your Micro-Raman Spectrometer**

Kathleen Martin[1], Gretchen Shearer[1]; [1]McCrone Associates, Inc.

Coupling a light microscope to a Raman spectrometer allows for spatial resolutions of less than 1 micrometer and thus greatly increases the range of possible applications for Raman spectroscopy. Use of a light microscope as a means of sample introduction, however, results in limited working distances and depths of field, and increases the laser power density at the sample. To overcome these limitations, some degree of sample preparation is often beneficial. In addition, sample preparation can eliminate matrix contributions to the spectra in cases where the microscope cannot adequately isolate an area for analysis. At the same time, the light microscope can act as more than a focusing element for the Raman laser. Polarized light microscopes are analytical instruments in their own right and can provide useful information about the physical character of a sample and can also be used to select components in a mixture based on morphology, color or birefringence. Our talk will discuss both sample preparation considerations and the use of the microscope portion of the micro-Raman to aid in sample analysis, with examples.

(479) **Combining Raman Spectroscopy and Differential Scanning Calorimetry**

Richard Spragg[1], Robert Alexander[1], Nancy Kawai[2], Kevin Menard[2]; [1]PerkinElmer LAS UK; [2]PerkinElmer LAS USA

We describe development and applications of a combined system for Raman spectroscopy and high speed Differential Scanning Calorimetry (DSC). Although both techniques are commonly applied to the same problems, simultaneous measurements have rarely been reported. DSC is widely used to investigate phase changes of materials as their temperature is changed, or isothermally. However the information obtained is essentially quantitative as this is a univariate technique that simply measures heat flows. Vibrational spectroscopy can provide complementary information, giving insight at molecular level into the changes accompanying thermal events or reactions. In addition the multivariate nature of Raman spectra means that it is possible to monitor simultaneous events with different spectral signatures that cannot be distinguished by DSC. Modern DSC practice has extended to using faster heating rates and smaller sample quantities than previously. This enhances sensitivity and improves the separation of overlapping transitions. However it increases the demands on the Raman instrumentation. The energy of the laser excitation represents a significant perturbation to the calorimeter that has to be minimised by controlling the laser power and duty cycle of the measurement. Fruitful areas for this combination of techniques include polymorphism, crystalline-amorphous transitions in synthetic polymers and pharmaceuticals, and resin curing reactions.

(480) **Potential-Dependent Acid/Base Chemistry of Silver-Immobilized 2-Mercaptobenzoic Acid Studied by Surface Enhanced Raman Spectroscopy**

Chaoxiong Ma[1], Joel Harris[1]; [1]University of Utah

Self-assembled monolayers (SAMs) of acid/base molecules are used for surface modification of materials to form biocompatible surfaces that are sensitive to solution conditions. Understanding the factors that influence the properties of these surfaces is crucial for further development of immobilization techniques, control of surface properties, and applications of the modified surfaces. The interfacial acid/base chemistry of 2-mercaptobenzoic acid (2-MBA) on a polycrystalline silver electrode was investigated by near-IR surface enhanced Raman scattering (SERS). The COO- bending mode at 840 cm-1 and C-COOH stretching mode at 800 cm-1 were used to determine the fraction of deprotonated and protonated 2-MBA. Potentials in the range of 0.0 V to –0.6 V (vs. Ag/AgCl) were applied to the surface while pH-dependent SERS spectra were acquired at each potential. The intensities of COO- bending mode and C-COOH stretching mode show a response that depends both on solution pH and on applied potential. Only at the solution pH lower than a threshold value, could the applied potential influence the pH response. This behavior can be ascribed to a strong interaction between Ag electrode and COO- of the immobilized 2-MBA that compete with acetate ions in buffer. The effective pKa of the immobilized 2-MBA varies with applied potential, where the pH response can be fit to the Poisson-Boltzmann equation while accounting for the potential distribution across the self-assembled monolayer. This study has demonstrated SERS to be a sensitive technique for probing the behavior of immobilized acid/base molecules, whose chemistry can be controlled by the solution pH and applied potential.

(481) **SRM 2244: Relative Intensity Correction Standard for 1064 nm Excitation**

Steven Choquette[1], Aaron Urbas[1], Stefan Leigh[1]; [1]NIST

This Standard Reference Material (SRM) is the latest in the SRM 224x series of glass artifact standards to correct for the instrument response function of Raman spectrometers. Existing SRM's 2241-2243, are used to correct the instrument response of Raman systems operating with 785 nm, 532 nm, and 488nm/514.5 nm laser excitation respectively. SRM 2244 is a certified spectroscopic standard for the correction of the relative intensity of Raman spectra obtained with instruments employing 1064 nm laser excitation. SRM 2244 consists of an optical glass that emits a broadband luminescence spectrum when excited with 1064 nm laser radiation. The relative spectral intensity of the glass luminescence has been determined through the use of a white-light, uniform-source, integrating sphere that has been calibrated for its irradiance at NIST. The shape of the luminescence spectrum of this glass is described by a polynomial expression that relates the relative spectral intensity to the wavenumber (cmtext-1) expressed as the Raman shift from the excitation wavelength of 1064 nm. This polynomial, together with a measurement of the luminescence spectrum of the standard, can be used to determine the spectral intensity-response correction that is unique to each Raman system. The resulting instrument-intensity-response correction may then be used to obtain Raman spectra that are instrument independent. This poster will discuss the properties of the glass, the certification procedure, and results of a round robin exercise used to vet the performance of the candidate SRM material. Additionally, initial results to extend its use to 980 nm excitation wavelengths will be presented.

(482) **Confocal Raman Microscopy of Optically-Trapped Lipid Vesicles: Investigation of the Polymerization of a Diacetylenic Lipid Membrane**

Jonathan Schaefer[1], Christopher Fox[1], Joel Harris[1]; [1]University of Utah

Polymerizable diacetylenic phospholipids are useful for developing stabilized bilayer membranes. Diacetylenic lipids undergo a 1,4 addition reaction when irradiated with UV light to form a polymer consisting of a conjugated alternating ene-yne backbone that adds stability to the vesicle membrane. The polymer formed by the 1,4 addition reaction is stable for long periods of time and is not destroyed osmotically by salt. The polymer is visibly colored and changes color with temperature, pH, and disruption of the polymer backbone through chemical interactions with the lipid head groups. This thermochromic behavior of the polymer has led to its use as a biological sensor because disruption of the polymer backbone and subsequent color change can be induced by the binding of molecules to the vesicle surface. The stable polymer membrane is a biologically compatible material that could be used as a delivery system for drugs. Despite the potential utility of these structures, the kinetics of the 1,4 addition reaction and color change in the resulting polymer are not well understood. Confocal Raman microscopy is an effective method for studying these materials. Optical trapping of single vesicles can be used to investigate reactions of phospholipids over time. The advantages of optical trapping are that the vesicle is trapped on the optical axis maximizing collection efficiency, reaction conditions mimic those of a vesicle dispersed in free solution, and fluorescence from the cover slip is avoided as the vesicle is levitated away from the surface. The advantages of confocal Raman microscopy is the sample does not need to be labeled, low sample concentrations are used, and signal outside the confocal volume is excluded. In this research confocal Raman microscopy was used to follow the kinetics of the 1,4 addition reaction, dependence of reaction rate on

UV light intensity, and thermochromic behavior of diacetylenic phospholipids in individual vesicle membranes.

(483) **Towards a Practical Clinical Approach for Automated Breast Histopathology**

Frances Pounder[1], Rohit Bhargava[1]; [1]University of Illinois at Urbana-Champaign

Automated molecular techniques to aid conventional morphologic diagnosis of breast cancer and are sought to assist with clinical tissue examination and intra-operative tumor identification. Fourier transform infrared (FT-IR) molecular spectroscopy is readily applicable for breast cancer histopathology, as this technique can be applied to tissue sections prepared for standard pathologic staining and analysis. An infrared spectrum provides a quantitative measure of tissue molecular composition. However, FT-IR imaging is required to visualize microscopic tissue structure and provide information on spatial tissue heterogeneity. This technique is complementary to current clinical diagnostic protocols, as it is non-destructive and does not require the application of any dyes or contrast agents. Using conventional stained tissue as a gold standard, we have demonstrated that computerized classification of FT-IR images can provide a reproducible indicator of tissue type (histology). Based on resulting false-color classified images, we present here an automated protocol to distinguish diseased and normal breast pathologic states based on tissue content and structure by evaluating the ratio of epithelial to stromal pixels in an optimal box-sized tissue region. This study employs tissue microarrays (TMAs) with 260 tissue samples from 90 breast cancer patients to provide a large population for classification algorithm development and validation. Classification is demonstrated on invasive tumors in the breast and corresponding metastatic tumors in lymph nodes. We next present initial preparations for clinical translation. Classification is validated on FT-IR TMA datasets acquired with several different instruments to demonstrate flexibility in clinical instrumentation. Automated classification protocols developed on FT-IR datasets acquired in transmission are demonstrated on TMA and surgical resection datasets acquired in reflection. This is an important step in clinical translation, as tissue substrate costs are significantly reduced by eliminating the necessity of mid-IR light transmission through the sample. This automated procedure of FT-IR tissue image classification could serve as a useful tool for breast cancer diagnosis and research.

(484) **Coherent Raman Studies of Germanium Sulfide Thin Film Deposition**

Patrick Whitham[1], Rene Rodriguez[1], BarJean Phillips[1]; [1]Idaho State University

Recently, studies on the properties of chalcogenide materials have indicated the possibility of using germanium sulfide materials in phase memory applications. Phase change memory devices store information by altering resistances within the phasic material through changes in micro structure. The deposition of GeXSeY by plasma enhanced chemical vapor deposition (PECVD) from germane and hydrogen selenide has been reported in the literature. Our work has focused on controlling the PECVD condition to deposit thin films of GeXSY with a desired stoichiometry from germanium tetrachloride an hydrogen sulfide. The relative mass flow rates, reactor pressure and deposition power may all affect the stoichiometry of the deposited germanium sulfide thin films. Here we report the use of coherent anti-stokes Raman scattering (CARS) to monitor the relative concentration of H2S in the plasma, and correlate these *in-situ* gas phase readings with the quality, morphology, and stoichiometry of the resulting germanium sulfide thin films.

(485) **Autocalibration of Process Raman Data Utilizing Multivariate Temperature and Pressure Modeling**

Wesley J. Thompson[1], Brian J. Marquardt[1]; [1]Applied Physics Lab, Univ. of Washington

Maintaining calibration in a dynamic process can prove challenging if temperature and pressure affect either the chemistry or the sampling optics. Customized Raman ballprobe immersion optics use sapphire as a focusing lens and could act as an internal standard for autocalibration of both wavelength and intensity. The goal of our current research is to understand the Raman response of the sapphire sampling optic to develop spectroscopic calibration models for applications requiring variable temperature and pressure changes. We have designed and built a lab scale high temperature/pressure vessel to generate the process conditions needed to develop the sapphire Raman calibration models. These models will utilize the sapphire Raman lines to ensure both wavelength and intensity calibrations over large temperature and pressure ranges. Preliminary data show that the spectral changes in sapphire are linear in both temperature and pressure with more of an effect from temperature. The models generated from this study will be applicable to process Raman systems where temperature and pressure gradients are prevalent. This presentation will describe the current state of the art pressure and temperature experimental apparatus, describe our Design of Experiment pressure and temperature experiments and present our current Raman multivariate models to autocalibrate for process changes.

(486) **Raman Spectroscopic Assessment of the Effects of Genetic Abnormalities on Bone Composition in a Mouse Model**

Michael Roberto[1], Jacqueline Cole[1], Chad Novince[2], Laurie McCauley[2], Ramiro Toribio[3], Michael Morris[1]; [1]University of Michigan Department of Chemistry; [2]University of Michigan School of Dentist; [3]Ohio State University College of Vet Med

As part of a broader study of the uses of Raman spectroscopy to characterize the effects of metabolic diseases and genetic abnormalities on bone tissue, we have examined the spectra of transgenic mice that have a defective parathyroid hormone related protein (PTHrP). PTHrP plays an important role in normal development, especially in the regulation of bone formation and metabolism. A transgenic mouse model with a defective PTHrP gene sequence was used to assess the biological functions of this particular protein. These mice often do not survive longer than a few days and display abnormal skeletal features, including uncharacteristic bone and tooth morphology. To date, the role of PTHrP in bone or tooth composition has not been examined. The objective of this study was to investigate the effects of PTHrP on bone mineral and matrix properties with Raman spectroscopy by comparing transgenic mice with a deficient PTHrP gene sequence to wild type mice with a normal PTHrP sequence. Three groups of mice were examined: wild type (+/+, n=4), heterozygous transgenic (+/-, n=6), and homozygous transgenic (-/-, n=3). For each mouse, one tibia was sectioned at the mid-diaphysis to create two regions for Raman analysis. Raman spectra were acquired with an 830-nm system at both the proximal and distal ends of each tibial section to assess both cortical and cancellous bone tissue, which may be affected differently by the PTHrP mutation. Standard measures of bone composition, including mineral/matrix ratio, carbonate/phosphate ratio, collagen cross-link ratio, and crystallinity, were computed and compared across the three groups. The homozygous transgenic mice exhibited the most pronounced skeletal abnormalities, and bone composition was most compromised in this group. Bone composition in the heterozygous transgenic mice was more similar to that of the wild type mice. Ours is the first reported study of bone composition in a mouse

model of a genetic defect other than osteogenesis imperfecta. The results demonstrate that Raman spectroscopy may be generally useful for characterizing bone tissue composition abnormalities caused by the defects.

(487) **UV Raman Spectra and Cross Sections of the G-Series Nerve Agents**

Steven D. Christesen[1], Jay Pendell Jones[2], Joseph M. Lochner[1], Aaron M. Hyre[1]; [1]U.S. Army Edgewood Chemical Biological Ctr; [2]ITT Advanced Engineering and Sciences

UV Raman spectroscopy is being applied to the detection of chemical agent contamination of natural and man-made surfaces. In support of these efforts, we have measured the UV Raman signatures of the G-series nerve agents GA (tabun), GB (sarin), GD (soman), GF (cyclosarin) and agent simulant diisopropyl methylphosphonate (DIMP) at 248 nm and 262 nm as well as their UV Raman and UV absorption cross sections. Of these chemicals, only GA exhibits any significant pre-resonance enhancement. We also show that reduction of the excitation wavelength from 262 nm to 248 nm effectively shifts the Raman spectrum away from a substantial sample fluorescence background implying a significant improvement in detection capability.

(488) **Hybrid Electrokinetic Localized Surface Plasmon Resonance Platform for Biomolecule Quantification in Complex Media**

Michael R Malone[1], Raul S Rivera[1], Karl S Booksh[1]; [1]University of Delaware

Surface plasmon resonance (SPR) coupled with electro-kinetic (EK) separation serve as the detection and isolation platform for lab-on-a-chip devices aimed at biological sample analysis. The traditional freely propagating SPR technique relying on a Kretschmann configuration, a prism based set up, has been abandoned in favor of localized surface plasmon resonance (LSPR). Localized surface plasmons, optical properties of nanoparticles, are utilized here in a spectral imaging format. The LSPR features of two different geometries, spherical and tetrahedral formed through gold citrate reduction and the nanosphere lithography method respectively are characterized in the presence and absence of externally applied potential gradients. The different geometries lead to different scattering characteristics and varying LSPR effects. Merging these two complimentary techniques has powerful potential in acquiring medically relevant information by determining concentrations of a variety of biomolecules in parallel from complex biological fluids using label-free detection in concert with a robust separation scheme utilizing focusing and isolation techniques.

(489) **Designing Novel Interfaces for Probing Protein Interactions with Carbohydrates and Lipids using Surface Plasmon Resonance and SPR Imaging**

Quan Cheng[1], Matthew Linman[1]; [1]Univ of California Riverside

Protein-carbohydrate and protein-lipid interactions are involved in many important cellular signaling processes. Various diseases states including cancer cell metastasis have been linked to these interactions. Gaining a fundamental understanding of these interactions is vital to our understanding of their biological significance and to the development of pharmaceutical treatment of the diseases. Surface plasmon resonance (SPR) and associated SPR imaging technique have gained widespread acceptance as the effective tool to probe biologically relevant interactions. Our group at UCR has focused on advancement of the SPR and SPRi methodology through the creation of novel surface chemistry and new materials to enhance the analysis in real-time. In this seminar, we report the development of new interface materials to monitor protein-carbohydrate and protein-lipid interactions in real-time. In additional to spectroscopic analysis, microarray approach with SPRi for high-throughput detection of protein-based interactions will be presented. A framework to study multiple biological interactions without special sample preparation in a highly reproducible manner will be discussed. Kinetic data, analytical figures of merit, and broad-based applicability of our approach will be presented. The surface methodology present herein could be used to identify and quantify binding patterns of numerous biologically relevant systems, opening new avenues for studying biological interactions.

(490) **X-Ray Characterization of Materials in 3D**

Brian Patterson[1], George Havrilla[1], Kimberly Defriend; [1]Los Alamos National Laboratory

Two analytical techniques are moving into the forefront of materials characterization. Micro x-ray computed tomography (micro CT) and confocal micro x-ray fluorescence (confocal XRF) both use x-rays to examine a sample in very complementary ways. Micro CT uses a micro-focus x-ray source that generates a cone beam of x-rays, creating a radiographic image of the samples 2D structure. Rotating the sample while radiographs are being collected generates a tomographic data set. From this data, a computed 3D rendering, based primarily upon x-ray absorption of the material with micrometer resolution, is possible. Confocal XRF uses a broad band x-ray tube source and a monolithic polycapillary optic to focus x-rays on a material. A second optic is placed in front of a simple Si pin diode x-ray detector collects the fluorescent x-rays emitted by the sample. Because of the system geometry, a 3D confocal volume of excitation and detection is possible by overlapping the two foci. The Si pin diode detector is x-ray energy and intensity sensitive, therefore an x-ray fluorescence spectrum is collected with both the x-ray energy (which elements are present) and x-ray intensity (measuring their concentration) at every location in a 3D volume. Micro CT has the advantages of quickly gathering high resolution 2D or 3D images of the sample. Unfortunately, the final 3D image is a calculated image, and there is no elemental information (unless performed on a synchrotron). Confocal XRF is inherently slower than micro CT because images are generated one voxel at a time, but the final image can be used to determine elemental composition of the sample at each voxel independently. Several samples will be shown to compare these two techniques. Samples include measuring the density of silica aerogels, examining machined polystyrene foams, a sputtered beryllium capsule doped with copper for nuclear fusion research, and an integrated circuit surface mount resistor.

(491) **Studies of Gadolinium-Doped Zinc Telluride Semiconductors by X-Ray Photoelectron and Auger Spectroscopy**

Dale L. Perry[1], Andrew Olson[3], Erik Topp[2], Zhix Ma[1], Samuel S. Mao[1]; [1]Lawrence Berkeley National Laboratory; [2]University of California, Berkeley; [3]Carleton College

Gadolinium-doped zinc telluride (ZnTe:Gd) has been characterized by X-ray photoelectron (XPS) and X-ray induced Auger electron spectroscopy (AES) in order to determine the chemical states and shifts in electronic energy levels of the elements present in the material. Chemical shifts of gadolinium, zinc, and tellurium photoelectron and Auger lines are compared to analogous lines in various other similar compounds that have been studied. Overlapping photoelectron and Auger lines are discussed with respect to performing detailed analyses. The use of Auger parameters in the study is described. This work was supported by the U. S. DOE under Contract No. DE- AC0205CH11231 and NA-22 of the NNSA.

(492) **A Prototype Pico Liter Deposition Device to Generate Reference Deposits for Direct Elemental Analysis using Micro X-Ray Fluorescence (MXRF)**

Ursula E. A. Fittschen[1], George J. Havrilla[1];
[1]Los Alamos National Laboratory

Modified ink jet printers have been used for various purposes, where reliable deposition of small volumes is needed [1]. Just recently this technology has been introduced for analytical chemistry using a modified HP DeskJet printer [2]. In this study an HP pico liter pipette prototype (TIPS thermal inkjet picojet system) was used. Its design allows for easy exchange of solutions for deposition and selection of the deposition volume in discrete steps between 1 and 300 pL with changes of the reservoir tip with no discernible memory effects. In this work different characteristics of the spotted drops and dried residues were examined including volume, diameter of dried droplets and the mass of delivered metal ions. The aim of this work is to demonstrate the extent this device can be used for calibration purposes. Aqueous single element and multi elemental standard solutions were used. The droplets were deposited on AP1® film (polypropylene), Si-wafer, aluminum filter, Teflon filter and PVC filter. An x,y,z stage was used to adjust the distance from substrate and TIPS and to generate patterns. Two different TIPS architectures with nominal spotting of 220pL and 35pL, 10pL, 5pL and 1pL the second were tested. The delivered elemental amounts were determined using MXRF. The results from the MXRF analysis show a good correlation between the count rate and the elemental amounts calculated from the delivered volumes with a relative standard deviation between 6 and 12%. The MXRF instrument used a nominal 50 micro meter X-ray spot. Additionally, the results were compared to those obtained from NIST 1832 and 1833 both thin multi elemental film standards designed for MXRF analyses. Correlations from 4 to 27% were found depending on the elemental line. The diameter of the dried residues covered a size range from 13±0.6µm to 58±4.9µm when a 10 g/L Ni solution was jetted depending on the droplet volume. LA-UR-08-03529 [1] De Gans, B.-J. et al. Adv. Mater. (2004), 16, 203-213 [2] Fittschen, U. E. A. et al. Anal. Chem. (2008), 80, 1967-1977

(493) **Assessing and Classifying the Spatial Distribution of E. coli Contamination by Means of Spectroscopic Imaging and Chemometrics**

Frank Vogt[1], Michael Gilbert[1], Rebecca Burke[1]; [1]University of Tennessee, Dept of Chemistry

Food contaminations with E. coli bacteria are a major concern for public health. Current techniques are based on sample extractions, time-consuming sample preparations and labor-intensive analyses. We present an approach that is based on FTIR spectroscopy using little to no sample preparation. Further, determining the type of bacterial contamination that patients have been exposed to is important for proper medical treatment. Three different strains of E. coli (B, C and K12) have been utilized for assessing chemometric classification methods which are used to evaluate FTIR spectra. To detect isolated bacteria colonies, extended areas must be analyzed at sufficient spatial resolution (few micrometers) in a reasonable time. For this purpose, spectroscopic imaging, a technique that acquires a large number of spectra from different sample locations, has been utilized. To ensure short data acquisition times a focal plane array has been used in conjunction with an IR microscope. Three approaches of chemometric data analysis for strain classification have been studied: 1) By means of conventional FTIR microscopy calibration spectra are obtained from carefully prepared E. coli samples containing one strain only. By correlation analyses the spectra of image cubes are then classified into one of these three classes. 2) Multivariate Image Analysis – the spectra of an image cube undergo a PCA; then three score images are color-coded in red, green and blue. In the final result, the distribution of different spectroscopic information is displayed as a color image. 3) By means of Multivariate Cure Resolution different factors are extracted from the aforementioned carefully prepared calibration samples. These factors are then used for modeling the different spectral signatures of spectroscopic imaging data. This determines the spatial distributions of the strains in extended sample areas. Macroscopic samples must be analyzed on a microscopic scale. Microscopes facilitate the latter but only in a small field of view. For this reason, several spectroscopic data cubes are acquired from neighboring sample areas and patched together. This results in very large data sets and unreasonably long data evaluation times. To overcome this, a data compression technique utilizing 3-dimensional wavelet transforms is applied as a preprocessing step.

(494) **Interplay of Chemometrics and Large-Scale Databases**

Brian Rohrback[1], Gregory Banik[2]; [1]Infometrix, Inc.; [2]Bio-Rad Informatics Division

The pharmaceutical PAT initiative has focused more attention on the use of multivariate instruments on-line. The addition of spectrometers and chromatographs to the control world clearly creates advantage in the monitoring and understanding of critical quality attributes, but the size of the data files and the sheer number of spectra and chromatograms can overwhelm the ability of a process database to manage. In the endeavor to build a resource for process quality improvement, companies are electing to store routine spectra as well as the data used to generate the multivariate model in the first place. Chemometrics can be used in several ways to reduce this ongoing data flow and enable technicians to keep the key process-relevant information within the plant historian. In addition, technologies that have proven valuable in the exploratory data analysis and modeling stage can also be deployed to improve on spectral search and aid the choices of what needs to be retained to suit the needs of process, support and research databases. Some of the chemometric approaches can be handled as stand-alone tasks, called automatically from a digital historian or an SPC system. Others are best combined with products originally designed for spectral library functions. The target of these combinations is to facilitate tasks such as: •Mining a process start up to quickly select a subset of spectra to use in chemometric model development; •Instantly evaluate a potentially errant chromatogram to see if a similar trace has been seen in any plant at any time in the past; and •Pull in spectral residuals and execute a database query to identify the cause of off-target features.

(495) **Wavelet Transform for Near Infrared Spectral Data Mining – Single Spectrum Disease Diagnosis**

Barry Lavine[1], Nikhil Miranjakar[1], Roumiana Tsenkova[2]; [1]Department of Chemistry, Oklahoma State University; [2]Faculty of Agriculture, Department of Eng

Diffuse reflectance NIR spectroscopy and pattern recognition methods were used to develop a potential method for detection of mastitis in cows during milking. The data set, which consisted of 500 NIR spectra of raw quarter and composite milk collected over a period of 6 months from 75 mastitic and healthy cows, was subjected to multivariate analysis to characterize and decode the complex signal patterns present in the data. A two-step procedure developed in our laboratory for analyzing diffuse reflectance spectral data was applied to this data set. First, the wavelet packet transform was used to denoise and deconvolute the spectra by decomposing each spectrum into wavelet coefficients that represent both the high and low frequency components of the signal. This decomposition process is iterated through successive wavelet packets until the required level of signal decomposition is achieved. Second, a genetic algorithm for pattern recognition analysis was

used to identify wavelet coefficients that could classify the diffuse reflectance spectra into the proper groups (mastitis versus normal) based on chemical differences. The pattern recognition GA employed both supervised and unsupervised learning to identify wavelet coefficients that optimize clustering of the spectra by diseased state in a plot of the two or three largest principal components of the data. Because principal components maximize variance, the bulk of the information encoded by the selected wavelet coefficients is about differences between classes in the data set. The pattern recognition GA identified informative wavelet coefficients by sampling key feature subsets, scoring their principal component plots, and tracking those samples that were most difficult to classify. The boosting routine used this information to steer the population to an optimal solution. After 300 generations, the pattern recognition GA identified a set of wavelet coefficients from which a discriminant could be developed. This result, although preliminary, is a strong indication of real differences in the NIR spectra of milk from healthy and mastitic cows. Furthermore, the period of lactation and the quarter from which the milk sample was obtained did not appear to be a significant covariant in this classification problem.

(496) **The Chemometrics Leading to Robust Calibrations for Low Signal-to-Noise Applications**

Jerry Workman; [1]Luminous Medical Incorporated

Robust modeling for challenging spectroscopy applications requires a comprehensive strategy for photon detection through to analyte prediction. This strategy initially involves instrument design characteristics specific to the analytical application requirements. In addition a series of automated expert algorithms must include metrics for evaluation of instrument status and modeling functionality in near real time. Calibration strategies include: experimental design optimization relative to sample characteristics, data preprocessing strategies, outlier detection methods, upset condition monitoring, and model applicability and integrity metrics. This paper discusses each of these issues and the selection criteria used for complex analyte signal discrimination through to instrument design and integration of multivariate algorithms for accurate prediction and monitoring of challenging spectroscopic analyte signals.

(497) **Developing Micro/Nano Solutions for Bioanalytical Chemistry using Low Resolution Tools**

Emanuel Carrilho[1]; [1]University of São Paulo

Bioanalytical Chemistry is a broad subject and an enormous field of opportunities. T o demonstrate its intrinsic inter and multidisciplinarity, we chose to develop both instrumentation and methods by bringing together the analytical validation and the biological specificity. The instrumentation is centered in microfluidic channels patterned over a varied of substrates ranging in the micro and nano scale features over glass, plastic, and paper, exploring fabrication tools at all levels of resolution. Examples of methods cover molecular biology tools and bioaffinity interaction and recognition.

(498) **DNA-Based Diagnosis of Greenhouse Fungal Pathogens on a 96-Channel Microfluidic Microarray Chip**

Paul Li[1], Lin Wang[1]; [1]Simon Fraser University

We have employed a microfluidic method in which probe creation does not require pin-spotting and fast hybridization is conducted on the same microarray chip for the detection of 3 greenhouse pathogens (Botrytis cinerea, Didymella bryoniae and Botrytis squamosa). In this method, 96 oligonucleotide probe line arrays were created on a glass substrate by a microfluidic printing method. Then, low amount of the DNA samples (1fmol oligonucelotides or PCR products) were introduced into the microchannels that were orthogonal to these probe lines. The hybridizations of 96 samples (21-mer complementary oligonuleotides and ~260-bp PCR products) were fulfilled at the channel-probe line intersections and in a short time (in 3 minutes). The optimization of probe immobilization and sample hybridization were described in detail. We have successfully detected and discriminated between two 260-bp PCR products with one-base-pair difference from closely related greenhouse plant fungal pathogens (Botrytis cinerea and Botrytis squamosa).

(499) **Biomedical Devices and Biosensors Based On Protein Attachment to Nanoparticles**

Alexey Vertegel[1]; [1]Clemson University

Enzymes as therapeutic agents offer several key advantages because of their high catalytic activity and unique selectivity. However, enzymes are often unstable, especially *in vivo*, and may be toxic. Use of nanoparticles as the protein carriers offers several important advantages. Enzymes conjugated to nanoparticles are known to possess both enhanced stability and high activity. Nanoparticles can also be used for targeted delivery, which reduces systemic toxicity of the attached enzymes. Our work is focused on the design of therapeutic nanodevices based on simultaneous conjugation of two of more functional proteins to the same nanoparticle. In the simplest case, such system can consist of a functional enzyme and targeting antibody, attached to a nanoparticle. Such approach has been used for the creation of prototypical therapeutic devices for dissolution of blood clots. We showed that simultaneous covalent attachment of targeting antifibrin antibody and tissue plasminogen activator (tPA) to 40 nm polystyrene latex nanoparticles results in effective targeting of tPA to fibrin clots and high fibrinolysis rates. This system is thus a promising therapeutic agent for post-myocardial infarction and stroke treatments. Other projects include targeted delivery of antimicrobial enzymes to clinically important bacteria, and nanodevices for treatment of secondary spinal cord injury based on simultaneous attachment of enzymes that address free-radical damage to neurons (superoxide dismutase) and glutamatergic toxicity (glutamate receptor ligand) to polybutylcyanoacrylate nanoparticles (provide targeted delivery to central nervous system). In more complicated designs, three or more different proteins can be simultaneously attached to nanoparticles. Thus, our approach can provide a new platform technology with a broad spectrum of applications.

(500) **Smaller is Better: Microfluidics Meet Surfaces**

Carlos D. Garcia[1], Maria Fernanda Mora[1], Carla E. Giacomelli[1,2], Jennifer Wehmeyer[1], Rena Bizios[1], Arturo A. Ayon[1]; [1]UT San Antonio; [2]Univ. Nacional de Cordoba - Argentina

Since their initial development, capillary electrophoresis microchips (uchip-CE) have shown a tremendous improvement in their capabilities to deal with real samples. In this regard, rapid, inexpensive and sensitive detection methods are absolutely necessary to achieve the goal of a true point-of-care testing device. In conjunction with microchips, electrochemical detection (ECD) is particularly attractive because of its analytical performance, versatility, and compatibility with microfabrication procedures. Considering the hypothesis that simple surface modifications in surface chemistry would produce significant improvements in the performance of uchip-CE-ECD, the most recent results from our lab will be discussed in this presentation. Along with basic background information, the effects of dynamic coatings on the separation and on electrochemical detection at the microchip scale will be discussed. Then, two strategies to integrate enzyme reactors and biosensors to the microchip will be presented. More information can be found at http://utsa.edu/chem/faculty/carlosGarcia/Garcia.html

(501) **Integrated Microfluidic System for Detection of Biomarkers in Biological Samples**

Hsiang-Yu Wang, Weichun Yang, Xiuhua Sun, Adam Woolley; [1]Brigham Young University

The presence and levels of certain biomarkers in an individual serve as key indicators in the diagnosis of cancers, Alzheimer's disease and many other illnesses. Traditional methods for detecting these biomolecules often involve multiple, complex and laborious processes. Microfluidic systems for biomarker detection are advantageous compared with conventional methods in several ways. First, integration of several processes into one device dramatically simplifies tasks and decreases the required amount of labor. Moreover, tiny sample size needed and potential for high sensitivity in detecting biomolecules make microfluidic systems an ideal platform for trace molecule analysis. Here, we focus on developing polymer-based, integrated microfluidic devices for the detection of targeted biomarkers inside cells or body fluids. We have successfully fabricated microchips from poly(methyl methacrylate) and performed separation of model analytes using these devices. A non-covalent labeling strategy for the fluorescence tagging of targeted biomolecules after separation has also been tested. We are presently designing a more sophisticated system for the extraction, concentration and detection of biomarkers in biomixtures. These devices should improve sensitivity and throughput in biomarker detection, while reducing assay cost, labor and complexity. This rapid and effective platform should provide great benefits for clinical diagnosis, medical research, and other areas in life sciences requiring detection of targeted molecules.

(502) **Active MOS Capacitive Sensor Array for Lab-on-a-Chip Applications**

Manu Sebastian Mannoor[1], Teena James[1]; [1]New Jersey Institute of Technology

Lab-On a-Chip devices represents a synergistic combination of microelectronics technology and molecular biology, which holds the promise of improving, the way many important molecular analyses are performed. In this work we introduce an active Metal-Oxide-Semiconductor (MOS) capacitive sensor for fast, massively parallel and highly selective nucleic acid analysis. Arrays of 50-100 Si-SiO2-Au sensing areas were fabricated using standard Si fabrication techniques. Multiple probe sequences were immobilized on the Au electrodes using alkyl thiol linkages. The immobilization and hybridization events were monitored by measuring the Capacitance-Voltage (C-V) characteristics across the sensing elements. Due to the intrinsic negative charge on the DNA molecules, during the immobilization of the single stranded probe sequence on the Au metal gate, the C-V characteristics show a measurable shift in the direction of negative gate bias. The presence of an additional layer of negatively charged DNA molecules due to hybridization with complimentary targets enhances this effect. Our experiments demonstrate that the rate and selectivity of hybridization reaction can be drastically improved by the application of an external electric field. Since oligomers in solution carry a net negative charge they can be transported towards the probe molecules immobilized on the sensor surface (Au) by application of a positive bias on the Au surface with respect to an electrode in solution. This electric field assisted transport of oligomers towards the immobilized probes will drastically enhance the rate of hybridization event. The movement of the target nucleotide molecules toward the immobilized probe sequences, facilitated by electric field can result in a concentrating effect of the target molecules near the surface enabling the binding of probe and target sequences at a much higher rate. The electric field induced transport of nucleotide molecules is also used for enhancing the selectivity of the sensing process. The sensor selectivity depends on the specificity of the binding between the target and probe sequences. The unhybridized target molecules which stay non-specifically bound on the sensor surface (Au electrode) will also contribute to the sensing signal. By applying an appropriate negative bias on the Gold (Au) surface these nonspecific target nucleotide molecules is released and repelled away from the sensing area, thereby eliminating their effect on the sensing signal. By adjusting the electric field to the appropriate level, selective dehybridization of the target-probe pair is also demonstrated, which is promising for single nucleotide polymorphism (SNP) analysis. This result is confirmed by the use for fluorescently labeled target sequences.

(503) **Luminescent Pyridine-bis(oxazoline) Complexes of Eu(III) and Tb(III)**

Ana de Bettencourt-Dias; [1]University of Nevada, Reno

Our group is interested in luminescent lanthanide ion Ln(III) complexes, in which the metal-centered emission is sensitized through the coordinated ligands.[1-3] Recently we started studying pyridine-bis(oxazoline)[4] as well as bis(pyridyl)amine as chelating and sensitizing ligands for Ln(III) emission. The structural and spectroscopic characterization of the resulting, highly luminescent lanthanide ion complexes and of their solutions and the improvement of ligand design based on observed efficiency trends will be discussed. 1. de Bettencourt-Dias, A., New isophthalato-based 2D coordination polymers of Eu(III), Gd(III) and Tb(III) - Enhancement of the terbium-centered luminescence through thiophene derivatization. Inorg. Chem. 2005, 44, 2734-2741. 2. de Bettencourt-Dias, A.; Viswanathan, S., Luminescent Eu(III) and Tb(III) complexes of a nitrothiophenylbenzoic acid derivative: structure and luminescence studies. Chem. Commun. 2004, 1024-1025. 3. de Bettencourt-Dias, A.; Viswanathan, S.; Ruddy, K., Intermolecular forces and functional group effects in the packing structure of thiophene derivatives. Cryst. Growth Des. 2005, 5, 1477-1484. 4. de Bettencourt-Dias, A.; Viswanathan, S.; Rollett, A., Thiophene-derivatized pybox and its highly luminescent lanthanide ion complexes. J. Am. Chem. Soc. 2007, 129, 15436-15437

(504) **Mobility and Diffusivity of Molecules Confined in Silica-Nanochannel as Studied by Time-Resolved Fluorescence Spectroscopy**

Toshio Kamijo[1], Akira Yamaguchi[2], Norio Teramae[3]; [1]Tohoku University

Diffusivities of solutes inside silica-nanochannel with a few to ten nm in diameter have been known to differ from those in bulk due to adsorption at the inner silica-wall of and/or rigidity of solvent molecules confined in the silica-nanochannel. Hence, the solute's diffusivity inside the one dimensional (1D) silica-nanochannel is expected to be different from bulk and that new separation mode could be realized, when the 1D silica-nanochannel is used as a nanofluidic channel for separation of solutes. Recently, we developed a hybrid nanoporous membrane composed of assemblies of silica-nanochannels inside columnar pores of a porous anodic alumina membrane (Yamaguchi et al., Nature Mater., 2004, 3, 337). Since the 1D silica-nanochannels are perpendicularly oriented to the membrane surface, they can be used for nanofluidic channels by embedding the membrane between two solution phases; for example, a separation membrane with a capability of nanometer-order size-exclusive separation and a chromatographic column in a HPLC system to separate small molecules. To clarify the separation mode in the 1D silica-nanochannel, diffusivity as well as mobilities of solutes and solvents are important issues to be solved. In the present study, the diffusivity and mobility of both solvent and solute molecules confined in the silica-nanochannel were examined on the basis of solvation relaxation time by time-

resolved fluorescence mesurments using C153 as a fluorescence probe. We examined solvation relaxation times using a series of alcohols with different alkyl chains. The solvation relaxation times obtained for alcohols with short alkyl chain (ethanol and butanol) confined in the silica-nanochannel (3.1 nm in diameter) were remarkably larger than those in bulk, whereas such remarkable difference was not observed for alcohols with long alkyl chains (hexanol and decanol). These results indicate that the motion of alcohols with short alkyl chain is restricted strongly inside the silica-nanochannel, suggesting that this restricted motion results in slowing down of salvation relaxation time in alcohol with a short alkyl chain confined in the silica-nanochacnnel.

(505) **Multiparameter Fluorescence Fluctuation Spectroscopy for Ultrasensitive Analysis of Nucleic Acids**

Alan Van Orden[1], Jaemyeong Jung[1], Keir Fogarty[1], Jeff McPhee[1], Eric Scott[1]; [1]Colorado State University

This presentation will discuss the development and application of multiparameter fluorescence fluctuation spectroscopy for monitoring the dynamic properties of RNA, DNA, and RNA- and DNA-protein complexes. Multiparameter fluorescence fluctuation spectroscopy combines the information content of single-beam fluorescence autocorrelation spectroscopy, dual-beam fluorescence cross-correlation spectroscopy, and photon counting histogram analysis. Based on this information, thermodynamic, kinetic, and mechanistic parameters about the folding/ unfolding and binding/ unbinding behavior can be uncovered. Combining these detection methods with continuous flow capillary electrophoresis provides information about the ionic atmosphere of the biomolecules being probed, and enables us to address the role of this atmosphere on the structural and dynamic properties of the biomolecules in solution.

(506) **Assays On-the-Fly: Rapid Identification of Aerosols using Fluorescent Beacons**

Matthew Hart[1], Horn-Bond Lin[1], Casey Jacobsen[1], Jay Eversole[1], Charles Merritt[1]; [1]Naval Research Laboratory

We are developing a method to label specific chemical or biological aerosols on-the-fly with fluorescent markers using an electrospray. Labeling molecules, with affinities to specific surface epitopes and produce a detectable change in emission characteristics upon binding, will be used to coat aerosols in an air stream. Specifically targeted aerosols could be labeled in this manner, allowing single particle identification in near real-time using a simple laser-induced fluorescence technique. This method would permit the use of solutions containing mixtures of different markers to simultaneously detect/identify multiple types of chemical or biological particles. In effect we would perform an immunoassay on the surface of individual particles as they flow, eliminating the need to sample into liquid or perform a washing process. The specifically labeled particles would then easily contrast among the dynamic ambient background of aerosols, which continues to be a formidable issue in the pursuit of rapid detection methods. Topics that are currently being investigated include the kinetics of molecular surface binding to an aerosol in flight and airflow modeling geometries for efficient particle coating.

(507) **Competitive Homogeneous Fluorescence Immunoassay (FIA) for Hapten Detection**

Annette Kupstat[1], Michael U. Kumke[1], Reinhard Niessner[2], Dietmar Knopp[2]; [1]University of Potsdam; [2]Technische Universitaet Muenchen

Homogeneous fluorescence immunoassays (FIA) are very attractive for the development of potential point-of-care (POC) tests in clinical/medical diagnostics as they are separation-free, making automation easy and permitting simple adaptation to existing automation. Benzo[a]pyrene (BaP) is highly carcinogenic and among other compounds responsible for lung cancer of smokers. Here, first results of a sensitive competitive homogeneous FIA for the detection of BaP (and metabolites) in human urine based on a new fluorescence probe and a tailor-made monoclonal antibody (Mab13) are presented. As the new fluorescence probe the organic dye sulforhodamine B (SRB) was covalently linked to the target analyte BaP. In the first experiments the photophysical parameters such as fluorescence quantum yield, fluorescence anisotropy, and fluorescence decay times were evaluated. The absorption spectrum of the fluorescent probe compared to those of the single fluorophores revealed the significant electronic coupling. A bathochromic shift of about 20 nm was found in the absorption related to the BaP moiety relative to free BaP. From the steady state and time-resolved fluorescence experiments it was concluded that an efficient intramolecular energy transfer occurs, in which BaP acts as the donor and SRB as the acceptor. In both measurements a quenching efficiency of about 60 percent was found. Switching from organic solvents like methanol to aqueous buffer systems a complete quenching of the BaP related fluorescence was observed. Upon addition of Mab13 a drastic increase of the BaP related fluorescence was found. In addition, the fluorescence anisotropy was increased as well. Both experimental results demonstrate the binding of the fluorescence probe to Mab13 and can be anticipated as detection scheme in a future homogeneous FIA application. The antibody-hapten binding was further analyzed in single molecule spectroscopy (SMS) experiments.

(508) **Room-Temperature Fluorescence Excitation-Emission Matrices for Comparing Textile Fibers as Physical Evidence**

Hector Goicoechea[2], Mathew Rex[1], Andres Campiglia[1]; [1]University of Central Florida; [2]Universidad Nacional del Litoral

This presentation focuses on the development of nondestructive analytical methodology capable of providing highly discriminating identification of textile fibers encountered as physical evidence in criminal investigations. We answer pertinent questions towards the successful achievement of our final goal. Experimental data collected via Room-Temperature Fluorescence (RTF) Spectroscopy and High-Performance Liquid Chromatography demonstrate the value of fluorescent impurities as reproducible sources of fiber characterization. The potential of room-temperature fluorescence excitation – emission matrices (RTF-EEM) as a valuable data format for comparing textile dyestuffs and/or fluorescence impurities without the need of previous chromatographic separation is demonstrated.

(509) **Catalytic Transformations of Biological Macromolecules in Single Nanopores Probed by 4ð Single Molecule Cross-Correlation**

Paul Bohn[2], Travis King[1,2], Zhen Wang[2]; [1]University of Illinois-Urbana-Champaign; [2]University of Notre Dame

Two goals of our work in nanofluidics are: (a) to develop an understanding of differential transport based on charge and molecular shape through optical and electronic measurements of single molecule transport in single, high-aspect-ratio cylindrical nanopores; and (b) to exploit intrapore molecular recognition events to understand the manner in which catalysis occurs in geometrically-confined spaces under flow. The approach to meeting these objectives centers on the creation of a known population of surface immobilized horseradish peroxidase (HRP) confined to a well-defined annulus in the center of a single nanopore and exploring the catalytic production of luminescent species through cross-correlation measurements in a specially

constructed dual-axis, counterpropagating 4ð laser induced fluorescence microscope. The construction and operation of the microscope will be described as well as its application to studying the kinetics of enzymatic reactions in geometrically constrained environments.

(510) **SERS - A Single Molecule Tool**

Katrin Kneipp[1,2], Harald Kneipp[1]; [1]Harvard University Medical School; [2]Harvard-MIT Division of Health Sciences

The remarkable 14-order-of-magnitude enhancement that can occur during Raman scattering from molecules on silver and gold nanostructures turns the normally weak inelastic scattering effect into a single-molecule probe. Structurally selective detection of single molecules and quantification of matter by counting single molecules represent the ultimate limit in chemical analysis and trace detection. The talk discusses the physics behind single molecule SERS including proofs for single molecule detection, as well the potential of extending single molecule SERS spectroscopy to two-photon excitation

(511) **Extreme Biosensing with Plasmons, Nanoparticles and Surface Enzyme Chemistry**

Robert Corn; [1]Chem Dept, Univ. of California-Irvine

Surface bioaffinity biosensors have become invaluable biotechnological tools for the rapid, multiplexed detection of biomolecules. In the last decade, a number of surface-sensitive spectroscopic techniques based on changes in the local optical index of refraction near an interface upon adsorption have emerged as attractive alternatives to traditional fluorescence-based detection methods for surface bioaffinity biosensing. In this talk we will discuss the fundamental issues in surface bioaffinity measurements and then describe our recent efforts to create the next generation of ultrasensitive biosensors which use a combination of surface enzyme chemistry and gold nanoparticle surface gratings. For example, nanoparticles and poly(A) RNA polymerase can be used together for ultrasensitive microRNA profiling measurements at femtomolar concentrations.

(512) **Nanoparticle Optical Property Modeling**

George Schatz; [1]Northwestern University

This talk will describe recent electrodynamics studies that my group has been involved in concerning the optical properties of silver and gold nanoparticles and nanostructures. This work has involved collaborations with Richard Van Duyne concerning extinction and SERS, with Chad Mirkin concerning plasmon excitation in gold nanodisk structures, and with Teri Odom concerning nanoparticle and nanohole array structures. Particular emphasis will be on the use of optical property measurements to detect molecules on the particle surfaces.

(513) **Nanoparticulate Quantitation Labels Based on SERS**

Michael Natan[1]; [1]Oxonica Materials Inc.

Oxonica Materials Inc. has developed a novel, patented nanoparticulate optical quantitation label based on surface enhanced Raman scattering (SERS). The particles comprise a 60-nm diameter Au nanoparticle cores (either as single particles or small aggregates), a layer of one of a group of organic molecules (the "reporter"), and a 30-nm thick silica (glass) coating. The spectrum of each tag consists solely of the Raman signal from the adsorbed reporter. By using different reporters, a large number of spectrally unique tags can be prepared, allowing a high level of multiplexing. The glass coating renders the particles exceptionally robust to changes in pH, temperature, and ionic strength, and yet enables facile subsequent chemical and/or biochemical functionalization. Moreover, because the particles are excited and detected in the near-IR, they are perfectly suited for use in complex, dirty matrices or materials that would confound results from traditional optical labels (e.g. fluorophores). Applications to multiplexed detection of cardiac markers for point-of-care diagnostics will be described.

(514) **Spectroscopic Studies of Environmentally Important Processes at Aqueous Surfaces**

Geraldine Richmond; [1]University of Oregon

Although the special properties of water have been valued and appreciated for centuries, as scientists we continue to be perplexed by the molecular make-up of water in all its forms. Equally perplexing is the surface of water, a surface that is involved in some of most important reactions in our atmosphere, a surface that can sculpt the landscape as it flows past rocks and soils, a surface that can break down the strongest of metals, and a surface across which essential nutrients and ions are constantly exchanged in life-sustaining processes in our bodies. In our laboratory we study environmentally important processes at aqueous surfaces using laser based spectroscopic techniques and molecular dynamics simulations. I will focus my talk on our recent studies of the intriguing behavior of water surfaces when in contact with molecules of importance in our environment.

(515) **Targeted Mass Spectrometric Immunoassays for Population Proteomics**

Dobrin Nedelkov; [1]Intrinsic Bioprobes Inc.

The need to systematically analyze protein variants across human populations is indisputable. Mass spectrometry is a unique approach capable of providing identifying information about specific protein structural modifications, without a priori knowledge of the modification. To enable high-throughput analysis of such protein modifications, we have developed affinity pipettes for selective retrieval of target proteins from complex biological fluids in preparation for mass spectrometric analysis. The resulting mass spectrometric immunoassays have been applied across large cohorts in an undertaking known as Population Proteomics - large-scale investigation of human proteins across and within populations to define and correlate protein variations. Such studies of protein diversity also explore the association of protein modifications with specific diseases, facilitating the discovery and validation of novel protein biomarkers. Presented here are the fundamentals of the mass spectrometric immunoassay approach and the results from several studies investigating human plasma protein microheterogeneity across the healthy population in the United States, as well as the correlation of specific protein variants with the presence of the disease.

(516) **Combining Protein Microarrays and Mass Spectrometry**

Robert J Cotter[1], Kenyon M Evans-Nguyen[1], Dwella M Nelson[1], Sheng-Ce Tao[1], Heng Zhu[1]; [1]Johns Hopkins University School of Medicine

We have recently demonstrated a method for MALDI-TOF analysis of protein arrays using patterned porous gold (PPG) surfaces. Gold-coated microscope slides are electrochemically functionalized and carboxy-terminated alkanethiol solution is "printed" to yield a pattern of hydrophilic self-assembled monolayer (SAM) spots. The substrate is then immersed in a hydrophobic, methyl-terminated alkanethiol solution to form a hydrophobic SAM background. Proteins or antibodies are covalently immobilized on the hydrophilic, carboxy-terminated spots. Mass spectra, MS/MS data, and MS images of species bound at antibody arrays probed with antigen-spiked solutions are then obtained using a Shimadzu CFR+ time-of-flight mass spectrometer. The enhanced surface area of the porous gold allows more protein to be immobilized in a given spot size, increasing the quantity of bound ligand and improving the limit of detection by an order of

magnitude. In addition, the high surface area of the porous gold amplifies the hydrophobicity imparted by the methyl-terminated SAMs, rendering these regions superhydrophobic. The superhydrophobic/hydrophilic pattern then contains the organic matrix solution within the hydrophilic protein spots and prevents cross-contamination due to matrix solution spreading between spots. Recently we have developed a lectin array with 94 distinct lectins on PPG. Glycoproteins captured at spots on the lectin array can be digested with trypsin on-spot and identified using mass fingerprinting. Additionally, lectin arrays on PPG can be probed with glycopeptides resulting from the trypsin digestion of glycoproteins in solution. MS interrogation of the captured glycopeptides yields information about the attached carbohydrates based on the spectra as well as the known affinities of the immobilized lectins.

(517) **Performing Enzyme Activity Assays with SAMs & Mass Spectrometry**

Steven Patrie[1,2]; [1]University of Texas Southwestern Medical Center; [2]University of Texas Dallas

We have previously shown that diverse protein and PTM-biomarkers can be rapidly isolated from humoral fluids with SAM-based immunosensors followed by characterization with SAMDI-TOF MS. This report expands the utility of our SAMDI approach to enzyme activity assays. We show optimal processing of immobilized protein and peptide substrates by endogenous enzymes present in humoral fluids. We will further apply the SAMDI approach to characterize clinically relevant enzyme activities in autoimmune disorders where protease activities perpetuate the immunological response.

(518) **Interfacing High-Performance Separation Systems with New High-Speed MALDI-TOF Mass Spectrometry**

Marvin Vestal[1], Stephen Hatton[1], Kevin Hayden[1]; [1]Virgin Instruments Corp.

A new family of high-performance MALDI-TOF systems has been developed using a modular design approach. Emphasis is on simplicity, reliability, and minimum cost consistent with high performance. Many of the major components are common to all systems, including a large-format (102x108 mm) sample plate and plate handling system with motion control, the laser optics and controls, vacuum system, digitizer and computer, and several electronics modules. A departure from earlier designs involves operating the ion source at or near ground potential with the drift space at elevated potential for analyzers requiring higher ion accelerating voltages. All of these instruments employ 5 khz lasers providing data acquisition 25 times faster than any existing commercial instrument. Novel MALDI-TOF sample plates employing collimated-hole structures allow capture and concentration of samples such as peptides, proteins and metabolites while simultaneously acting as a sink for carrier solvents. The plates provide an efficient interface between separation and MALDI mass spectrometry. With reversed-phase LC separation these plates quantitatively capture samples eluting at flow rates about one hundred times higher than with current LC-MALDI and several hundred times higher than current LC-ESI protocols. This allows separations employing orders of magnitude greater initial sample capacities to be efficiently coupled to MS and MS-MS and specifically addresses the issue of dynamic range of sample concentration as the primary bottleneck limiting the utility of mass spectrometry as a tool for global analyses of biological systems. Recent applications of these new sample plates and MALDI-TOF instruments to tissue imaging, direct analysis of 2-D gels, and protein arrays are described.

(519) **Micropatterned Fluid Lipid Bilayers Created using a Continuous Flow Microspotter**

Kathryn Smith[1], Bruce Gale[2], John Conboy[1]; [1]Department of Chemistry, University of Utah; [2]Department of Mechanical Engineering

Micropatterned lipid bilayer arrays (MLBAs) are attractive platforms for the high-throughput detection and analysis of biomolecules such as proteins because of their high resistance to nonspecific biomolecule adsorption and non-fouling nature. We have developed a new method for creating MLBAs using a 3D microfluidic system. An array of fluid lipid membranes is patterned onto a glass substrate using a continuous flow microspotter (CFM™). The microspotter consists of a series of individually addressable microchannels, allowing the production of 48 multi-component bilayers on a single substrate. These arrays are shown to be good models of biological membranes, allowing for a diverse assortment of biological and chemical interactions to be explored in a controlled manner *in vitro*. Protein-ligand and small molecule-membrane binding on MLBAs will be discussed. The system's capability of performing multianalyte assays has potential applications in many fields such as biosensing, drug discovery, proteomics and clinical diagnostics.

(520) **Tissue Imaging of Antitumor Drugs with MALDI-TOF/TOF and MALDI-FTMS**

Emily Creedon[2], Stefen Laukien[2], Paul Kowalski[1], Jane-Marie Kowalski[1], Michael Easterling[1], Katherine Kellersberger[1], Claire Sauvageot[3], Nathalie Agar[4]; [1]Bruker Daltonics; [2]The Rivers School; [3]Dana Farber Cancer Inst., Harvard Med; [4]Brigham & Women's Hospital, Harvard Med

Matrix Assisted Laser Desorption Ionization - Time of Flight / Time of Flight (MALDI-TOF/TOF) was used successfully to detect and image the distribution of small molecule drugs in tissue specimens. The two drugs in this study, temozolomide (mw: 194.06 Da) and erlotinib (mw: 393.17 Da), are, respectively, used and under investigation for use as adjuvant treatment of malignant brain tumors by interfering with cell growth. Tissue specimens from mice that were treated orally with either temozolomide or erlotinib were imaged using an Ultraflex III MALDI-TOF/TOF and a MALDI Fourier Transform Mass Spectrometer (FTMS) (Bruker Corp., Billerica, MA) to evaluate drug distribution in selected organs. Temozolomide was found in brain and liver tissue, while erlotinib was found in liver and kidney tissue. The distribution of erlotinib was confirmed by MALDI FTMS, by means of the FTMS' high resolution and high mass accuracy. The MALDI TOF-TOF method proved useful by way of selective ion monitoring with tandem mass spectrometry analysis (TOF/TOF) to confirm the identity of the substance in question in the presence of interfering substances from the tissue. The TOF-TOF mode isolates parent ions, fragments them, and provides a spectrum of the resulting fragment ions. Since every parent ion generates a unique fragmentation pattern, the identity of molecules can be confirmed by interpreting this fragment spectrum. MALDI Mass Spectrometry Imaging (MSI) displays the drug's spatial distribution in the tissue by providing a pixelated image, with a color gradient corresponding to the intensity of the drug signal. The presented results demonstrate the ability to detect and to resolve spatial distribution of a drug directly from tissue specimens using two distinct mass spectrometry approaches. The significance of the information is enhanced by co-registering the molecular images to high-resolution digital pictures of the tissue stained to reveal histopathological features.

(521) **MC-ICPMS: The Year in Review**

Charles Douthitt; [1]Thermo Scientific

The first MC-ICPMS, the Plasma 54, was introduced by VG Elemental in 1992. While there were certainly high hopes that the combination of an ICP source and a TIMS collector array would lead to a very interesting instrument, nobody really had any idea of how interesting it would become. 15 years later, there are now >200 MC-ICPMS installed in 32 countries around the world, and >2100 papers in the refereed literature, and the interest in the technique shows no signs of slacking off. At the time of writing, there are two manufacturers (down from a high of four) and the size of the market is running around 15 units per year, worldwide. The latest hardware developments include increasing implementation of on-line chromatography, both LC and GC; the commercial introduction of femtosecond lasers. Application highlights include high precision measurements of Cl, Br, S and Se, continued development of high precision measurements of U-series allowing unprecedented resolution of the recent time scale recorded in speleothems, and progress in dating of zircons by combined U-Pb and Lu-Hf.

(522) **Lead Isotopic Analysis as a Versatile Tool for Provenance Determination**

Frank Vanhaecke[1], Eleonora Balliana[1,2], Carlo Barbante[2], Christophe Cloquet[3,1], David De Muynck[1], Esperanza Garcia-Ruiz[4], Paz Marzo[4], Martin Resano[4], Paul Vallelonga[2], ; [1]Ghent University, Belgium; [2]Ca'Foscari Uni + IDPA-CNR, Venice, Italy; [3]CRPG - Nancy, France; [4]University of Zaragoza, Spain

The isotopic composition of Pb shows natural variations because three of its isotopes are radiogenic. As a result, Pb isotopic analysis – preferably carried out using multi-collector ICP - mass spectrometry – can be deployed for provenancing studies. In this presentation, real-life applications from various fields will be discussed. Antarctic ice can be considered as a chronological archive, documenting changes in the composition of the atmosphere over long periods of time. By drilling ice cores, this "archive" can be investigated and such a study has shown changes in the concentration of Pb in the ice layers accompanied by significant variations in the isotopic composition of Pb. This observation is attributed to changes in the source areas and different transport mechanisms over glacial/interglacial time periods and to the development of industrial activities in the Southern hemisphere in more recent times. In an attempt to obtain some insight into the Potential Source Areas (PSA) of the Pb influx, soil was sampled at different locations in South America, South Africa, Australia and New Zealand. The isotopic composition of Pb in these soil samples was determined and the results obtained compared to the Pb isotopic signature in the ice core. Also another study focused on Pb in the environment, but on a much more local scale. Lichen (Hypogymnia physodes) was sampled from the bark of a tree and was transplanted to five different sites: the reference site itself, two peri-urban sites, a site in proximity of a densely trafficked highway and a final one close to industrial activities (all of which located in the NE part of France). On each site, two different set-ups were used, one in which the lichen was covered by a Plexiglas plate, protecting it from direct wet deposition, and another, in which the lichen was not covered. Both the concentration of Pb and its isotopic composition were monitored as a function of time. Interpretation of the data obtained could not be accomplished on the basis of Pb coming from different sources and thus showing a different isotopic composition only, and the effect of a different Pb loading of the fine and the coarse fraction of atmospheric aerosol had to be taken into account. A final study focused onto the investigation of Medieval Spanish glazed ceramics. By selectively probing the glaze layer via laser ablation, the isotopic composition of the abundantly present Pb could be determined and conclusions could be drawn as to the origin of the Pb used in the manufacturing of the artefacts.

(523) **Mo Stable Isotope Fractionation: From Marvel to Mechanism**

Laura Wasylenki[1], Tracy Lund[1], Colin Weeks[2], Thomas Spiro[2], John Bargar[3], Ariel Anbar[1]; [1]Arizona State University; [2]University of Washington; [3]Stanford Synchrotron Research Laboratory

The advent of MC-ICP-MS has opened up vast new frontiers in isotope science; elements from lithium to uranium are now known to fractionate during atmospheric, biological, geological, oceanic, and extraterrestrial processes. One of the first "non-traditional" stable isotope systems studied was molybdenum, which fractionates strongly (0.9‰/amu) between seawater and ferromanganese sediments. This phenomenon is of interest to geochemists studying the early earth, as Mo isotope signatures in ancient rocks reflect the degree to which the ancient ocean was oxygenated [1]. Using a combination of experimental, computational, and analytical methods, we determined the molecular-scale mechanism by which adsorption of Mo to birnessite (Mn oxyhydroxide) causes such a surprisingly large fractionation of Mo isotopes (0.9‰/amu). Our work with Mo has led us to a general hypothesis about how large isotope effects arise during adsorption of metals to minerals or other substrates. From simple experiments we learned that, while the fraction of Mo adsorbed takes >72 hours to reach steady state, isotopic fractionation between dissolved and adsorbed Mo is constant as a function of time and amount adsorbed. This kinetic discrepancy led us to suspect that isotope exchange occurs between MoO42-, the predominant aqueous species, and a trace aqueous species enriched in light isotopes that preferentially adsorbs to birnessite [2]. Density functional theory calculations identified MoO3(H2O)3 as this trace species [3], suggesting that octahedral coordination of Mo in MoO3(H2O)3 versus tetrahedral coordination in MoO42- drives the isotope effect. Indeed, EXAFS patterns indicate that adsorbed Mo is in octahedral coordination. Interestingly, Mo adsorbed to ferrihydrite (Fe oxyhydroxide) fractionates by only 0.45‰/amu. Preliminary fitting of EXAFS spectra for this system indicates a mixture of tetrahedrally- and octahedrally-coordinated Mo on the surface. Thus sorbent surface structure is also a critical control on isotope fractionation. Mechanistic understanding of isotope fractionation during metal adsorption will likely be a useful new tool for investigating interactions between dissolved metals and solid surfaces. [1] Anbar and Rouxel (2007) Ann. Rev. Earth. Sci. 35, 717. [2] Wasylenki et al., in revision, Geochim. Cosmochim. Acta. [3] Weeks et al. (2007) J. Phys. Chem. A. 111, 12434.

(524) **Advances in High-Precision U-Series Analyses using MC-ICPMS**

Victor Polyak[1], Yemane Asmerom[1]; [1]University of New Mexico

Uranium-series (U-series) isotope measurements involve extreme ratios (> 10^6 in the case of $^{232}Th/^{230}Th$ in silicate rocks and minerals) and elements with low ionization efficiency [e.g. ~ 10^{-4} for Th by thermal ionization mass spectrometry (TIMS)], with some isotopes in femto (10^{-15}) gram quantities. The evolution of U-series analyses from alpha spectrometry, TIMS and now to multi-collector inductive coupled mass spectrometry (MC-ICPMS) has resulted in significant analytical gains, both in precision and throughput. MC-ICPMS in combination with a desolvating nebulizer provides at least a factor of 100 improvement in ionization efficiency over TIMS, which translates to a factor of 10 improvement in precision ($1/\sqrt{n}$, n=number of ions counted). We recently installed a Thermo Neptune MC-ICPMS equipped with nine Faraday cups, five channeltron detectors, and a secondary electron multiplier (SEM) and optimized for U-series measurement.

Samples are introduced using a CETAC Aridus II desolvating nebulizer, which improves signal intensity by at least a factor of 5. Faraday cups can be dynamically coupled with either$10^{12}\Omega$, $10^{11}\Omega$ or $10^{10}\Omega$ feedback resistors. The cups can handle ion currents up to $5x10^{-10}$ A (equivalent to 500 V with $10^{10}\Omega$ feedback resistor). For uranium isotope analysis ^{238}U is collected in a cup with a $10^{10}\Omega$ resistor, ^{236}U and ^{233}U (spikes and used for mass fractionation correction) are coupled with $10^{12}\Omega$ resistors and ^{235}U with a $10^{11}\Omega$ resistor. ^{234}U is measured on the SEM simultaneously, after establishing Faraday-SEM gain using a known isotope standard. The $10^{12}\Omega$ resistors provide a factor of three improvement in signal to noise ratio, allowing for the measurement of ion currents in the range of 10^{-14} A in a Faraday cup, because the resistor noise (Johnson noise) only increases by the square root of resistance. However, because of their slow response time, they are best suited for static measurements. For both silicate and carbonate Th measurements the ^{229}Th (spike), ^{232}Th are measured on Faraday cups coupled with $10^{12}\Omega$ resistors, while the much smaller ^{230}Th peak is measured on the SEM. Analyses that used to take about 3 hours on the TIMS can now be done in about 20 minutes with better precision.

(525) **Accurate and Precise Determination of Hg Isotope Ratios and Isotope Fractionation Induced by Vapor Generation**

Lu Yang[1], Ralph Sturgeon[1]; [1]NRCC

The introduction of multicollector ICP-MS (MC-ICP-MS) has allowed highly precise determination of Hg isotope ratios in various samples1-2. However, this remains a challenging task and in this presentation a procedure is described for such measurements in NIST SRM 3133 Hg standard. Although thallium was added to the samples for mass bias correction, it was not assumed that identical mass bias was suffered for both elements. From a natural logarithmic plot of measured 202Hg/200Hg against 205Tl/203Tl, the slope and the intercept of each session of measurements was calculated and used to obtain mass bias corrected 202Hg/200Hg. A value of 1.285333±0.000192 (mean and one standard deviation) for 202Hg/200Hg in NIST Hg 3133 was obtained from 40 measurement sessions. This value was then used for mass bias correction for other Hg isotope pairs in the samples based on a Russell exponential law correction. Isotope ratios of 0.015342 ± 0.000014, 1.68784 ± 0.00051, 2.3058 ± 0.0014, 1.3131 ± 0.0012, 2.9636 ± 0.0035, and 0.6795 ± 0.0012 (recommended value and expanded uncertainty, k=2) were obtained for 198Hg/196Hg, 199Hg/198Hg, 200Hg/198Hg, 201Hg/198Hg, 202Hg/198Hg and 204Hg/198Hg, respectively. Recent publications from several research groups have demonstrated per mil level variations of the Hg isotopic composition in both natural samples and induced by chemical manipulation1-2. This suggests that Hg isotopes may be a useful new tool for fingerprinting sources of Hg in the environment and to study a wide variety of chemical and biological processes in nature. Mercury fractionation induced during vapor generation in the laboratory will be reported for reduction reactions using SnCl2, NaBH4, NaBEt2 and a UV field. 1. J. D. Blum and B.A. Bergquist, Anal. Bioanal. Chem. 2007, 388, 353-359. 2. W. Zheng, D. Foucher and H. Hintelmann, Anal. At. Spectrom. 2007, 22, 1097-1104.

(526) **Mass Independent Fractionation of Mercury Isotopes in Environmental Samples**

Holger Hintelmann[1], Wang Zheng[1], Klaus Gantner[2], Derek Muir[2], Xinbin Feng[3]; [1]Trent University, Peterborough ON; [2]Environment Canada, NWRI, Burlington ON; [3]Chinese Academy of Sciences, Guiyang

The measurement of isotope fractionation, originally established for studying biogeochemical pathways of light elements was recently extended to almost the entire periodic table. Mercury is one of the heaviest stable elements and an intriguing isotope system, where classical mass-dependent fractionation (MDF) as well as unique mass-independent fractionation (MIF) of odd isotopes is observed. Processes such as photochemical reduction of inorganic mercury lead to MIF and provide a unique isotope abundance fingerprint that could be used in addition to MDF to track Hg in the environment. We systematically investigated photoreduction of ionic Hg in natural waters to identify, which environmental parameter affects Hg isotope fractionation. Filtered lake water with a residual dissolved organic carbon (DOC) content of 12 mg/L was amended with 10 µg/L of Hg and irradiated using a solar simulator. Reduced Hg(0) was continuously purged from the reactor and trapped in acidic permanganate solution. Every 2 hours, sub-samples were collected for a total reaction time of 10 hours, after which 30 % of the initial Hg was reduced. The Hg isotope composition of the residual aqueous Hg and the reduced Hg(0)-product of the reaction was determined. The data revealed not only strong fractionation caused by the photoreduction, but also a significant MIF. The remaining Hg was depleted with light isotopes, showing a $\delta^{202}Hg$ of +0.46 ‰, while the reduced Hg was enriched with light isotopes at -0.80 ‰. The even isotopes of Hg were preferentially reduced resulting in an even greater enrichment of ^{199}Hg and ^{201}Hg in solution. The corresponding $\Delta^{199}Hg$ and $\Delta^{201}Hg$ values were +1.77 and +2.22 ‰, respectively, for Hg remaining in solution and -6.43 and -7.94 ‰, respectively, for the photoreduced Hg. To put the laboratory data into context, we compared Hg isotope ratios in sediments and fish from Arctic inland lakes, and measured samples from a mercury mining area, artisanal zinc smelting area, and sediments from two reservoirs, which were contaminated with mercury from different anthropogenic sources.

(527) **Isotopic Reference Materials for the 21st Century**

Robert Vocke[1], Jacqueline Mann[1];
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Recent developments in multicollector thermal ionization and inductively coupled plasma mass spectrometry (MC-TIMS and MC-ICPMS, respectively) have lead to isotope ratio measurements with precisions approaching 100 ppm or better. The accuracy of such measurements would normally be benchmarked by isotopic Certified Reference Materials (iCRMs). However, the currently available iCRMs from various National Metrological Institutes have total uncertainties for their absolute isotopic ratios that are no better than a few parts in 10,000. The uncertainty of the absolute isotopic ratio of an iCRM is governed by the uncertainty of the synthetic mixtures of enriched isotopes that bracket the isotopic ratios in the candidate material and are used to correct the measured ratios to an absolute value. The resulting iCRMs, while accurately characterized at the 0.3 to 1 per mil level, are still too imprecise by at least two orders of magnitude. Up to the mid-1990s, terrestrial isotopic fractionation had been observed only in the 'light' elements (Hydrogen through Sulfur). Variations in isotope abundances of the 'heavier' elements were due to the accumulation of daughter isotopes from radioactive decay. Recent MC-TIMS and MC-ICPMS measurements however started showing isotopic variations in other heavy elements such as Hg, Fe, Se, Cr, Mo, Tl, Cu, and Mg. These are elements whose isotope abundances were previously thought to be unfractionated and as a consequence isotopic standards were not developed for many of these elements. These discoveries were then followed by the recognition of mass independent isotopic fractionation effects for O, S and now Hg. At ppm levels of precision, such measurements are subject to not-well-understood biases introduced by the mass spectrometers that appear to be element and instrument specific. No universally accepted approach is currently employed to make these measurements and

there are no trustworthy reference materials to test measurement protocols against. NIST is in the process of producing a new generation of highly homogeneous isotopic reference materials that will both become the basis for artifact based delta scale measurements and provide an effective way to correct for such biases.

(528) **Nanoholes Arrays Sensors Prepared using Lithography**

Jean-Francois Masson[1]; [1]Universite de Montreal

The spectroscopic properties (excitation wavelength, sensitivity and dynamic range) of nanoholes arrays were determined in relation with the physical properties (shape, thickness and periodicity) of nanotriangles and nanoholes arrays. These arrays are prepared using nanosphere lithographic techniques with monodisperse polystyrene spheres of 450 nm (CV < 3%). Glancing angle deposition (GLAD) deposition of Au on a ordered nanosphere monolayer results in a thin (0-20 nm) array of nanoholes. Otherwise, plasma etching a nanosphere monolayer reduces the size of the spheres and allows the preparation of thicker nanoholes arrays (0-150 nm). AFM and SEM characterization of the arrays reveals that GLAD prepared arrays have hexagonal holes and that plasma treatment results in circular-shaped holes. Domains of several mm2 are obtained with both techniques. Varying the deposition angle and the thickness of the array with GLAD optimized the excitation wavelength in the near infrared (between 750 nm and 1000 nm). The sensitivity of these arrays is typically between 200 and 500 nm/RIU; with a domain of linearity between 1.33 RIU and 1.42 RIU. Plasma treated arrays are optically active in the 500-600 nm region, resulting in a sensitivity of approx. 200-300 nm/RIU. However, the arrays prepared with a plasma pre-treatment exhibit a significantly narrower optical response, thereby improving the resolution. Both techniques result in the reproducible preparation of nanoholes arrays. These arrays are the first step towards highly sensitive biosensors.

(529) **SPR Microscopy Combined with a Microfluidic Flow Cell Array as a Platform for Immunogenicity Assays**

Jennifer Shumaker-Parry[1]; [1]University of Utah

The increased use of therapies based on proteins and monoclonal antibodies for a broad range of diseases has brought safety and efficacy issues to the forefront. A focus on immunogenicity response to these therapies brings challenges in the development of assays to provide sensitive, accurate assessment of anti-drug antibody binding interactions. The challenge begins with the first step of evaluating immune response to therapies – the detection of the presence of anti-drug antibodies. Issues with ELISA-based assays motivate the development of a new approach based on the combination a novel microfluidic flow cell array (MFCA) with SPR microscopy. The microfluidic device provides 48 separate flow channels that can be used simultaneously for biomolecule immobilization and subsequent biomolecule interaction analysis. Because the biomolecules can be immobilized *in situ*, exposure to harsh environments can be avoided, a major benefit for protein immobilization. In addition, the biomolecule immobilization process can be monitored in real time by SPR microscopy. This versatile, high-throughput biomolecule interaction analysis platform is being developed for immunogenicity assays to measure anti-drug antibody interactions with drug molecules. The high-throughput nature of the integrated system allows a large number of replicate experiments, including control experiments, to be performed simultaneously on the same sensor surface in a short time. The integrated system also will be applicable for more general high-throughput protein-array based analysis.

(530) **Engineering Stable Nanostructures for Enhanced Optical Detection**

Amanda Haes[1], Maryuri Roca[1], Kyungtag Ryu[1]; [1]University of Iowa

Precise control over the size, shape, and local environment of nanoparticles is vital for the development of new technologies based on these materials and their novel properties. This is especially important in understanding how these size-dependent properties impact the detection of biological and chemical targets. This work focuses on the synthesis and modification of silver and gold nanoparticles for enhancing and facilitating both the detection and separation of target molecules. We will reveal that solution-phase gold nanoparticle cores can be entrapped in porous silica cages through novel nanoparticle engineering. Silica shells offer robust protection of the metal nanoparticles against aggregation thereby preserving the novel optical properties; however, this shell prevents direct interaction between the metal core and analytes limiting applications in nanoparticle-enhanced spectroscopies. By removing the innermost layer of the silica shell, we have engineered optically stable gold nanoparticles that are protected by silica membranes which can be used to screen analytes using both localized surface plasmon resonance spectroscopy and surface-enhanced Raman scattering. Detection of both biological and environmental species will be discussed.

(531) **Electrochemical SPR Studies of Acid Thiol Chemisoption**

Roger Terrill[1], Arthur Cheng[1], Shaowei Chen[1]; [1]San Jose State University; [2]UC Santa Cruz

In acid-thiol adsorption to Au the competition between unfavorable electrostatic repulsion and favorable Au-S bonding enthalpy is influenced by factors such as acid protonation, ion pairing and Debye-screening. Our SPR studies have shown that the mass density of these charged layers is affected principally by pH, with lower pH favoring lower SAM density. The interfacial electrochemical potential also plays an important role and these studies attempt to address this factor in a quantitative way.

(532) **Pure Plasmons: The Control of Plasmon Frequency and Bandwidth in Conducting Metal Oxides**

Josh Guske[1], Alina Efremenko[1], Mark Losego[1], Jon-Paul Maria[1], Stefan Franzen[1]; [1]North Carolina State University

The development of surface plasmon resonance (SPR) spectroscopy on novel conducting substrates permits the control of materials parameters to create plasmons that are free from interference of band-to-band transitions. Using Fouier-Transform Surface Plasmon Resonance (FT-SPR) detection we demonstrate the prediction of plasmons using Fresnel equations that agrees with experiment with no adjustable parameters. The control of materials parameters leads to series of indium tin oxide (ITO) thin layers with different film thicknesses, conductivity and mobility. By measuring SPR using a θ-2θ stage with near-infrared radiation in the Kretschmann configuration we now show that the surface bulk plasmon can be directly detected in very thin films (<50 nm). In films ranging from 70 – 250 nm thickness the surface plasmon polariton (SPP) can be detected. In this thickness range, the conductivity can be controlled by changing the oxygen partial pressure during annealing and the mobility can be altered by changing the argon gas pressure during sputtering. Moreover, the SPP can be induced by adding layers of gold nanoparticles that have an effective charge carrier density that is close to that of ITO. This is the opposite of the effect of metallic gold layers on ITO, where the mismatch of the plasma frequencies causes quenching of the SPP in ITO. These effects will be discussed as a general feature of hybrid plasmonic materials.

(533) **Designing Novel Interfaces for Probing Protein Interactions with Carbohydrates and Lipids using Surface Plasmon Resonance and SPR Imaging**

Quan Cheng[1], Matthew Linman[1]; [1]Univ of California Riverside

Protein-carbohydrate and protein-lipid interactions are involved in many important cellular signaling processes. Various diseases states including cancer cell metastasis have been linked to these interactions. Gaining a fundamental understanding of these interactions is vital to our understanding of their biological significance and to the development of pharmaceutical treatment of the diseases. Surface plasmon resonance (SPR) and associated SPR imaging technique have gained widespread acceptance as the effective tool to probe biologically relevant interactions. Our group at UCR has focused on advancement of the SPR and SPRi methodology through the creation of novel surface chemistry and new materials to enhance the analysis in real-time. In this seminar, we report the development of new interface materials to monitor protein-carbohydrate and protein-lipid interactions in real-time. In additional to spectroscopic analysis, microarray approach with SPRi for high-throughput detection of protein-based interactions will be presented. A framework to study multiple biological interactions without special sample preparation in a highly reproducible manner will be discussed. Kinetic data, analytical figures of merit, and broad-based applicability of our approach will be presented. The surface methodology present herein could be used to identify and quantify binding patterns of numerous biologically relevant systems, opening new avenues for studying biological interactions.

(534) **Raman Spectroscopy for Bioprocess Development**

Harry Lee[1], Gustavo Gil[1], Paolo Boccazzi[1], Anthony Sinskey[1], Rajeev Ram[1], Elizabeth Bruce[1]; [1]Massachusetts Institute of Technology

During process development, when media composition, growth conditions, and overall process behavior is expected to change from experiment to experiment, explicit calibration methods based on physical models can be more appropriate than implicit calibration approaches. In addition, explicit calibration methods based on physical models offers the potential for being able to transfer calibrations performed on one system to another. We will discuss the challenges of applying these methods for on-line analysis of bioprocesses in order to rapidly assess the impact of process changes to performance.

(535) **Near-Infrared Spectroscopy: A Versatile Tool for the Pharmaceutical Industry**

Christopher John[1], James Roberts[1], Megan Miller[2], Feng Yang[2], Maria Cruanes[1], Manoharan Ramasamy[3]; [1]Merck-MRL-PAC; [2]Merck-MRL-Vaccines and Biologics; [3]Merck-MRL-AS&QT-Specialty Analytical

Near-Infrared (NIR) Spectroscopy is an ideal tool for the analysis of pharmaceutical dosage forms. The technique is complimentary to Raman and provides fast, non-destructive analysis for the quantitation and identification of a wide variety of pharmaceutical components. For example, NIR spectroscopy has successfully demonstrated the ability to quantitate and identify active pharmaceutical ingredients (API), polymorphic forms, functional excipients and moisture content in various dosage forms. The Pharmaceutical Analytical Chemistry Technology Development Lab will present data showing the flexibility of this tool for implementation in a Ph I drug development environment. Specifically, a research based spectroscopic toolkit was implemented to quantitate polymorph content in tablets, content uniformity in solid dosage forms, quantitation of functional excipients, and moisture content in a lyophilized vaccine product.

(536) **Does Crystal Structure Trump Chemistry? Raman Spectroscopy of Isostructural Solvates**

CJ Pommier[1], Raymond Scaringe[1], John DiMarco[1], Michael Galella[1], Mary Malley[1]; [1]Bristol-Myers Squibb

Polymorphism and pseudopolymorphism are characteristic phenomena of many pharmaceutical compounds. Importantly, different polymorphs or solvates can have different physicochemical properties such as solubility and impurity profile. In some cases, more than one kind of solvent can fit into crystal structures that have the same or very similar solid-state API packing arrangements. The Raman spectra of some of these crystal structure "families" have been observed to be very similar, even though the stoichiometry of the solid is entirely different. This talk will present some examples of Raman spectra of similar solvates, explain the pitfalls of relying solely on Raman spectroscopy for identification of crystal forms, and speculate on what may be the cause of the similarity in the Raman spectra through comparison of different spectroscopies.

(537) **Raman Spectroscopy of Biopharmaceuticals for Counterfeit Detection and Quality Assurance**

John Kauffman[1], John Spencer[1], Connie Gryniewicz[1], Lucinda Buhse[2], Benjamin Westenberger[1], Hongping Ye[1], John Reepmeyer[1], Wei Ye[1]; [1]FDA Div. of Pharmaceutical Analysis, St. Louis, MO

Protein therapeutics are typically analyzed by methods that require wet chemical sample preparation protocols, which are often complex and always time consuming. Spectroscopic methods for rapid screening of these products are advantageous for process control, and are also potentially useful for maintaining a safe and effective supply of protein-based pharmaceutical products. However, electronic and vibrational spectra of large proteins are complicated, resulting in the need for chemometric methods to elucidate compositional information. Examples of rapid screening methods based on Raman spectroscopy of insulin and heparin sodium will be presented. Insulin methods have been developed to distinguish insulins having different origins and formulations, as well as insulins that have been modified by external stresses such as heat and agitation. Heparin sodium methods have been developed to detect the presence of oversulfated chondroitin sulfate in active pharmaceutical ingredient (API). The rapid spectroscopic methods have been compared with standard methods of analysis including CE, HPLC, size exclusion chromatography and mass spectrometric methods. The results provide insight into the advantages and limitations of vibrational spectroscopies for rapid screening of therapeutic biopolymers.

(538) **Spearman Rank Correlation: A Robust Method for Determining High-Throughput Raman and pXRD Crystalline Solid Spectra Statistical Distances**

B. Andre Weinstock[1]; [1]TransForm Pharmaceuticals Inc.

A high-throughput (HT) combinatorial system has been developed for discovery of novel polymorphs, salt forms, co-crystals, hydrates, and solvates of crystalline active pharmaceutical ingredients (APIs)1. Raman and powder X-ray diffraction (pXRD) spectroscopies are employed individually and in tandem as rapid non-invasive techniques to measure API crystal properties. A relatively simple, fast, and robust method of spectral clustering is required to aid in the discovery of unique polymorphs, salt forms, etc. from tens to thousands of HT sample spectra. The application of Spearman rank correlation coefficients to spectral pairs followed by hierarchal clustering meets these criteria for several reasons. First, the use of Spearman rank correlation preferentially maintains and examines abscissa information (peak locations, peak widths) and normalizes and marginalizes ordinate information (peak intensities). This is directly applicable to correlating spectral

information in Raman and pXRD spectroscopies where peak intensities are relative and highly subject to noise. Second, the use of a rank correlation is inherently nonparametric2 and therefore requires minimal spectral processing and user subjectivity to be effective. Finally, the mathematics involved are simple and lend themselves to analyzing large spectral databases quickly. While not a novel use of Spearman rank correlation3, an explanation of how and why the method is superior for this application will be offered. Comparisons will be shown to other statistical distance methods on both synthetic and real spectral databases. 1.Morissette, S.L., Almarsson, O., Peterson, M.L., Remenar, J.F., Read, M.J., Lemmo, A.V., Ellis, S., Cima, M.J., & Gardner C.R. Advanced Drug Delivery Reviews 56 (2004) 275-300 2.Numerical Recipes in C: The Art of Scientific Computing Second Editon. Press, W.H., Teukolsky, S.A., Vetterling, W.T., & Flannery, B.P. Cambridge University Press, Cambridge, England, UK, 1992 ISBN 0 521 43108 5, pp. 639-642 3.Gilmore, C.J., Barr, B., & Paisley, J., Journal of Applied Crystallography 37 (2004) 231-242

(539) **Transmission Raman Spectroscopy for Quantitative Analysis**

Olof Svensson[1], Anders Sparén[1], Jonas Johansson[1], Staffan Folestad[1], Mike Claybourn[2]; [1]PAR&D, AstraZeneca R&D Mölndal, Sweden; [2]PAR&D, AstraZeneca R&D Macclesfield , UK

The development of transmission mode Raman spectroscopy of bulk samples has opened new opportunities for Raman analysis of pharmaceuticals. In spite of the many advantageous features of Raman spectroscopy, a significant disadvantage of pharmaceutical Raman spectroscopy has so far been sub-sampling of solid samples, such as tablets. However, with the development of transmission Raman a greatly improved sampling depth has been attained. In this work, quantitative analysis of simple pharmaceutical formulations using the new approach of transmission Raman spectroscopy has been investigated and compared with conventional backscatter mode Raman. The experimental set-up consisted of a Raman probe-based spectrometer with 785 nm excitation for measurements in backscatter mode. In transmission mode the same system was used to detect the Raman scattered light, while an external diode laser of the same type was used as excitation source. Quantitative partial least squares models were developed for both measurement modes. The results for tablets show that the prediction error for an independent test set was lower for the transmission measurements with a relative root mean square error of about 2.2 % as compared with 2.9 % for the backscatter mode. Furthermore, the models were simpler in the transmission case where only a single PLS component was required to explain the variation. The main reason for the improvement using the transmission mode is a more representative sampling of the tablets, compared with the backscatter mode. Capsules containing mixtures of pharmaceutical powders were also assessed by transmission only. The quantitative results for the capsule content were good, with an RMSEP of 3.6 w/w % for an independent test set. The advantage of transmission Raman over backscatter Raman spectroscopy has been demonstrated for quantitative analysis of pharmaceutical formulations and the prospects for reliable, lean calibrations for pharmaceutical analysis is discussed. Work is in progress on more complex formulations and the results from this study will be presented.

(540) **Two Dimensional Correlation Spectroscopy to Graphically Represent Instrument Similarity for Calibration Transfer**

Franklin Barton[1], James der Haseth[1], Arnold Eilert[2]; [1]Light Light Solutions, LLC; [2]Unity Scientific, Inc.

When looking at a series of instruments to move an assay into the processing plant environment there are some vital questions that must be answered. First and foremost is the instrument robust enough for the environment. An examination of the reliability statistics of installed instruments usually answers this question. Second, can my laboratory calibration be transferred to the instrument? Third, Since I will be employing multiple instruments in a process, how similar are they in the total network. This last one will indicate the amount of calibration maintenance needed. While there are existing algorithms to do the needed calibration transfer it is imperative to understand the differences between instrument platforms and the differences between identical instruments. The calibration transfer programs provide the user with a numerical figure of merit for comfort, RMSEP, R2, etc. What is needed is a graphical representation of the differences that will give a reasonable picture of instrument similarity. Two dimensional correlation spectroscopy (2DCOS) has been used to characterize instrumental differences which will affect performance, stability and reliability. The 2DCOS programs were re-written in MATLAB ver. 6.51 to provide a common format with the newer instruments and the special purpose instruments which utilize MATLAB for data functions. This study utilizes seven instruments from one manufacturer, two series of instruments and two sample presentation geometries.

(541) **Application of IR Correlation Spectroscopy to Conjugated Polymer Materials**

Georgia Arbuckle-Keil; [1]Rutgers University

Polymers such as poly(p-phenylene vinylene)(PPV) and derivatives of PPV are of great interest due to their opto-electronic properties. Most of these highly conjugated polymers are rigid and insoluble. By preparing these materials via a precursor route, the polymers can be cast into thin flexible films. The bulk mechanical (dynamic mechanical analysis) and opto-rheological properties of several PPV polymers have been characterized. This infra-red analysis provides insight into the opto-rheological properties of these polymers including molecular information. An example of the ability of IR correlation spectroscopy to distinguish and successfully identify phenylene ring stretches along a polymer backbone from ring stretches associated with a phenoxy substituent will be illustrated by spectral analysis of poly(2-phenoxy p-phenylene vinylene). Assignments were supported by density functional theory (DFT) calculations and validate the interpretations made based on dynamic IR spectroscopy.

(542) **Characterization of Hydrostatic Pressure Effect on the Phase Transitions of a Weakly Interacting Block Copolymer by Two-Dimensional Correlation Spectroscopy**

Young Mee Jung[1], Hye Jeong Kim[2], Seung Bin Kim[3], Jin Kon Kim[2]; [1]Dept. of Chemistry, Kangwon National University; [2]Dept. of Chemical Engineering, POSTECH; [3]Dept. of Chemistry, POSTECH

In this presentation, we have applied two-dimensional (2D) correlation spectroscopy to the pressure-dependent IR spectra of polystyrene-block-poly(n-pentyl methacrylate) copolymer (PS-PnPMA) to investigate in detail the hydrostatic pressure effect on the phase transition of PS-PnPMA. PS-PnPMA was shown to exhibit a closed-loop phase behaviour, where, upon heating, a lower disorder-to-order transition (LDOT) was found at lower temperature, and an upper order-to-disorder transition (UODT) was observed at higher temperature. The size of closed-loop consisting of both LDOT and UODT became smaller with increasing pressure, which is consistent with results obtained from small angle neutron scattering. At a lower temperature region, with increasing pressure, PnPMA chains become frozen because of cluster formation of alkyl chain. Main chains in PS block move first. On the other hand, at a higher temperature region, it is difficult to maintain the ordered states due to side chain motion. Specially,

PnPMA block is more flexible than PS block due to the difference of specific volume, which indicates UDOT is more sensitive than LDOT with pressure. Results of 2D correlation analysis will be discussed in details.

(543) **Enhancing S/N in Nanosecond Time-Resolved IR Emission Spectra from Transient Radicals through 2-D Correlation Analysis**

Hai-Lung Dai[1], Michael Wilhelm[2], Mathew Nikow[2]; [1]Department of Chemistry, Temple University; [2]Department of Chemistry, University of PA

Based on the principles of the generalized two-dimensional vibrational spectra correlation analysis, an approach for deciphering the correlation among the spectral peaks of two different spectra is developed for revealing the IR emission features associated with a common transient radical. The cross-spectral correlation is based on the premise that, though in different spectra, the spectral features of the same species should have the same time-evolution of intensity. This 2DCSC has been applied to analyzing nanosecond time-resolved emission spectra obtained, by a Fourier transform IR spectrometer, for samples consisting of the vibrationally excited transient radicals including cyanooxomethyl (OCCN), ketenyl (HCCO), and vinyl (C2H3). We have examined the relative signal-to-noise (S/N) enhancement as obtained through extraction of the diagonal elements of the synchronous correlation map following two dimensional correlation analysis of both self- and cross-spectral correlation. It is found that when there is time-dependent decay in spectral intensity, the S/N enhancement achieved through correlation is somewhat superior to that through simple averaging. Frequency shift with time diminishes the enhancement in all analyses. The effect of self- vs cross-correlation on S/N enhancement is directly related to the number of spectra used in the treatment. Additionally, for series exhibiting frequency shift, it is observed that correlation analysis yields spectra which are more representative of the original time-dependent data sets.

(544) **New Method for Time-Resolved Structural Characterization with Polarization Modulation FTIR Spectroscopy**

Christian Pellerin[1], Yongri Liang[1], Robert Prud'homme[1], Damien Mauran[1]; [1]University of Montreal

Polarization modulation infrared linear dichroism (PM-IRLD) is often used to study the orientation and relaxation in polymers and thin films. It provides high sensitivity, good time resolution, and the spectral selectivity of IR spectroscopy for multi-component and multiphase systems. Nevertheless, the technique only provides dichroic difference spectra, which can lead to the loss of important information about the structure of the sample, for instance its conformational changes, crystallization, etc. In this work, we demonstrate a new method, called polarization modulation infrared structural absorbance spectroscopy (PM-IRSAS), that can measure simultaneously the polarized spectra and the dichroic difference spectra. This allows calculating structural absorbance spectra in real-time to follow structural changes with a 200 ms time resolution. Illustration of the new approach will be given for the fast deformation of poly(ethylene terephthalate), as well as for following its cold crystallization. It is also demonstrated that PM-IRSAS improves the accuracy of the orientation function determination by quantitatively taking into account sample thinning and band absorbance changes during the measurements.

(545) **Quantitative Study of Protein Conformation and Orientation in Single Silk Fibers by Golden Gate Attenuated Total Reflectance Infrared Spectroscopy**

Michel Pezolet[1], Maxime Boulet-Audet[1], Thierry Lefevre[1], Thierry Buffeteau[2]; [1]Laval University; [2]Universite de Bordeaux I

Polarized attenuated total reflectance (ATR) infrared spectroscopy is an efficient technique to determine the orientation and conformation of a large variety of samples, but it is more difficult to apply to very small specimens such as silk fibers. The Golden Gate single-reflection ATR accessory that uses diamond as an ATR element and a focalized beam turns out to be highly efficient to study quantitatively the orientation and conformation of a single cocoon silk filament of the silkworm Bombyx mori that is about 10 μm in diameter. For orientation measurements, rotating the sample instead of the electric field greatly simplifies the theoretical analysis and keeps the penetration depth of the infrared radiation constant. A sample holder that can be fitted on the Golden Gate system has thus been developed to allow the accurate rotation of the sample and to obtain spectra with a low, non damaging and reproducible pressure on the fiber. To validate the method, spectra have been recorded as a function of the angle θ between the fiber axis and the polarization of the incident radiation. The data have been fitted following the cosine square dependency of the absorbance with respect to the angle θ. The procedure has been applied to the spectral components of the amide I bands, as determined from spectral decomposition. Multiple angle measurements turn out to be quite useful to correct systematic angle errors and validate the accuracy of the curve-fitting parameters of the band decomposition. By using the calculated dichroic ratio, a parameter $\langle P_2 \rangle$ of -0.46 ± 0.01 has been calculated for the antiparallel β-sheets and of -0.04 ± 0.02 for the remaining structures. From the orientation-insensitive spectrum A_0, the amount of β-sheets has been estimated to 49 ± 3%. The results obtained from only two measurements with the electric field of the incident radiation parallel and perpendicular to the fiber axis has demonstrated that ATR can be used routinely in quantitative studies of the molecular orientation and conformation of macromolecules.

(546) **Spatial Compression and Noise Scaling for Improved Multivariate Analysis of Hyperspectral Fluorescence Images**

David Haaland[1], Howland Jones[1], Michael Sinclair[1], Bryan Carson[1]; [1]Sandia National Laboratories

Images obtained from hyperspectral fluorescence microscopes can yield significant new information and better quantitative details and contrast from biological samples relative to images obtained from more traditional filter-based fluorescence microscopes. In order to efficiently extract the information contained in the hyperspectral images, we have been applying multivariate curve resolution (MCR) alternating least squares methods to the data. In order to achieve improved sensitivity and quantitation, we recently have been scaling the data for the presence of both Poisson noise and read noise present in the images. Scaling is an approximation to a full weighted least squares MCR approach, but is required to reduce the computational burden on these very large data sets that approach 1 GB in size. The effectiveness of this approximation is image dependent and depends on the spatial distribution and dynamic resolution of the image both spectrally and spatially. The scaling also does not take into account the small but pervasive correlated noise in the data. We have found that the correlated noise is randomly distributed spatially and therefore its effect on the analysis can be reduced by spatial binning of the image. Spectral binning also is found to reduce the effect of correlated noise. Spatial and spectral binning also can serve to dramatically

decrease the computational time required for the MCR extraction of the pure component emission spectra. We find that spatial binning can serve to improve the appropriateness of the scaling approximation to the full weighted least squares MCR solution. The combination of spatial compression and noise scaling will be demonstrated with the MCR analysis of experimentally-derived hyperspectral images of biological samples and to simulated hyperspectral images obtained using the MCR results obtained from the real images. The speed advantages and the improvement in the accuracy of the MCR analyses will be demonstrated with this combination of spatial compression and noise scaling. Sandia is a multi-program laboratory operated by Sandia Corporation, a Lockheed Martin Company, for the United States Department of Energy under Contract DE-ACO4-94AL85000. A portion of this work was supported by the Microscale Immune Studies Laboratory Grand Challenge LDRD

(547) **Quantification of Synthetic Fuel Content and Property Prediction Compensation in Fuel Blends using Near-Infrared Spectroscopy and Partial Least Squares**

Jeffrey Cramer[1], Robert Morris[1], Mark Hammond[1], Braden Giordano[2], Susan Rose-Pehrsson[1]; [1]U.S. Naval Research Laboratory; [2]Nova Research, Inc.

Many bulk fuel properties can be predicted from partial least squares (PLS) modeling of near-infrared (NIR) spectra. Since these predictive models are based on correlating fuel properties to compositional features, this presents a particular challenge when modeling synthetic or alternate fuels that have radically different compositions than training set petroleum fuels. In the near term, these types of models and the associated analytical instrumentation will be expected to function effectively when evaluating fuel blends containing up to 50% Fischer-Tropsch (FT) synthetic fuel originating from a single source (a simple, or binary, blend) or multiple sources (a complex blend). The following work describes a PLS modeling strategy statistically capable of quantifying synthetic fuel content within 6.9% of its true value 95% of the time according to binary experimental data. The resulting synthetic fuel content prediction can then be used to compensate for errors found in those fuel property predictions (themselves based on existing PLS models constructed without the benefit of pure or blended synthetic fuel training samples) that are affected by the same underlying chemical factors in binary fuel blends. This strategy is validated using both artificially constructed and real NIR fuel blend data.

(548) **Analytical Chemistry and Multi-Block Modeling for Improved NIR Spectral Interpretation**

Charles Miller; [1]Eigenvector Research, Inc

The practical advantages of near-infrared spectroscopy for rapid analysis are well-documented. However, some commonly-cited disadvantages of NIR technology are its inherently low analytical selectivity, and its subsequent heavy reliance on empirical calibration procedures that do not require fundamental understanding of the chemistry and physics of the problem. Although it has been shown that these disadvantages do not necessarily limit one's ability to develop practically useful NIR methods, they can nonetheless affect one's "confidence" in these methods, which impacts long-term acceptance and viability of this very useful technology. What many folks might not realize is that the non-destructive nature of NIR analysis enables an interesting possibility for obtaining a deeper fundamental understanding of NIR methods on a problem-specific basis. Specifically, one could run "parallel" analyses of a set of suitably-representative standards by both NIR and another multivariate analytical technique that is more selective. The resulting data could then be analyzed using multi-block chemometric modeling methods, to explore the correlation structure between then two analytical methods. With carefully-designed experiments, such multi-block analyses can enable more confident assignments of specific NIR spectral features to specific underlying chemical or physical phenomena. This approach to improved NIR understanding will be demonstrated using several different datasets obtained from relatively well-characterized polymer systems. The application of this approach to more complex systems will then be discussed.

(549) **Identification of Protein Secondary Structure UVRR Spectral Motifs using Trilinear-MCR of 2D Excitation Raman Shift Matrices**

Renee JiJi[1], John Simpson[1]; [1]University of Missouri

Ultraviolet resonance Raman (UVRR) is a powerful analytic technique for the study of the structural elements in biomolecules. In particular, UVRR can be used to determine the content of each major secondary structural domain type (alpha-helix, beta-sheet, and disordered) present in a protein at lower sample concentrations than needed infrared absorption (IR and has the potential to convey more structural information than either IR or circular dichroism (CD). Previously, we have demonstrated that multivariate curve resolution (MCR) could be used to resolve discrete alpha-helical and disorder spectral profiles from 2D multi-excitation UVRR spectra of myoglobin, a predominantly alpha-helical protein. In an attempt to improve the quality of these spectral profiles and extend the analysis to more complex proteins we have collected the multi-excitation UVRR spectra of nine proteins at eight excitation wavelengths ranging from 195 to 209 nm. These 2D UVRR protein spectra were subjected to MCR-ALS featuring trilinearity constraints. The results of this study will be presented.

(550) **Pattern Recognition Methods for Real-Time Monitoring Applications of Near-Infrared Spectroscopy**

Gary Small[1]; [1]University of Iowa

Many analytical chemistry applications require real-time monitoring of a system or process in order to detect failures, ensure desired product specifications, or maintain optimal experimental settings. In such applications, a premium is placed on the degree of automation, both from the standpoint of the measurement process and the subsequent analysis of the measured data. Near-infrared spectroscopy has gained popularity in automated monitoring scenarios because minimal sample preparation is typically required and because rugged, relatively low-cost instrumentation is available that can be installed at the measurement site. In this presentation, near-infrared spectroscopy will be employed in real-time monitoring scenarios, coupled with the use of pattern recognition methods to implement threshold monitoring of analyte concentrations. The application addressed here focuses on the detection of nocturnal hypoglycemia (low glucose levels) in diabetic patients. Since there is no obvious symptom before hypoglycemia, the occurrence of this condition during sleep can lead to serious health consequences for the patient. It is thus desirable to develop a nocturnal hypoglycemic alarm which will wake diabetic patients during sleep if hypoglycemia occurs. Currently, the standard method to monitor blood glucose levels is a test-strip procedure based on the collection of a small sample of capillary blood. However, this approach suffers from invasiveness and intermittence and is unsuitable in a continuous monitoring scenario while the patient is asleep. To address this limitation, we are developing near-infrared spectroscopic methods for this application. For an *in vivo* measurement, application of infrared light to tissue is painless and can be applied continuously. In this research, we are employing supervised pattern recognition methods to identify the occurrence of hypoglycemia from an analysis of the recorded spectra. Data will be presented from both *in vitro* measurements using two different model systems, as well as from

direct *in vivo* tissue measurements of laboratory rats. With both types of measurements, near-infrared spectra are collected continuously during glucose excursions designed to simulate the nocturnal profile of a sleeping patient. The presentation will focus on how to develop a robust and stable pattern recognition model that can detect hypoglycemic events and can account for time-based spectral variation.

(551) **Two-Dimensional Gas Chromatography / Time-of-Flight Mass Spectrometry with Chemometric Data Analysis**

Jamin C. Hoggard[1], Robert Synovec[1]; [1]University of Washington

Comprehensive two-dimensional (2D) separation methods are emerging as powerful tools for the analysis of complex samples. Truly comprehensive 2D methods inherently provide, from a chemometric perspective, second order data. Additionally, if 2D separations are coupled with a multi-channel detector, such as time-of-flight mass spectrometry (TOFMS) or multi-wavelength absorbance, then a third order data structure is obtained, which has distinct advantages when it comes to data analysis. Thus, it is critical to design and implement 2D separation instrumentation in a comprehensive fashion. Information gleaned from comprehensive 2D separations can then be optimized using chemometrics software (i.e., multivariate data analysis). Each component eluting from the first column should be represented by at least three (in phase) or four (out of phase) separations on the second column, as dictated by the first column peak width and the modulation period as defined by the run time on the second column. The ultimate goal is to analyze the entire sample (within a sample set), while maintaining resolution gained by the first column, and maintaining good quantitative accuracy and precision. These principles will be the focus of this presentation, inter-relating the instrumentation and software requirements needed, in concert with understanding retention time precision issues and methods to correct these issues. Chemometric methods that provide discovery-based, multivariate feature selection, followed by data mining using the peak deconvolution method PARAFAC will be presented. Recent work in the metabolomics field using comprehensive two-dimensional gas chromatography coupled with TOFMS is described (GC x GC – TOFMS), although the principles apply to all comprehensive 2D separations (eg., LC x LC – Multi-wavelength Absorbance).

(552) **Application of the Raman Microscope to Forensic Science**

Sergey Mamedov[1], Eunah Lee[1], Fran Adar[1], Andrew Whitley[1], Jon Goldey[1]; [1]Horiba Jobin Yvon

Raman microscopy was developed in the early to mid 1970s for chemical analysis with 1*f*Ým spatial resolution. Early motivation was to identify contaminants that appeared in manufactured products. However it was quickly applied to all types of materials analysis. Raman analysis has been recognized to have potential for solving an entire variety of problems of forensic science. However, one of the barriers to exploiting this potential has been the overhead of the technology , the cost of the equipment, its footprint, and the level of skill required for successful use. New Raman microscopes have been introduced at about half the cost of larger research systems, and they take up no more lab table space than an ordinary optical microscope. During this talk, this new equipment will be described, as well as forensic applications including identification of illicit drugs in their containers, counterfeit currency, fibers permanently embedded in epoxy. It will be shown that commercial software is available that can provide quick identification of materials whose spectra have been collected in a library, or just matched to suspect material samples.

(553) **Crystal Tests as a Separation Method for the Rapid Analysis of Illicit Drugs by IR Microspectroscopy**

Pauilne Leary[1]; [1]Smiths Detection

The value of Microcrystal Tests for the identification of unknowns is well established within the scientific community. For over 100 years, scientists have been selectively separating ions and compounds of interests from complex matrices, and then documenting their identification by virtue of the characteristic crystal complexes formed during the reaction. These tests were successfully applied to the field of illicit drug analysis. In recent years, however, standards of admissibility of scientific evidence within the Courts have challenged the validity of these tests for identification. One of the primary reasons for this is because it is purported that evaluation of a sample's chemical composition can not be performed simply by looking at the shapes and sizes of the crystals formed, even if appropriate positive and negative controls are used during the analysis. As a result, analytical methods such as gas chromatography-mass spectrometry (GC-MS) and high-performance liquid chromatography (HPLC) have become standard practice in laboratories testing illicit drug samples. These methods meet the standards of admissibility established within the judicial system. Advances in infrared instrumentation, however, are changing the role and the value of Microcrystal Tests within the field of illicit drug analysis. It is now possible to collect an infrared spectrum from a single crystal. No longer is the analyst relying upon the appearance of the crystal formed to identify the unknown, but rather to selectively and with great sensitivity isolate the compound of interest from its matrix. Then, infrared spectral data can be collected from either a single crystal or cluster of crystals to discern the sample's chemical composition within seconds. The ability to perform this type of analysis is very powerful and has significant advantages over other analytical techniques. For instance, infrared spectral data can not only be used to identify the chemical composition of the parent compound, but also to detect differences in solid-state forms of these compounds. This ability to differentiate solid-state form, as well as the speed and accuracy of the measurement, are significant advantages over methods such as HPLC and GC-MS.

(554) **FT-IR Microspectroscopy of Individual Starch Granules Detects the Presence of Chemical Modification**

Yanjie Bai[1], Yong-Cheng Shi[1], David Wetzel[1]; [1]KSU Microbeam Molecular Spectroscopy Lab

Single starch granules with a median size of ca. 30um are analyzed by FT-IR microspectroscopy one at a time to assess the existence of chemical modification sites. A two-phase reaction mixture is used to produce modified starch. Assessing the targeted modification level is not a problem when dealing with a bulk sample. The uniformity of distribution is not readily verifiable by normal means. The procedure used in this work involved conducting a census among more than 100 individual granules from individual laboratory produced batches of modified starch. The absorption bands of organic functional groups were used to produce a GO/NO GO classification for each granule one at a time. A similar procedure was used for more than 100 granules of the native starch from which the modified starch was produced. In commerce, the 3% modified product used for food applications is commonly produced by dilution of a more concentrated modified starch. I n this study, to simulate such a product, a 15% modified starch product was blended with sufficient native starch from the same lot used to produce the 15% concentration. Individual granules were analyzed microspectroscopically in an attempt to determine the actual ratio of modified to native granules. By centering a 15um X 15um spot from a confocal image plane masked beam on each granule, a spectrum was produced. The peak area for the carbonyl (1740 cm-1) was radioed to that of the carbohydrate band. T he

results of all three of these unique experiments are presented to summarize the utility of this painstaking but nevertheless revealing technique that documents the granule-to-granule modification population.

(555) **The Challenges of Trace Evidence – In the Field, Laboratory and Court**

John Reffner[1]; [1]Trace Consulting

Scientific analysis of trace evidence is an exciting, challenging and frustrating field of forensic investigations. Everything in our environment is potentially trace evidence. Trace evidence is not limited by size, shape or composition. It is the lingering vapors of an accelerant in the rubble of a suspicious fire. It is the impression of a fabric on the fender of a vehicle involved an accident. It is a plastic coating on a counterfeit drug package. But nothing is evidence until it is found and documented. When evidence is recovered, modern methods of analysis provide information that assists the courts in adjudicating an action. However, the courts have rules that impose limits on the admissibility of evidence. Because of the complexities of modern analytical methods, it is difficult for juries to understand scientific findings. This is especially true in the adversarial courtroom. What does it mean if a fiber found on a victim has the same infrared spectrum as a fiber found on the prime suspect? What if these fibers have the same color? What if these fibers have the same visible light absorption spectrum? What if they have the same cross-sectional shape and size? What if they have the same elemental composition? Are you certain that they came from the same source? What is the error rate? Are we ever certain of anything? What is reasonable scientific certainty? These are some of the challenges the trace evidence examiners must face. Analytical chemistry and spectroscopy are important technologies to detect and evaluate evidence in legal procedures. While applying scientific methods to matters of law defines forensic science, forensic science is not restricted to criminal actions. Environmental regulations, civil litigation and intellectional property law are included in forensic science. Analytical chemists think of trace as meaning a small quantity, but to the forensic scientist, trace has an extended meaning. Trace evidence is used to track or link events. The best outcome of the analysis of trace evidence is to discover a path, linking past events.

(556) **Studies on the Feasibility of using Chemometric Modeling of Spectral Data for the Determination of Post-Mortem Intervals on Skeletal Remains**

Patricia Diamond[1], Marianna Busch[1], Kenneth Busch[1], Jody Dogra[1]; [1]Center for Analytical Spectroscopy

In forensic investigations, establishing the time of death is a key piece of evidence. Forensic scientists frequently categorize human remains in terms of their post-mortem interval (PMI), which is the time elapsed since a person died. In areas like Texas that have extreme climates with high heat and high humidity, excarnation of the remains can occur relatively quickly. Under these conditions, the determination of the PMI is frequently problematic because of the rapid decomposition of the tissues routinely used to determine PMI. Determining the PMI from skeletal remains is currently not possible for lack of accurate methods. What methods that do exist are best for deciding whether a bone is of forensic interest (less than 50 years old) or anthropologic interest. The objective of this study was to determine whether spectroscopic examination of bone could be used to predict the PMI of skeletal remains. It was hypothesized that changes in the water content and organic makeup of skeletal remains would occur following death, and that these changes could be followed spectroscopically and correlated with the PMI. Since pigs are often used in forensic field studies because of their similarity to humans, we have chosen to focus our initial studies on pig femurs. In this paper, we report on a series of parallel spectroscopic studies using both NIR reflectance and UV/visible emission and absorption spectroscopy obtained with pig femurs in the laboratory over a period of several months. We will further report on the use of multivariate regression modeling, specifically PLS-1, for correlating small spectral changes that occur over time with the PMI of bone samples. Finally, the success of the regression models in accurately predicting the PMI of pig femurs will be discussed.

(557) **Laser Induced Fluorescence Spectral Classification and Selective Electrostatic Collection of Individual Biothreat Aerosol Particles**

Vasanthi Sivaprakasam[1], Jay Eversole[1], Timothy Pletcher[2], David Keller[2]; [1]Naval Research Laboratory; [2]Sarnoff Corporation

Detection of low concentrations of aerosolized biological threats in a timely manner is hampered by the presence of large quantities of extraneous aerosol material in whole samples of airborne particles that can confound subsequent analysis and lead to undesirably high false positives or a reduced probability of detection. We have developed an aerosol particle sorting and capture system, the Biological Aerosol-Capture-and-Enrichment (BioACE), that provides high quality samples for analysis in which the biological material is enriched by rejecting background clutter. The BioACE system uses an all-optical measurement sub-system to interrogate single aerosol particles in the 0.5 μm to 10 μm size range in the inlet air flow, and classify each one as either a potential-threat or as a non-threat. This aerosol interrogation unit is based on an UV-LIF excitation system that sequentially generates laser pulses at 266 nm and 355 nm. Fluorescence signatures in 4 discrete emission bands are captured for each aerosol particle at for both excitation wavelengths in order to characterize the particle composition. Also, novel two cw beam technique was developed to measure the velocity of each particle on-the-fly that is able to unambiguously determine the relative position of the particle in respect with the two beams by exploiting polarization properties. This information is used for initiating the timing sequence and setting an appropriate delay to capture the particles of interest. This particle classification information is then used to trigger an electrostatic capture mechanism which charges identified particles and deposits them onto a conductive substrate. Non-threat particles are not charged and discarded with the exiting airflow. The resulting sample is therefore greatly concentrated relative to its initial total aerosol percentage. This enables various analytical techniques that require a relatively clean sample for accurate results. Initial sorting results on 2 μm dye doped PSL particles show a collection efficiency of greater than 65% for the particles of interest and a rejection efficiency of greater than 85%. We have been able to successfully classify different types of bioaerosols including proteins and bacteria (vegetative cells and spores) and distinguish them from several common interferents with high performance criteria.

(558) **Detection of Biological Compounds using a Fluorescence-Based Detection System**

Brian Dable[1], Geoff Wilson[1], Steve Estrada[1], Everett Perry[1], Jim Brady[1], Mike Carrabba[1]; [1]Hach Homeland Security Technologies

Sensors that can detect the presence of specific biological compounds to provide an early warning or secondary confirmation of an early warning are desired for protecting during a terrorist attack. This presentation will describe a novel detection method for detecting the presence of pathogens by using a combination of fluorescence detection and chemometric analysis. Using discreet wavelengths of light to measure the fluorescence emission of an unknown sample that may contain several compounds, an algorithm may be applied to resolve the data into "pure" mixture

component spectra. Comparison of these pure spectra to a reference library containing known pathogens can be used to validate the presence of desired compounds within the unknown mixture.

(559) **Unusual Photophysical Behavior of Pyrazolo[3,4-b]Quinoline in Low-Temperature n-octane Matrices**

Freek Ariese[1], Joost S. de Klerk[1], Arjen N. Bader[1], Cees Gooijer[1], Monika Sterzel[2], Mariusz Pilch[2], Andrzej Danel[3], Szczepan Zapotoczny[2]; [1]Laser Centre Vrije Universiteit Amsterdam; [2]Jagiellonian University, Krakow, Poland; [3]Agricultural University, Krakow, Poland

The aim of the current work is to understand the photochemical behavior of pyrazolo[3,4-b]quinoline (PQ). Three tautomeric forms are possible for this molecule and upon lowering the temperature dimer formation can be observed in alkane solvents. During cooling the dimer is formed and a strongly fluorescent solution of PQ in n-octane becomes non-fluorescent. Surprisingly, after irradiating the sample for several minutes at temperatures below 30 K a narrow-banded Shpol'skii-type fluorescence spectrum is obtained. The system was studied using low-temperature absorption and fluorescence spectroscopy over the 300-5 K temperature range. Very fast excited-state proton transfer processes via a tunneling mechanism are responsible for the efficient quenching of PQ dimer fluorescence at low temperatures. Deuteration significantly slows down these proton transfer processes and in that case a fluorescent dimer is observed that is slowly converted into two fluorescent monomers during irradiation at cryogenic temperatures. The processes were found to be reversible. A scheme will be presented to explain the observations.

(560) **Single Molecule Fluorescence Anisotropy Measurements to Monitor and Quantify Biomolecular Complexation**

Sean M. Burrows[1], Dimitri Pappas[1]; [1]Texas Tech University

Our research focuses on the application of single molecule fluorescence anisotropy measurements to monitor and quantify biomolecular complexation reactions. The long-term goal of this work is to develop new enabling technologies to elucidate cellular/molecular function. We have previously studied and published work on quantifying molecular recrossing events as a tool to observe photon saturation and photobleaching of several single fluorophore molecules. Our current work focuses on observing and measuring the extent of binding in a biologically relevant system, the NeutrAvidin-Biotin System. Using single molecule fluorescence anisotropy, we are able to quantify binding and observe both heterogeneities and rare events. In contrast, ensemble measurements would only yield an averaged anisotropy value, and mixed populations (i.e. both free and bound probes present in solution) and rare events are lost. This presentation will detail our latest results in the area of single molecule complexation studies. The number of bound and free biotin-fluorophore probes were determined based on fluorescence anisotropy values. The effect of probe and protein concentrations was studied. In addition, competitive reactions with unlabeled probe (biotin) were also studied. Future work will focus on improving the analytical figures of merit and the implementation of this technology to observe bimolecular complexations in living cells. Specifically, we will look at fluorescent-tagged inhibitors of protein function as a drug screening model.

(561) **In-Capillary Protein Detection using Laser Induced Native Fluorescence of the Aromatic Amino Acids**

Matthew Heywood[1], Paul Farnsworth[1]; [1]Brigham Young University

We have developed a protein detector based on laser-induced fluorescence of naturally existing aromatic amino acids. The excitation source is a compact solid-state laser. The 1064-nm output of the Nd:YAG laser is frequency quadrupled to produce radiation at 266 nm. This deep-UV radiation is well-suited for excitation of tryptophan, tyrosine, and phenylalanine. The laser radiation is directly focused through the wall of a fused-silica separation capillary for capillary electrophoresis (CE). Fluorescence is collected and focused by a reflective objective to a PMT. The detector has been tested using buffered solutions containing tryptophan. One challenge with the fluorescence detection of aromatic amino acids is that they are easily photobleached. We will present an analysis of the effects of photobleaching due to laser power and exposure time of the fluorophore on the performance of the protein detector. Limits of detection for Tryptophan, Tyrosine and several proteins using laser induced native fluorescence will also be presented.

(562) **Fluorescence Microscopy Analysis of Surface Immobilized Phospholipid Vesicles**

Emily Heider[1], Moussa Barhoum[1], Karl-Heinz Gericke[2], Joel Harris[1]; [1]University of Utah; [2]Technische-Universitaet Braunschweig

Controlling and analyzing phospholipid vesicle structure is important in liposome applications including drug delivery, biomimetic membrane studies and chemical analysis. Extrusion of hydrated lipid suspensions is often employed to produce vesicles of uniform size. Herein, a method is described for the analysis of individual vesicles to obtain information on the size, lamellarity, and structure of vesicles produced by extrusion. In contrast to methods for bulk analysis (i.e. fluorescence and dynamic light scattering), microscopy provides information about vesicles that is not averaged, and heterogeneities in vesicle populations can be characterized. Phosphatidylcholine vesicles containing small fractions of biotin-modified phospholipid and fluorescently labeled phospholipid were immobilized through a biotin-avidin-biotin interaction above the surface of an biotin-modified glass coverslip. Biotin was attached to the surface in a mixed cyano monolayer by reaction with exposed amine binding sites for N-hydroxysuccinimide ester-PEO4-biotin. Membrane lamellarity was analyzed by producing vesicles with 0.5% of the phospholipid head groups modified with 7-nitro-2,1,3-benzoxadiazol-4-yl (NBD), which fluoresces at 540 nm when excited at 470 nm. After recording initial fluorescence intensities for each immobilized vesicle, a solution of sodium dithionite ($Na_2S_2O_4$) was passed through the flow cell to reduce the nitro group of the NBD and quench the fluorescence. Since the dithionite ion ($S_2O_4^{2-}$) does not permeate the membrane, only the outer layer was reduced and the remaining fluorescence from the inner lipid layers was measured. From the fractional loss of fluorescence intensity, the number of interior lipid leaflets can be quantified. The microscope images were analyzed by fitting the bright vesicle spots to 2-dimensional Gaussian functions and the intensities measured as the integrated signal under the peak. The observed vesicles showed a distribution of size, lamellarity, and structure. Surface immobilization can also be an important tool in analyzing other applications involving vesicles. One such application is the concentration of drugs within vesicles using a pH gradient. Doxorubicin is a fluorescent chemotherapeutic agent that has been marketed as vesicle-encapsulated Doxil. The kinetics of the concentration process are of interest and can be investigated for multiple individual vesicles in parallel by fluorescence microscopy.

(563) **Analytics in a Live Cell using SERS**

Janina Kneipp[3], Harald Kneipp[1], Margaret McLaughlin[2], Burghardt Wittig[4], Dennis Brown[1,2], Katrin Kneipp[1]; [1]Harvard University, Medical School,; [2]Renal Unit, Massachusetts General Hospit; [3]Humboldt University, Chemistry Departmen; [4]Institute for Molecular Biology and Bio

Exploring the chemical composition of endosomes has thus far not been possible without fractionation, purification, i.e. *in vitro* approaches. Surface enhanced Raman scattering (SERS) enables probing cellular chemistry in individual endosomes in a live single cell. Gold nanoparticles can serve as biocompatible mobile nanosensors. They deliver chemical information by providing the enhanced Raman spectra of intrinsic cellular molecules in their vicinity. Moreover, the SERS signature of a "reporter molecule", attached to the gold nanoparticle, which exhibits a pH-sensitive Raman spectrum, can deliver information on the acidity in the endosome. In this way, SERS enables sensitive probing of the molecular structure in a cellular compartment along with measuring the local pH value. Measurements can be performed in the second and millisecond time scale, i.e. on the time line of cellular processes. The sensitive probing of molecular structural changes and pH in a live cell at subendosomal resolution has the potential to provide a new means to improve our understanding of cellular processes on the molecular level.

(564) **Novel Nanorod Array Substrates for High Sensitivity Biopathogen Sensing**

Richard Dluhy[1], Jeremy Driskell[1], Vinh Hoang[1], Yiping Zhao[1], Paul Rota[2], Ralph Tripp[1]; [1]University of Georgia; [2]Centers for Disease Control

Development of diagnostic methods for rapid and sensitive identification of viruses and other biomedical pathogens is essential for the advancement of therapeutic and intervention strategies necessary to protect public health. Current diagnostic methods for viruses in particular, e.g. isolation, PCR, antigen detection and serology, are time-consuming, cumbersome, or lack sensitivity. We have investigated the use of aligned Ag nanorod arrays, prepared by oblique angle vapor deposition (OAD), as surface-enhanced Raman scattering (SERS) substrates for the identification and classification of viral pathogens. The OAD method of substrate preparation facilitates the selection of nanorod size, shape, density, alignment, orientation, and composition, while the procedure is reproducible and relatively simple to implement. The current talk will address aspects of the fundamental nanostructural design of metallic nanorod arrays and their influence on SERS enhancement, as well as the development of a spectroscopic assay for virus detection based on these unique nanostructured SERS probes. We will also present results of multivariate statistical analyses on the SERS spectra of different pathogenic species that indicate that it is possible to identify, differentiate and classify viruses and other biomolecules based on their intrinsic SERS spectra, even down to the individual strain level.

(565) **Barcoding Bacteria: A SERS Based Methodology for Rapid Bacterial Identification**

Lawrence Ziegler[1], W. Ranjith Premasiri[1], Donald Moir[2], Ishan Patel[1]; [1]Boston University; [2]Microbiotix, Inc

We have a developed a diagnostic platform for the identification of bacteria by exploiting the phenomenon of surface enhanced Raman spectroscopy (SERS). The use of SERS in combination with microscopy capabilities has allowed the development of a diagnostic assay that is fast, species and strain specific, sensitive, portable and simple to operate for the identification of bacteria that have been recovered from human bodily fluids as well as environmental settings. Relative to polymerase chain reaction (PCR) based techniques, SERS microscopy offers advantages in terms of speed, ease-of-use, cost, portability and infection mixture resolution. The SERS based platform for vegetative bacterial cell identification consists of four key components: (1) a microfluidic front end for bacterial enrichment and application of the resulting small volume to the SERS substrate, (2) a reproducible SERS substrate, (3) a portable Raman microscopy instrument and (4) software protocols for identification. An Au nanoparticle cluster covered *in situ* grown SiO2 matrix resulting from a metal doped sol-gel is shown to extremely effective in producing reproducible SERS spectra of bacteria excited at 785 nm. Principal component analysis (PCA) based procedures are used in order to quantitatively characterize the reproducibility, specificity and diagnostic capabilities of this SERS based methodology. The novel feature employed here is the reduction of our spectral input vectors to barcodes based on the sign of the second derivative of the spectrum. SERS spectra exhibit much more distinct spectral signatures than corresponding non-SERS Raman spectra of the same bacteria essentially due to the distance dependence of the SERS enhancement mechanism. SERS species specificity is maintained after exposure to human blood. An example of the diagnostic specificity of this SERS aproach relevant to a contemporary health problem in the United States is the ability to rapidly (~minutes) distinguish MRSA, the anti-biotic resistant Staphylococcous aureus bacteria from MSSA, a closely related non-drug resistant Staphylococcous aureus strain.

(566) **Application of SERS to Structure-Functional Characterization of Complex Biosystems**

George Chumanov[1], Jacquitta KaTrina Daniels[2], David Evanoff[1]; [1]Clemson University; [2]Sporian Microsystems, Inc

The localization of *f*Ò-carotene and lycopene in low-density lipoproteins (LDL) isolated from human plasma were determined from the sharp distance dependence of the SERS signal. SERS substrate was modified with self-assembled monolayers of carboxy-terminated linear alkanethiols of different length. The negative charge of the surface groups mimicked the binding region of the LDL receptor. It was concluded that both carotenoids are located near the positively charged protein domain on the surface of LDL particles. Capitalizing on the short distance dependence of SERS, a mismatch in s double stranded DNA was identified. Enhanced Raman spectra only originated from nucleotides that were in direct contact with SERS surface. Hydrogen bonding in double stranded DNA prevented Raman scattering from aromatic rings to be enhanced and no SERS spectra was observed. However, hydrogen bonding was disrupted when a mismatch was present resulting in an open region that produced strong characteristic SERS spectra. SERS spectroscopy was applied to measure the kinetics of dipicolinic acid (DPA) release from B. subtilis (an anthrax stimulant) spores during germination. Germination was initiated by L-alanine and was monitored by the increase of DPA SERS signal over time. The kinetics was measured as a function of the germinant concentration and temperature. The SERS sensitivity allowed monitoring of the DPA release from a single B. subtilis spore thereby providing the ultimate detection limit.

(567) **Probabilistic Modeling for Small Molecule Identification in LC-SERS Experiments**

Royston Goodacre[1], Iqbal Shadi[1], Richard O'Connor[1], Roger Jarvis[1]; [1]The University of Manchester

Two of the great advantages of Raman spectroscopy, and to a certain extent surface-enhanced Raman scattering (SERS), are chemical specificity and true quantitation. In the field of metabolomics[1] these properties, along with nM sensitivity and good dynamic range, are desired for biochemical profiling of small molecules in biological samples. Currently, the technologies most

widely used in this area are liquid chromatography (LC) or gas chromatography (GC) coupled to a mass spectrometer (MS) detector. In addition, nuclear magnetic resonance (NMR) spectrometry is used widely within the sibling metabonomics community, which is more focused on pharmaceutical areas of research. Each of these techniques has disadvantages which mean that they are not entirely fit for purpose. NMR is reproducible and sensitive, but sample throughput is slow and instruments are expensive to purchase, house and maintain. GC/LC–MS have much greater rates of sample throughput, but the mass spectra obtained from the analysis are not strictly quantitative. There is clearly space within this field for new technologies that offer inexpensive, rapid and truly quantitative analysis of biological samples. To this end we have developed LC-SERS for metabolomics and will demonstrate this on a simple idealized mixture as well as bacterial cell extracts. Although not as sensitive as the current technologies listed above, we believe that this method could provide a useful complementary analysis procedure to add to the metabolomics toolkit. An additional requirement when taking such an approach is that the biochemicals measured through the system can be identified and mapped back to biochemical networks. Therefore, we have developed a database of 150 spectra of chemical standards relevant to biology, and will show how the probabilistic data modeling methods have been used to automate the process of deconvoluting LC-SERS data.

(568) **Immunoassay Sensor Based on Surface-Enhanced Raman Scattering on Gold SOLS for Detecting Biological Molecules**

Ava Dykes[1], Lori Kamemoto[1,2], Anupam Misra[1], Shiv Sharma[1]; [1]University of Hawaii; [2]John A. Burns School of Medicine

The realization that early detection is the key to treatment of many maladies has spurned the need for the sensitive detection of biological markers beyond the nanomolar scale. Current methods, such as fluorescence assays and flow cytometry, are limited in their sensitivity by the characteristics of the fluorophores used. Photobleaching, quenching, and spectral overlap are among some barriers to detection beyond current limits. Recent advances in surface-enhanced Raman scattering, with sensitivity comparable to fluorescence, have renewed interest in Raman spectroscopy as a clinical tool. We have examined SERS enhancement on commercial gold particles as well as gold sol prepared in our laboratory using rhodamine 6G dilute solutions. We found that SERS enhancement with 785nm laser excitation increases with decreasing particle size. To further study this finding, we have developed immunosensors with both gold sol and 40nm gold nanoparticles. Conjugation of monoclonal antibodies to gold nanoparticles via the bifunctional Raman reporter molecule, 5, 5'-dithiobis (succinimidyl-2-nitrobenzoate) (DSNB) allows for the sensitive detection of target proteins in addition to those advantages associated with SERS-based detection, narrow spectral bandwidth and resistance to photobleaching and quenching. We have measured SERS spectra of protein A and prostate specific antigen (PSA) using separate yet similar antibody-based detection methods. A range of concentrations of protein A were immobilized on nitrocellulose membrane then labeled via incubation with anti-protein A linked to DSNB reporter-gold nanoparticle complexes. PSA dilutions were evaluated by first capturing free PSA using monoclonal anti-free PSA antibody coupled to gold-coated glass slides. Subsequent probing with a complementary tracer antibody conjugated to the DSNB reporter-gold nanoparticle complex resulted in a highly specific sandwich-type assay. Both methods offer improved sensitivity to both conventional and previously-tested SERS-based detection methods.

(569) **To Charge or Not to Charge: Ions at Aqueous Interfaces**

Geraldine Richmond; [1]University of Oregon

Inorganic ions, and molecular ions present at the surface of aqueous solutions can have a strong influence on the behavior of many complex physical, chemical and biological processes. To advance our knowledge of the role that these charged species play in these systems, we need to develop a molecular level picture of how ions, including acids and bases, adsorb at aqueous surfaces and how these ions enhance or diminish the adsorption of other species at these surfaces. This presentation will focus on what we are learning about charged ions at a water surface, with a particular focus on the differences between how these ions behave at an air/water interface compared to an interface between water and hydrophobic liquids and films. Our studies that combine nonlinear spectroscopic measurements at surfaces and molecular dynamics calculations provide intriguing insights into this relatively unexplored but important area of interfacial science.

(570) **Vibrational Spectroscopy of Water Interfaces**

Yuen-Ron Shen[1]; [1]University of California, Berkeley

Surface-specific sum-frequency spectroscopy (SFS)is unique in its ability to generate vibrational spectra for water interfaces, from which information on water interfacial structures can be deduced. The spectra in general can be characterized by water-like and ice-like features as well as a dangling OH peak if the interface is hydrophobic. Thus, water interfaces appear to have the structure of a heavily disordered, dynamically varying, hydrogen-bonding network. Attempts to extract more detailed structural information from the spectra, however, have led to confusion. The problem arises because the spectra obtained by conventional SFS cannot be used to uniquely characterize the vibrational resonances. We have developed phase-sensitive SFS capable or generating spectra analogous to absorption or emission spectra that can directly characterize the vibrational resonances. Application to water interfaces allows us to construct more detailed physical pictures of various types of water interfaces. We find that all water interfaces appear as a randomly distorted ice surface, with rapidly decreasing order moving into the bulk, but the net polar orientations of different water species at the interface can be very different. The topmost layer is occupied by H-bonded DAA and DDA molecules, which are also H-bonded to the DDAA molecules underneath. (D and A refer to donor and acceptor bonds, respectively.) A small fraction of such DDAA molecules has symmetric tetrahedral H-bonding geometry resembling that of ice and gives rise to the ice-like feature in the spectrum. Large anions, hydroniums, and perhaps hydorxyls in aqueous solution can approach the interface. They do not significantly disturb the topmost layer structure, but can create a positive or negative surface field that reorients the DDAA molecules in the subphase. This work was supported by NSF-STC WaterCAMPWS and DOE.

(571) **Coupling of Cholesterol-Rich Lipid Phases in Asymmetric Bilayers**

Lukas Tamm[1], Volker Kiessling[1], Chen Wan[1]; [1]University of Virginia

Cholesterol-rich liquid-ordered domains with lipid compositions typically found in the outer leaflet of plasma membranes induce liquid-ordered domains in adjacent regions of asymmetric lipid bilayers with apposed leaflets composed of typical inner leaflet lipid mixtures as visualized by epifluorescence microscopy and confirmed by single molecule diffusion measurements in supported bilayers (1). To further examine the nature of transbilayer couplings in asymmetric cholesterol-rich lipid bilayers, the effects on the lipid phase behavior of different combinations of asymmetric lipid bilayers were investigated (2). We established several systems with natural extracted and synthetic lipid

combinations that exhibited coexisting liquid-ordered (lo) and liquid-disordered (ld) domains in a supported bilayer format. We found that lo phase domains were induced in all quaternary inner leaflet combinations composed of PCs, PEs, PSs, and cholesterol. Ternary mixtures of PCs/PEs/Chol, PCs/PSs/Chol also exhibited lo phases on top of outer leaflet lo phases. However, with the exception of brainPC extracts, binary PC/Chol mixtures were not induced to form lo phases by adjacent outer leaflet lo phases. Higher melting lipid adducts of PEs and PSs are needed for lo phase induction in the inner leaflet. It appears that the phase behavior of the inner leaflet mixtures is dominated by their intrinsic melting temperatures, rather than by their specific headgroup class. The targeting of various proteins to asymmetric lipid domains of different composition will be discussed. 1. Biophys. J. 91:3313-3326 [2006] 2. Biochemistry 47:2190-2198 [2008]

(572) **Quantitative Determination of Interfacial Populations at the Single-Molecule Level**

Joel Harris[1], Joshua Wayment[1], Christopher Fox[1]; [1]University of Utah

The accurate determination of small numbers of molecules is a challenging measurement problem in chemical analysis. Quantitative analysis of small populations of molecules at surfaces is needed to understand a variety of analytical processes including adsorption, catalysis, and reactions with surface-bound ligands. While single-molecule imaging has produced exciting results for characterizing small numbers of molecules, the results are not usually interpreted on a quantitative basis due to the significant challenge of preparing standard samples having known surface concentrations. To address this challenge, quantitative deposition of molecules at fractional monolayer coverages onto surfaces from solution can be implemented using a substrate-withdrawal technique. Molecules are deposited at very low surface concentrations and detected by fluorescence microscopy to validate the quantitative accuracy of single-molecule counting. Excitation conditions are optimized for reliable counting of individual molecules and are applied to quantifying the binding of small proteins to supported lipid bilayer membranes. For studying ligand-binding reactions at liquid/solid interfaces, reactive sites are incorporated at very small concentrations into a monolayer of a diluent silane so that reactive sites spaced by several micrometer distances. Small antigens are bound to these reactive sites and used to image binding and unbinding events of labeled antibodies to specific ligand sites on the surface, producing an immunoassay performed at the single-molecule level. Binding isotherms and equilibrium constants can be determined without standardization of the fluorescence response. Rate constants for unbinding and binding can be determined directly from histograms of on-off times in the fluorescence image. The experiment is massively parallel where hundreds of reactive sites undergo thousands of reactions in a single observation.

(573) **A Molecular View of Low Work Function Metal-Organic Contacts in Photonic Devices**

Jeanne E. Pemberton[1], Robert J. Davis[1], Matthew C. Schalnat[1]; [1]University of Arizona

Low work function metals are commonly used as electron injection (cathode) contacts on electron transport layers in photonic devices such as organic light emitting diodes (OLEDs). Although the fundamental charge injection physics of such interfaces has been well described, the interfacial chemistry associated with these contacts is poorly understood and characterized. Efforts to characterize the chemistry of such interfaces using surface Raman spectroscopy have been undertaken in this laboratory. In this presentation, work in which contacts of Ag, Al, Ca and Mg are formed with tris-(8-hydroxyquinoline) aluminum (Alq3), a widely used electron-transport/light-emitting layer in OLEDs, will be discussed. Surface Raman spectroscopy of these interfaces documents significant molecular structural change in thin, amorphous Alq3 layers upon vapor-deposition of small amounts of these metals in UHV. Ag is unreactive with Alq3; however, results suggest the formation of metal-organic adducts for Al, Ca and Mg at the interface along with the formation of different types of graphitic carbon depending on the metal deposited. These findings will be presented and their implications for device performance considered. Attempts to correlate the structural changes observed by Raman spectroscopy with theoretically-predicted Alq3 metal adducts will also be discussed.

(574) **Structure, Functional Properties, and Analytical Applications of Poly(Lipid) Bilayer Membranes**

Scott Saavedra[1]; [1]University of Arizona

In some types of applications, the utility of fluid phospholipid bilayers as biocompatible structures in sensors and other types of molecular devices may be compromised by their chemical and mechanical instability. One strategy to address this problem is the use of synthetic lipids, substituted with reactive groups, to create polymerized bilayer structures. We have been investigating cross-linking polymerization of dienoyl-functionalized lipids in an effort to enhance the stability of liposomes, giant vesicles, and planar supported bilayers. An appropriate choice of lipid composition and polymerization method yields structures that are elastomeric yet stable to conditions that would destroy a fluid membrane (e.g. exposure to air, surfactants, solvents). In addition to extensive structural characterization, we have examined functional properties of these poly(lipid) structures, specifically their resistance to nonspecific protein adsorption, their permeability to ions and small molecules, and the activity of incorporated transmembrane proteins. Arrays of substrate-supported poly(lipid) membranes suitable for fluorescence and mass spectral analysis of ligand binding have also been a recent focus.

(575) **Correcting Isotope Ratio Inaccuracies Encountered with ICP-TOF-MS**

Adam Rowland[1], James Holcombe[1]; [1]University of Texas at Austin

The use of TOF mass analyzers with ICP mass spectrometers is generally assumed to be a viable means of obtaining accurate and precise isotopic ratio data in applications such as tracer studies, IDMS and chronological dating. While precision has been amply demonstrated, the accuracy of the ratios is flawed. The error originates from the need to use analog signal information in place of ion counting and the subsequent errors originating at the detector and within the detection circuitry. An explanation of the fundamental source of the inaccuracies and a means by which these errors can be minimized will be presented. Several examples will be used to illustrate the effectiveness of the approach.

(576) **Plutonium Isotope Ratio Measurements at Femtogram-Attogram Levels by Single and Multicollector ICP-MS using Inline Selective Electrochemical Preconcentration and Stripping**

Martin Liezers[1], Scott A. Lehn[1], Khris B. Olsen[1], Orville T. Farmer (lll)[1], Douglas C. Duckworth[1]; [1]Pacific Northwest National Laboratory

A selective and efficient method of plutonium electrochemical complexation and isolation on to an anodized glassy carbon electrode has been developed using a flow through cell. Because plutonium preconcentration and release is simply controlled by the applied cell potential, large transient concentration enhancements can be achieved whilst rejecting uranium. This presentation will focus on the analytical performance characteristics of plutonium isotope ratio measurements using this electrochemically-modulated

separation approach in-line with both single and multi-collector ICP-MS at femtogram to attogram concentrations.

(577) **High Accuracy and Precision Multi-collector TIMS Uranium Isotope Metrology**

Stefan Buerger[1], Rebecca B. Thomas[1], Richard M. Essex[1], Kattathu Mathew[1], Peter Mason[1]; [1]DOE New Brunswick Laboratory

The availability of accurate and precise isotopic abundance values for uranium certified reference materials (CRM) is crucial in various fields of science, including nuclear fuel cycle studies from ore to disposal, geo- and cosmochronology, the investigation of illicit nuclear trafficking, nuclear safeguards, and non-proliferation. New approaches are being explored to assess peak tailing, background contributions, and ion counting yield calibration to measure minor isotope ratios more accurately and reduce corresponding uncertainties in the certified isotope ratios. New Brunswick Laboratory is applying these approaches to the certification of the isotopic ratios for NBL CRM 112-A (natural uranium) and CRM 116 (high-enriched uranium). Examples from these certification efforts will be presented. The role of GUM (Guide to the Uncertainty in Measurement) uncertainty evaluation in multi-collector TIMS analysis will be discussed.

(578) **Analysis of High Activity Nuclear Waste: Laser Ablation ICP at 100 Million Rads!**

Steven Hughes[1], Joseph W. Brady[1], Robert Fry[1]; [1]Spectra-LAse

High volume processing of nuclear waste into radioactive glass (for secure long term storage in an approved facility), and creation of an MSDS storage certificate for each batch of glass, requires rapid elemental analysis in a hostile environment where many sub-samples are so “hot” they literally glow “bright blue”. At radiation levels of 1,000 – 2,000 rads/hr, many instrument components are rapidly destroyed. Conventional key component ratings are often only 500 – 1,000 rads total accumulated exposure, so failure is likely within 60 minutes (or less). The “RAD-8” is a new laser ablation system designed by Spectra-LAse, Inc, to analyze radioactive glass in a Radiation “Hot Cell”, coupled to an adjacent glove-box ICP spectrometer. This paper outlines unusual design parameters of the RAD-8 which allow it to withstand up to 100 million (108) rads total accumulated exposure, facilitating an expected instrument life of 6 – 12 years, operating 15 h/day, 20 days/month.

(579) **Trace Element Analysis by DC Arc**

Jeffrey Miller[1], David Gallimore[1], Ning Xu[1]; [1]Los Alamos National Laboratory

The Actinide Analytical Chemistry group (C-AAC) within Chemistry Division at Los Alamos National Laboratory works with the Plutonium Manufacturing & Technology Division on several non-proliferation projects. One of these projects involves processing Pu-238 to be used in heat source and radioisotope thermoelectric generator development technology. The Pu-238 program is required to meet project specifications for the amount of trace elements to be allowed in the final product. Due to the Pu-238 final product being heat treated to very high temperature to form a ceramic, this material is not easily dissolved in our typical acid mixtures. Therefore, we utilize a DC Arc solid-sampling method of analysis to measure a wide variety of analytes in the high-fired Pu-238 material. However, the equipment used in this DC Arc method is greater than 30 years old and is no longer made. We are not able to buy parts or get any professional service to maintain or fix the DC Arc stand, spectrograph, or micro photometer should this equipment fail. In order to maintain our solid-sampling analysis capability, we endeavored to update our method using newer equipment and technology. In conjunction with Teledyne Instruments Leeman Labs, we will interface a Prodigy spectrometer with a glovebox DC Arc stand separated by an optical, quartz window. This report describes the existing method of DC Arc and the actions that are currently being taken to develop this method using this newer equipment and technology to meet the project specifications for the Pu-238 program.

(580) **Site Selective Passive Eu(III) Binding Affinities to Datura innoxia Plant Cell Walls using Saturated Luminescence Spectroscopy**

Jessica Moore[1], Debbie Serna[1]; [1]New Mexico State University, Chemistry Department

A part of the legacy of the cold war era consists of many square miles of land contaminated with significant amounts of lanthanide and actinide metals. Current technologies for the remediation of these areas include the physical removal of the top-most several feet of ground for relocation. An alternate technology involves the application of plants that are able to accumulate these metals from the soil and transport them into their shoots. A significant contribution of the mechanisms of intra-plant transport of metals involves the passive binding of these metal ions to chemical functionalities located on the cell walls of the different plant tissues. As a model system, the binding of metal ions to fragments of cultured cells from the plant Datura innoxia has been investigated in our laboratory. In an effort to understand passive metal-ion binding to this chemically heterogeneous material, the binding of a lanthanide metal ion (Eu3+) has been investigated. Previous work identified at least four unique binding environments. Recent developments have enabled site-specific quantitation of metal binding to this material through optical saturation of the 5D0 excited state of the Eu(III) within each chemical environment. Application of regularized regression analysis of the resulting environment-specific binding isotherms has enabled the determination of pH-dependent metal ion binding affinities for each type of site on the cell wall of this plant material. These results will be presented. The implications of these determinations for the application of D. innoxia for phytoremediation will be discussed.

(581) **Introducing Molecular Recognition to Surface Plasmon Resonance Sensors using Composite Metal-Polymer Coatings**

Nicola Menegazzo[1], Jing Wang[1], Soame Banerji[1], Wei Peng[1], Yoon-Chang Kim[1], Karl Booksh[1]; [1]University of Delaware

Polymer membranes can be tailored to impart chemically selective response and improved sensitivity to surface plasmon resonance (SPR)-based sensors. Preliminary results utilizing ultrathin (~10nm) polyelectrolyte membranes displayed reliable and selective detection of vapor-phase ammonia at sub-100 ppm levels, with negligible response to interferants such as methane and hydrogen sulfide. In addition, molecularly imprinted polymers yielded a selective response to liquid-phase 200 ppm glucose in undiluted urine. Application of surface modification strategies to SPR sensing is necessary due to the non-specific nature of refractive index changes, measured as a shift in energy minima (lambdaSPR). In addition, small molecules, such as ammonia, induce negligible changes in refractive index restricting access to direct monitoring strategies. Enrichment of compounds into polymers result in swelling, improving the measured response. Polymer coatings were further surficially modified with metal (gold or silver) nanoparticles, providing additional signal amplification due to changes in resonance energy coupling conditions between the base metal and the nanoparticles.

(582) **Development of Compact Sensing System by the Localized Surface Plasmon Resonance**

Ryosuke Hasui[1], Takeo Nishikawa[1], Satoshi Fujita[1], Hideyuki Yamashita[1], Yutaro Okuno[1]; [1]OMRON Corporation CORE Technology Center

In this paper we report the developed LSPR sensor device in comparison with the conventional device and the detection of AFP. In late years, the study of the localized surface plasmon resonance (LSPR) sensor has been investigated as the detection method of the biological molecules. The characteristic of the LSPR sensor is that the real time monitoring is possible and a mark to the biological molecule is unnecessary. In addition, the noise factors such as temperature fluctuation can be eliminated since the sensor can localize the sensing area closer to the interface. Until now, we confirmed, by AFP (cancer tumor marker) detection, the possibility of applications to the biosensor of the sensor chip made by our nanoimprinting technique which allowed good reproducibility and the mass production. Our purpose of this study is to develop the LSPR sensor device newly in order to improve the usability and to clarify the detection limit through the detections of AFP with the above-mentioned LSPR sensor device. The conventional SPR device was large-scale size to have a temperature adjustment system. In addition, a pump flowing such as buffer was necessary separately from the main unit. As a result of device development, our device is small size (W9.8 x D9.8 x H5.9inch) because of having no temperature adjustment system, and the compact constitution establishing the pump in the main unit of the device inside. Therefore, we remarked that our device has high operability in comparison with the conventional device. Furthermore the detection limit of APP was 100ng/ml less than the cutoff-value of AFP (200ng/ml), and it was clear that the performance of our LSPR sensor device was equal to laboratory environment. From these results we found that our LSPR sensor device was available to the high sensitivity detections and would contribute in various fields such as health monitoring, food industry, and environmental monitoring.

(583) **Combining SPR with Other Analytical and Surface Techniques for Studies and Separation of Proteins**

Feimeng Zhou[1], Yongjun Li[1], Ming Du[1], Juan Xiang[2]; [1]California State University, Los Angeles; [2]Central South University, P. R. China

In this presentation, surface plasmon resonance (SPR) combined with other analytical and surface techniques (including electrochemical SPR, HPLC coupled on-line with SPR, the tandem use of scanning electrochemical microscopy and SPR, and imaging SPR used in conjunction with ellipsometry) will be described. The versatility of these novel coupled techniques in interrogating properties of proteins at the surface/solution interface and in addressing biological problems will be demonstrated. The applications include studies of infinitesimal changes in protein conformation initiated by redox reactions, metal sequestration of release by metallothioneins (a cysteine-rich metalloprotein), detection by a dual channel SPR of chromatographically separated proteins, and monitor thin film growth with SPR imaging.

(584) **A Surface Impedance Imaging Technique**

Kyle Foley[1], Xiaonan Shan[1], Nongjian Tao[1]; [1]Arizona State University

We demonstrate here a surface impedance imaging technique based on sensitive dependence of surface plasmon resonance (SPR) on local surface charge density. By applying a potential modulation to a sensor surface, we are able to simultaneously obtain three images: the dc component and the amplitude and phase of the ac component. The dc image measures local molecular binding activity on the surface, as found in the conventional SPR imaging technique, and the ac images are directly related to the local impedance of the surface. Our experimental data can be analyzed quantitatively in terms of the simple free electron gas model for the sensor surface and the Randles equivalent circuit model for interfacial impedance.

(585) **Swellable Polymer Particles for Optical Sensing**

Barry Lavine[1], Mary Kim[1], Donald Brown[1]; [1]Department of Chemistry, Oklahoma State University

Theophylline-imprinted polymer particles of N,N-propylacrylamide were prepared by dispersion polymerization and deposited onto a gold SPR slide by spin coating. Ten drops of a methanol suspension of the particles were placed in the center of the sample slide, which was spun at 500 rpm for 5 seconds and 3000 rpm for 25 seconds. The slide was then allowed to dry for two days in a desiccator before rehydration. A polyvinyl alcohol hydrogel membrane prepared *in situ* before rehydration, encapsulated the spin coated polymer particles, preventing their detachment from the gold. The polymer particles formed a layer that was both sensitive and specific. The addition of as little as 40ppb theophylline was sufficient to cause a change in the refractive index, which we were able to detect by SPR. Higher concentrations of theophylline produced larger changes in the refractive index. In contrast, the particles showed no response to distilled water or 1.0x10-2 M caffeine. (Caffeine only differs from theophylline by a single methyl group.) The full scale response of the imprinted particles to the template occurs in less than 10 minutes. Swelling is reversible, and independent of ionic strength. Replicate precision is less than 10-4 RI units. A unique aspect of the polymer particles is the use of light crosslinking rather than heavy crosslinking. Swellable polymer particles that respond to pH and metal ions have also been prepared by dispersion polymerization. The polymer particles show a larger response over a narrower pH range than that predicted by the Henderson-Hasselbach equation. The pKa of the polymer particles can be tuned by varying the degree of crosslinking or the pKa of the pH sensitive commoner used in the formulation. One potential application of these pH sensitive polymer particles is monitoring the progress of open-heart surgery, where pH serves as a measure of tissue ischemia. Gastric pH sensing is yet another potential application. For metal ions, the polymer particles respond by swelling when exposed to alkali and alkaline earth metals whereas they shrink in respond to transition metal ions.

(586) **Plasmonic Electrode Assemblies for Multi-Modal Sensing and Intelligent**

Paul W. Bohn[1], Sean P. Branagan[1]; [1]University of Notre Dame

Our work investigates the construction and characterization of an integrated architecture capable of implementing the linked tasks of detection, identification and chemical transformation. These unit operations are coupled in a unique element: a plasmonic nanocapillary array reactor, PNAR, that is capable of supporting technically diverse, but inter-related, functions: (a) flow control, (b) detection of small deviations in the dielectric function of a fluid, (c) highly-specific identification through enzyme-linked bioelectrochemistry and (d) chemical transformation of the detected species. We are exploring how PNARs can achieve highly selective chemical sensing by exploiting the multimodal character of the plasmonic and electrochemical responses in a single structure which uniquely combines the elements of flow, plasmonics and electrochemistry. Currently our focus is on using the PNAR as an SPR sensor, the architecture also doubling as a fluid gate, such that bulk flow is brought into intimate contact with the chemical sensor, when the fluid is electrokinetically driven from one microfluidic channel to another. The analytes are required to flow through nanometer-diameter capillaries and forced into the evanescent field

of the propagating plasmon, thereby greatly improving detection efficiency. Optically, this configuration also offers an ideal situation for SPR imaging.

(587) **TERS – A Potential Tool for Direct Sequencing**

Volker Deckert[1,2], Elena Bailo[1], Tanja Deckert-Gaudig[1]; [1]ISAS; [2]TU Dortmund

Tip enhanced Raman scattering (TERS) combines conventional Raman spectroscopy with scanning probe techniques. An optically active silver or gold coated scanning probe microscopy tip on top of the specimen is illuminated with a laser. This provides a unique tool not only to obtain highly enhanced Raman signals together with a high lateral-resolution of around 20 nm, but also an unique surface enhancing substrate that allows the quantitative comparison of the results at different locations. While a major challenge is the optimization of the probes with respect to high enhancement factors and high lateral resolution using experimental approaches as well as theoretical and modelling tools, a major aim of our research is the application of this method to analytical problems in the life sciences. We will show the comparison of Raman and surface enhanced Raman spectra of various bio related molecules with TERS experiments. TERS studies of nano crystals of DNA monomers will be investigated emphasising the geometry of the field enhancing probe. Direct measurements on a single RNA strand will be discussed with respect to enhancement, resolution and direct sequencing capabilities of he method. In a similar approach TERS spectra of monolayers of amino acids immobilised on gold nanocrystals have been obtained. Again the results will be discussed with respect to a label free sequencing method.

(588) **Making CARS Better**

Eric Potma[1]; [1]University of California, Irvine

Coherent anti-Stokes Raman scattering (CARS) microscopy is gaining popularity as a biomedical imaging tool. CARS offers label-free imaging based on vibrational contrast at image acquisition rates comparable to fluorescence microscopes. The current detection sensitivity of CARS to a variety of compounds such as lipids, water and select molecular agents have already produced an impressive array of biomedical imaging studies. In this contribution we will present an overview of several recent CARS imaging studies and discuss various strategies to move CARS to the next level of detection sensitivity.

(589) **Non-Invasive Raman Spectroscopy and Mapping of Musculoskeletal Tissue using Spatially-Separated Delivery and Collection Optical Fibers**

Jacqueline Cole[1], Matthew Schulmerich[1], Kathryn Dooley[1], Michael Morris[1]; [1]University of Michigan, Ann Arbor, MI

Fiber-optic Raman probes provide unique opportunities to characterize the composition of tissues noninvasively. Using spatially-separated delivery and collection fibers to minimize the fluorescence background of surface layers, we recover subsurface bone tissue signals from through-the-skin measurements despite interference from overlying soft tissues (e.g., skin, muscle, tendon). Compositional properties are correlated with aspects of bone health. By observing changes in composition, we can assess the status of various metabolic and genetic diseases and their effects on bone tissue without the use of ionizing radiation. With several different probe designs we examine bone tissue in specimens of various sizes, ranging from mice and rats through canines to humans. For these probes, we alter the geometry and placement of the excitation light and collection field of view using various lenses and fiber arrays to control the sampling area size and the delivery-collection separation, which determines the penetration depth. Current probe configurations include delivery via a laser ring or a laser line and collection via a close-packed circular disk or rectangular array of fibers. Because these designs are flexible, we can maximize the rejection of Raman scatter from skin and make accurate subsurface measurements with short acquisition times. The same basic technology is applied to other novel and related measurement schemes. For example, we use light scattering with spatially-offset probes in bone tissue to monitor the presence of small cracks, which often precede overall bone fracture. Using a fiber-optic probe, we have demonstrated Raman tomography in a canine limb, where we reconstructed the Raman signal from the bone through more than 25 mm of tissue. Image-guided Raman spectroscopy, a method that combines anatomical information from typical medical imaging techniques with spectroscopic measurements, allows us to visualize bone spectra at a contrast of 145:1 with respect to the spectra from surrounding soft tissues. Using animal models that mimic human tissue properties, we will present our newest developments in these optical probe technologies and exciting new findings in noninvasive Raman spectroscopy, Raman tomography, and light scattering. These advances point toward Raman-based diagnostics that can be implemented in a clinical environment.

(590) **Static Coded Apertures for Diffuse and Imaging Spectroscopy**

David Brady[1]; [1]Duke University

Static mask coded aperture spectrographs may increase the spectral efficiency of Raman instruments by 1-2 orders of magnitude. This talk reviews the impact of this increased efficiency on the SNR of spectral estimation and on chemometric analysis. We focus in partcular on the potential to surpass the classic "multiplex advantage" of Hadamard codings outlined by Harwit and Sloan using nonlinear estimators. We describe chemometric applications in tissue diagnostics and pharmacuetical analysis. We also describe extensions to coded aperture snapshot spectral imaging (CASSI) systems.

(591) **SERS-Melting: A New Method for Distinguishing Mutations in DNA Sequences**

Sumeet Mahajan[1], James Richardson[1], Tom Brown[1], Phil Bartlett[1]; [1]School of Chemistry, University of Southampton

The development of simple, low cost, reliable, high-throughput methods to detect genetic variations in DNA is crucial for the development of DNA-based diagnostics and forensics. In a typical solid-phase analytical system, single-strand DNA (ssDNA) is immobilized on the substrate as the 'probe' sequence and then hybridized to 'target' sequences from solution. The resulting DNA duplexes (dsDNA) are then denatured, typically, either by ramping up the temperature or by washing with solutions of decreasing ionic strength (stringency washing). Mutations are detected by monitoring the denaturation process; mutations destabilize the duplex to varying degrees depending on the number of mismatches as compared to the perfectly complementary target and therefore denature more readily. Presently, fluorescence is the most widely used method for following dehybridization. In this work a novel sensitive and reproducible method that uses surface enhanced (resonance) Raman scattering (SERS or SERRS) for monitoring denaturation of dsDNA on sphere segment void gold substrates is described. This denaturation is driven thermally or electrochemically. Using this method we can distinguish between wild type, a single point mutation (1653C/T), and a triple deletion (ÄF508) in the CFTR gene using synthetic sequences. The sensitivity of detection of this method has been found to be at the 0.02 attomole level, as determined by electrochemical techniques. To establish the practical utility of our SERS-melting method we also show that it can be used to differentiate PCR products, as in a real situation. Employing electrochemically induced melting we are easily able to distinguish unpurified PCR amplicons of the wild

type and ÄF508 mutation in CFTR gene using our SERS monitoring methodology.

(592) **Raman Analysis of Common Gases using a Multi-Pass Capillary Cell (MCC)**

Christopher Gordon[1], William Pearman[1], Chance Carter[2], Michael Angel[1], James Chan[2]; [1]University of South Carolina; [2]Lawrence Livermore National Laboratory

The Raman analysis of common, non-absorbing gases was performed using an 18@1 fiber-optic probe coupled to a multi-pass capillary cell (MCC) for signal enhancement. The MCC is fabricated by metal-coating, using silver or other highly reflective metals, the inside of a 1-2 mm diameter glass capillary using commercially available silvering solutions and provides enhancements up to 30-fold over measurements using the fiber-optic probe alone. The design of the MCC is simple and the device is easy to incorporate into an experimental setup making it suitable for uses in remote and *in-situ* analysis. Although the MCC is functionally similar to other liquid-core waveguides that have been previously described in the literature, the MCC is not based on total internal reflection and so the refractive index of the analyte is not important to the operation of the device. The principle of operation of the MCC is similar to mirror-based multiple pass Raman cells, however, the MCC is not expensive, alignment is trivial and an optical path length up several meters in length is possible. With our first-generation MCCs made with silver-coated capillaries, limits of detection were determined to be 0.02% and 0.2% for CH4 and CO2 respectively. In this talk we will discuss optimization of the MCC and issues involved in its use.

(593) **Detection of Disease in Individual Exfoliated Cells from Oral and Cervical Cytological Samples by Infrared Micro-Spectroscopy**

Max Diem[1], Benjamin Bird[1], Miloš Miljkoviæ[1], Jennifer Schubert[1], Kostas Papamarkakis[1], Melissa Romeo[1]; [1]Northeastern University

We have collected tens of thousands of high quality images and infrared spectra from individual exfoliated cells. To this end, we map an entire sample substrate, onto which exfoliated cells are deposited via liquid-based cytology methods, in an imaging infrared spectrometer at high spatial resolution, and reconstruct cellular spectra from the individ-ual pixel spectra. Furthermore, we have developed hard- and software to automatically collect high resolution visual images of all cells detected in the infrared map, after stain-ing and at 40X magnification, and link the images and spectra in a relational database. We are presently analyzing hundreds of samples from cervical cancer screening, and dozens of samples from oral cancer screening, using the methodology described above. The total number of cellular spectra and images collect to far is approaching 100,000. At the level of individual cells, it is possible to detect infection of the cells by viruses (e.g., herpes simplex and human papilloma virus) by processing spectral data via methods of multivariate analysis, such as principal component analysis. The maturation of cells in the squamous epithelium, as well as the transition from normal to cancerous states, af-fect the cellular in a reproducible manner such that the spectra can be correlated to the progress of disease. These results, which have been attempted by a number of re-search groups over the past decade, represent the first evidence that it is possible to carry out medical diagnoses of individual cells on a cell-by-cell basis by infrared spec-troscopy.

(594) **Infrared Chemical Imaging with a Solid Immersion Lens**

Chris Michaels[1]; [1]NIST

Infrared (IR) spectral microscopy exploits the chemical specificity of infrared absorbance spectroscopy to allow the mapping of constituents of heterogeneous materials. The spatial resolution of conventional IR microscopes is in the 20-30 micrometer range, limiting its utility for the chemical imaging of some materials. The application of hemispherical solid immersion lenses (SIL) is an approach to increasing the spatial resolution attainable in chemical imaging with an infrared microscope. The hemispherical SIL lens can produce images with minimal geometric aberration, wherein the effective numerical aperture and magnification are increased by a factor of the SIL material index of refraction. A microscope designed for exploration of IR SIL chemical imaging based on a hemispherical ZnSe SIL, an InSb focal plane array detector and a broadband IR laser source will be described. The imaging characteristics of this system are reported, including the spatial resolution improvements achieved in the imaging of organic test samples.

(595) **Vibrational Infrared Spectroscopic Imaging of Protein Acetylation: Pharmacodynamic Assessment of Histone Deacetylase Inhibitors**

Tsoching Chen[1], Jane Trepel[1], Ira Levin[1]; [1]National Institutes of Health

Vibrational infrared spectroscopic imaging techniques are used to monitor cellular protein acetylation mediated by a histone deacetylase inhibitor (HDACi), an anticancer pharmacologic agent. The anticancer activity of histone deacetylase inhibitors is ascribed to the hyperacetylation of both core nucleosomal histones and non-histone proteins critical to the maintenance of the malignant phenotype. After incubating peripheral blood mononuclear cells *in vitro* with an HDACi, SNDX-275, a benzamide drug derivative used in clinical trials, vibrational spectral changes in the methyl and methylene stretching mode regions as well as the amide I spectral interval were detected and quantified. These spectral changes reflect concentration dependent increases in protein acetylation. Metrics based upon these spectral differences were applied to spectra of peripheral blood mononuclear cells (PBMCs) from patients treated *in vivo* with this pharmacologic agent. The data demonstrate a new approach to a sensitive assessment of global molecular modifications that is independent of antibodies, requires minimal cell processing, and is easily adapted to high-throughput screening.

(596) **FTIR Imaging of Multiple Sclerosis Animal Models**

Donald McNaughton[1], Sally Caine[1], Vivienne Juan[1], Philip Heraud[1], Claude Bernard[1]; [1]Monash University

High spatial resolution infrared images can be routinely and quickly obtained using array detectors at sufficient S/N to follow the progression of disease. The higher spatial resolution and better S/N provided by synchrotron FTIR mapping at the expense of time can often provide further insights into the molecular and structural changes due to disease and the two methods together can more readily provide a basis of disease understanding and possible diagnosis. Multiple sclerosis is one of the most common neurological diseases in the young with an unclear pathogenesis and unpredictable progression. The disease markers are essentially localized areas of demyelination and inflammation. No direct animal model exists for the disease but insight into the pathogenesis of MS is best modeled by the earlier stages of disease progression in experimental autoimmune encephalomyelitis (EAE) in mice. EAE, an autoimmune system-mediated response inducible by injection of major myelin proteins or myelin oligodendrocyte glycoprotein (MOG), is marked by extensive inflammation, demyelination, and axonal damage which mimic MS lesions in humans. We have applied both FPA and synchrotron IR microscopic imaging to analyse the chemical and structural changes that occur in the cerebellum during the progression and prevention of EAE. We demonstrate that pathological changes in

the cerebellum, not visualized by conventional histology, or by confocal microscopy are detected before the clinical onset of EAE. Notably in severe EAE, loss of lipid and increase in nucleic acids co-localizing at lesion sites, correlated with inflammation and demyelination. Each structure of the cerebellum including the lesions could be identified by unique spectral fingerprints such that artificial neural networks (ANNs) could be trained to classify different tissue or pathology in independent samples with high specificity and sensitivity, thus demonstrating the potential of this approach as an automated and unbiased pathology detection system. Finally, we show that the protein secondary structure, alpha-helix and beta-pleated sheet, likely involving myelin-specific proteins, is different in mice vaccinated with Nogo-A, a protein that inhibits neurite outgrowth, as compared to EAE animals. These findings reveal that this methodology can also yield valuable information pertaining to the molecular basis of therapeutic agents.

(597) **Diagnosis of Colorectal Adenocarcinoma by MIR Microspectroscopic Imaging**

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The past decade has witnessed substantial progress towards the application of infrared microspectroscopy as an useful diagnostic tool for spectroscopic characterization of histological specimens. The combination of IR spectroscopy with microscopy, new technical developments such as sensitive multichannel detectors, and the implementation of multivariate concepts of data analysis permit high-quality infrared microspectroscopic imaging of tissue specimens. The IR imaging methodology provides spatially resolved structural and compositional information of the histological specimens and opens in combination with computer based multivariate image reassembling techniques wide perspectives for routine use in the clinical environment. After 15 years of research it is now an accepted standard that IR spectra of cells, or tissues, can be considered as complex spectral fingerprints which cannot be always completely understood in an analytical sense. It is therefore advantageous to analyze the spectral fingerprints by pattern recognition techniques, preferentially of the supervised type, such as multilayer perceptron artificial neural networks (MLP-ANN), or support vector machines (SVM). As the concept of supervised classification requires a teaching phase, in which labeled subsets of tissue reference spectra are analyzed, the compilation and validation of the teaching spectra will be the main challenge to render IR microspectroscopic expert systems applicable in practice. Thus, it is believed that the development of a non-subjective IR based tissue characterization technique will be dependent on the collection of data bases of teaching spectra ideally containing a representative number of standardized spatially resolved IR microspectra of relevant normal and pathologic tissue structures. The aforementioned aspect is important because despite all the fascinating perspectives, promising technical developments and exciting research papers, progress towards the translation of the technique into a practical application is less evident. The lack of available spectral reference data bases is now identified as a factor which limits the transfer of the technique from the research laboratory to the clinical environment. In our presentation we will discuss topics relevant to the collection of spectral data bases such as spectral quality criteria, measurement standards, measurement conditions and more. The presentation will be based on experimental results of colorectal adenocarcinoma studies.

(598) **Optimized Mid- IR Imaging for Clinical Translation**

Rohit Bhargava[1], Frances Keith[1], Anil Kodali[1], Jason Ip[1], Michael Walsh[1]; [1]University of Illinois at Urbana-Champaign

A number of groups have demonstrated the potential of IR spectroscopy and imaging approaches in determining tissue structure (histology) and disease states (pathology). There is a need, however, to develop these successes into integrated protocols that are ready for clinical translation. In this presentation, we present efforts to optimize both the data acquisition and classification process. Simplified data acquisition is shown to improve the rate of examination significantly, compared to current methods. Optimization of experimental parameters for classification demonstrates that several orders of magnitude faster scanning can be achieved by careful integration of various facets of diagnostic histopathology by spectroscopic imaging.

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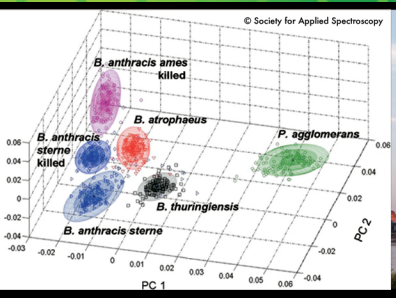

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