FACSS 2006

FINAL PROGRAM
BOOK OF ABSTRACTS

Federation of Analytical Chemistry & Spectroscopy Societies
Society for Applied Spectroscopy National Meeting

September 24-28, 2006

Disney's Contemporary Resort

Lake Buena Vista, Florida

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TABLE OF CONTENTS

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

FACSS National Office
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WELCOME TO FACSS 2006

On behalf of the Governing Board and the Executive Committee, it is my pleasure to welcome you to Lake Buena Vista and Disney's Contemporary Resort for the 33rd annual meeting of the Federation of Analytical Chemistry and Spectroscopy Societies (FACSS), and the annual meeting for both the Society for Applied Spectroscopy (SAS) and the Coblentz Society.

To maintain the long tradition of FACSS as a premier fall chemistry meeting, the organization is continuing to evolve in response to the changing needs of chemists. This year, FACSS has been significantly enriched by the new FACSS affiliation of the American Society for Mass Spectrometry (ASMS). While many ASMS members have been FACSS attendees for years, this is the first time that ASMS participates as an official FACSS Member Society.

The FACSS Program is also continuing to evolve in response to constructive comments from attendees and leadership. A new format for the technical program was implemented at the 2004 conference that was designed to encourage mixing, discussion, and exchange of ideas. In this format, which was largely continued this year, each day will begin with plenary presentations by an internationally acclaimed speaker and/or winner of an award presented at FACSS. Each half day, the technical program will consist of only eight highly focused, concurrent oral sessions. Daily poster sessions are scheduled so they do not compete with oral sessions to maximize their visibility and impact, and awards will be given daily for outstanding posters. In direct response to last year's attendee input, we are deliberately offering as many casual opportunities as possible for networking by taking advantage of the opportunities offered by the Disney facilities and our Program and Exhibit hall. Official social events this year will further enhance your FACSS experience, and include the welcome mixer Sunday evening, the exhibit opening early Monday evening, coffee breaks during the Tuesday and Wednesday poster sessions in the exhibit hall, and the Wednesday Evening Event. For the first time, the FACSS Exhibit will include a hands-on workshop, to facilitate exchange of technical ideas between exhibitors and attendees. We encourage you to take full advantage of the meeting's workshops, employment bureau, and social activities. We hope you will provide additional feedback on your FACSS experience this year.

This year's technical program features cutting edge symposia in the topical areas of atomic spectroscopy, bioanalytical chemistry, chemometrics, forensics, Raman spectroscopy, mass spectrometry, molecular spectroscopy, nanoscience, process analytics, and surface plasmon resonance. The FACSS Program is looking to the future of analytical chemistry and spectroscopy with symposia featuring young principal investigators and a symposium highlighting student award winners. The conference will kick off with "Spectroscopy on the Red Planet: More than Meets the Eye" by Hap McSween of the University of Tennessee and the Thursday plenary "Ultrahigh-Resolution Mass Spectrometry for Separation and Identification of Complex Analytical, Biological, and Environmental Organic Mixtures" will be presented by Alan Marshall of Florida State University. Key lectures will be given throughout the meeting in recognition of the following award winners: Charles Mann Award winner Michael Morris of the University of Michigan, William F. Meggers Award winners Pavel Matousek, Ian Clark, Edward Draper, Michael Morris, Allen Goodship, Neil Everall, Mike Towrie, William Finney, and Anthony Parker, and Lester W. Strock Award winner Paul Farnsworth of Brigham Young University. Richard D. Sacks will be recognized posthumously for his contributions to science, as the 2006 recipient of the ANACHEM Award. Information about the awards and the recipients can be found in this program.

Lake Buena Vista is a fabulous area; please plan time into your schedule to enjoy it. Well-known attractions can be enjoyed on the Disney properties, which are directly accessible by monorail from the meeting site. Many other attractions are easily accessible, and there are numerous world class restaurants and souvenir shops in the area. We will be having our Wednesday Evening Event at the Adventurers' Club on Walt Disney's Pleasure Island.

This year's meeting would not be possible if it were not for a fantastic team of people that freely volunteer copious amounts of time, passion, thought and effort. When you see someone wearing a "Committee Ribbon" on their name tag, please take the time to thank them for their efforts.

If you have constructive comments or suggestions, complimentary or otherwise, please mention them and fill out one of our annual FACSS attendee questionnaires so that FACSS can better serve your meeting needs in the future---or, even better, become involved in the FACSS organization; we can always use new ideas and energy!

Diane Parry
2006 Governing Board Chair

GENERAL INFORMATION

LOCATION: All conference symposia, workshops and exhibits will be held at *Disney's Contemporary* 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 by registration.

POSTER SESSIONS.

Sunday SAS Sponsored Student Poster Session – *Nutcracker Ballroom*
- Poster Session and Welcome Mixer 5:00 – 7:00 PM

Monday Poster Session – *Nutcracker Ballroom 2*
- Morning Session 9:00 – 10:30 AM

Tuesday Poster Session – *Fantasia Ballroom H/J*
- Morning Session 9:00 – 10:30 AM
- Afternoon Session 1:45 – 3:15 PM

Wednesday Poster Session – *Fantasia Ballroom H/J*
- Morning Session 9:00 – 10:30 AM
- Afternoon Session 1:45 – 3:15 PM

Thursday Poster Session – *Fantasia Ballroom H*
- Morning Session 9:00 – 10:30 AM
- Afternoon Session 1:45 – 3:15 PM

Your poster should remain up all day. If your poster number is an odd number (1, 3, 5, etc.), the presenting author must be present 9:00 - 9:45 AM and 1:45 – 2:30 PM on the assigned day. If your poster number is an even number (2, 4, 6, etc.), the presenting author must be present 9:45 – 10:30 AM and 2:30 – 3:15 PM on the assigned day. One exception to this schedule is the Monday poster session when authors only are required to be by their posters in the morning.

FACSS WORKSHOPS. A list of workshops, descriptions, and the locations begin on page 33. You must register for a FACSS workshop at the conference registration desk.

EMPLOYMENT BUREAU. The bureau will be located in Grand Republic D, second level. The center will be open Monday through Wednesday, 9:00 AM to 5:00 PM and 9:00 AM – 3:00 PM on Thursday. Registration forms are available at the employment bureau. See page 35 for additional information.

EXHIBITS. The exhibition is located in Fantasia Ballroom H/J and will be open as follows**:** See page 25 for details.

Monday (Opening Reception)	**4:30 – 6:30 PM**
Tuesday – Wednesday	**9:00 AM – 5:00 PM**

BREAKS. Monday Breaks will be held in the Nutcracker Ballroom 2. Tuesday and Wednesday breaks will be held in the Exhibit Hall (Fantasia Ballroom H/J), and Thursday breaks will be held in Fantasia H.

INTERNET ACCESS. Complimentary wireless internet access will be available to all conferees. Access is located in the Fantasia Ballroom/Exhibit Hall and Foyer. Click on wireless network named "FACSS."

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

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 will be allowed in the technical sessions.**

SPECIAL EVENTS.

SUNDAY

3:20 – 5:00 PM **"What's Hot" Exhibitor Presentations**, *Fantasia E/F*

5:00 – 7:00 PM **Welcome Mixer and SAS Sponsored Student Poster Session**, FACSS and SAS Award Presentations, *Nutcracker Ballroom*

MONDAY

8:00 AM **Plenary Lecture:** Spectroscopy on the Red Planet: More than Meets the Eye, **Harry Y. McSween, Jr.,** University of Tennessee**,** *Fantasia Ballroom G*

1:15 – 2:15 PM "**What's Hot" Exhibitor Presentations,** *Fantasia E/F*

4:30 – 6:30 PM **Reception for Exhibit Opening** (wine, beer, snacks, live music), *Fantasia Ballroom H/J*

TUESDAY

8:00 AM **ANACHEM AWARD**: From Exploding Wires to Rapid chromatography: The Legacy of a High Speed Scientist and Gentle Mentor, **Richard D. Sacks,** *posthumous:* University of Michigan, presented by James Holcombe, University of Texas, Austin, *Fantasia Ballroom G*

8:30 AM **Charles Mann Award:** Growing, Walking and Falling. The Role of Raman Spectroscopy in the Study of Musculoskeletal Tissue, **Michael Morris,** University of Michigan, *Fantasia Ballroom G*

12:30 **GE Advanced Materials sponsored Student/Professional Panel Discussion and Brown Bag Lunch. "I'm Graduating Soon. What's Next?"** *Grand Republic C. Sign up at conference registration desk.*

WEDNESDAY

8:00 AM **Applied Spectroscopy William F. Meggers Award:** Subsurface Probing in Diffusely Scattering Media Using Spatially Offset Raman Spectroscopy**, Pavel Matousek***,* Rutherford Appleton Laboratory, *Fantasia Ballroom G*

8:30 AM **Lester W. Strock Award:** Probing Plasmas with Photons**, Paul Farnsworth,** Brigham Young University*, Fantasia Ballroom G*

7:00 PM **FACSS Wednesday Evening Event.** Downtown Disney® Pleasure Island **Adventurers Club** (information at conference registration desk). *Ticket required*

THURSDAY

8:00 AM **Plenary Lecture:** Ultrahigh-Resolution Mass Spectrometry for Separation and Identification of Complex Analytical Biological, and Environmental Organic Mixtures**, Alan G. Marshall,** Florida State University, *Fantasia Ballroom G*

COMPANION REGISTRATION. Companion registration is offered for persons accompanying conference registrants. Does not include access to symposia or exhibit hall other than for exhibit opening. Cost is $45 and includes the following:

- Sunday Evening Welcome Mixer and SAS Student Poster Session
- Monday, 4:30 – 6:30 PM, Exhibit Hall Opening Reception
- Monday, 9:00 AM, coffee and pastries, *Pastoral 2*
- Tuesday, 9:00 AM, coffee and pastries, *Board Room*

EVENTS OF SPECIAL INTEREST TO STUDENTS

Sunday Evening, *Nutcracker*

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

Monday

- Employment Bureau in Grand Republic D
  Monday – Wednesday 8:30 AM – 5:00 PM; Thursday 8:30 AM – 3:00 PM

Tuesday

- 12:30, GE Advanced Materials Sponsored Student/Professional Panel Discussion and Brown Bag Lunch. "I'm Graduating Soon. What's Next?" in Grand Republic C. *Sign up at conference registration desk.*

Wednesday

- 9:00 AM – 5:00 PM, Professional Analytical Chemists in Industry: A Short Course for Undergraduate Students; Sandy Murawski, *Procter and Gamble*, instructor. *No charge. Register at the conference registration desk.*

WEDNESDAY EVENING

7:00 PM **FACSS EVENT.** Join the festivities Wednesday evening at Downtown Disney® Pleasure Island **Adventurers Club**. The Adventurers Club is one of the eight clubs at Pleasure Island, and you won't find anything else quite like it on the island. The Adventurers Club presents an interactive entertainment experience in a setting reminiscent of the fictional 1930's gentleman adventurer club, as depicted in Hollywood films of that era. Your evening will include a full buffet dinner with salad, entree (chicken, beef and fish) and coffee. Beverages will be available via cash bars. The fun does not need to end at the Adventurers Club because your admission to the FACSS Adventurers Club dinner also includes admission to Pleasure Island and all its amenities for the remainder of the evening (Admission alone is a $20 value!). Make your reservation for this unique evening early. Admission is limited to 150 people. *Cost for the event: $50*

INDEX TO ADVERTISERS

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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Surface Plasmon Resonance	**Karl S. Booksh**, *Arizona State University*
SAS Student Poster Session	**Bonnie Saylor** and **Victor Hutcherson**, *Society for Applied Spectroscopy*

FACSS CHAIRS

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Diane Parry

Procter and Gamble

Diane Parry is currently an Associate Director for the Procter and Gamble (P&G) Company in Cincinnati, Ohio. She leads P&G's Global Household Care Business Analytical Department with over 100 members in six countries. Diane is married to an analytical chemist, and has two daughters, ages 15 and 17. She received her bachelor's degree in Biology in 1982 from the University of Cincinnati. After graduation, Diane worked as a laboratory technician for the University of Cincinnati College of Medicine, making and measuring the efficacy of serum and monoclonal antibodies and running a research Fluorescence Activated Cell Sorter (FACS!). In 1984, Diane moved to P&G to apply her FACS-acquired laser and computer interfacing skills to P&G's research program in Raman Spectroscopy. With the encouragement of her P&G scientist mentors, Diane left P&G and returned to graduate school full-time at the University of Utah in 1986, joining the research group of the talented and energetic Professor Joel Harris. Her graduate work in infrared and Raman spectroscopy of molecular interactions at non-conducting surfaces led to a post-doctoral research position at IBM's Almaden Research Center in San Jose, California, with Dr. Michael Philpott. At IBM, Diane worked to develop experimental data for comparison with computational chemistry results. Diane was re-recruited by the Procter & Gamble Company from IBM, and returned to Cincinnati and P&G in 1991 to work in the Analytical Department that she currently leads. Since her second hiring by P&G, Diane has completed 10 years of industrial broadening assignments in formula design, process design, and consumer research, before returning to an analytical chemistry assignment. For those 10 years, Federation of Analytical Chemistry and Spectroscopy Societies meetings, and memberships in the American Chemical Society, the Society for Applied Spectroscopy, and the Coblentz Society kept Diane up-to-date on advances in analytical science. Since she returned to analytical work for P&G in 2002, Diane has found these external organizations and their meetings and publications to be a regular source of new ideas on how measurement science can influence industrial research and development. Diane and a team of P&G colleagues have taught the Analytical Chemists in Industry Short Course at FACSS for many years. Diane first joined the FACSS Governing Board as an ACS Analytical Division representative in 2002.

GENERAL CHAIR

Christine M. Wehlburg

MITRE Corporation

Christine M. Wehlburg is a member of the technical staff at MITRE in McLean, Virginia where her background in hyperspectral imaging sensors and data analysis transitioned from a national labs research laboratory to national security issues within the US intelligence community. Dr. Wehlburg spent 7 years at Sandia National Laboratories contributing to several spectroscopy-based programs including the development of a prototype fluorescence-based instrument with an industrial partner, FT-IR hyperspectral imaging analysis of materials and constructing an ion mobility spectrometer/mass spectrometer instrument in support of Sandia's work in IMS portal technology. Her current work focuses on remote sensing satellite systems and the advanced algorithms required to analyze that data.

Dr. Wehlburg completed her Bachelors of Science in Chemistry (1991) and received her Ph.D. in Physical Chemistry (1997) at the University of Florida. Her doctoral research under the direction of Prof. Martin Vala involved infrared spectroscopic investigations of matrix-isolated carbon clusters and PAH ions. Dr. Wehlburg serves on the board of the Coblentz Society and was the previous Workshops Chair for the Federation of Analytical Chemists and Spectroscopy Societies (FACSS) Conference.

FACSS CHAIRS

PROGRAM CHAIR

S. Douglass Gilman

Louisiana State University

Doug Gilman is an Associate Professor at Louisiana State University in Baton Rouge, LA, where he has been a member of the Chemistry faculty since 2004. Doug started his path towards becoming a scientist by heading south to Harvey Mudd College in Claremont, CA in 1985. He carried out undergraduate research in organic synthesis under the direction of Bill Daub, and he completed a B.S. degree in Chemistry in 1989 Doug then headed east for graduate school at Penn State University. At Penn State Doug eventually figured out that he liked bioanalytical chemistry better than organic synthesis and was lucky enough to land in the laboratory of Andy Ewing. While completing his Ph.D. under Andy's guidance, Doug had the opportunity to spend three years in the desk next to past FACSS Governing Board Chair and Program Chair, Mark Hayes – a fellow Californian. He also met his wife, Indu Kheterpal, in the Ewing Group at Penn State.

Doug left State College, PA to take a postdoctoral position with Bruce Hammock, an LSU alum. Doug was an NIH postdoctoral fellow in Hammock's group in Entomology and Environmental Toxicology at UC Davis. In 1997 Doug headed to the Southeast to start as an Assistant Professor at the University of Tennessee in Knoxville. While at the University of Tennessee he received an NSF CAREER Award (2001) and was promoted to Associate Professor (2003). In 2004 Doug moved further south to LSU. Doug's research program at LSU focuses on the development of new bioanalytical techniques to study enzyme inhibition and protein aggregation. He also studies electroosmotic flow dynamics in capillaries and microfluidic devices.

Doug first attended FACSS in Philadelphia in 1992. He gave his first talk at FACSS as student in Detroit in 1993. Since 2000 when FACSS was in Nashville, Doug has given several talks and organized and chaired many symposia for the meeting. He was the Bioanalytical Section Co-Chair for FACSS 2002 in Providence with Chuck Henry, and he was Awards Chair in 2005 in Quebec City. Doug is a member of SAS and the Analytical Division of ACS.

Outside of science and work, most of Doug's time today is devoted to activities of interest to his children, Rohin (6) and Priya (5). Doug's wife, Indu, is an Assistant Professor and Director of the Proteomics Facility at the Pennington Biomedical Research Center in Baton Rouge. Doug grew up in Exeter, California in the San Joaquin Valley just below Sequoia National Park, and his favorite activities are backpacking and basketball. His son is *finally* interested in playing basketball, but mountains are proving difficult to find in South Louisiana. Another theme in Doug's life seems to be associations with football schools (Penn State, LSU and Tennessee). Doug and his wife are mainly loyal Penn State fans, but Doug is also a Fresno State Bulldog fan and is looking forward to their visit to Baton Rouge after FACSS.

EXHIBITS CHAIR

Michael Carrabba

Hach Homeland Security Technology

Dr. Mike Carrabba is currently the Director of Hach 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 and in 2004 he received the FACSS Charles Mann Award for Applied Raman Spectroscopy. He is also a member of the Society for Applied Spectroscopy (SAS) and Coblentz Society. On the home front, his wife, Dr. Mary Widmark Carrabba, a highly skilled Infrared microscopist and the former treasurer for SAS, complements Mike's Raman background

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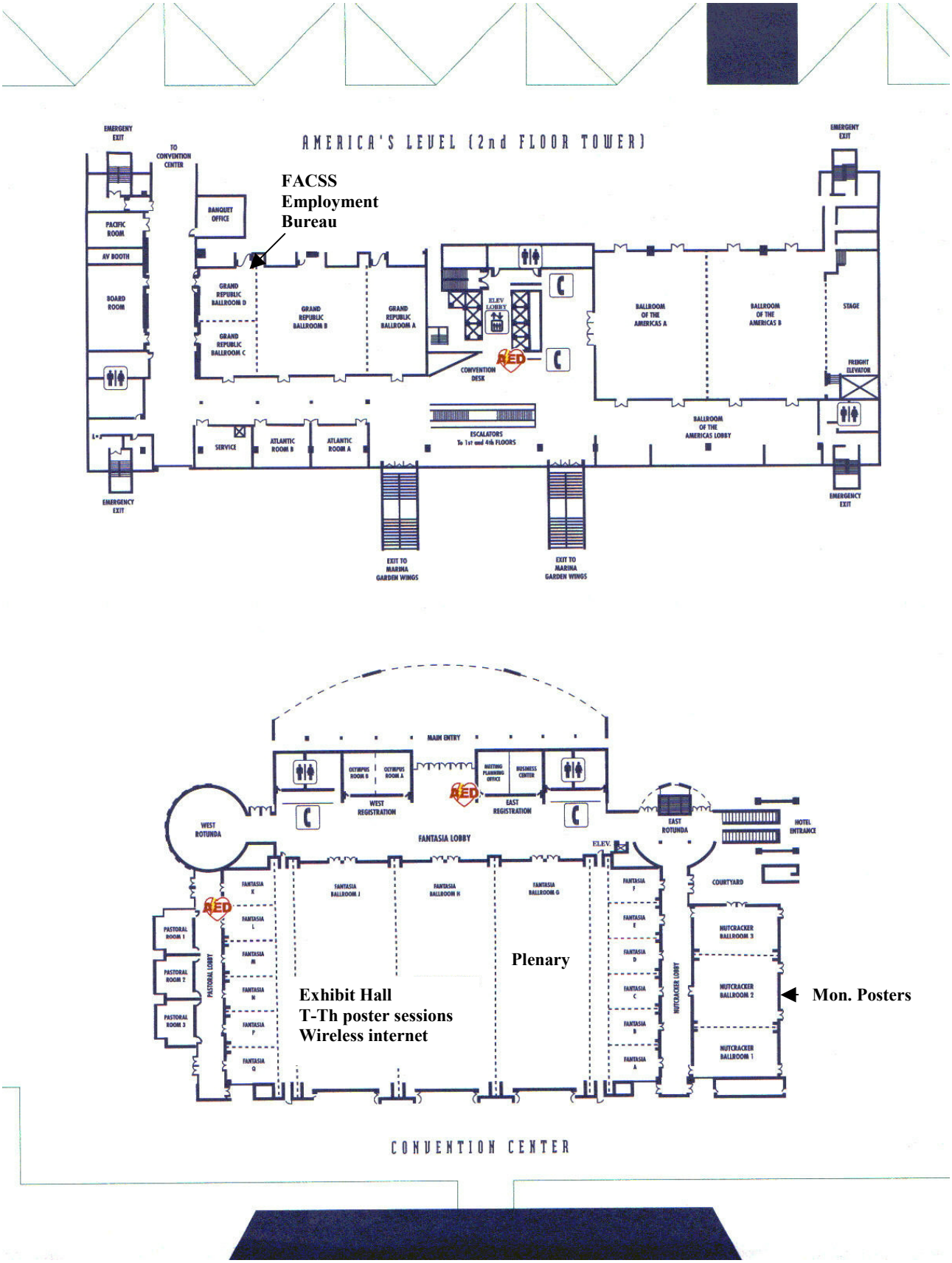
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PASTORAL ROOM 2
PASTORAL ROOM 3
PASTORAL LOBBY
NUTCRACKER BALLROOM 3
NUTCRACKER BALLROOM 2
NUTCRACKER BALLROOM 1
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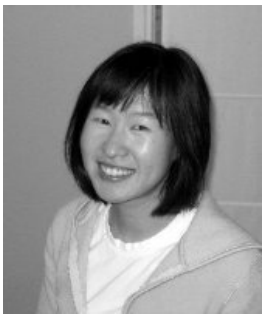
FACSS AWARDS

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



Andrea Tao
University of California, Berkeley

Presentation, Wednesday, 11:10 AM, Fantasia M

Andrea Tao is beginning her fifth year as a chemistry graduate student with Prof. Peidong Yang at UC Berkeley, where she is an NSF Graduate Research Fellow. Her research interests lie in the assembly and optical properties of metallic nanostructures. She holds an A.B. from Harvard University, where she graduated with honors in Chemistry and Physics in 2002. There, Andrea worked under Prof. George Whitesides in the Dept. of Chemistry on the self-assembled construction of a flexible LED display device. Through summer internships, she has also had the opportunity to work under Prof. James Harris at Stanford University and in the R&D Dept. at Biosite Diagnostics, Inc. in her hometown of San Diego, California. Andrea was also a high school research intern at UC San Diego with Prof. Michael J. Sailor, studying the surface-dependent photoluminescence of porous silicon. She attributes her interest in basic scientific research to these wonderful mentorships and has continued this tradition by mentoring undergraduate students throughout her graduate career.

TOMAS HIRSCHFELD SCHOLAR

Tim M. Brewer
Clemson University

Presentation, Monday, 2:30 PM, Fantasia C

Tim M. Brewer earned his B.S. degree in chemistry from Millikin University, Decatur, Illinois in 2002. He is currently doing doctoral research at Clemson University in Clemson, South Carolina under the direction of Dr. R. Kenneth Marcus. His primary research interest is focused on novel techniques for detecting and monitoring biomolecules by both mass and atomic spectrometries. He began his research career analyzing solid materials with radio frequency glow discharge optical emission spectrometry. He has also extensively done work on imaging and analysis of nanoparticles using field emission scanning electron and transmission electron microscopies for Savannah River National Laboratories. He helped in the development of biomolecule detection by glow discharge spectrometeries and is one of the first to use particle beam glow discharge for the analysis of Fe-metalloproteins. Recently, he has been working on speciation and species-specific analysis of biomolecules and toxic metals. His accomplishments in the area include the specific detection of nucleotides and Fe-containing metalloprotiens by particle beam glow discharge optical emission spectrometry. At present he is focusing on the comparison of inductively coupled plasma and particle beam glow discharge sources for the identification of biomolecules following HPLC separation.

FACSS AWARDS

FACSS STUDENT AWARD

Daniel B. Bassil

University of Missouri - Columbia

Presentation, Monday 4:10 PM, Fantasia C

Daniel B. Bassil was born in Hadeth El-Joubbeh, Bshari; Lebanon, where he went to the "Mission Laïque Française" High School. He received his Bachelor of Science degree in Chemistry in 2000 from the Lebanese University II, Beirut. He was awarded a scholarship from the International Centre for Advanced Mediterranean Agronomic Studies (Paris, France) and received his Master's degree in 2002 from their Institute (M.A.I.Ch.) in Chania, Greece. His thesis research involved the evaluation of the antioxidant properties of 2-*S*-cysteinylcaffeic acid. He joined the Department of Chemistry at the University of Missouri – Columbia in August 2002. He is currently pursuing his PhD in analytical chemistry under the supervision of Professor Sheryl A. Tucker. His research project, investigating the host-guest properties of self-assembling nanocapsules using fluorescent reporter molecules, is a collaboration with Professor Jerry L. Atwood in the department. The main appeal to the scientific community of these nanocapsules is their ability to mimic living cells that self-assemble, such as viruses and proteins. Daniel's research illustrates the potential utility of these assemblies as molecular transporters. He has received national and departmental research awards and university travel awards in recognition of these research efforts. Daniel has four refereed publications and scientific conference presentations and is a member of the American Chemical Society, Society for Applied Spectroscopy and Inter-American Photochemical Society. Daniel's main activities outside of research consist of playing table tennis and racquetball. In July 2006, he won a bronze medal in the doubles table tennis competition at the Show-Me State Games held in Jefferson City, MO.

FACSS STUDENT AWARD - HONORABLE MENTION

Marion Lawrence-Snyder, *University of South Carolina*. Presentation, Monday 3:30 PM, *Fantasia C*
Maria Fernanda Mora, *University of Texas at San Antonio*. Presentation, Thursday 4:15 PM, *Fantasia C*

TOMAS HIRSCHFELD AND FACSS STUDENT AWARDS
Call for Applications for 2007

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 2007 FACSS meeting in Memphis, TN (October 14-18, 2007). In 2006 two Tomas Hirschfeld Scholars and one FACSS Student Award were made. 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 award.

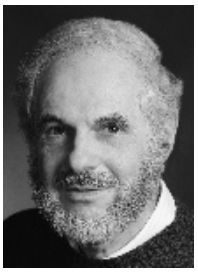
The submissions process involves completing the web site submission form, and submitting three sets of the following:

a) the form
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 2007**.** Go to www.facss.org to submit an application.

CHARLES MANN AWARD

For Achievements in the Field of Applied Raman Spectroscopy



Michael Morris

University of Michigan

Presentation, Tuesday 8:30 AM, Fantasia G

Michael Morris is professor of chemistry at the University of Michigan and a member of the university's Biomedical Engineering faculty, its Comprehensive Cancer Center and its Core Center for Musculo-skeletal Research. He presently serves on the editorial boards of Applied Spectroscopy, Journal of Biomedical Optics and Calcified Tissue International. His honors include the ACS Division of Analytical Chemistry Award in Spectrochemical Analysis, the Anachem Award, the SAS New York Section Gold Medal and several University of Michigan awards.

His research interests include Raman spectroscopy and Raman imaging. He is a pioneer in the analytical applications of Raman spectroscopy, particularly in its uses in microscopy and imaging. He has made important contributions to Raman spectroscopic instrumentation based on holographic and liquid crystal optics and has been a leader in development of computational techniques for multivariate Raman image processing and three-dimensional Raman imaging. He has worked on applications of Raman microspectroscopy and imaging to materials as diverse as mineralized tissue and synthetic polymer blends. He was among the leaders of the first wave of coherent Raman spectroscopy and developed successful methods for coherent spectra free of non-resonant background.

Morris has been an active researcher in biomedical Raman spectroscopy for over 25 years. His contributions include physical biochemical studies of flavoproteins, bile pigments and neurotransmitters. In the last several years his laboratory has led the development of Raman spectroscopy for study of musculoskeletal tissues. He and his co-workers have published on bone biomechanics, mechanisms of tissue mineralization and non-invasive spectroscopic assessment of bone quality.

Professor Morris is noted as well for his many contributions to Raman instrumentation. He was one of the first to use volume holograms as Raman instrument components and the first to perform Raman hyperspectral imaging. His work in this field includes the development of Hadamard multiplexed Raman spectroscopic imaging, and Powell lens line scan imaging. His software innovations include development of the first multivariate methods for Raman spectroscopic image processing and development of digital deconvolution methods for three-dimensional Raman imaging. He was also the first to do Raman-detected capillary electrophoresis and the first to do Raman-detected electrophoresis in a microchip.

Michael Morris has been an important contributor to FACSS meetings since the founding of the conference some thirty years ago. He has often served as a session organizer and an invited speaker and has developed and offered a popular FACSS short course on Analytical Raman Spectroscopy.

SOCIETY FOR APPLIED SPECTROSCOPY AWARDS

DISTINGUISHED SERVICE AWARD

Recognizing members for their long-time service to the society

Joseph Caruso

University of Cincinnati

Professor Caruso received his Ph.D. from Michigan State University under the direction of Alexander Popov. After a one-year postdoctoral fellowship with J. J. Lagowski at The University of Texas - Austin, he joined the faculty of the University of Cincinnati as assistant professor of analytical chemistry and proceeded through the ranks. During this time he has authored or co-authored over 300 scientific publications, has more than 6000 citations and presented over 250 invited lectures at universities and at scientific meetings.

Professor Caruso=s research interests are trace elemental analysis by atomic spectrometric methods. The principle instrumental focus is both inorganic and organic mass spectrometry as detectors for various chromatographic separation types. A strong interest of the group continues to be chemical speciation with element specific detection. Application of these methods to environmental remediating plants, metalloproteins, chemical warfare agents are of high current interests. In particular, the use of metallomic approaches (full characterization of metal in a cell or sample) is of the highest interest in applying to specific problems.

Professor Caruso is a member of the American Chemical Society, Canadian Spectroscopy Society, Society for Applied Spectroscopy and Fellow of the Royal Society of Chemistry. He has been honored by Eastern Michigan University with its 1990 Distinguished Alumni Award, by the American Chemical Society with the 1992 Cincinnati Chemist of the Year Award, the Federation of Analytical Chemistry and Spectroscopy Society with the 1994 Anachem Award, and with the 2000 Spectrochemical Analysis Award given by the Analytical Division of the American Chemical Society. In 2005 he gave the Procter and Gamble Honorary Lecture at the University of Massachusetts B Amherst. He recently received the 2006 Excellence in Doctoral Mentoring Award from the University of Cincinnati. He serves or has served on numerous editorial or advisory boards:

HONORARY MEMBERSHIP AWARD

Recognizing those individuals who have made exceptional contributions to spectroscopy

Charles Wilkins

University of Arkansas

Charles Wilkins was born in Los Angeles on August 14, 1938 and attended school there until graduation in June, 1956. Following that, he went to Chapman College in Orange, Ca graduating in 1961. Following a year at Arizona State University, he transferred to University of Oregon in Eugene, and was awarded the Ph.D. in Chemistry in 1966. After a postdoctoral year at the University of California, Berkeley Dr. Wilkins joined the University of Nebraska as an Assistant Professor of Chemistry and rose to the position of Professor of Chemistry. In 1981 he moved to the University of California, Riverside as a Professor of Chemistry and, shortly before the move became Distinguished Professor of Chemistry. In 1998 Dr. Wilkins moved to the University of Arkansas, Fayetteville where he was appointed to his present position as a Distinguished Professor of Chemistry and Biochemistry.

Dr. Wilkins research interests include analytical chemistry; Fourier transform nuclear magnetic resonance, infrared, and mass spectrometry; laboratory computer applications in chemical instrumentation, fundamentals of gas phase ion-molecule reactions; and bioanalytical chemistry.

Dr. Wilkins is a member of American Chemical Society, American Society for Mass Spectrometry, American Association for the Advancement of Science, Society for Applied Spectroscopy, Sigma Xi. He has served on numerous editorial boards and is the recipient of several prestigous awards and honors including Lester W. Strock Award, Society for Applied Spectroscopy, 1982, 7th Annual H.W. Davis Lectures, University of South Carolina, 1984, Society of Analytical Chemists of Pittsburgh Lecture, Pennsylvania State University, 1984; Pittsburgh Analytical Chemistry Award, 1994, Faculty Research Lecturer, University of California, Riverside, 1994, 1993 Tolman Medal, Southern California American Chemical Society, Eli Lilly Distinguished Speaker in Analytical Chemistry, Indiana University, 1995, 1996 New York Section of the Society for Applied Spectroscopy Gold Medal Award, 1997 American Chemical Society Franklin & Field Award for Outstanding Achievement in Mass Spectrometry; 1996 Elected Fellow of the American Association for the Advancement of Science; Chevron Lecturer, University of California, Berkeley, 1997, 2002 Eastern Analytical Symposium Award for Outstanding Achievements in the Fields of Analytical Chemistry, 2003 Arkansas Alumni Faculty Distinguished Achievement Award B Research, University of Oregon Department of Chemistry Alumni Achievement Award, Distinguished Awardee in Pure Science, 2004, and Fulbright College Master Researcher Award, University of Arkansas, 2005.

SOCIETY FOR APPLIED SPECTROSCOPY AWARDS

FELLOWS AWARD

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

Bonner Denton

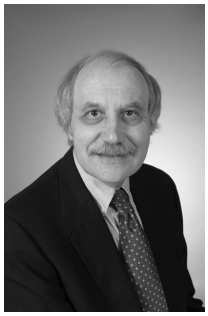
Unversity of Arizona

M. Bonner Denton is Professor of Chemistry at the University of Arizona. His research interests include applying the latest technological advances in electronics, physics, optics, astronomy, acoustics, mechanical engineering and computer science toward developing new and improved chemical instrumentation and analytical methods. His multifaceted but strongly interlocking program ranges from new frontiers of mass, plasma emission and Raman spectrometry through intelligent instrumentation. Denton is currently developing revolutionary new detection technology for mass and ion mobility spectrometry. Professor Denton received a Bachelor of Science in Chemistry and a Bachelor of Arts in Psychology from Lamar University in Beaumont, Texas. He then attended the University of Illinois at Champaign-Urbana, receiving his Ph.D. in Analytical Chemistry. His awards include an Alfred P. Sloan Research Fellowship, an Outstanding Young Men of America Award, the 1989 ACS Division of Analytical Chemistry Award in Chemical Instrumentation, the 1991 Society of Applied Spectroscopys Lester Strock Award, the Spectroscopic Society of Pittsburghs 1998 Spectroscopy Award, the American Chemical Society Division of Analytical Chemistry's 2001 Award in Spectrochemical Analysis, and the Royal Society of Chemistrys 2004 Theophilus Redwood Lectureship. He has served on the Advisory Board of the journal, Analytical Chemistry, and on the Editorial Advisory Board of the Journal of Automated Methods & Management in Chemistry. He was President of the Society for Applied Spectroscopy, and serves as Associate Editor for the journal, Applied Spectroscopy. He is a past Chair of the Analytical Division of the American Chemical Society.

Joel Harris

University of Utah

Joel M. Harris received his B.S. degree from Duke University in 1972 and a Ph.D. from Purdue University in 1976. That same year, he was appointed to the faculty of the University of Utah, where he has taught for the past 30 years. Harris=s research has focused on analytical chemistry and spectroscopy of trace-level species in liquids and at liquid/solid interfaces. He and his students have developed photothermal spectroscopy methods, multidimensional analysis of time-resolved spectroscopic data, and single-molecule counting techniques. They have pioneered surface-selective methods for investigating interfacial molecular transport, adsorption, and binding in chemical analysis and separations. Harris is a Fellow of the American Association for the Advancement of Science. He is the recipient of an Alfred P. Sloan Fellowship, the Coblentz Award in Molecular Spectroscopy, the University of Utah Distinguished Research Award, the ACS Division of Analytical Chemistry Award in Chemical Instrumentation, the SAS New York Section Gold Medal Award in Spectroscopy, the Pittsburgh Analytical Chemistry Award, the Utah Award in Chemistry, and the ACS Award in Analytical Chemistry. He is currently Editor-in-Chief of *Applied Spectroscopy*.



Nicolo Omenetto

University of Florida

Nicoló Omenetto obtained his Doctor degree in Chemistry (*Laurea*) from the University of Padua (Italy) in 1964. He was then appointed as Assistant Professor at University of Pavia (Italy) in 1969 and became Professor of Spectrochemistry (*Libera Docenza*) in 1971. He spent three years (1971-73, 1978-79) as Post Doc Associate at the University of Florida in Gainesville, working with Jim Winefordner. In 1979, he was appointed at the Joint Research Centre of the European Commission in Ispra (Italy) until 2001, when he moved to the University of Florida, where he is currently a Professor in the Department of Chemistry.

Dr. Omenetto has been a member of the Advisory Board of "Journal of Analytical Atomic Spectroscopy", Royal Society of Chemistry, U.K., "CRC Critical Reviews in Analytical Chemistry", and Talanta He was also a Titular Member of IUPAC, Commission V-4 ("Spectroscopic Nomemclature"). He has served as European Editor for Atomic Spectroscopy of the journal "Applied Spectroscopy" during the period 1986-1993. Dr. Omenetto is currently a member of the "Society for Applied Spectroscopy", and a member of the AOptical Society of America@. Since 1994, he is Co-editor of the journal ASpectrochimica Acta, Part B : Atomic Spectroscopy@. He has published over 200 papers and has given many invited talks at various international conferences. He has edited and co-edited two books on the use of lasers in analytical spectroscopy.

The research interests of Dr. Omenetto have been directed towards the theory and applications of atomic and molecular spectroscopic methods of analysis. Particular emphasis has been given to the use of tunable lasers and to the development of techniques such as atomic and molecular fluorescence, atomic ionization, photo-thermal, photo-fragmentation, and laser induced plasma spectroscopy. In addition to these developments, fundamental diagnostic studies in atom reservoirs such as flames and plasmas have been pursued, improving the understanding of the interaction between the laser and the atomic/molecular systems investigated. More recently, the interest has been focused on environmentally important topics, such as, for example, the analytical feasibility of detecting atmospheric pollutants and trace metals in particulate matter by laser fluorescence, and the characterization of atmospheric particles in real time with the technique of time resolved laser induced fluorescence and laser ionization/glow discharge time of flight mass spectrometry.

Charles Wilkins

University of Arkansas

See page 13 for additional information on Charles Wilkins.

SOCIETY FOR APPLIED SPECTROSCOPY AWARDS

GRADUATE STUDENT AWARD

Recognizing a graduate student for outstanding research in spectroscopy

George Chan
Indiana University

Poster Presentation, Wednesday, abstract #342

George Chan is currently pursuing a Ph.D. in analytical chemistry at Indiana University at Bloomington under the direction of Distinguished Professor Gary M. Hieftje. Born and raised in Hong Kong, George received his B.Sc. degree, with first class honors, majoring in chemistry from The University of Hong Kong (HKU) in 1997. At HKU he performed undergraduate research in the laboratory of Professor Wing-Tat Chan on developing an analytical technique to overcome volatilization interferences in graphite furnace atomic absorption spectrometry by coupling a capacitively coupled plasma inside the graphite furnace atomizer as an additional atomization source. After receiving his B.Sc. degree, he continued his graduate study in the Wing-Tat Chan research group at HKU and received his M.Phil. degree in 2000, majoring in analytical chemistry. During his graduate study at HKU, he worked on a collaborative research project with Dr. Richard Russo at Lawrence Berkeley National Laboratory on investigating matrix effects in inductively coupled plasma-atomic emission spectrometry (ICP-AES) during laser ablation sampling. He also studied the characteristics of direct sample insertion as an alternative solid-sample introduction technique for ICP spectrometry during his stay in HKU. He started his graduate research at Indiana University with Professor Gary Hieftje in 2002. His current research interests include understanding matrix-effect mechanisms and analyte excitation mechanisms in ICP-AES, and development of diagnostic tools to identify interelement matrix effects and methods to alleviate them. The work aims to clarify the origin of matrix interferences, to better understand the excitation and ionization mechanisms for analyte species and their relationships to matrix effects. He has received a Hong Kong Croucher Foundation Scholarship from 2002-2005 and the American Chemistry Society Division of Analytical Chemistry Graduate Fellowship sponsored by GlaxoSmithKline for 2005-2006. Mr. Chan has been recognized by the Chemistry Department at Indiana University by receiving awards for the best research by a first-year graduate student and by a graduate student completing his fifth semester of study.

Philipp Kukura
University of California, Berkeley

Philipp Kukura received his B.A. in Chemistry from the University of Oxford in 2001, his Master in Chemistry degree from the University of Oxford in 2002, and his Ph.D. in Chemistry from the University of California, Berkeley in May 2006. His Ph.D. advisor was Professor Richard A. Mathies. Dr. Kukura=s Ph.D. thesis is entitled AReal-Time Structural Observation of Ultrafast Chemical Reaction Dynamics with Femtosecond Stimulated Raman.@ His published papers include an article in *Science* (2005, 310, 1006-1009), which was also featured in *Nature* and *C&E News*. A chapter on AFemtosecond Raman Spectroscopy@ co-authored with Richard A. Mathies will be published in the *Annual Review of Physical Chemistry*, 2007. Dr. Kukura is currently employed at the Physical Chemistry Laboratory, ETH, Zurich, Switzerland.

SOCIETY FOR APPLIED SPECTROSCOPY AWARDS

WILLIAM F. MEGGERS AWARD

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

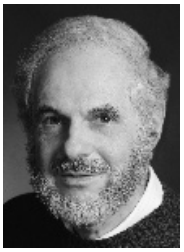
Presented to: Pavel Matousek, Ian P. Clark, Michael Towrie, Antony W. Parker, Edward R.C. Draper, Allen E. Goodship, Michael Morris, William F. Finney, and Neil Everall for the paper entitled ASubsurface Probing in Diffusely Scattering Media Using Spatially Offset Raman Spectroscopy@ Volume 59 Number 4.

Presentation, Wednesday 8:00 AM, Fantasia G

Dr Pavel Matousek has worked at the Central Laser Facility, Rutherford Appleton Laboratory (RAL), England for over 15 years. His research has focused on steady state and time-resolved Raman spectroscopy and nonlinear optics. He led the developed of Raman Kerr gated concept for the rejection of fluorescence from Raman spectra in solutions (EPSRC grant GR/L83943), currently the most effective suppression method in existence enabling the detection of Raman spectra in the presence of up to million times more intense fluorescence. He and his collaborators subsequently applied the method to fluorescence rejection in powders and time-resolved Raman photon migration studies in turbid media, a strand of research for which he shares 2002 Meggers Award with his colleagues Everall, Hahn, Parker and Towrie. Later on, he and his collaborators were the first to apply the Kerr gated concept to the subsurface Raman spectroscopy of powders and tissue. He also proposed the use of an Optical Parametric Chirped Pulse Amplification (OPCPA) concept for the generation of multi-petawatt peak powers. Recently, this concept became a part of a proposal for a European laser driven fusion facility HiPER. His current research focuses on the development of NSOM techniques and advanced biomedical and pharmaceutical non-invasive imaging techniques utilising Raman spectroscopy. His accomplishments in this area include a proposition for Spatially Offset Raman Spectroscopy (SORS) which he and his collaborators are currently developing for in-depth probing of pharmaceutical products and human tissue. He is a programme manager for the Ultrafast Raman Spectroscopy Facility and also leads SORS technique development programme at RAL. He has over 130 journal publications and 5 patent filings and is a member of the EPSRC Peer Review College.

Dr Ian Clark obtained a BSc in Chemistry from the University of Nottingham, UK, in 1994. He continued at Nottingham for his PhD ("Time-resolved infrared spectroscopy of organometallic excited states", 1997) under the supervision of Prof J Turner FRS. From 1997 to date Dr Clark has been employed at CCLRC Rutherford Appleton Laboratory, Oxfordshire, UK, initially taking a post in the Ultrafast Spectroscopy Laboratory within the Central Laser Facility. For the past seven years Dr Clark has been the Programme Manager of the Nanosecond Science Laboratory within the same facility. Research interests include Raman spectroscopic techniques, including sampling methods and more recently the use of muons as a probe for free radicals.

Dr Edward Draper PhD is a Chartered Mechanical Engineer and Chartered Scientist with many years experience of research into mechanobiology of skeletal tissues. For the first ten years of his career he ran a clinical bioengineering service in Edinburgh within the National Health Service. At that time his attention was increasingly drawn towards how healing bones are affected by their mechanical environment and this led him towards academic research. Since joining the team headed by Professor Allen Goodship in 2000 as a joint appointment between the Royal Veterinary College and Imperial College London, Dr Draper has developed a keen interest in the variation of the mechanical properties of skeletal tissues between individuals both in health and disease. His current research attentions are into novel minimally-invasive techniques of detecting and monitoring both material strength and elastic moduli of tissues such as cartilage, the annulus of the intervertebral disc and bone; these new techniques include genotyping specific single nucleotide polymorphisms that are known to affect these tissues and a range of spectroscopic techniques, as well as a range of more traditional measurements of the physical properties of tissues.



Michael Morris
University of Michigan

See page 12 for additional information.

WILLIAM F. MEGGERS AWARD - continued

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

Professor Allen Goodship graduated in veterinary science in 1972, his PhD thesis related to functional adaptation of bone, both at the University of Bristol. He maintained a research interest in the pathobiology of skeletal tissues. His contributions to research in this field have centred upon the optimisation of skeletal structures in relation to their functional roles. At the University of Bristol he was Head of the Department of Anatomy and led the Comparative Orthopaedics Research Unit. In 1996 he moved to a joint appointment between the Royal Veterinary College and University College London. In 2000 he was appointed as Director of the Institute of Orthopaedics and Muscloskeletal Science at UCL. The translational research in mechanobiology of skeletal tissues has led to changes in the understanding of bone repair, degenerative disease of tendons and the enhancement of integration of orthopaedic prostheses with biological tissues and structures. Recently the research has been directed to interactions between the material properties of skeletal tissue matrices and the structural architecture of the skeletal system. The evaluation of matrix composition and its relationship to genetic and functional factors has led to the interaction with a broader based multidisciplinary team in utilisation of spectroscopic techniques both to enhance the understanding of bone matrix composition, and to explore the application in non-invasive assessment of bone quality.

Neil Everall gained his BSc in Chemistry and Chemical Physics in 1981 from the University of York, UK, and his PhD (researching picosecond Raman spectroscopy) in 1986 from the University of Durham, UK. After a Post Doctoral position at the Rutherford Appleton Laboratory (Oxford, UK), developing high power UV lasers, he joined ICI in 1988 to establish a Raman Spectroscopy facility at its Corporate Research Centre. For the last 12 years he has led the infrared and Raman spectroscopy activity at ICI's Measurement Science Group at Wilton in the North East of England. Everall's research interests centre on the development and application of vibrational spectroscopy for characterising materials and industrial processes. In recent years this has included infrared and Raman studies of polymer structure (primarily polymerisation mechanisms, microstructure, crystallinity and molecular orientation), modelling the spatial response and depth resolution of the confocal Raman microscope, process analysis with Raman spectroscopy, and materials characterisation using infrared and Raman mapping/imaging. More recently he has been studying Raman photon migration in opaque media, and has also been revisiting the issues that determine the working resolution of the Raman microscope. Everall has published over 70 refereed articles, several book chapters and 1 Patent, and is currently a European Associate Editor for Applied Spectroscopy. He is also on the editorial advisory board for the Asian Journal of Spectroscopy, and was an Associate Editor of the Handbook of Vibrational Spectroscopy, a five-volume text edited by John Chalmers and Peter Griffiths and published in 2001. Everall is a member of the organising committee of the UK Infrared and Raman Discussion Group, and is a Fellow of the Royal Society of Chemistry. He is also a member of the EPSRC Peer review college. In 2002 he was awarded, along with co-authors Hahn, Matousek, Parker and Towrie, the "Meggers Award" by the Society for Applied Spectroscopy, and in 2003 he received the Williams-Wright Award from the Coblentz Society. He was appointed an ICI Company Research Associate in 2003.

Dr Mike Towrie is programme manager for the Central Laser Facility time resolved IR facilities and detector developments concentrating on the research and development of advanced laser technology and gas and condensed spectroscopic and imaging techniques. This work has lead to the world leading ultrafast vibrational spectroscopy facilities with highlights including the first dual picosecond OPA for time resolved resonance Raman system (EPSRC GR/J76392), the Meggers Award winning Optical Kerr Gated Raman spectrometer (ESPRC GR/L83943) and PIRATE the highly sensitive IR time resolved spectrometer with unique femtosecond to microsecond time resolved capability. He is currently engaged in the development of the ULTRA system a next generation time resolved vibrational spectrometer designed for life science research. He leads the Tweezers Nanoprobe project aiming to marry the remarkable attributes of laser tweezers with those of scanning probe microscopy (SPM) to provide the first three-dimensional (3D) optical imaging and force probe instrument with nanometre and sub picoNewton resolution. He has over 100 publications.

William F. Finney, PhD obtained his BS from the State University of New York at Binghamton in 1994. He received his PhD from Syracuse University in 2002 while working with Professor Joseph Chaiken. In his dissertation "Noninvasive in vivo tissue modulated quantitative Raman spectroscopy of human blood." In this work it was demonstrated that the Raman spectrum of blood could be obtained noninvasively and in-vivo. With the support of LighTouch Medical, Inc. and in collaboration with the Joslin Diabetes Center at the State University of New York Upstate Medical University this work also provided proof of principle that blood glucose concentrations could be followed by this method. Following this work, Dr. Finney joined the research group of Professor Michael D. Morris at the University of Michigan. At Michigan he worked on several projects including probing changes in bone caused by physiological level forces using Raman spectroscopy and hexafluorosilicate hydrolosys. Dr. Finney is currently a postdoctoral fellow at the Illinois Institute of Technology where he is working with Sandra Bishnoi to study peptide interactions with SERS active substrates.

WILLIAM F. MEGGERS AWARD - continued

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

Professor Anthony Parker is Head of the Lasers for Science Facility group within the Central Laser Facility based at Rutherford Appleton Laboratory, Oxfordshire, UK. He obtained his BSc degree from Trent University and went on to do his PhD at Warwick University, investigating the electron transfer properties of excited state nucleic acid bases. He then did a 1 year Post Doc at The Royal Institution of Great Britain followed by a brief spell in industry with Applied Photophysics. In 1987 he joined RAL and over the past 19 years has gained expertise in using time resolved laser spectroscopy to investigate photochemical and photobiological reactions. A major part of this has been in developing time resolved vibrational spectroscopy, both resonance Raman and infrared, for investigating the structure, reactivity and dynamics of intermediates formed in fast reactions. At present he is focusing on developing lasers and spectroscopy for the biological and medical research communities and encouraging their broader uses for UK science programmes. He is a member of the International Organising Committees for Time Resolved Vibrational Spectroscopy, International Conference on Raman Spectroscopy and European Conference on the Spectroscopy of Biological Molecules and actively supports the development of laser science on the African Continent through his advisory role for the National Laser Centre in South Africa. In 2002 he shared the "Meggers Award" from the Society for Applied Spectroscopy with his colleagues Everall, Hahn, Matousek and Towrie. He has previously held the post of Technical Director at LaserThor from 1999 to 2003. He is honorary visiting Professor at both University of Salford and University College London and has over 150 publications and 2 shared patents.

LESTER W. STROCK AWARD

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

Paul Farnsworth

Brigham Young University

Presentation, Wednesday 8:30 AM, Fantasia G

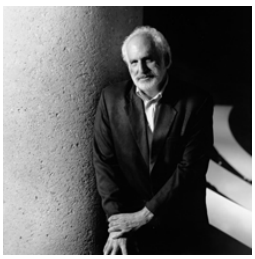
Professor Paul Farnsworth is currently chair of the Department of Chemistry and Biochemistry at Brigham Young University. He earned his B.S. degree in 1977 from BYU, then went on for doctoral work at the University of Wisconsin in Madison under the direction of John Walters. He did postdoctoral work with Gary Hieftje at Indiana University, and then returned to BYU as an assistant professor in 1983. He has had two appointments as a visiting scientist at the Joint Research Center of the European Commission in Ispra, Italy, the first in 1989 and the second in 1998, working in the laboratories of Nicolò Omenetto.

Professor Farnsworth=s primary research interests are laser and atomic spectroscopy. He began his research career studying energy transport and excitation mechanisms in inductively coupled plasmas used as emission sources. He has slowly evolved into a mass spectrometrist, but retains his interest in optical spectroscopy. In recent years he has been using laser-excited fluorescence as a tool to study ion transport through the vacuum interface of an inductively coupled plasma mass spectrometer. His initial work on ion transport was recognized with the *Spectrochmica Acta* atomic spectroscopy award in 1998. He has also ventured into the molecular world with the development of detectors for proteins based on two-photon excited fluorescence.

Dr. Farnsworth has served as editor for the journal *Applied Spectroscopy* since 1997, and has had primary responsibility for the development of the online edition of the journal. He was editor of *Spectrochimica Acta Electronica* from 1994-2001 and is currently a member of the editorial board of *Spectrochimica Acta, part B.* He served as program chair for the 2005 FACSS meeting in Quebec City.

ANACHEM AWARD

The ANACHEM Award was established in 1953 and 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. The Award was presented as a part of the ANACHEM Conference through 1972. After 1972, the ANACHEM Award has been presented at the International FACSS Conference as a part of a special symposium arranged and given by former students and colleagues.



Richard D. Sacks, *posthumous*

University of Michigan

Presented by James A. Holcombe, University of Texas, Austin

Presentation, Tuesday 8:00 AM, Fantasia G

The late Richard D. Sacks, Professor of Chemistry received his B.S. Chemistry from the University of Illinois (Champaign) in 1965, and his Ph.D. in Analytical Chemistry from the University of Wisconsin at Madison in 1969 (with John Walters). He began his career as an assistant professor at the University of Michigan that same year and was promoted to associate professor in 1974 and full professor in 1979. He served numerous roles within the UM Chemistry Department including a term as associate chair for graduate studies from 1987-1992.

Professor Sacks was internationally recognized for his pioneering work on analytical instrumentation. During the early part of his career, his research focused on novel atomic emission spectroscopic methods, including direct solid-sample elemental analysis. In the 1970's he developed exploding thin film platforms for solids analysis that combined simplicity of sample introduction with unprecedented low detection limits. In the mid-1980s, he turned his attention to innovative approaches to high-speed gas chromatographic separations of complex mixtures of volatile organic compounds. His methodologies reduced measurement times for complex mixtures almost 100-fold and attracted great academic and industrial interest, eventually leading to formation, with several of his students, of a spin-off company, Chromatofast Inc., that commercialized instrumentation invented in the Sacks laboratory. In recent years he helped to lead efforts at the University to create wireless micro-analytical systems for environmental, homeland security, and deep-space applications.

During his career, Prof. Sacks and his coworkers published more than 150 research papers on these topics and presented their findings at scientific conferences all over the world. He served as mentor to many Ph.D. graduate students, who have gone on to distinguished careers in academia, industry and government laboratories.

Sacks was also a truly outstanding educator, teaching both undergraduate and graduate students the principles of modern analytical chemistry and instrumentation. Over this period, he was a driving force in modernizing the analytical chemistry curriculum at Michigan. He developed completely new courses on chemical instrumentation at the undergraduate level and, at the graduate level, he introduced courses on electronic measurements and microcomputer control of analytical instruments, as well as modern separations methods.

Prof. Sacks was a candidate for the ANACHEM Award prior to public knowledge of the cancer that ultimately claimed his life. This is the first time the award, given annually since 1953, has been given posthumously.

In addition to a half-day symposium with papers by former students and colleagues, the traditional Plenary Lecture will be given in his stead by his former Ph.D. student Prof. James Holcombe. The title is: "From exploding wires to rapid chromatography: The legacy of a high speed scientist and gentle mentor."

Prof. Sacks is survived by his wife Kristine and his daughter Jenny.

[Note: The Department of Chemistry at the University of Michigan has established the Richard D. Sacks Memorial Travel Award used to support yearly travel awards for analytical chemistry graduate students to present their research at technical conferences. For more information, call the Chemistry Department at 734-615-9852]

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SOCIETY AND COMMITTEE MEETINGS AND EVENTS

FACSS

All meetings will take place at *Disney's Contemporary* Resort.
Saturday, September 23, *Board Room*
1:00 PM Long Range Planning committee
Sunday, September 24, *Board Room*
7:00 PM Program Committee
7:30 PM Web Site meeting
Wednesday, September 27, *Board Room*
9:00 AM 2007 Planning/Budget Committee
10:00 AM Budget Committee for Memphis
11:00 AM Budget Committee for Reno
1:00 PM Budget and Finance Committee
Thursday, September 28, *Board Room*
1:00 PM Executive Committee
7:00 PM Governing Board

ASTM

All meetings will take place at *Disney's Contemporary* Resort.
Monday, September 25
1:30 – 3 PM E13.10 Molecular Spectroscopic Optical Imaging, *Board Room*
3 – 4:30 PM E13.08 Raman Spectroscopy, *Board Room*
6:00 PM Raman Reception, *Ballroom of the Americas B*

COBLENTZ

All meetings will take place at *Disney's Contemporary* Resort.
Monday, September 25, *Board Room*
8:00 PM Board Meeting

SOCIETY FOR APPLIED SPECTROSCOPY

All meetings will take place at *Disney's Contemporary* Resort.
Sunday, September 24, *Board Room*
7:30 AM – 6 PM SAS Executive Committee Meeting
12:00 – 1:30 PM SAS Executive Committee Luncheon
Monday, September 25
12:00 – 1:30 PM Publications Committee Meeting/Lunch *Atlantic A*
Tuesday, September 26
4:30 – 6:30 PM SAS Governing Board Meeting, *Atlantic A*
7:00 – 9:00 PM SAS Wine and Cheese Reception, *Ballroom of the Americas A (members only)*

SAS Members are Cordially Invited to Attend the SAS Wine and Cheese Reception

Tuesday, September 26, 2006, 7:00 p.m.
Ballroom of the Americas A
Disney's Contemporary Resort

This is a member's only event.

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Ahura Corporation	Booth 59
Andor Technology	Booth 52
AXSUN Technologies	Booth 65
B&W Tek, Inc.	Booth 45
BioTools, Inc.	Booth 55
Bruker Optics, Inc.	Booth 1
Carl Zeiss MicroImaging, Inc.	Booth 61
Centice Corporation	Booth 16
Ceram Optec Industries	Booth 36
CETAC Technologies	Booth 5
ChemImage Corporation	Booth 57
Coblentz Society	Booth 53
Delta Nu	Booth 63
Eigenvector Research, Inc.	Booth 40
Elsevier - Materials Today	Table Top
FACSS	Booth 64
FiberTech Optica, Inc.	Booth 50
GenTech Scientific, Inc.	Booth 19
Hamilton Sundstrand Corporation	Booth 68
High Tech Photonics	Booth 41
Hitachi High Technologies America	Booth 60
HORIBA Jobin Yvon	Booth 37,38
ICP Information Newsletter, Inc.	Booth 61
JASCO, Inc.	Booth 46
Kaiser Optical Systems, Inc.	Booth 10
Lab Manager Magazine	Table Top
Mesophotonics Ltd	Booth 47
Ocean Optics, Inc.	Booth 42
OPOTEK, Inc.	Booth 4
PerkinElmer Life & Analytical Sciences	Booth 39
Pittsburgh Conf of Analytical Chem	Booth 69
Reed Business Information	Table Top
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Society for Applied Spectroscopy	Booth 6, 7,8
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Spectroscopy Magazine	Booth 48
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Thermo Electron Corp.	Booth 17, 18
Upchurch Scientific	Booth 66
Varian, Inc.	Booth 2,3
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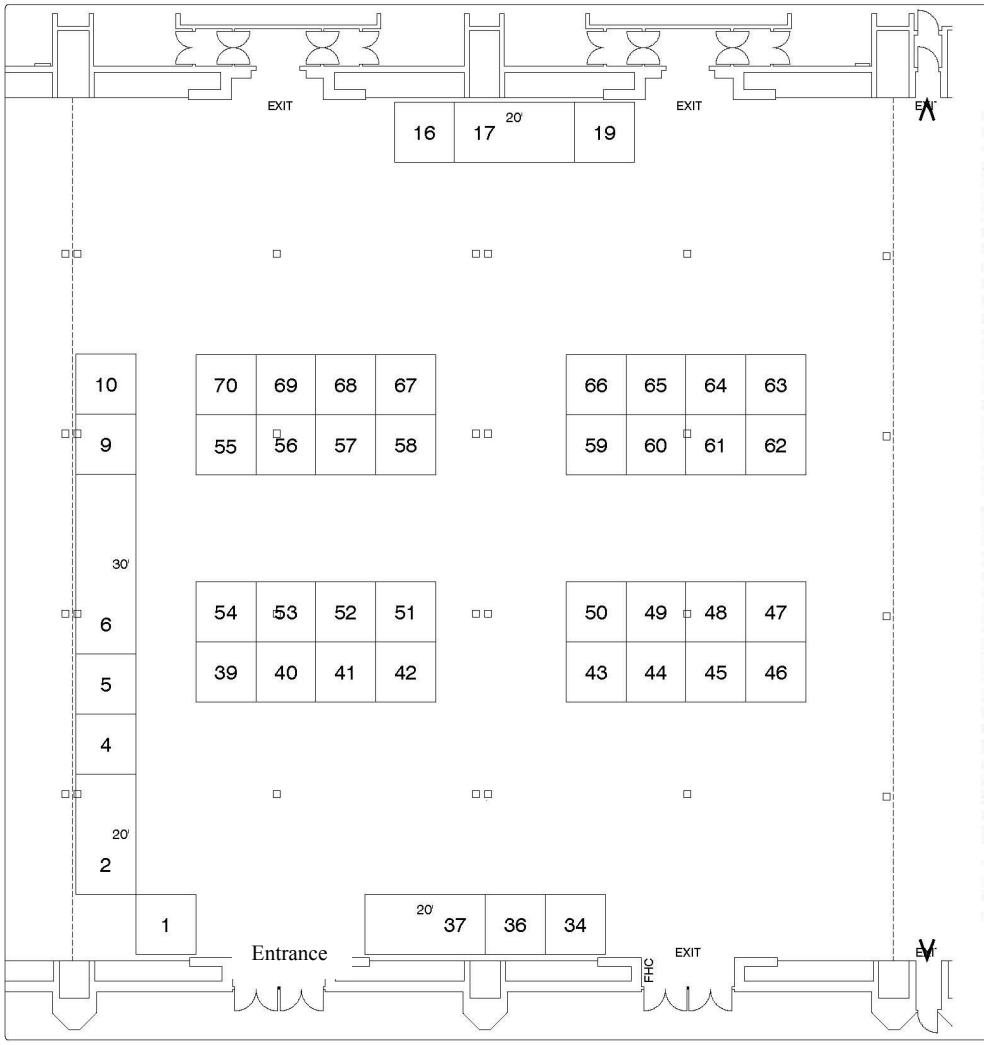

EXHIBITOR DESCRIPTIONS

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FACSS **Booth 11**
2019 Galisteo Street, Bldg I-1
Santa Fe, NM 87505
Phone: 505 820 1648

FACSS 2007 will be held October 14 – 18 in Memphis, TN at the Memphis Cook convention Center. The conference hotel will be the Memphis Marriott Downtown Hotel, which is adjacent to the convention center. Make it a point to stop by the booth to talk to the organizing committee about the conference and be sure to visit the FACSS web site www.facss.org for FACSS 2007 updates.

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85 N. Whitney Street
Amherst, MA 01002-1869
Phone: 413 256 8942
www-unix.oit.umass.edu/~wc2006

ICP Information Newsletter, Inc. is a nonprofit corporation established in 1997 to foster science education, research, and study in spectroanalytical chemistry. The corporation comprises three divisions: the *ICP Information Newsletter*, a monthly publication with international distribution that gathers all conference and published information related to plasma spectrochemistry; the Winter Conference on Plasma Spectrochemistry, a biennial meeting with international participation featuring state-of-the-art research developments in plasma spectrochemistry, and the University Research Institute for Analytical Chemistry, the research and development branch that provides specialty plasma spectrochemical analyses, method development, training, consulting, and applied research with ICP atomic emission spectrometry and ICP mass spectrometry. The 2006 Asia-Pacific Winter Conference on Plasma Spectrochemistry is scheduled for Bangkok, Thailand, November 27-December 2, 2006, and the 2008 Winter Conference is planned for Temecula, California, January 6-12, 2008. Visit www-unix.oit.umass.edu/~wc2006 or contact wc2006@chem.umass.edu for program and registration details. The *ICP Information Newsletter* now in its thirty-second year of publication is currently distributed to subscribers in computer-readable format on CD-ROM.

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Lab Manager Magazine(TM), a Vicon publication, addresses lab managers and other decision makers in their dual roles as scientist and manager. The magazine (www.labmgr.com) is designed to help lab managers of every discipline balance effective administrative practices with superior scientific techniques, to promote scientific analysis and discovery. Lab Manager Magazine will publish bi-monthly in 2006; in 2007, its frequency will increase to monthly publication. It is available free of charge – in print and/or digital format -- to qualified subscribers.

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Ocean Optics, a diversified electro-optics technology firm is the leading supplier of optical sensing and spectroscopy solutions. Our vision is to expand the frontiers of optical sensing and to make it the foundation on which innovative, life-changing ideas are built. We have pioneered laser ablation with our LIBS innovations, providing you with turn-key and modular systems to fit your needs. Ocean Optics can provide you with Raman solutions to fit your needs and your budget. With diverse applications in chemistry, biological research, environmental monitoring, and science education, our extensive line of complementary technologies include spectrometers, chemical sensors, metrology instrumentation, optical fibers, and thin films and optics. Visit our website www.OceanOptics.com for more information.

OPOTEK, Inc. **Booth 4**
2233 Faraday Avenue
Suite E
Carlsbad, CA 92008
Phone: 760 929 0770
www.opotek.com

Manufacturer of efficient, compact, and broadly tunable solid-state laser systems based on its Optical Parametric Oscillators (OPO). These products stand out in their efficiency, reliability and robustness. Applications include photochemistry, photobiology, medical-diagnostics, spectral imaging and environmental monitoring. The systems are computer controlled and simple to use.

EXHIBITOR DESCRIPTIONS

PerkinElmer Life & Analytical Sciences **Booth 39**
710 Bridgeport Avenue
Shelton, CT 06484
Phone: 203 402 6878
http://las.perkinelmer.com

We serve a number of growing industries and markets including the environmental, pharmaceutical, chemical, petrochemical, semiconductor, academic research, biotechnology, and clinical screening segments. Our instruments, reagents, consumables and service offerings help our customers solve complex analytical problems that require innovation, precision and reliability. Our instruments and related software applications measure a range of substances from biomolecular matter to organic and inorganic materials. Our total application-driven laboratory solutions help our customers speed drug discovery, enhance research productivity, meet strict regulatory requirements, improve time-to-market, and increase manufacturing efficiencies.

Pittsburgh Conf of Analytical Chem **Booth 69**
300 Penn Center Blvd., Ste 332
Pittsburgh, PA 15235
Phone: 412 859 0818
www.pittcon.org

Stop by our booth to find out more about Pittcon 2007, the premier conference and Exhibit in the world of Laboratory Science. No matter what your field of study, if you work in a laboratory, you'll find the products, services and technical information you need to do it better.

Reed Business Information **Table Top**
Rue des Palais 100
Brussels 10:30, Belgium

Renishaw, Inc. **Booth 44**
5277 Trillium Blvd.
Hoffman Estates, IL 60192
Phone: 847 286 9953
www.renishaw.com

Renishaw Raman spectrometers are configurable to include multiple excitation sources from the UV through the NIR. Our unique confocal Raman systems automate laser switching and alignment, integrate fiber-optic-launch for remote sampling, allow easy integration of AFM and SEM instruments, allow macro-sampling, and global Raman imaging. Renishaw Raman microscopes utilize kinematic optics that allow easier customization and more wavelength options to meet the most demanding Raman analysis needs.

RoMack, Inc. **Booth 70**
PO Box 615
Lightfoot, VA 23090
Phone: 757 258 4805
www.romackfiberoptics.com

RoMack,Inc., manufacturers fiberoptic assemblies, components and related products specifically tailored for spectroscopic, laser, pharma amd medical applications. Products include probes, fiberoptics, connectors, adapters, patchcords, bundles, arrays, imagers, collimators, couplers, tapers and filter packages. RoMack,Inc. routinely takes concept to product, creating solutions to the most difficult problems.

Royal Society of Chemistry **Booth 49**
Thomas Graham House
Science Park, Milton Road
Cambridge, UK CB4 0WF
Phone: 44 1223420066
www.rsc.org

Visit the RSC booth to pick up a copy of one of our internationally renowned journals including those covering analytical science The Analyst, JAAS and Lab on a Chip and general titles such as Chemical Communications and Chemical Society Reviews. Membership and other information on the RSC activities is also available. The RSC is the largest organisation in Europe for advancing the chemical sciences. Supported by a worldwide network of members and an international publishing business, our activities span education, conferences, science policy and the promotion of chemistry to the public.

Saudi Aramco **Booth 43**
9009 West Loop Street
Houston, TX 77096
Phone: 713 432 4675
www.jobsataramco.com

The Saudi Arabian Oil Company (Saudi Aramco) is the world's largest crude oil producer and exporter, holding approximately one-fourth of global oil reserves. It also ranks among the leading producers of natural gas and in refining capacity. Saudi Aramco employs experienced professionals in all fields supporting its energy operations.

Savillex Corporation **Booth 62**
6133 Baker Road
Minnetonka, MN 55345
Phone: 952 935 4100
www.savillex.com

Savillex Corporation has been manufacturing PFA labware products for over 30 years. We currently offer over one thousand products including; vials, digestion vessels, syringes, inline filters, jars, impingers, sub-boiling stills and various transfer containers. In addition, we offer a full line of PFA sample introduction systems and have the capability to custom mold products to meet the specific requirements of our customers.

SCP SCIENCE **Booth 9**
348 Route 11
Champlain, NY 12919-4816
Phone: 800 361 6820
www.scpscience.com

Founded in 1980, SCP SCIENCE is a successful privately owned manufacturer and distributor of analytical equipment, supplies, standards, reagents, and certified reference materials for the inorganic analytical laboratories market. The company manufactures supply items including digestion systems; calibration, quality control and certified reference material standards; and specialized glassware for the atomic spectroscopy market. In distribution, the company supplies analytical instruments for spectroscopist primarily in Canada.
Products:
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PlasmaTEST Instrument Control Standards
PlasmaFORM ICP-MS Skimmer and Sampler cones
MAT Family of Certified Reference Materials
peCHECK Performance Evaluation Standards
AccuSPEC Standards and Reagents
Organo-metallic Standards

EXHIBITOR DESCRIPTIONS

Shimadzu Scientific Instruments, Inc. **Booth 56**
7102 Riverwood Dr.
Columbia, MD 21046
Phone: 410 381 1227
www.shimadzu.com

Shimadzu offers a full line of analytical instrumentation, including UV Visible and Fluorescence Spectrophotometers; FTIR Spectrometers; Automated FTIR Microscope; HPLC systems and components; LC/MS; Gas Chromatography; GC/MS; Data Stations for Spectroscopy and Chromatography; Thermal Analyzers, TOC, Atomic Absorption Spectrometers, ICP, Particle Size Analyzers, Balances, Capillary Rheometers, Mooney Viscometers, Universal Testing Equipment and more.

Society for Applied Spectroscopy **Booth 6, 7,8**
201B Broadway Street
Frederick, MD 21701-6501
Phone: 301-694-8122
www.s-a-s.org

The Society for Applied Spectroscopy is an association of scientific professionals who have organized to advance and disseminate knowledge and information concerning spectroscopy and other allied sciences. We've served the scientific community for over 40 years and are the publishers of Applied Spectroscopy. Visit our booth for membership information.

SpectroPure / Ricca Chemical Company **Booth 67**
2862 G Road
Fults, IL 62244
Phone: 314 302 8782
www.spectropure.com

SpectroPure / Ricca Chemical offers a complete line of atomic spectroscopy products - AA, ICP, ICP-MS, as well as standardized solutions for analytical laboratories, reagent chemicals in small packages, and certified NIST traceable secondary standards. Multi-element ICP standards are listed by EPA method. Made to a higher standard - yours.

Spectroscopy Magazine **Booth 48**
485 Route 1 South, Bldg F, 1st Fl
Iselin, NJ 08830
Phone: 732 346 3081
www.spectroscopyonline.com

Spectroscopy is the only publication dedicated to delivering a complete information solution to the largest circulation of spectroscopists in North America. By providing peer-reviewed, technical and applications-oriented information in every issue, Spectroscopy enables substantial productivity improvement in the laboratories of the spectroscopists leading the way in all areas of spectroscopy www.spectroscopyonline.com

StellarNet, Inc. **Booth 58**
14390 Carlson Circle
Tampa, FL 22626-3003
Phone: 813 855 8687
www.stellarnet-inc.com

StellarNet delivers extreme solutions for a variety of spectroscopy measurements in the Lab or in the Field. Our ruggedized fiber optic instruments are made to be portable and deliver high S/N performance at a low cost. Detector arrays include CCD, PDA, and NIR-InGaAs (512 & 1024 pixel) for UV-VIS-NIR applications from 190-2200nm. Up to eight spectrometers can be attached to desktop or portable PC via USB-2.0 interface for simultaneous measurements. Come see our - 1) concave grating UV-VIS spec for fluorescence measurements using LED excitation. 2) the Dual-DSR (dual detector super range) spec for reflectance measurements 400-1700nm. 3) NIRX-SR spec for 900-2200nm cuvette measurements. 4) PORTA-LIBS battery operated elemental analysis. Our free SpectraWiz software enables quantitative measurements for SpectroChemistry, SpectroRadiometry, SpectroColorimetry, OES, and LIBS spectroscopy. Customizable LabVIEW and VBA+Excel programs also included on CDROM with software training videos. Visit our website for more information at www.StellarNet-Inc.com.

Teledyne Leeman Labs Inc. **Booth 34**
6 Wentworth Drive
Hudson, NH 03051
Phone: 603 886 8400
www.leemanlabs.com

Thermo Electron Corp. **Booth 17, 18**
5225 Vernona Road
Madison, WI 53711
Phone: 608 273 6822
www.thermo.com

Upchurch Scientific **Booth 66**
619 W. Oak Street
Oak Harbor, WA 98277
Phone: 800-426-0191
www.upchurch.com

Upchurch Scientific®, an ISO 9001 company, manufactures precision fluid transfer components from high-performance engineering thermoplastics and corrosion-resistant metals for analytical laboratory and biotechnology applications. The product line offers solutions for applications requiring exceptional chemical compatibility, mechanical strength, biocompatibility and temperature resistance. Stop by our booth to discuss integrating our fluidic connection solutions for your spectroscopy needs.
Products and Services:
New products of particular interest: chromatography fittings for high temperature (200°C) and ultra-high pressure 28,000 psi (1930 bar). Standard products include: fittings (threaded, luer, barb, unions, adapters, tees/crosses, etc.), polymer tubing (such as PEEK™, Teflon®, Tefzel®, Radel®, Halar®); stainless steel and titanium tubing; valves, unions, adapters, backpressure regulators, inline check/relief valves; guard columns/accessories; components for lab-on-a-chip, and other micro/nanoscale applications. Assembly and kitting products and services include custom tubing (sizes, lengths, materials), fittings and connectors, as well as custom forming, labeling and packaging. As part of the IDEX® Health and Science Technologies group, Upchurch Scientific also offers micro- and nanoscale valves from sister business unit Rheodyne®. Capabilities include in-house injection molding, extrusion, precision machining

EXHIBITOR DESCRIPTIONS

Varian, Inc. **Booth 2,3**
3120 Hansen Way D-111
Palo Alto, CA 94304
Phone: 650 424 4962
www.varian.com

Varian, Inc. is a world leader in scientific instruments' technologies. Varian serves environmental, industrial, chemical, life science, and heath care customers. We will be presenting our latest range of FTIR, UV, AA, ICP, and ICP-MS products. To learn more about our exciting new products, the 700-ES series of ICP-OES instruments and the 810/820-MS ICP-MS, please visit us at Booth #2.

WITec GmbH **Booth 51**
101 Tomaras Ave.
Savoy, IL 61874
Phone: 877 948 3201
www.WITec.de

WITec is manufacturer of high resolution optical and scanning probe microscopy solutions for scientific and industrial applications. A modular product line allows the combination of different microscopy techniques guaranteeing highest flexibility for a wide range of applications. WITec will showcase the new alpha300 microscope generation. This series includes the Confocal Raman 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 is acquired in less than 100 ms and stored on the computer. This multi-spectrum file can then be analysed with respect to various peak characteristics 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.

FACSS 2007
Memphis Cook Convention Center
October 14 – 18, 2007
Exhibition Dates: October 15 – 17
Conference Hotel: Memphis Marriott Downtown Hotel
Go to www.facss.org to register for your booth.
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FACSS/SAS WORKSHOPS

Workshops are a valuable component of FACSS and are conducted by leading experts. There is an additional charge for workshops

Following are the rates for workshops unless otherwise indicated.

	half day	full day	2 day
Conferees:	$150	$300	$500
Students:	$25	$50	$100
Non-Conferees	$250	$400	$700

ANALYTICAL RAMAN SPECTROSCOPY

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

Sunday, 8:30 AM – 12:30 PM, *Pastoral 1*

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. Attendees who elect this option may take advantage of a reduce rate for the Hands-on Raman Workshop

INFRARED SPECTRTAL INTERPRETATION: A STRATEGIC APPROACH

Brian C. Smith, *Spectros Associates*

Sunday, 8:30 AM – 5:00 PM and Monday, 9:00 AM – 5:00 PM, *Pastoral 3*

A 2 day overview of how to interpret infrared spectra to determine unknown molecular structures. The course begins with what peak positions, heights, and widths mean and how to use this info to distinguish functional groups from each other. A 10-step strategy to successfully interpret spectra is presented along with how to deal with mixtures and how to perform identities properly. The bulk of the course is an examination of the important infrared bands of a wide variety of economically important molecules. Reference spectra are studied in detail, and many problem spectra are worked on in class with the help of your expert instructor. The course finishes with a discussion of how library searching and spectral subtraction make interpretation easier. Course attendees receive a free copy of Dr. Smith's more than 200 PowerPoint slides that will make learning fast and easy.

HANDS-ON RAMAN

Exhibitors, Instrumentation Company Representatives

Conferees $50, Students $10, Non-Conferees $150

Sunday, 1:00 – 5:00 PM, *Fantasia K/L*

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 including: HORIBA Jobin Yvon, WiTec, Renishaw, B&W Tek, Kaiser Optical, Mesophotonics, Bruker Optics, Ahura, DeltaNu, ChemImage, Hamilton Sundstrand, and Ocean Optics.

CHEMOMETRICS WITHOUT EQUATIONS (OR HARDLY ANY) – HANDS ON!

Barry M. Wise, Jeremy M. Shaver, Willem Windig; *Eigenvector Research, Inc.*

Conferees $550, Students $150, Non-Conferees $750 (includes computer use)

Monday and Tuesday, 9:00 AM – 5:00 PM, *Atlantic B*

Chemometrics without Equations concentrates on two areas of chemometrics: 1) exploratory data analysis and pattern recognition, and 2) regression. Participants will learn to safely apply techniques such as Principal Components Analysis (PCA), Principal Components Regression (PCR), and Partial Least Squares (PLS) Regression. 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).

PRACTICAL APPLICATIONS OF LCMS FOR SMALL MOLECULES

Michael P. Balogh, *Waters Corporation*

Monday, 9:00 AM – 5:00 PM, *Grand Republic C*

A one day course introduces the most commonly applied HPLC-to-mass spectrometry techniques and examines in detail the most widely used related technologies. High throughput, high sensitivity and ease-of-use considerations are illustrated with applications from industrial and environmental analyses as well as pharmaceutical interests. Course materials include video aids and a wide variety of practical applications to demonstrate ionization techniques and components while examining what makes an LC/MS method successful and where some of the common errors are made. An extensive Glossary as well as reference materials created specifically for LC/MS practice is included.

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

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

Tuesday, 9:00 AM – 1:00 PM, *Pastoral 3*

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

FACSS/SAS WORKSHOPS

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

James W. Rydzak, *GlaxoSmithKline;* **Christian Hassell**, *AMTI*

Tuesday, 9:00 AM – 5:00 PM, *Pastoral 2*

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.

PROFESSIONAL ANALYTICAL CHEMISTS IN INDUSTRY: A SHORT COURSE FOR UNDERGRADUATE STUDENTS

Sandy Murawski, *The Procter & Gamble Company*

Tuesday, 9:00 AM – 5:00 PM, *Fantasia Q*

The objective of this workshop is to provide insight into the work of industrial analytical chemists. In a highly interactive forum, participants will explore the role of analytical chemist as problem solver using real problems encountered at Procter & Gamble. Participants have an opportunity to try their hand at solving real consumer product chemistry problems, and to get answers to some of their questions on industrial chemistry careers. The course is targeted at third-year undergraduates who have had some exposure to instrumental analysis; however, new undergraduate students, graduate students, and chemistry teachers have all reported that they found the short course highly beneficial. For additional information go to: www.pg.com/science/prof_chemists.jhtml

INFRARED CHEMICAL IMAGING

E. Neil Lewis, Frederick Koehler, Janie Dubois,

Spectral Dimensions, Inc.

Tuesday, 1:30 – 5:30 PM, *Pastoral 1*

Infrared and near-infrared chemical imaging instruments are relatively new tools to non-invasively visualize the chemical heterogeneity of various samples. They provide both a qualitative and quantitative assessment of the molecular composition and architecture of a diverse array of heterogeneous materials. As a result, chemical imaging can be used to assess the quality and performance of new and existing complex materials and products. Topics covered in this half-day course will include: imaging spectrometer technologies, focal-plane array detectors and data processing methods and software. We will frame the instrumentation discussion with a strong emphasis on the value and practical applications of the technology for biological, polymeric and pharmaceutical problem solving.

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

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

Tuesday, 1:30 – 5:30 PM, *Pastoral 3*

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 and 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

ATTACK THE VARIANCE: AN INTRODUCTION TO ROBUST METHOD DESIGN

Drew Manica, Erica Kyllo, and **Nancy Jestel**;

GE Advanced Materials

Wednesday, 9:00 AM – 5:00 PM, *Pastoral 3*

This workshop will cover statistical design strategies (DOE & Robust Design) for building robust new methods and improving existing methods. Learn how critical experimental factors can be identified and controlled for measurement improvement as well as how deliberate experimental design can capture variability to produce a more robust measurement. Robust design methodologies accommodate variability present in the experimental factors themselves and in the measurement process in such a way that undesirable variation of the final result is minimized. Consequently, both an optimal and robust measurement system can be developed simultaneously. Hands-on breakout sessions will include the use of statistical software.

CHEMOMETRICS IN MASS SPECTROMETRY

Barry M. Wise, Willem Windig, Jeremy M. Shaver;

Eigenvector Research

Conferees $350, Students $75, Non-Conferees $450

Wednesday, 9:00 AM – 5:00 PM, *Atlantic B*

Chemometrics in Mass Spectrometry covers methods for dealing with the discontinuous spectra produced by MS. Hyphenated instruments, such as GC/MS and LC/MS are also discussed. Participants will learn how overlapping peaks, such as resulting from GC/MS, can be resolved into separate peaks for each of the components and their associated single component spectra using self modeling mixture analysis. The newly developed technique has the same functionality as the well known SIMPLISMA method. Methods for extracting high quality mass chromatograms from complex data such as resulting from LC/MS with electro spray will also be covered. Methods that extract small differences between very similar samples, such as different batches of the same material, will also be discussed. The course includes hands-on computer time for participants to work example problems using PLS_Toolbox.

NEAR INFRARED SPECTROSCOPY: MEASUREMENT PRINCIPLES AND INTERPRETATION

Jerry Workman, *Molecular Spectroscopy and Microanalysis, Thermo Electron Corporation*

Wednesday, 9:00 – 5:00 PM, *Pastoral 2*

Near infrared spectroscopy is used for many applications where multicomponent molecular vibrational analysis is required in the presence of interfering substances, such as high moisture content, or when sampling is constrained to in situ conditions. The near infrared spectra consist of overtones and combination bands of the fundamental molecular absorptions found in the mid-infrared region. Near infrared spectra consist of generally overlapping vibrational bands that are non specific and non-resolved. Spectra measured using this wavelength region also contain information related to the optical and physical properties of materials. The use of chemometric mathematical data processing can be used to calibrate for qualitative or quantitative analysis despite these apparent spectroscopic limitations. This workshop will describe the methods and techniques applied to make effective near infrared measurements for most applications, including: natural products, fine chemicals, pharmaceuticals, hydrocarbons, polymers and rubbers, medical applications, and other materials. In addition, a detailed overview and workshop will be given on interpretation of near infrared spectra, including the use of spectra-structure correlation charts provided to participants.

FACSS/SAS WORKSHOPS

SUPERCRITICAL FLUID CHROMATOGRAPHY: A TECHNOLOGY TO INCREASE THE EFFICIENCY & QUALITY OF CANDIDATE

Jennifer L. Lefler, *Applications and Technology Manager, Thar Technologies, Inc*

Wednesday, 9:00 AM – 1:00 PM, *Pastoral 1*

As the environment for discovering and developing potent pharmaceuticals becomes more competitive and more costly, companies are looking to identify potential lead compounds earlier in the process. Employing purification methods to facilitate the route to candidate selection is gaining in popularity. Technologies, such as preparative liquid chromatography (LC), have yielded in the isolation of impurities from potential lead molecules. Yet these techniques involve tremendous man hours and consume/generate large volumes of hazardous, liquid waste. An attractive alternative to preparative scale LC is a closely related technology, Supercritical Fluid Chromatography (SFC). The bulk of the mobile phase is carbon dioxide (CO2), which is highly tunable in its chromatographic properties and is easily removed from the collected fraction. Supercritical CO2 also demonstrates lower viscosity than traditional LC solvents, thereby enabling geometric scalability with reduced penalty of back pressure or pressure drop across a column, and follows the basic chromatographic principles understood by most end-users. This course will discuss the importance of pumping and regulating supercritical carbon dioxide in its chromatographic instrumentation and to demonstrate the scalability from conduct method development to purification for chiral and achiral matrices. We wish to demonstrate through several applications of the ease of use of the technology, as well as, demonstrate its economic and environmental attractiveness.

MOLECULAR MICROSPECTROSCOPY

André Sommer; *Molecular Microspectroscopy Laboratory, Miami University*

Wednesday, 1:30 – 5:30 PM, *Pastoral 1*

The workshop will present an overview on the fundamentals of molecular microspectroscopy and will provide specifics regarding current instrumentation and current applications. Topics to be covered include: elements of optical microscopy and how they relate to the design and performance of infrared and Raman microscopes, sample preparation for each method and industrial problem solving using the combined techniques. The instructor has over 25 years of industrial problem solving experience using the featured methods and has taught at 16 of the Molecular Microspectroscopy Short Courses held annually at Miami University.

FACSS EMPLOYMENT BUREAU

The FACSS Employment Bureau will be available during the 2006 FACSS Conference to both job applicants and employer representatives. The Employment Bureau is a free service that provides job and applicant listings, message boards, and interviewing booths. Participants must be registered for the conference. Separate files will be available for job opportunities and applicant resumes. Registered participants may review these files during Employment Bureau hours. Either applicants or employers may request on-site interviews.

LOCATION. The employment bureau is located in Grande Republic D, second level
HOURS. 9:00 AM – 5:00 PM, Monday – Wednesday and 9:00 AM – 3:00 PM on Thursday

- **Applicants** should submit the FACSS Employment Bureau Applicant Form and a personal one-page resume. The Applicant Form is designed to allow easy review by employer representatives. Applicants also should include a formal resume. Applicants who wish to exclude their resume from the resume book should check the appropriate box on the registration form.
- **Employers** should submit the Employer Form. Books containing all applicant approved resumés will be available for purchase and will be mailed after the conference.

ON-SITE REGISTRATION. Applicants and employer representatives must sign in with the Employment Bureau upon arrival at the meeting. Applicant Resumé forms and Employer forms will be available for review. Interview booths will be available during Employment Bureau hours. The Employment Bureau will schedule 30-minute interviews upon request from either employers or applicants. Interview notices and messages will be posted on message boards. It is recommended that Employment Bureau participants check the message boards at approximately two-hour intervals during the day.

SPECIAL INVITATION TO STUDENT ATTENDEES:
Tuesday, 12:30, GE Advanced Materials sponsored Student/Professional Panel Discussion and Brown Bag Lunch. "I'm Graduating Soon. What's Next?" Grand Republic C, second level. *Sign up at conference registration desk*

PROGRAM HIGHLIGHTS

SUNDAY	MONDAY	TUESDAY	WEDNESDAY	THURSDAY
	07:30 Wake up coffee	07:30 Wake up coffee	07:30 Wake up coffee	07:30 Wake up coffee
8:30 AM – 5:00 PM FACSS/SAS Workshops	Plenary Session *Fantasia G* 8:00 AM Harry Y. McSween, Jr. *University of Tennessee*	Plenary Sessions *Fantasia G* 8:00 AM ANACHEM Award Richard D. Sacks, posthumous, *University of Michigan*; presented by James A. Holcombe, *University of Texas, Austin* 8:30 AM Charles Mann Award Michael Morris *University of Michigan*	Plenary Sessions *Fantasia G* 8:00 AM Applied Spectroscopy William F. Meggers Award Pavel Matousek *Rutherford Appleton Laboratory* 8:30 AM Lester W. Strock Award Paul Farnsworth *Brigham Young University*	Plenary Session *Fantasia G* 8:00 AM Alan G. Marshall *Florida State University*
	9:00 AM – 5:00 PM Workshops	9:00 AM – 5:00 PM Workshops	9:00 – 5:00 PM Workshops	
	9:00 – 10:30 AM Poster Session and Break *Nutcracker Ballroom 2*	9:00 – 10:30 AM Poster Session and Break *Fantasia J/H*	9:00 – 10:30 AM Poster Session and Break *Fantasia J/H*	9:00 – 10:30 AM Poster Session and Break *Fantasia H*
		9:00 AM – 5:00 PM Exhibits Open *Fantasia J/H*	9:00 AM – 5:00 PM Exhibits Open *Fantasia J/H*	
	10:30 AM – 12:30 PM Oral Symposia	10:30 AM – 12:30 PM Oral Symposia	10:30 AM – 12:30 PM Oral Symposia	10:30 AM – 12:30 PM Oral Symposia
	12:30 PM Lunch on own	12:30 PM Lunch on own	12:30 PM Lunch on own	12:30 PM Lunch on own
	1:15 – 2:15 PM "What's Hot" Symposium *Fantasia E/F*			
		1:45 – 3:15 PM Poster Session and Dessert Reception *Fantasia J/H*	1:45 – 3:15 PM Poster Session and Dessert Reception *Fantasia J/H*	1:45 – 3:15 PM Poster Session and Break *Fantasia H*
3:20 – 5:00 PM "What's Hot" Symposium *Fantasia E/F*	2:30 – 4:30 PM Oral Symposia	3:15 – 5:15 PM Oral Symposia	3:15 – 5:15 PM Oral Symposia	3:15 – 5:15 PM Oral Symposia
5:00 – 7:00 PM Welcome Mixer and SAS Sponsored Student Poster Session *Nutcracker Ballroom*	4:30 – 6:30 PM Exhibit Opening Reception *Fantasia J/H*	6:00 PM Raman Reception *Ballroom of the Americas A*		
		7:00 PM SAS Reception *(SAS members only)* *Ballroom of the Americas B*	7:00 PM FACSS Event Downtown Disney® Pleasure Island Adventurers Club *Tickets required*	

PROGRAM OVERVIEW

SUNDAY

3:20 PM "What's Hot" Symposium – oral presentations by FACSS 2006 exhibitors describing some of their latest products**.** *Fantasia E/F*

5:00 PM Welcome Mixer and SAS Sponsored Student Poster Session, *Nutcracker Ballroom*

MONDAY MORNING

8:00 AM **PLENARY LECTURE,** *Fantasia G*
Spectroscopy on the Red Planet: More than Meets the Eye; Harry Y. McSween, Jr., page 42

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

9:00 – 10:30, Posters, *Nutcracker Ballroom 2,* page 42
Correlation Spectroscopy
Chemometrics
Pharmaceutial and Process Analysis
Education

10:30 – 12:30, Symposia, page 44
Optical Detection in Bioanalysis, *Fantasia A/B*
New Methods for Characterization of Chiral Pharmaceuticals, *Fantasia C*
FACSS Young Investigators I, *Fantasia D*
Imaging Mass Spectrometry, *Fantasia E/F*
Symposium to Honor the Retirement of Peter C. Jurs, *Fantasia K/L*
2-D Correlation Spectroscopy I, *Pastoral 1*
Raman Imaging, *Nutcracker 1*
Other Ways to Get the Job Done with ICPMS – Sample Introduction Alternatives I, *Nutcracker 3*

MONDAY AFTERNOON

1:15 PM What's Hot" Symposium – oral presentations by FACSS 2006 exhibitors describing some of their latest products. *Fantasia E/F, page 45*

2:30 PM **SYMPOSIA,** page 46
Applications of Nanoparticles and Other Techniques, *Fantasia A/B*
Student Awards Sympsoium, *Fantasia C*
FACSS Young Investigators II, *Fantasia D*
NIR Used as a Process Analytical Tool, **sponsored by CNIS, a technical affiliate of SAS**, *Fantasia E/F*
Chemometrics and Industry: A Successful Marriage?, *Fantasia K/L*
2-D Correlation Spectroscopy II, *Pastoral 1*
Navigating an Entangled Web: Raman Spectroscopy of Polymeric Systems, *Nutcracker 1*
Other Ways to Get the Job Done with ICPMS – Sample Introduction Alternatives II, *Nutcracker 3*

TUESDAY MORNING

8:00 AM **PLENARY LECTURES,** *Fantasia G*
Anachem Award, Richard D. Sacks, *posthumous*, page 48
Charles Mann Award, Michael Morris, page 48

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

9:00 – 10:30, Posters, *Fantasia J/H,* page 48
Nanoscience and Microscopy
Surface-enhanced Raman Spectroscopy
Laser-induced Breakdown Spectroscopy
Materials
Environmental
Separations
Bioanalytical

10:30 – 12:30, Symposia, page 51
ANACHEM Award, *Fantasia A/B*
Recent Advances in Forensic Sciences I, *Fantasia C*
Applications of NIR Spectroscopy – Diversity in Action, **sponsored by CNIS, a technical affiliate of SAS**, *Fantasia D*
Analysis of Dissolved Organic Matter in Seawater Using Mass Spectrometry, *Fantasia E/F*
Chemometrics for Sensors, *Fantasia K/L*
Surface Plasmon Resonance I, *Fantasia M*
Separation of Carbon Nanotubes I, *Fantasia N*
Pharmaceutical Raman: Process and Screening Applications, *Nutcracker 1*
Atomic Spectroscopy in the Clinical Laboratory, *Nutcracker 3*

TUESDAY AFTERNOON

1:45 PM **SYMPOSIA AND POSTER SESSIONS**

1:45 – 3:15, Posters, *Fantasia J/H,* page 48
For listing, see above.

3:15 – 5:15, Symposia, page 53
Recent Advances in Forensics Sciences II, *Fantasia C*
Innovations in NIR – Advancing the Field, **sponsored by CNIS, a technical affiliate of SAS**, *Fantasia D*
Microchips and Mass Spectrometry, *Fantasia E/F*
Multivariate Imaging, Wavelets, and Genetic Algorithms for 21st Century Applicaitons, *Fantasia K/L*
Surface Plasmon Resonance II, *Fantasia M*
Separation of Carbon Nanotubes II, *Fantasia N*
Charles Mann Award, *Nutcracker 1*
From Elemental Speciation to Metallomics, *Nutcracker 3*

PROGRAM OVERVIEW

WEDNESDAY MORNING

8:00 AM **PLENARY LECTURES,** *Fantasia G*
William F. Meggers Award, Pavel Matousek, page 56
Lester W. Strock Award, Paul Farnsworth, page 56

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

9:00 – 10:30, Posters, *Fantasia J/H,* page 56
Atomic Mass Spectrometry
Atomic Spectroscopy
Infrared Spectroscopy
Fluorescence

10:30 – 12:30, Symposia, page 59
Microchip-CE, *Fantasia A/B*
Spectroscopy and Mass Spectrometry in Forensic Sciences I, *Fantasia C*
Raman Microscopy, *Fantasia D*
Field Deployable Mass Spectrometers, *Fantasia E/F*
Process Analysis: Spectroscopic Monitoring Tools, **organized by SAS Process Analytical Technical Section**, *Fantasia K/L*
Nanotubes and Nanowires for Sensing, *Fantasia M*
Advances in IR Spectroscopy, **sponsored by the Coblentz Society**, *Fantasia N*
William F. Meggers Award: New Approaches in Raman Spectroscopy of Turbid Media, *Nutcracker 1*
Ion Processsing, Detection and Laser Sampling in Plasma Source MS, *Nutcracker 3*

WEDNESDAY AFTERNOON

1:45 PM **SYMPOSIA AND POSTER SESSIONS**

1:45 – 3:15, Posters, *Fantasia J/H,* page 56
For listing, see above.

3:15 – 5:15, Symposia, page 61
Standard CE & HPLC of Biomolecules, *Fantasia A/B*
Spectroscopy and Mass Spectrometry in Forensic Sciences II, *Fantasia C*
Illuminating the Biological World with Raman Microscopy, *Fantasia D*
Applications in Atomic Spectoscopy, **organized by the SAS Atomic Spectroscopy Technical Section**, *Fantasia E/F*
Process Analysis: Interfaces for Spectroscopic Measurements, **sponsored by the Coblentz Society**, *Fantasia K/L*
Electron Transfer Chemistry of Nanostructured Materials, *Fantasia M*
Probes for Spectroscopic Bio-analysis, **sponsored by the Royal Society of Chemistry**, *Nutcracker 1*
Lester W. Strock Award: Ion Generation, Transport and Detection in MS, *Nutcracker 3*

THURSDAY MORNING

8:00 AM **PLENARY LECTURE: Ultrahigh-Resolution Mass Spectrometry for Separation and Identification of Complex Analytical, Biological, and Environmental Organic Mixtures**, Alan G. Marshall, *Fantasia G,* page 64

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

9:00 – 10:30, Posters, *Fantasia H,* page 64
Molecular Mass Spectrometry
Forensic Sciences
Raman Spectroscopy

10:30 – 12:30, Symposia, page 66
Frontiers in Analytical Spectrochemistry I Honoring Gary Horlick, *Fantasia A/B*
Highlighting Diversity in Forensic Applications of Mass Spectrometry, *Fantasia C*
Bioelectronics and Biosensors, *Fantasia D*
Vapor Generation for Atomic Spectroscopy, *Fantasia E/F*
Process Analysis: New Spectroscopic Technologies, **sponsored by the Coblentz Society**, *Fantasia K/L*
Applications of Novel Materials for Fluorescence Spectroscopy, *Pastoral 1*
Gas Analysis by IR Spectroscopy, **sponsored by the Coblentz Society**, *Pastoral 2*
In Situ Raman analysis in Non-traditional Environments, *Nutcracker 1*

THURSDAY AFTERNOON

1:45 PM **SYMPOSIA AND POSTER SESSIONS**

1:45 – 3:15, Posters, *Fantasia H,* page 64
For listing, see above.

3:15 – 5:15, Symposia, page 68
Frontiers in Analytical Spectrochemistry II Honoring Gary Horlick, *Fantasia A/B*
Electrophoretic Separations, *Fantasia C*
Advances in Nebulization and Plasma Spectrometry, *Fantasia D*
Innovations in Fourier Transform Mass Spectrometry, *Fantasia E/F*
Developments in Luminescence Spectroscopy and Instrumentation, *Pastoral 1*
Advances in Vibrational Spectroscopy, *Pastoral 2*
Combining Raman and Scanning Probe Microscopy – Are We There Yet? *Nutcracker 1*

TECHNICAL PROGRAM OVERVIEW BY TOPIC

AWARD SESSIONS

Monday PM
Student Awards Symposium, *Fantasia C*
Tuesday AM
ANACHEM Award, *Fantasia A/B*
Tuesday PM
Charles Mann Award, *Nutcracker 1*
Wednesday AM
Applied Spectroscopy William F. Meggers Award: New Approaches in Raman Spectroscopy of Turbid Media, *Nutcracker 1*
Wednesday PM
Lester W. Strock Award: Ion Generation, Transport and Detection in MS, *Nutcracker 3*

ATOMIC SPECTROSCOPY

Monday AM
Other Ways to Get the Job Done with ICPMS – Sample Introduction Alternatives I, *Nutcracker 3*
Monday PM
Other Ways to Get the Job Done with ICPMS – Sample Introduction Alternatives II, *Nutcracker 3*
Tuesday AM
Atomic Spectroscopy in the Clinical Laboratory, *Nutcracker 3*
ANACHEM Award, *Fantasia A/B*
Tuesday PM
From Elemental Speciation to Metallomics, *Nutcracker 3*
Wednesday AM
Ion Processsing, Detection and Laser Sampling in Plasma Source MS, *Nutcracker 3*
Wednesday PM
Applications in Atomic Spectoscopy, **SAS,** *Fantasia E/F*
Lester W. Strock Award: Ion Generation, Transport and Detection in MS, *Nutcracker 3*
Thursday AM
Vapor Generation for Atomic Spectroscopy, *Fantasia E/F*
Thursday PM
Advances in Nebulization and Plasma Spectrometry, *Fantasia D*
Frontiers in Analytical Spectrochemistry II Honoring Gary Horlick, *Fantasia B*

BIOANALYTICAL

Monday AM
Optical Detection in Bioanalysis, *Fantasia A/B*
FACSS Young Investigators I, *Fantasia D*
Raman Imaging, *Nutcracker 1*
Imaging Mass Spectrometry, *Fantasia E/F*
Monday PM
Applications of Nanoparticles and Other Techniques, *Fantasia A/B*
Tuesday AM
Recent Advances in Forensic Sciences I, *Fantasia C*
Atomic Spectroscopy in the Clinical Laboratory, *Nutcracker 3*
Surface Plasmon Resonance I, *Fantasia M*
Analysis of Dissolved Organic Matter in Seawater Using Mass Spectrometry, *Fantasia E/F*
Tuesday PM
Recent Advances in Forensic Sciences II, *Fantasia C*
Microchips and Mass Spectrometry, *Fantasia E/F*
From Elemental Speciation to Metallomics, *Nutcracker 3*
Charles Mann Award, *Nutcracker 1*
Wednesday AM
Microchip-CE, *Fantasia A/B*
Wednesday PM
Standard CE & HPLC of Biomolecules, *Fantasia A/B*
Probes for Spectroscopic Bio-analysis, **RSC,** *Nutcracker 1*
Illuminating the Biological World with Raman Microscopy, *Fantasia D*
Thursday AM
Bioelectronics and Biosensors, *Fantasia D*
Thursday PM
Innovations in Fourier Transform Mass Spectrometry, *Fantasia E/F*
Advances in Nebulization and Plasma Spectrometry, *Fantasia D*

CHEMOMETRICS

Monday AM
Symposium to Honor the Retirement of Peter C. Jurs, *Fantasia K/L*
Monday PM
Chemometrics and Industry: A Successful Marriage? *Fantasia K/L*
Tuesday AM
Chemometrics for Sensors, *Fantasia K/L*
Tuesday PM
Multivariate Imaging, Wavelets, and Genetic Algorithms for 21st Century Applications, *Fantasia K/L*

CORRELATION SPECTROSCOPY

Monday AM
2-D Correlation Spectroscopy I, *Pastoral 1*
Monday PM
2-D Correlation Spectroscopy II, *Pastoral 1*

FLUORESCENCE

Monday PM
Applications of Nanoparticles and Other Techniques, *Fantasia A/B*
Thursday AM
Applications of Novel Materials for Fluorescence Spectroscopy, *Pastoral 1*
Thursday PM
Developments in Luminescence Spectroscopy and Instrumentation, *Pastoral 1*

TECHNICAL PROGRAM OVERVIEW BY TOPIC

FORENSIC SCIENCE

Tuesday AM
Recent Advances in Forensic Sciences I, *Fantasia C*
Tuesday PM
Recent Advances in Forensic Sciences II, *Fantasia C*
Wednesday AM
Spectroscopy and Mass Spectrometry in Forensic Sciences I, *Fantasia C*
Wednesday PM
Spectroscopy and Mass Spectrometry in Forensic Sciences II, *Fantasia C*
Thursday AM
Highlighting Diversity in Forensic Applications of Mass Spectrometry, *Fantasia C*

IMAGING and MICROSCOPY

Monday AM
Imaging Mass Spectrometry, *Fantasia E/F*
Raman Imaging, *Nutcracker 1*
Wednesday AM
Raman Microscopy, *Fantasia D*
Thursday PM
Combining Raman and Scanning Probe Microscopy – Are We There Yet? *Nutcracker 1*

IR and NEAR IR

Monday PM
NIR Used as a Process Analytical Tool, **CNIS,** *Fantasia E/F*
Tuesday AM
Applications of NIR Spectroscopy - Diversity in Action, **CNIS,** *Fantasia D*
Tuesday PM
Innovations in NIR – Advancing the Field, **CNIS,** *Fantasia D*
Wednesday AM
Advances in IR Spectroscopy, **Coblentz,** *Fantasia N*
ThursdayAM
Gas Analysis by IR Spectroscopy, *Pastoral 2*
ThursdayPM
Advances in Vibrational Spectroscopy, *Pastoral 2*

MASS SPECTROMETRY

Monday AM
Imaging Mass Spectrometry, *Fantasia E/F*
Other Ways to Get the Job Done with ICPMS – Sample Introduction Alternatives I, *Nutcracker 3*
Monday PM
FACSS Young Investigators II, *Fantasia D*
Other Ways to Get the Job Done with ICPMS – Sample Introduction Alternatives II, *Nutcracker 3*
Tuesday AM
Analysis of Dissolved Organic Matter in Seawater Using Mass Spectrometry, *Fantasia E/F*
Recent Advances in Forensic Sciences I, *Fantasia C*
Tuesday PM
Microchips and Mass Spectrometry, *Fantasia E/F*
Wednesday AM
Field Deployable Mass Spectrometers, *Fantasia E/F*
Spectroscopy and Mass Spectrometry in Forensic Sciences I, *Fantasia C*
Ion Processsing, Detection and Laser Sampling in Plasma Source MS, *Nutcracker 3*
Wednesday PM
Spectroscopy and Mass Spectrometry in Forensic Sciences II, *Fantasia C*
Lester W. Strock Award: Ion Generation, Transport and Detection in MS, *Nutcracker 3*
Thursday AM
Highlighting Diversity in Forensic Applications of Mass Spectrometry, *Fantasia C*
Frontiers in Analytical Spectrochemistry I Honoring Gary Horlick, *Fantasia A/B*
Thursday PM
Innovations in Fourier Transform Mass Spectrometry, *Fantasia E/F*
Frontiers in Analytical Spectrochemistry II Honoring Gary Horlick, *Fantasia A/B*

NANOSCIENCE

Monday AM
FACSS Young Investigators I, *Fantasia D*
Monday PM
Applications of Nanoparticles and Other Techniques, *Fantasia A/B*
Tuesday AM
Separation of Carbon Nanotubes I, *Fantasia N*
Tuesday AM
Separation of Carbon Nanotubes II, *Fantasia N*
Wednesday AM
Nanotubes and Nanowires for Sensing, *Fantasia M*
Wednesday PM
Electron Transfer Chemistry of Nanostructured Materials, *Fantasia M*
Thursday AM
Bioelectronics and Biosensors, *Fantasia D*
Thursday PM
Combining Raman and Scanning Probe Microscopy – Are We There Yet? *Nutcracker 1*

PROCESS ANALYSIS AND PHARMACEUTICAL

Monday AM
New Methods for Characterization of Chiral Pharmaceuticals, *Fantasia C*
Monday PM
NIR Used as a Process Analytical Tool, **CNIS,** *Fantasia E/F*
Tuesday AM
Pharmaceutical Raman: Process and Screening Applications, *Nutcracker 1*
Wednesday AM
Process Analysis: Spectroscopic Monitoring Tools, **SAS,** *Fantasia K/L*
Wednesday PM
Process Analysis: Interfaces for Spectroscopic Measurements, **Coblentz,** *Fantasia K/L*
Thursday AM
Process Analysis: New Spectroscopic Technologies, **Coblentz,** *Fantasia K/L*

TECHNICAL PROGRAM OVERVIEW BY TOPIC

RAMAN

Monday AM
Raman Imaging, *Nutcracker 1*

Monday PM
Navigating an Entangled Web: Raman Spectroscopy of Polymeric Systems, *Nutcracker 1*

Tuesday AM
Pharmaceutical Raman: Process and Screening Applications, *Nutcracker 1*

Tuesday PM
Charles Mann Award, *Nutcracker 1*

Wednesday AM
Raman Microscopy, *Fantasia D*
Applied Spectroscopy William F. Meggers Award: New Approaches in Raman Spectroscopy of Turbid Media, *Nutcracker 1*

Wednesday PM
Illuminating the Biological World with Raman Microscopy, *Fantasia D*
Probes for Spectroscopic Bio-analysis, **RSC,** *Nutcracker 1*

Thursday AM
In Situ Raman Analysis in Non-traditional Environments, *Nutcracker 1*

Thursday PM
Combining Raman and Scanning Probe Microscopy – Are We There Yet? *Nutcracker 1*

SEPARATIONS and MICROFLUIDICS

Monday PM
FACSS Young Investigators II, *Fantasia D*

Tuesday AM
Separation of Carbon Nanotubes I, *Fantasia N*
ANACHEM Award, *Fantasia A/B*

Tuesday PM
Separation of Carbon Nanotubes II, *Fantasia N*
Microchips and Mass Spectrometry, *Fantasia E/F*

Wednesday AM
Microchip-CE, *Fantasia A/B*

Wednesday PM
Standard CE & HPLC of Biomolecules, *Fantasia A/B*

Thursday PM
Electrophoretic Separations*, Fantasia C*

SURFACE PLASMON RESONANCE

Tuesday AM
Surface Plasmon Resonance I, *Fantasia M*

Tuesday PM
Surface Plasmon Resonance II, *Fantasia M*

TECHNICAL PROGRAM SUNDAY

"What's Hot" Symposium, *Fantasia E/F*

3:20 **Advanced Chemistry Development Inc**. "From Spectra to Material to Structure and Back — Expert Software Systems"
3:30 **Varian, Inc.,** "The Unique Collision Reaction Interface (CRI) for ICP-MS."
3:40 **Upchurch Scientific, Inc.,** "Low Flow Components for Spectroscopic Applications."
3:50 **Axsun Technologies,** "The Incredible Shrinking Spectrometer."
4:00 **Shimadzu Scientific Instruments, Inc.,** High sensitivity UV-Vis-NIR measurements with Shimadzu's three detector spectrophotometers
4:10 **HORIBA Jobin Yvon, Inc–Optical Spectroscopy Division** "The Benefits of Modular Raman Spectrometers"
4:20 **HORIBA Jobin Yvon, Inc.–Raman Spectroscopy and EDXRF Div**. "The Latest Developments in Raman Spectroscopy"
4:30 **Ahura Corporation**
4:40 **Mesophotonics Ltd.,** "Enhanced Sensitivity, Stability and Reproducibility in Trace Level Detection using Klarite SERS Substrates"
4:50 **Kaiser Optical Systems, Inc.,** ATEX Certified RamanRXN3 Process Raman Analyzer: A New Process Analytical System for the 21st Century

5:00 SAS Sponsored Student Poster Session, *Nutcracker Ballroom*

TECHNICAL PROGRAM – MONDAY
Plenary and Posters

8:00 AM, Plenary Session, *Fantasia G*

Harry Y. McSween, Jr.

(1) **Spectroscopy on the Red Planet: More than Meets the Eye**; Harry Y. McSween Jr., University of Tennessee

Dr. Harry (Hap) McSween is University Distinguished Professor of Science and former head of the Department of Earth and Planetary Sciences at the University of Tennessee. He holds an undergraduate degree (B.S.) in chemistry from The Citadel and graduate degrees in geology from the University of Georgia (M.S.) and Harvard (Ph.D.). Unlike most geochemists, McSween's attention is drawn to rocks falling from the heavens rather than to those already underfoot. For more than 27 years NASA has funded his research on meteorites, and he has published numerous scientific papers dealing with the petrology and cosmochemistry of meteorites and their implications for understanding how the solar system formed and evolved. He was one of the original proponents of the idea that a handful of unusual meteorites came from Mars, and he has worked extensively on martian meteorites. Dr. McSween was a member of the science team for the Mars Pathfinder spacecraft mission in 1997. He currently serves on the TES science team for Mars Global Surveyor and is a Co-investigator for the THEMIS instrument on Mars Odyssey. This instrument is presently mapping the Martian surface from orbit. He is also a co-investigator for the Mars Exploration Rovers now operating on Mars and for the Dawn spacecraft mission, which will study two large asteroids from orbit. McSween is particularly interested in communicating the excitement of science to the public. He is the author of three recently published popular books introducing planetary science, as well as a textbook in geochemistry. Dr. McSween is the recipient of the Leonard Medal of the Meteoritical Society and is a Fellow of the American Academy of Arts and Sciences. He is also the namesake for asteroid 5223 McSween.

MONDAY POSTER SESSION
9:00 – 10:30 AM
Nutcracker Ballroom 2

All Monday posters should be put up in Nutcracker Ballroom between 7:30 – 8:00 AM and removed between 5:00 – 6:00 PM. If your poster board is an odd number (1, 3, 5, etc.) , the presenting author must be present 9:00 – 9:45 AM on Monday. If your poster board number is an even number (2, 4, 6, etc.), the presenting author must be present 9:45 – 10:30 AM on Monday.

Correlation Spectroscopy

Board #

1 (2) **Self-Modeling Curve Resolution (SMCR) by Hybrid Genetic Algorithms (HGA)**; Hideyuki Shinzawa[1], Makio Iwahashi[2], Yukihiro Ozaki[1]; [1]Kwansei-Gakuin University; [2]Kitasato University

2 (3) **Perturbation-Correlation Moving-Window Two-Dimensional Correlation Analysis Applied to Temperature-Dependent IR Spectra of Cellulose I beta**; Akihiko Watanabe[1,2], Shigeaki Morita[1], Yukihiro Ozaki[1]; [1]Kwansei Gakuin University; [2]Yasuma Co. LTD

3 (4) **Biophysical Studies on Mutated Surfactant Protein C Using Infrared Spectroscopy and 2D Correlation Analysis**; Yu Zhu[1], Saratchandra Shanmukh[1], Shin-ichi Morita[1], John E Baatz[2], Richard A Dluhy[1]; [1]Chemistry Department, University of Georgia; [2]Dept Pediat, Div Neonatol,Med Univ S CA

4 (5) **Moving Window Correlation Analysis of Photoluminescence Images of Biotinylated CdTe – Streptavidin Au Bioconjugates**; Alyssa Thomas[1], Hugh Richardson[1] ;[1]Dept of Chemistry and Biochemistry Ohio University

5 (6) **2D Correlation Analysis of Thin Film Water on alpha-Al2O3 (0001): A Theoretical Comparison**; Alyssa Thomas[1], Hugh Richardson[1]; [1]Dept of Chemistry and Biochemistry, Ohio University

6 (7) **Characterization of Interaction in Weakly Interacting Block Copolymer by Two-Dimensional Hetero-Spectral Analysis of Wide Angle X-ray Scattering and Infrared Spectroscopy**; Hye Jeong Kim[1,3], Young Mee Jung[2,4], Jin Kon Kim[1,3], Seung Bin Kim[2,3]; [1]Department of Chemical Engineering; [2]Department of Chemistry; [3]Pohang University of Science and Technol; [4]Kangwon National University

Chemometrics

Board #

7 (8) **Detection of Fires Aboard Naval Vessels using Cermet Sensor Arrays**; Kirsten Kramer[1], Susan Rose-Pehrsson[1], Mark Hammond[1], Kevin Johnson[1], Daniel Gottuk[2], James Lynch[2], Duane Tillett[3], Holger Streckert[3]; [1]Naval Research Laboratory; [2]Hughes Associates, Inc.; [3]General Atomics

8 (9) **Investigation of Bagged Kernel Partial Least Squares (KPLS) and Boosting KPLS**; Hideyuki Shinzawa[1], Jian-Hui Jiang[2], Pitiporn Ritthiruangdej[3], Yukihiro Ozaki[1]; [1]Kwansei-Gakuin University; [2]Hunan University; [3]Kasetsart University

9 (10) **Spectral Studies of Enantiodiscrimination with Chiral Ionic Liquids**; Jody Harvey[1], Marianna Busch[1], Kenneth Busch[1]; [1]Baylor University

TECHNICAL PROGRAM – MONDAY
Posters 9:00 – 10:30 AM

Board #

10 (11) **A Practical Algorithm to Remove Cosmic Spikes in Raman Imaging Data for Pharmaceutical Applications**; Lin Zhang[1], Mark Henson[1]; [1]Pfizer Global R&D

11 (12) **The Harmony/Parsimony Tradeoff in Multivariate Calibration**; John Kalivas[1], Forrest Stout[1]; [1]Idaho State University

12 (13) **Water Sorption Process into a Biocompatible Polymer Film: Self-Modeling Curve Resolution Analysis of ATR-IR Spectra**; John Kalivas[1], Forrest Stout[1]; [1]Idaho State University

13 (14) **Application of Row-wise Constraints in Multivariate Curve Resolution for Spectral Unmixing of Highly Overlapped Components**; David Melgaard; [1]Sandia National Laboratories

14 (15) **Chiral analysis by Regression Modeling of Fluorescence Spectral Data Obtained with a CCD Fluorescence Spectrophotometer**; Selorm Modzabi[1], Marianna Busch[1], Kenneth Busch[1]; [1]Baylor University

15 (16) **Whole Product Analysis by 1H NMR and Multivariate Statistics**; Laura H. Lucas[1], Molly P. Armstrong[1], Mike Rothgeb[1], Carrie Furnish[2], Charles D. Eads[2]; [1]Procter and Gamble, Household Care Analytical; [2]Procter and Gamble, Discovery Analytical

16 (17) **Determination of the Enantiomeric Composition of High-Percentile Range Samples by Multivariate Regression Modeling of Spectral Data**; Jemima Ingle[1], Marianna Busch[1], Kenneth Busch[1]; [1]Baylor University

17 (18) **Interactive Self-modeling Image Analysis**; Willem Windig[1], R. Scott Koch[1]; [1]Eigenvector Research, Inc.

18 (19) **New Approach for Spectroscopic Analysis Applied to Infrared Spectroscopy**; Marie Scandone[1], Gregory Banik, Ph.D.[1], Ty Abshear[1], Omoshile Clement, Ph.D.[1]; [1]Bio-Rad Laboratories, Inc., Informatics Division

19 (20) **MCR Analysis of Spectral Data Files**; Jon Schoonover[1], Jennifer Butler[1], Cole Paffett[1], Jonathan Cox[1]; [1]Los Alamos National Laboratory

20 (21) **Chemometric Analysis of Bio-Aerosol Agents Using a LIF Biological Agent Monitor**; Brian Dable[1], Geoff Wilson[1], Jim Brady[1], Mike Carrabba[1]; [1]Hach Homeland Security Technologies

21 (22) **Performance of a NIR Multivariate Optical Computing Based Instrument on a Binary Organic Mixture**; Luisa T.M. Profeta[1], Michael L. Myrick[1]; [1]University of South Carolina

22 (23) **PARAFAC-Based Estuarine Water Fingerprinting**; Gregory Hall[1], Jonathan Kenny[2]; [1]U.S. Coast Guard Academy; [2]Tufts University

23 (24) **Classifications in Biospectroscopy using a Non-Generational Genetic Algorithm for Automated Preprocessing and Wavelength Selection**; Francis Esmonde-White[1], David Burns[1]; [1]McGill University

24 (25) **Eureka: An Online Research Data Archiving and Analysis Portal for Faculty**; Stuart Chalk[1]; [1]University of North Florida

25 (26) **Classification of Textiles by Diffuse Near-infrared Reflectance Spectroscopy**; Christopher Davis[1], Dennis Rabbe[1], Kenneth Busch[1], Marianna Busch[1], Alton Hassell[1], Judith Lusk[1], [1]Baylor University

26 (27) **Quantitative Crystal Form Determination by XRPD Partial Least Squares**; Michael Dotlich[1], John Mannin[1], Sharon Snorek[1]; [1]Eli Lilly and Company

Pharmaceutical and Process Analysis

Board #

27 (28) **Use of a Portable Electrochemical Sensor to Evaluate Packaging Container Effectiveness**; Gregory Webster[1], William Buttner[2], Joseph Stetter[2]; [1]Pfizer Global R&D; [2]Illinois Institute of Technology

28 (29) **Forensic Analysis of Micro-Particle Contaminant in Biopharmaceutical Manufacturing**; Guiyang Li[1], Zai-qing Wen[1], Gianni Torraca[1], Chanel Yee[1]; [1]Forensic Analysis Group, GCAR, Amgen Inc.

29 (30) **Scatter Correction of Transmission NIR Spectra by Photon Migration Data for Analysis of Intact Pharmaceutical Samples**; Christoffer Abrahamsson[1], Tomas Svensson[1], Stefan Andersson-Engels[1], Sune Svanberg[1], Jonas Johansson[2], Staffan Folestad[2]; [1]Lund Institute of Technology, Sweden; [2]AstraZeneca R&D Mölndal, Sweden

30 (31) **FT-IR Reflectance Imaging and Multivariate Analysis for Characterization of Defects in Pharmaceutical Tablet Modified Release Coatings**; Yang Liu[1], Mark Henson[1], Rafael Arguelles[2]; [1]Pfizer Inc, PGRD; [2]Pfizer Inc, PGM

31 (32) **Non-invasive Characterization of Pharmaceutical Tablets using Gas in Scattering Media Absorption Spectroscopy (GASMAS)**; Tomas Svensson[1], Jonas Johansson[2], Stefan Andersson-Engels[1], Sune Svanberg[1], Staffan Folestad[2]; [1]Lund University; [2]Astra Zeneca R&D, Mölndal

32 (33) **Evaluation of Critical Experimental Parameter Settings for Tablet Content Uniformity Measurement Using Near Infrared Transmission Spectroscopy**; Dong Xiang[1], Paul Gargiulo[1], Jason Teelucksingh[1], Florian Battung[1], Rosario LoBrutto[1], James Pazdan[1], Busolo Wabuyele[1]; [1]Novartis Pharmaceuticals

33 (34) **Comparison of Transmission and Diffuse Reflectance Modes in Near-Infrared (NIR) Spectroscopic Measurements of Pharmaceutical Tablets**; Jason Teelucksingh[1], Dong Xiang[1], Rosario LoBrutto[1], Stephanie Metz[1], Paul Gargiulo[1], Richard Vivilecchia[1], Busolo Wa Wabuyele[1]; [1]Novartis Pharmaceuticals Corporation

34 (35) **Application of Vibrational Circular Dichroism Spectroscopy at BMS**; Ming-Hsing Huang[1], Linda Phillips[1], Yingru Zhang[1], Steve Gozo[1], Jack Gougoutas[1]; [1]Bristol-Myers Squibb

35 (36) **Multivariate Data Analysis of Near Infrared Chemical Imaging Measurements for Tablet Content Uniformity Study**; Wei Huang[1], Busolo Wa Wabuyele[1], Patrick Chen[1], Dong Xiang[1], Boyong Won[1], Yusuf Sulub[1], Joseph Etse[1], Richard Vivilecchia[1]; [1]Novartis Pharmaceutical Corporation

36 (37) **High Throughput Raman Chemical Imaging Analysis of Pharmaceutical Products**; Matthew Nelson[1], Linda Batykefer[1], David Tuschel[1], Patrick Treado[1]; [1]ChemImage Corporation

37 (38) **Estimation of Optical Constants from Diffuse Reflectance Measurements of Turbid Media Using Fractal Analysis**; Fabiano Pandozzi[1], Claudia E. W. Gributs[1], Dirk Bandilla[1], David H. Burns[1]; [1]McGill University

38 (39) **Factors Affecting the Production of Broadband Acoustic Emission Signals and Their Use in Particle Characterisation**; Alison Nordon[1], Nichola Townshend[1]; [1]University of Strathclyde

39 (40) **Monitoring Wood Composites Manufacture Using Near Infrared Spectroscopy**; Tim Rials[1], Nicolas Andre[1], Tim Young[1]; [1]The University of Tennessee

Education

Board #

40 (41) **The Analytical Sciences Digital Library: A Growing Resource for Pedagogy in the Analytical Sciences**; Alexander Scheeline[1], Cynthia Larive[2]; [1]University of Illinois at Urbana-Champaign; [2]University of California at Riverside

41 (42) **An Undergraduate Lab for Lead in Ancient Bronze Coins by Atomic Absorption Spectrometry**; Mary Kate Donais[1], Ashley Dumas[1], Kathleen Golden[1], Abby Pelletier[1]; [1]Saint Anselm College

42 (43) **Spectroscopy Myth Busters: FTIR Spectra Collected with Diffuse Reflectance and Attenuated Total Reflectance Accessories can be Searched Against Transmission Libraries**; Eric J Bukowski[1], John A Monti[1], Shannon M Richard[1]; [1]Shimadzu Scientific Instruments

43 (44) **Brewing Beer to Teach Analytical Chemistry**; William Lammela; [1]Nazareth College

Monday Morning, Fantasia A/B
OPTICAL DETECTION IN BIOANALYSIS
Organizer and Presider: Hossein Ahmadzadeh

10:30 (45) **Nanoscale Antennae for Luminescent Lanthanide Cations Emitting in the Visible and Near-Infrared Domains**; Stephane Petoud[1]; [1]University of Pittsburgh

11:10 (46) **Surface Second Harmonic Generation Imaging for the Detection of Biomolecule Adsorption to Patterned Ligand Arrays**; John Conboy[1], Trang Nguyen[1]; [1]University of Utah

11:30 (47) **Novel Phthalocyanine-Based Near-IR Fluorophores: Development and Bioanalytical Applications**; Steven Soper; Louisiana State University

11:50 (48) **Surface Enzymatic Processing of Nucleic Acid Microarrays for Enhanced SPR Imaging Biosensing**; Hye Jin Lee[1], Robert Corn[1]; [1]Univ. of California-Irvine, Dept. of Chemistry

12:10 (49) **Histology-guided Sampling Hyphenated with Capillary Electrophoresis and Laser Induced Fluorescence Detection**; Hossein Ahmadzadeh[1], LaDora Thompson[2], Edgar Arriaga[3]; [1]California State Polytechnic University; [2]University of Minnesota; [3]University of Minnesota

Monday Morning, Fantasia C
NEW METHODS FOR CHARACTERIZATION OF CHIRAL PHARMACEUTICALS
Organizer and Presider: Rina K. Dukor

10:30 (50) **Chiral Technology Toolboxes**; Oliver McConnell; [1]Wyeth Research

10:50 (51) **A Nanoscale Approach to Chiral Discrimination**; Regina Valluzzi[1]; [1]Evolved Nanomaterial Sciences

11:10 (52) **Application of VCD Spectroscopy to the Determination of the Structures of Natural Products, Pharmaceuticals, Peptides, Peptidomimetics, Supramolecules: Recent Developments**; Philip Stephens; [1]University of Southern California

11:30 (53) **Magneto-Optical Enantiomeric Detection**; Phillip Gibbs[1]; [1]Stheno Corporation

11:50 (54) **Solid State Vibrational Circular Dichroism and X-ray Crystallography: The Absolute Configuration of an α-Hydroxy-Betalactam**; Linda Phillips[1], Michael Galella[1], Ming Huang[1], Yingru Zhang[1], Stephen Gozo[2], Jack Gougoutas[1]; [1]Bristol-Myers Squibb PRI, Princeton, NJ; [2]Bristol-Myers Squibb PRI, Hopewell, NJ

12:10 (55) **Pharmaceutical Applications of VCD: Reaction Monitoring and Solid-Phase Analysis of APIs and Excipients**; Laurence A. Nafie[1,2], Xiaolin Cao[1,2], Shengli Ma[1], Rosina Lombardi[1], Teresa B. Freedman[1], Rina K. Dukor[2]; [1]Syracuse University; [2]BioTools, Inc.

Monday Morning, Fantasia D
FACSS YOUNG INVESTIGATORS I
Organizer: S. Douglass Gilman; Presider: Paul Farnsworth

10:30 (56) **Advancing Spectroscopic Imaging to Time-Resolved Chemical Sensing in Three Spatial Dimensions**; Frank Vogt[1], Michael Gilbert[1], Robert Luttrell[1]; [1]University of Tennessee

10:50 (57) **Optical Spectroscopies for Biological Structure at Interfaces**; Kimberly Briggman[1]; [1]NIST

11:10 (58) **Inorganic Colloidal Nanocrystals for Biological Labeling**; Yunwei Charles Cao; University of Florida

11:30 (59) **Engineering the Selectivity of Nanopatterned Surfaces for Protein Assays by Combining AFM Characterization and Nanoscale Lithography**; Jayne C. Garno[1]; [1]Louisiana State University

11:50 (60) **Exploring Nanostructured Surfaces For Novel Electrochemically Based Sensing Devices**; Diego Diaz[1], [1]University of Central Florida

12:10 (61) **Liquid-Deposited Carbon Nanotube Networks: A New Electronic Material**; Marcus D Lay, Pornnipa Vichchulada, Tasaday E Lynch; [1]University of Georgia

Monday Morning, Fantasia E/F
IMAGING MASS SPECTROMETRY
Organizer and Presider: David Russell

10:30 (62) **Imaging Mass Spectrometry: Principle and Applications**; Pierre Chaurand[1], D. Shannon Cornett[1], Richard M. Caprioli[1]; [1]Vanderbilt University

10:50 (63) **Applications of Advanced High Speed Laser Optics for Imaging Mass Spectrometry**; Stacy D. Sherrod[1], Edward T. Castellana[1], David H. Russell[1]; [1]Texas A&M University

11:10 (64) **Imaging MALDI MS with an Orthogonal TOF Mass Spectrometer**; Werner Ens[1], Gamini Piyadasa[1], Oleg Krokhin[1], Hui Qiao[1], Victor Spicer[1], Kenneth Standing[1]; [1]University of Manitoba

11:30 (65) **Mass Spectrometry in the Brain: from Single Cells to Imaging**; Jonathan Sweedler[1], [1]University of Illinois

11:50 (66) **Comparison of UV and IR Atmospheric Pressure MALDI Mass Spectrometry in Biomolecular Imaging**; Akos Vertes[1], Yue Li[1]; [1]The George Washington University

12:10 (67) **Multidimensional Identification and Structural Characterization of Peptides and Proteins – Imaging Ion Mobility-Mass Spectrometry**; John A. McLean[1], David H. Russell[2]; [1]Vanderbilt University; [2]Texas A&M University

TECHNICAL PROGRAM – MONDAY
Orals 10:30 AM – 12:30 PM and 1:15 – 2:15 PM Vendor Presentations

Monday Morning, Fantasia K/L
SYMPOSIUM TO HONOR THE RETIREMENT OF PETER C. JURS
Organizer and Presider: Barry K. Levine

10:30 (68) **PhD Scientists for the 21st Century**; Thomas Isenhour[1]; [1]Old Dominion University

10:50 (69) **Multivariate Calibration Strategies for Near-Infrared Glucose Sensors**; Gary Small[1]; [1]University of Iowa

11:10 (70) **Is PLS a General Paradigm for Multivariate Data Analysis in Chemistry?** Barry Lavine[1], Nikhil Mirjankar[1], Mehul Vora[1];[1]Oklahoma State University

11:30 (71) **Multi-sensory Approach to Improved Situational Awareness**; Susan Rose-Pehrsson[1], Christian Minor[2], Kevin Johnson[1], Jeff Owrutsky[1], Stephen Wales[1], Daniel Gottuk[3], Daniel Steinhurst[2]; [1]Naval Research Lab; [2]Nova Research, Inc; [3]Hughes Associates, Inc

11:50 (72) **Student-Designed Undergraduate Research Projects**; Debra Egolf, [1]Marietta College

12:10 (73) **Advances in Protein QSPR and Surface Analysis**; Curt Breneman[1]; [1]Rensselaer Polytechnic Institute

12:30 (74) **Chemometrics, Computational Chemistry, and Cheminformatics Over the Decades**; Peter Jurs; [1]Penn State University

Monday Morning, Pastoral 1
2-D CORRELATION SPECTROSCOPY I
Organizers: Wei Zhao, Isao Noda, Hugh Richardson
Presider: Richard A. Dluhy

10:30 (75) **2D Raman Correlation Spectroscopy Study of Emulsion Polymerization Reaction**; Isao Noda[1], William Allen[1], Seth Lindberg[1]; [1]The Procter & Gamble Company

10:50 (76) **Noise Perturbation in Functional Principal Component Analysis Filtering for Two-Dimensional Correlation Spectroscopy: Its Theory and Application to Infrared Spectra**; Yukihiro Ozaki[1], Yun Hu[1], Boyan Li[1], Harumi Sato[1], Isao Noda[2]; [1]Kwansei Gakuin University; [2]The Procter & Gamble Company

11:10 (77) **Moving Window Correlation Analysis of Photoluminescence Images of Single and Aggregated Gold Nanoparticles**; Hugh Richardson[1], Alyssa Thomas[1], Zachary Hickman[1], Alexander Govorov[1]; [1]Ohio University

11:30 (78) **Cross Spectra Correlation Analysis and Its Application to Time-Resolved FTIR Spectroscopy of Transient Radicals**; Hai-Lung Dai, William McNavage; [1]Department of Chemistry, University of Pennsylvania

11:50 (79) **Spectroscopic Studies of Gas Interactions with Carbon Nanotubes**; Christopher Matranga; [1]NETL - U. S. Dept. of Energy

12:10 (80) **pH Unfolding of Apomyoglobin Studied with Two-Dimensional Hetero-Correlation Spectroscopy**; Maxwell Geng[1], Gufeng Wang[1]; [1]University of Iowa

Monday Morning, Nutcracker 1
RAMAN IMAGING
Organizer and Presider: Kelly Akers

10:30 (81) **High Spatial Resolution Raman Spectral Imaging of Human Cells**; Max Diem[1], Christian Matthäus[1]; [1]Northeastern University

10:50 (82) **In situ Raman Microspectroscopic Detection of Focally Elevated Creatine in Transgenic APP Mouse Brain**; Kathleen Gough; [1]Department of Chemistry, University of Manitoba

11:10 (83) **Macro- and Micro-Investigation of Arterial Tissue by Optical Coherence Tomography and Raman Spectroscopy**; Lin-Ping Choo-Smith[1], Mark Hewko[1], Alex Ko[1], Jeffrey Werner[1], Elicia Kohlenberg[1], Sebastien Delorme[2], Rouwayda El-Ayoubi[2], Michael Sowa[1]; [1]NRC-Institute for Biodiagnostics; [2]NRC-Industrial Materials Institute

11:30 (84) **Adventures in Wonderland: Through the Biofilm**; Truis Smith-Palmer[1], Christophe Sandt[1], Judith Pink[1], David Pink[1]; [1]St Francis Xavier University

11:50 (85) **Micro-Raman Studies of Dental Materials**; Richard Larsen[1], Tim Williams[1], Mark Latta[2]; [1]Jasco, Inc.; [2]Creighton University

12:10 (86) **Cell and Tissue Imaging With SERS Nanotags: Surface Enhanced Raman Scattering Meets Medicine**; Michael Natan;Oxonica, Inc.

Monday Morning, Nutcracker 3
OTHER WAYS TO GET THE JOB DONE WITH ICPMS – SAMPLE INTRODUCTION ALTERNATIVES I
Organizer and Presider: James A. Holcombe

10:30 (87) **Weird Science: ICPMS without a nebulizer!** Frank Vanhaecke[1], Luc Moens[1], Martín Resano[1,2]; [1]Ghent University, Dept. of Analytical Chemistry; [2]University of Zaragoza

11:10 (88) **Electrothermal Vaporization Processes for Plasma Sample Introduction**; Greet de Loos[1]; [1]Delft University of Technology

11:50 (89) **ETV-ICPMS: When can it solve analytical problems better and easier?** James Holcombe[1], Adam Rowland[1], Thomas Kreschollek[1]; [1]University of Texas at Austin

12:10 (90) **Benefits and Applications of On-Line Electrochemically-Modulated Separations for ICP-MS**; Douglas C. Duckworth[1], William J. Clark, Jr.[1], Gary J. Van Berkel[1], Debra A. Bostick[1]; [1]Oak Ridge National Laboratory

Monday Afternoon, Fantasia E/F
"WHAT'S HOT" EXHIBITOR PRESENTATIONS
Organizer and Presider: Michael Carrabba

1:15 – 1:25 **PerkinElmer Life and Analytical Sciences**

1:25 – 1:35 **Opotek, Inc.** "Spectral Imaging and 3D LIF instruments based on Tunable Lasers"

1:35 – 1:45 **GenTech Scientific, Inc**. "The 3 "S's" of Refurbished Analytical Equipment - Selection, Service, & Savings"

1:45 – 1:55 **Savillex Corporation. "**PFA Sample Introduction Systems from Savillex Corporation"

1:55 – 2:05 **Eigenvector Research, Inc.**

2:05 – 2:15 **WiTec Instruments Corp.**

TECHNICAL PROGRAM – MONDAY
Orals 2:30 – 4:30 PM

Monday Afternoon, Fantasia A/B
APPLICATIONS OF NANOPARTICLES AND OTHER TECHNIQUES
Organizer and Presider: David Benson

2:30 (91) **Nanoparticulate Optical Labels Based on Surface Enhanced Raman Scattering: Progress and Opportunities**; Michael Natan[1]; [1]Oxonica, Inc.

3:10 (92) **Nanoscale Plasmonics for Ultrasensitive Biosensor Development**; Amanda J. Haes[1]; [1]The University of Iowa

3:30 (93) **Quantum dot FRET-based Sensors for Bioassays**; Zeev Rosenzweig[1], Georgeta Crivat[1], Darwin Reyes[2], Michael Giatan[2], Laurie Locascio[2], Nitsa Rosenzweig[1]; [1]Department of Chemistry-University of New Orleans; [2]Analytical Chemistry Division-NIST

3:50 (94) **The Development of Quantum Dot Aptamer-based Biosensors for the Detection of Thrombin**; Marla Swain[1], Vivekanand Shete[1], Frank Hernandez[2], David Benson[1]; [1]Wayne State University; [2]Universitat Rovira i Virgili

4:10 (95) **Monitoring Protease Kinetics with Quantum Dot Bioconjugates**; Igor L. Medintz[1], Aaron R. Clapp[2], Philip Dawson[3], Hedi Mattoussi[2]; [1]Center for BMSE - U.S. Naval Research Laboratory; [2]DOS - U.S. Naval Research Laboratory; [3]The Scripps Research Institute

Monday Afternoon, Fantasia C
STUDENT AWARDS SYMPOSIUM
Organizer: S. Douglass Gilman; Presider: Rebecca Dittmar

2:30 (96) **Determination of "Free" Iron from Iron Metalloproteins via Liquid Chromatography-Particle Beam/Hollow Cathode and Inductively Coupled Plasma-Optical Emission Spectroscopy**; *Tomas Hirschfeld Scholar,* Tim Brewer[1], Kenneth Marcus[1]; [1]Clemson University

2:50 **SAS Poster Winner**

3:10 **SAS Poster Winner**

3:30 (97) **LIBS in Extreme Environments: The Feasibility of Sequential-Pulse LIBS for Deep-ocean Analysis**; *FACSS Student Award Honorable Mention*, Marion Lawrence-Snyder[1], S. Michael Angel[1], William F. Pearman[1]; [1]The University of South Carolina

3:50 **SAS Poster Winner**

4:10 (98) **Host-guest Properties of Novel, Self-assembling, Hexameric Pyrogallol[4]Arene Nanocapsules**; *FACSS Student Award*, Daniel B. Bassil[1], Sheryl A. Tucker[1], Scott J. Dalgarno[1], Jerry L. Atwood[1]; [1]University of Missouri – Columbia

4:30 **SAS Poster Winner**

Monday Afternoon, Fantasia D
FACSS YOUNG INVESTIGATORS II
Organizer: S. Douglass Gilman; Presider: Michael W. Blades

2:30 (99) **Coupling Depolarized RALS and MALS to Size-Exclusion Chromatography**; Andre Striegel; Florida State University

2:50 (100) **Detection of Biologically Relevant Phenolic Compounds using CE and Microchip-CE**; Carlos D. Garcia[1], Yongsheng Ding[1], Maria Fernanda Mora[1], Eric Mejia[1]; [1]The University of Texas at San Antonio

3:10 (101) **Microfluidic Hydrogels as an Alternative to Biomolecule Immobilization**; Gloria Thomas[1], Hui Chen[1], Bindu Nanduri[2], Shane Burgess[2]; [1]Mississippi State University, Chemistry Department; [2]MS State University, Center for Veterinary Medicine

3:30 (102) **Glycoprotein Analysis for Vaccine Development**; Heather Desaire; [1]University of Kansas

3:50 (103) **Forensic Discrimination of Diesel Samples**; Ruth Waddell[1], Dahlia I. Campbell[2], Amber Hupp[2], Victoria L. McGuffin[2]; [1]Forensic Science Department, Michigan State University, [2]Department of Chemistry, Michigan State University

4:10 (104) **A Minimal Fragmentation Real Time Aerosol Mass Spectrometry**; Allan Bertram[1], Pedro Campuzano[1], Emily Simpson[1], Sarah Hanna[1], Damon Robb[1], Michael Blades[1], John Hepburn[1]; [1]University of British Columbia[4]

Monday Afternoon, Fantasia E/F
NIR USED AS A PROCESS ANALYTICAL TOOL
Organizer: Katherine A. Bakeev; Presider: Brandye Smith-Goettler

2:30 (105) **The Use of Process Analytical Technology (PAT) in Primary Pharmaceutical Manufacturing**; Jose Menezes[2], Licinia Rodrigues[1], Joao Lopes[2], Teresa Alves[1]; [1]CIPAN SA; [2]Center for Biological & Chemical Engineering

3:10 (106) **Process Induced Transformations of Erythromycin Dihydrate During Drying**; Meike Roemer[1], Jyrki Heinämäki[1], Inna Miroshnyk[1], Niklas Sandler[2], Jukka Rantanen[3], Jouko Yliruusi[1]; [1]University of Helsinki; [2]University of Otago; [3]University of Copenhagen

3:30 (107) **Getting Value Out of Your Process Analytical Results – Getting the Data to Where it Can be Acted on**; Larry McDermott[1]; [1]Axsun Technologies

3:50 (108) **Comparison of Reaction Calorimetry and In-line Near Infrared Spectrometry for Monitoring of Esterification in a Novel Reactor**; Pamela Allan[1], David Littlejohn[1], Alison Nordon[1], Kathryn Hipkins[2]; [1]University of Strathclyde; [2]Powder Systems Limited (PSL)

4:10 (109) **Development and Transfer of a Near Infrared Identity Method for Polymorphic Form**; CJ Pommier[1], Shawn Yin[1], Anisha Patel[1]; [1] Bristol-Myers Squibb

Monday Afternoon, Fantasia K/L
CHEMOMETRICS AND INDUSTRY: A SUCCESSFUL MARRIAGE?
Organizer and Presider: Jerry Workman

2:30 (110) **Chemometrics and Instrumentation: Where Have We Succeeded and Where Have We .. Not Succeeded**; Garry Ritter[1]; [1]Thermo Electron Corporation

2:50 (111) **A Successful Marriage between Chemometrics and Industry? I Could Tell You but Then I'd Have to Kill You**; Barry M. Wise[1]; [1]Eigenvector Research, Inc.

3:10 (112) **Chemometrics – What's it good for?**; Jerry Workman; [1]Thermo Electron

3:50 (113) **Considerations and Applications of Chemometrics for On-line Classification and Prediction**; Dongsheng Bu[1], Scott Gordon[1], Ranga Vittala[2]; [1]Camo Software Inc.; [2]Camo Software India Pvt. Ltd.

4:10 (114) **Chemometrics and the FDA's PAT Initiative**; Howard Mark[1]; [1]Mark Electronics

Monday Afternoon, Pastoral 1
2-D CORRELATION SPECTROSCOPY II
Organizers: Wei Zhao, Isao Noda, Hugh Richardson
Presider: Hugh Richardson

2:30 (115) **Quantitative 2D IR Correlation Analysis of Dynamic Interfacial Reorganization - A Model-Based Approach**; Richard Dluhy[1], Saratchandra Shanmukh[1], Yu Zhu[1], Shin-ichi Morita[1]; [1]University of Georgia

2:50 (116) **Two-way Multivariate Correlation as an Information Theoretic Tool for Measuring Analytical Orthogonality**; Peter Harrington;Ohio University

3:10 (117) **Rediscovering the Power of Conventional 2DCOS with Global Phase Correlation Analysis for Studying Phase and Sample Modulation Systems**; Eric Jiang[1], Alexander Grenov[1]; [1]Thermo Electron Corporation

3:30 (118) **Global Phase Angles for Specific Analytical Systems in Generalized Two-Dimensional Correlation Spectroscopy**; Shin-ichi Morita[1], Yu Zhu[1], Saratchandra Shanmukh[1], Richard Dluhy[1]; [1]University of Georgia

3:50 (119) **Investigation of Hydrogen Bonding Microenvironments in Methanol using Density Functional Calculations and Infrared Absorption Spectroscopy**; Daniel Besemann[1], Ryan Haws[1], Brody Anderson[1], Boyd Johnson[1]; [1]Hamline University

4:10 (120) **A Theory and Applications of Perturbation-Correlation Moving-Window Two-Dimensional Correlation Spectroscopy**; Shigeaki Morita[1], Akihiko Watanabe[1], Hideyuki Shinzawa[1], Isao Noda[2], Yukihiro Ozaki[1]; [1]Kwansei-Gakuin University; [2]The Procter & Gamble Company

Monday Afternoon, Nutcracker 1
NAVIGATING AN ENTANGLED WEB: RAMAN SPECTROSCOPY OF POLYMERIC SYSTEMS
Organizer and Presider: Nancy L. Jestel

2:30 (121) **Orientation in LLDPE Blown Films by Polarized Raman Spectroscopy**; Amod Ogale[1], Giriprasath Gururajan[1], Srinivas Cherukupalli[1]; [1]Clemson University

2:50 (122) **Raman of Structural Modifications of Silica Glass**; Carl W. Ponader[1]; [1]Corning Incorporated

3:10 (123) **Raman Spectroscopic Analysis of Release Mechanism in Drug Delivery Systems**; Shaw Hsu; [1]University of Massachusetts (Amherst)

3:30 (124) **Advanced Automated Spectroscopic Data Analysis for High Throughput Materials Research**; Tzu-Chi Kuo[1], Harry H. Luo[2], Shao-Ching Hung[1], M. Anne Leugers[1]; [1]The Dow Chemical Company; [2]Symyx Technologies, Inc

3:50 (125) **Adsorption on Nanosurfaces: A Raman Spectroscopy Investigation**; Maher Amer; [1]Wright State University

4:10 (126) **Raman Spectroscopy as a Probe of the Structure & Configuration**; Bruce Chase[1], John Rabolt[2], Meghana Kahade[2]; [1]DuPont; [2]University of Delaware

Monday Afternoon, Nutcracker 3
OTHER WAYS TO GET THE JOB DONE WITH ICPMS – SAMPLE INTRODUCTION ALTERNATIVES II
Organizer: James A. Holcombe
Presider: M. T. C. de Loos-Vollebregt

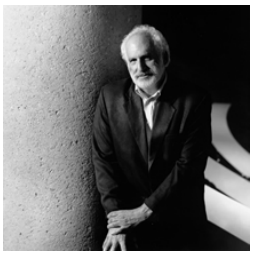
2:30 (127) **Solids Sampled Directly: ICPMS Analysis with Laser Ablation Introduction**; Lawrence Neufeld[1]; [1]New Wave Research, Inc

2:50 (128) **Novel Strategies for Sample Introduction into and by Glow Discharges**; Gary M. Hieftje[1], Francisco J. Andrade[1], Michael R. Webb[1], Gerardo Gamez[1], Steven J. Ray[1]; [1]Department of Chemistry, Indiana University

3:10 (129) **Panel Discussion - Fact Or Fiction? Looks Good On Paper, But How Is It In The Real World?** Panel Members: G. deLoos, D. Duckworth, G. Hieftje, L. Neufeld, R. Sturgeon, F. Vanhaecke. Moderator: J. Holcombe

TECHNICAL PROGRAM – TUESDAY
Plenaries

ANACHEM Award
8:00 AM Plenary Session, *Fantasia G*

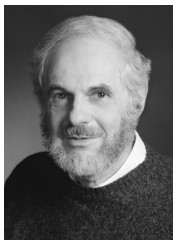


Richard D. Sacks, *posthumous*

(131) **From Exploding Wires to Rapid Chromatography: The Legacy of a High Speed Scientist and Gentle Mentor**; Presented by James A. Holcombe;University of Texas

Refer to page 19 for additional information.

Charles Mann Award
8:30 AM Plenary Session, *Fantasia G*



Michael Morris

(132) **Growing, Walking and Falling. The Role of Raman Spectroscopy in the Study of Musculoskeletal Tissue**; Michael D. Morris;University of Michigan

Refer to page12 for additional information.

TUESDAY POSTER SESSIONS
9:00 – 10:30 AM and 1:45 – 3:15 PM

Fantasia H/J

All Tuesday posters should be put up in Fantasia H/J between 7:30 – 8:00 AM and removed between 5:00 – 6:00 PM. If your poster board is an odd number (1, 3, 5, etc.) , the presenting author must be present 9:00 – 9:45 AM and 1:45 – 2:30 PM on Tuesday. If your poster board number is an even number (2, 4, 6, etc.), the presenting author must be present 9:45 – 10:30 AM and 2:30 – 3:15 PM on Tuesday.

Nanoscience and Microscopy

Board #

1 (133) **Adsorption of Pyrazolone[HPMS],Calix[4]-arene**; Mehdi Vadi, Anne Boos, Zouhair Asfari

2 (134) **Dispersion and Functionalization of Single-Walled Carbon Nanotubes**; Dan Wang[1], Liwei Chen[1]; [1]Ohio University

3 (135) **In situ AFM Investigation of the Effects of Concentration and Writing Parameters When Nanografting Functionalized n-alkanethiol SAMs on Au(111)**; Algernon Kelley[1], Johnpeter Ngunjiri[1], Jayne Garno[1]; [1]Louisiana State University

4 (136) **Studying Biomolecular Reactions at the Nanoscale: In Situ Studies of Proteins Patterned by Nanografting and Surface Activation Chemistry**; Johnpeter Ngunjiri[1], Brian Lewandowski[1], Jayne Garno[1]; [1]Louisiana State University

5 (137) **Mapping Magnetic Nanomaterials on Surfaces using Selective Modulation**; Brian Lewandowski[1], Johnpeter Ngunjiri[1], Jayne Garno[1]; [1]Louisiana State University[4]

6 (138) **In situ AFM Studies of the Assembly of Porphyrins on Flat Surfaces**; Zorabel M. LeJeuene[1], Jie-Ren Li[1], Jayne Garno[1]; [1]Louisiana State University

7 (139) **Application of Arrays of Protein Nanostructures Produced Using Particle Lithography for Investigation of Biomolecular Reactions on Surfaces**; Jie-Ren Li[1], Zorabel M. LeJeuene[1], Jayne C. Garno[11]Louisiana State University

8 (140) **Electrochemistry of 2-Dimensional Carbon Nanotube Networks**; Pornnipa Vichchulada, Tasaday E Lynch, Marcus D Lay; University of Georgia

9 (141) **Near-Field Spectroscopy for the Investigation of Various Materials**; Richard Larsen[1], Yoshihito Narita[2]; [1]Jasco, Inc.; [2]Jasco Corporation

10 (142) **Thermal Behavior of J-aggregates in Mixed Langmuir-Blodgett (LB) Films of Merocyanine Dye Investigated by UV-visible and IR Absorption Spectroscopy**; Tateno Shinsuke[1], Hirano Yoshiaki[1], Ozaki Yukihiro[1]; [1]Kwansei Gakuin University

11 (143) **Thermal Behavior of H-aggregates inMixed Langmuir-Blodgett (LB) Films with Merocyanine Dye Investigated by UV-visible and IR Absorption Spectroscopy**; Yoshiaki Hirano[1], Shinsuke Tateno[1], Yukihiro Ozaki[1];[1]Kwansei Gakuin University

12 (144) **Towards Quantitative Simulation of Two Photon Absorption Profiles for Multi-Photon Imaging Applications**; Sergio Tafur[1], Artem Masunov[1]; [1]University of Central Florida

13 (145) **Molecular Spectroscopy of Acoustically Levitated Samples**; Jork Leiterer[1], Andreas F. Thünemann[1], Stefan Florek[2], Michael Okruss[2], Ute Resch-Genger[1], Knut Rurack[1], Markus Grabolle[1], Ulrich Panne[1]; [1]Federal Institute for Materials Research and Testi; [2]Institute for Analytical Sciences (ISAS); [3]to Institution 1: ng (BAM)

14 (146) **Nanometer Scale Center of Gravity Analysis of Single Quantum Dot Fluorescence. A New Tool for Study of Local Variation of Bone Tissue Biomechanical Properties**; Kurtulus Golcuk[1], Thomas M. Vanasse[2], Michael D. Morris[1], Steve A. Goldstein[2];[1]Department of Chemistry, University of Michigan; [2]ORL, Orthopaedic Surgery, U.of Michigan

15 (147) **Laser Desorption Mass Spectrometry and Atomistic Modeling of Hydrogen Physisorption for Alloy-Doped Carbon Nanostructures**; Michael Miller[1,2], Grant Merrill[2];[1]Southwest Research Institute; [2]University of Texas at San Antonio

16 (148) **Confocal Micro X-ray Fluorescence:3 Dimensional Elemental Mapping**; George Havrilla[1], Brian Patterson[1]; [1]Los Alamos National Laboratory

17 (149) **Microchannel Device filled with Fluorescence Standards for the Characterization of Spectral Scanning Fluorescence Microscopes**; Ulrich Panne[1], Ute Resch-Genger[1], Katrin Hoffmann[1], Roland Nitschke[2]; [1]BAM; [2]Albert-Ludwigs-Universität Freiburg

18 (150) **Photoactivated Self-Assembly of TiO2 Nanoparticles on Sidewalls of Single-Walled Carbon Nanotubes**; Yeonsu Jang[1], Hyeonsuk Shin[2], Yoonmi Lee[1], Yeonwook Jung[1], Heecheul Choi[1], Seungbin Kim[1]; [1]Department of Chemistry POSTECH; [2]Department of Chemistry, Cambridge

Surface-Enhanced Raman Spectroscopy

Board #

19 (151) **Multimodal Multiplex Raman Spectroscopy**; Mike Fuller[1], Prasant Potuluri[1], Mike Sullivan[1]; [1]Centice

20 (152) **Observation of Optical Coupling between Surface-enhanced Raman Scattering and Localized Surface Plasmon Resonance from Single Ag Nanoaggregates**; Kenichi Yoshida[1], Tamitake Itoh[2], Yasuo Kikkawa[1], Vasudevan Biju[2], Mitsuru Ishikawa[2], Yukihiro Ozaki[1]; [1]Kwansei-Gakuin University; [2]AIST

21 (153) **Structural Characterization of J- and H-Aggregates in Mixed LB Films with Merocyanine Dye Investigated by Raman Scattering Spectroscopy**; Ari Maio[1], Yoshiaki Hirano[1], Kenichi Yoshida[1], Luhei Lu[1], Atsuko Kobayashi[2], Keiko Tawa[2], Yukihiro Ozaki[1];[1]Kwansei Gakuin University; [2]AIST

22 (154) **Surface-Enhanced Raman Spectroscopy: from Research Tool to a Routine Analytical Technique**; Caterina Netti, Helen Stanford, Pushwinder Kaur, David Reece, Stephen Allen; [1]Mesophotonics Ltd

23 (155) **Discrimination of Biologically Revelant Threat Materials via Surface Enhanced Raman Spectroscopy**; Jason Guicheteau[1], Darren Emge[1], Aaron Hyre[1], Leanne Argue[1], Steven Christesen[1]; [1]US Army ECBC

24 (155A) **Surface enhanced Raman Detection of Pathogenic Bacteria with Antibody Functionalized Raman Nanoprobes**; Li-Lin Tay[1], Shannon Ryan[1], Jamshid Tanha[1]; [1]National Research Council Canada

25 (156) **Characterization and Application of Silver Nanorod SERS Substrates as Viral Biosensors**; Sarat Shanmukh[1], Les Jones[3], Rene Alvarez[3], Yiping Zhao[2], Ralph Tripp[3], Richard Dluhy[1]; [1]Department of Chemistry, University Of Georgia; [2]Department of Physics, University Of G; [3]Department of Infectious Diseases, UGA

26 (157) **Multilayer Enhanced Gold Film Over Nano-structured SERS Substrates for Extended Shelf-life and Sensitivity**; Brian Cullum[1], Honggang Li[1], Caitlin Baum[1], Jian Sun[1]; [1]U. of MD-Baltimore County

27 (158) **Development of a Surface-Enhanced Raman Spectroscopy Protocol for Identification of Potential Osteoarthritis Biomarkers**; Karen Dehring[1,4], Gurjit Mandair[3,4], Blake Roessler[2,4], Michael Morris[3,4]; [1]Department of Biomedical Engineering; [2]Department of Internal Medicine; [3]Department of Chemistry; [4]University of Michigan

28 (159) **SERS and DFT of 4''-trimethylsilylethylsulfanyl-4,4'-bis-(phenyleneethynylene)benzenethiol on Ag nanospheres**; Melissa Fletcher, Alberto Vivoni[2], Orest Glembocki[3], Sharka Prokes[3], James Lui[3], Joshua Caldwell[3], Martin Moore[3], Stephen Choquette[4], Charles Hosten[1]; [1]Howard University; [2]Inter American University; [3]Naval Research Laboratory; [4]National Institute of Standards and Tech

Laser-Induced Breakdown Spectroscopy

Board #

29 (160) **Glass Sample Discrimination by Laser Induced Breakdown Spectroscopy (LIBS)**; Candice Bridge[1], Micheal Sigman[1], Joseph Powell[2], Katie Steele[1], Jean MacInnis[1], Mary Williams[1]; [1]National Center for Forensic Science at UCF; [2]South Carolina Law Enforcement Dept.

30 (161) **The Analysis of Commercial Blasting Agents by Laser Induced Breakdown Spectroscopy (LIBS), with Emphasis on Methods for Heterogeneous Samples**; Katie Steele[1], Michael Sigman[1], Candice Bridge[1], Jean MacInnis[1], Zach Parker[1]; [1]National Center for Forensic Science, UCF

31 (162) **LIBS Analysis of Blood Samples in Clinical Applications**; Dale LeCaptain[1], Kishore Singirikonda[1]; [1]Central Michigan University

32 (163) **A Critical Assessment of Different Analytical Approaches to the Direct Determination of Carbon in Soil by LIBS**; Lydia Edwards[1], Benjamin W Smith[1], Nicolo Omenetto[1], Igor Gornushkin[1], Joda C Wormhoudt[2], Andrew Freedman[2], James D Winefordner[1]; [1]University of Florida; [2]Aerodyne Research, Inc.

33 (164) **Forensic Glass Identification by Laser Induced Breakdown Spectroscopy (LIBS)**; Esperanza Rodriguez[1], Uwe Heitmann[2], J. R. Almirall[3], Igor Gornushkin[1], Ben Smtith[1], Nico Omenetto[1], James Winefordner[1]; [1]University of Florida, Department of Chemistry, Ga; [2]Institute for Analytical Sciences, Berl; [3]Florida International University, Miami

34 (165) **Multi-Element Analysis of Cast Iron by Laser Induced Breakdown Spectroscopy using Ortogonal Pre-Ablation Spark and High-Resolution Echelle Spectrometer**; Igor Gornushkin[1], Uwe Heitmann[2], Nico Omenetto[1], Ben Smith[1], James Winefordner[1], M. Mueller[3]; [1]University of Florida, Department of Chemistry; [2]ISAS - Inst for Analytical Sciences; [3]BAM - Federal Inst Materials Res Testing

35 (166) **Standard-Free Quantitative Analysis in Laser-Induced Breakdown Spectroscopy: Experimental Evaluation of Existing Algorithms and Theoretical Modeling Approaches**; Kathleen Herrera[1], Igor B. Gornushkin[1], Elisabetta Tognoni[2], Benjamin W. Smith[1], Nicolo Omenetto[1], James D. Winefordner[1], M. Mueller[3]; [1]Department of Chemistry, University of Florida; [2]Applied Laser Spectroscopy Lab, Institute for Chemical Physical Processes Research Area of National Research Council, Pisa, Italy; [3]Federal Inst Materials Res and Testing

36 (167) **Evaluation of Optical Thickness of Laser Induced Plasma by Duplication Factor Approach**; Igor Gornushkin[2], Uwe Heitmann[1], Galan Moore[2], M. Mueller[3], Ben Smith[2], James Winefordner[2], Nico Omenetto[2]; [1]ISAS- Institute for Analytical Sciences, Berlin; [2]University of Florida, Dept of Chemistry; [3]BAM - Federal Inst for Res and Testing

37 (168) **Laser Ablation ICP Optical Emission Spectrometry analysis of Semiconductor Components as specified by WEEE and RoHS Compliance**; Craig Seeley[1], David Pfeil[1], Garry Kunselman[1]; [1]Teledyne Leeman Labs

38 (169) **Double Pulse Laser Induced Breakdown Spectroscopy (DP-LIBS) in Metallic Alloys. Matrix Influence Studies**; Mauro Alberto Martinez L.[1], Vincent Piscitelli S.[1], Alberto Jose Fernandez C.[1], Jhanis Jose Gonzalez Ch.[2], Richard E. Russo[2]; [1]Universidad Central de Venezuela; [2]Lawrence Berkeley Laboratory

39 (170) **Laser Induced Breakdown Spectroscopy in the VUV Range**; Ulrich Panne[1], Maike Mueller[1], Saara Kaski[1], Helmut Becker-Ross[2], Stefan Florek[2]; [1]Federal Institute of Materials Research BAM; [2]ISAS Berlin

40 (171) **To Gate or Not to Gate in Laser Induced Breakdown Spectroscopy (LIBS)**; Ulrich Panne[1], Maike Mueller[1], Igor Gornushkin[2]; [1]Federal Institute of Materials Research BAM; [2]Dept. of Chemistry, Univ. Florida

Materials

Board #

41 (172) **NMR Spectroscopy of Solid Lead Materials**; Cecil Dybowski[1], Alicia Glatfelter[1], Shi Bai[1], Dale L. Perry[2]; [1]University of Delawre; [2]Lawrence Berkeley National Laboratory

42 (173) **Thin Films Characterization Using Several Complementary Spectrometric Techniques**; Albert Brennsteiner[1], Julien Malherbe[2], Olivier Donard[2], Hervé Martinez[2], Sébastien Mazan[3], Franck Niveau[4], Célia Tauziede[1], Coralie Naudin[1], Céline Eypert[1], Jean-Paul GASTON[1];[1]HORIBA Jobin Yvon; [2]University of Pau; [3]PSA Peugeot Citroën; [4]Renault SA

43 (174) **Kinetic and Characterization Studies of the Formation of Barium Monomolybdate in Equimolar Powder Mixture of BaCO3 and MoO3**; Latifa Alhajji[1]; [1]Kuwait Institute Science Research

Environmental

Board #

44 (175) **Evaluation of a Standardized Micro-Vacuum Sampling Method for Collection of Surface Dust**; Kevin Ashley[1], Gregory Applegate[1, 2], Tamara Wise[1], Joseph Fernback[1], Michael Goldcamp[2]; [1]CDC/NIOSH, Cincinnati, OH; [2]Wilmington College, Wilmington, OH

45 (176) **Characterization of Hyperaccumulating Plants Employed for Phytoremediation of Arsenic and Lead**; David Butcher[1], James Bolick[1], Youngsoo Cho[1]; [1]Western Carolina University

46 (177) **Handheld Field Sensors For Indoor Air Pollutants**; Claire Robertson[1], Lorraine Gibson[1], Amy Cheung[1], Walter Johnstone[1], Claire Watt[1]; [1]University of Strathclyde

47 (178) **Kinetics and Catalytic Reactions as Applied to Trace Analysis**; Surendra Prasad[1]; [1]The Univ. of the South Pacific

48 (179) **Analysis of Nerve Agent Degradation Compounds Using the Vanadomolybdate Reagent**; Stuart Chalk[1], Tanya Alvers[1]; [1]University of North Florida

49 (180) **Flow Based Inkjet Reagent System for Cyanide Analysis**; Stuart Chalk[1], David Cacace[1], Heidi Ashbaugh[1], Sara Bledsoe[1], Naomi Kouri[1]; [1]University of North Florida

50 (181) **Flow Analysis of Mixtures of Arsenite, Arsenate, Phosphate and Methylphosphonic Acid Using Vanadomolybdate**; Stuart Chalk[1], Doris Kosova[1], Leah Reed[1]; [1]University of North Florida

51 (182) **Novel Focused Semi Open Microwave Instrument for Elemental Speciation Studies**; Greg Barlow[1], David Barclay[1], Elaine Hasty[1]; [1]CEM Corporation

52 (183) **A Field-Portable GC with Multi-stage Preconcentration, Dual-Column Separation, and Chemiresistor-Array Detection for VOC Analysis**; Qiongyan Zhong[1], William Steinecker[1], Rebecca Veeneman[1], Edward Zellers[1]; [1]University of Michigan

53 (184) **Instrument Gain for a 24ml Ozone-Nitric Oxide Reaction Cell**; Ronald Whiddon[1], Igor Gornushkin[1], Benjamin Smith[1], Nicoló Omenetto[1], James D. Winefordner[1]; [1]University of Florida

Separations

Board #

54 (185) **Effect of a Temperature Gradient on Retention Time and Efficiency for Solvating Gas Chromatography**; Steven Goates, John-David McElderry, Marisa Stark; [1]Brigham Young University

55 (186) **Guanosine Gels for Sequence Dependent DNA Separations in Capillary Electrophoresis**; William Case[1], Keren Glinert[2], Linda McGown[1]; [1]Rensselaer Polytechnic Institute; [2]Princeton University

56 (187) **Novel Label-Free Method for Real-Time Flow Rate Monitoring in a Capillary Based on Liquid Core Optical Ring Resonators**; Hongying Zhu[1], Ian M. White[1], Jonathan Suter[1], Hesam Oveys[1], Xudong Fan[1]; [1]Biological Engineering Dept, Univ. of Missouri

57 (188) **Separation of Uranyl Species by Capillary Electrophoresis**; Greg Klunder[1], Julie Herberg[1]; [1]LLNL

58 (189) **De-noising and Baseline Drifting Correction of Electropherograms on Real-Time Bases**; Alejandro Solis[1], Matthew Rex[1], Andres Campiglia[1], Pedro Sojo[2]; [1]Dept. of Chemistry, University of Central Florida; [2]Fac. de Ciens., Univ. Cent. de Venezuela

59 (190) **Cavity Ring-Down Spectroscopy Coupled to Liquid Chromatography: Extension to Tunable Sources and UV Wavelengths**; Freek Ariese[1], Lineke van der Sneppen[1], Arjan E. Wiskerke[1], Cees Gooijer[1], Wim Ubachs[1]; [1]Laser Centre Vrije Univ. Amsterdam, Netherlands

60 (191) **Separation of Gold Nanorods with Capillary Electrophoresis to Achieve Better Limits of Detection for Mercury in Water**; Matthew Rex[1], Florencio Hernandez[1], Andres Campiglia[1]; [1]University of Central Florida

61 (192) **Simultaneous Estimation of Glimepiride and Pioglitazone in Bulk and in Pharmaceutical Formulation by HPLC and HPTLC Methods**; Bhavesh Shah

62 (193) **Assessment of Anabolic Compounds**; Nisar Ahmed;[1]Kuwait Institute Science Research

Bioanalytical

Board #

63 (197) **System for Studying Enzyme Kinetics in a Levitated Drop Reactor**; Alexander Scheeline[1], Christopher Field[1], Zakiah Robinson[1], Haylee Trout[1]; [1]University of Illinois at Urbana-Champaign

64 (198) **Fabrication and Characterization of a Superoxide Sensor for in vivo and in situ Studies**; Alexander Scheeline[1], Rebekah Wilson; [1]University of Illinois at Urbana-Champaign

65 (199) **Bis(carbocyanine) Near-Infrared Dyes as an Analytical Tool**; Gabor Patonay[1], Jun Seok Kim[1], Maged Henary[1], Lucjan Strekowski[1]; [1]Georgia State University

66 (200) **Application of Bipolar Semiconductor Microchip System to DNA Chip**; Joon Myong Song[1], Min-Sung Yang[2], Ho Taik Kwan[2]; [1]College of Pharmacy, Seoul National University; [2]Celltek Co. Ltd, Ansan-si, South Korea

67 (201) **Synchrotron Infrared Microspectroscopy Determines Secondary Protein Structure of Wheat Endosperm in situ Relative to Protein Quality**; David Wetzel[1], Tiffany Fisher[1], Virgil Smail[1], Hicran Koc[1], Emily Bonwell[5]; [1]Kansas State University

68 (202) **Imaging of Tissue Phantoms Constructed of Biological Fluorophores Embedded in Mesoporous Particles**; Yulia Skvortsova[1], Maxwell Geng[1]; [1]The University of Iowa

69 (203) **Probing Folding Pathways: Apomyoglobin Folding at High Salt Conditions**; Yi Gao[1], Lei Geng1; 1The University of Iowa

70 (204) **Ratiometric Fluorescence Imaging of Water Transport in Subcellular Organelles of Live Cells using D2O as a Contrast Agent**; Adriana Chaurra[1], Kenneth Christensen[1]; [1]Clemson University

71 (205) **Monitoring Conformational Rearrangements in Bacillus anthracis Protective Antigen Using FRET Microscopy**; Kenneth Christensen[1], Nathaniel Smith[1], Thomas Caldwell[1]; [1]Clemson University

72 (206) **Comparison of Fluorescent Probes and Probe Technologies for Visualizing mRNAs in Brain Tissue**; Linda Nieman[1], Rachel Rohde[1], John Guzowski[2], Jerilyn Timlin[1]; [1]Sandia National Labs; [2]University of California, Irvine

73 (207) **PCR-free Nucleic Acid-based Biosensing using Magnetic Microparticle Carriers with a Fluorescent Polymer Hybridization Transducer**; Denis Boudreau[1], Sebastien Dubus[1], Boris Le Drogoff[2], Jean-François Gravel[1], Benoît Voisin[1], Teodor Veres[2]; [1]Dept. Chemistry and COPL, Laval University; [2]Industrial Materials institute, NRC

74 (208) **Gene Expression for Pro-Inflammatory Proteins Following the Deposition of Particles onto A549 Cell Culture**; George Agnes[1], Danielle Balik[1], Allen Haddrell[1], Stephan van Eeden[2]; [1]Simon Fraser University; [2]James Hogg iCAPTURE Centre

75 (209) **Rapid Small Volume Analysis of Serum Myoglobin via Modulated Supraparticle Fluoroimmunoassays.**; Matthew Petkus[1], Mark Hayes[1], Antonio Garcia[1]; [1]Arizona State University

76 (210) **Fiber Optic Surface Plasmon Resonance Biosensors For Clinical Monitoring of Acute Myocardial Infraction Biomarker**; Michael R Malone, Karl Booksh; [1]Arizona State University

Tuesday Morning, Fantasia A/B
ANACHEM AWARD
Organizer and Presider: David Coleman

10:30 (211) **Sacks-cess in Science: an Optical Elution**; Alexander Scheeline[1]; [1]University of Illinois at Urbana-Champaign

10:50 (212) **Following in Grandfather's Footsteps: Research in High Speed Gas Chromatography Performed by Atomic Spectroscopists**; Frank Dorman[1], Richard Sacks[2], Rebecca Wittrig[1], Christopher English[1], TIncutta Veriotti[2]; [1]Restek Corporation; [2]University of Michigan

11:10 (213) **Taming the Pulsed Plasma: Lessons Learned From a Fearless Mentor**; Joel Goldberg; [1]University of Vermont

11:30 (214) **Sacks Lab Chemistry at the Engineering Interface: Gas Chromatography for the WIMS and MACE Projects**; Megan McGuigan[1,2], Richard Sacks[1], Cory Fix[1], Gordon Lambertus[1], Mark Libardoni[1,2], Amy Payeur[1], Peter Stevens[1], Shaelah Reidy[1]; [1]University of Michigan; [2]LECO Corporation

11:50 (215) **Richard Sacks and the Path to a Micro-GC**; Ted Zellers, Kensall Wise, Gordon Lambertus, Shaelah Reidy, Massoud Agah[4], Joseph Potkay, Qiongyan Zhong, Chia-Jung Lu[2], Joshua Whiting[3], Hanseup Kim; [1]University of Michigan; [2]Fu Jen Caholic University, Taiwan; [3]Sandia National Laboratories; [4]Virginia Polytechnic University

12:10 (216) **Short Reflections by Friends and Colleagues**; David M. Coleman; [1]Wayne State University

Tuesday Morning, Fantasia C
RECENT ADVANCES IN FORENSIC SCIENCES I
Organizer and Presider: Bruce McCord

10:30 (217) **Single Fiber Dye Analysis by Liquid Chromatography Mass Spectrometry (LC-MS) with SWGMAT Dye Extraction Protocol**; Derek Dorrien[1], Michael E. Sigman[1]; [1]University of Central Florida

10:50 (218) **Microextraction/Capillary Electrophoresis/Mass Spectrometry for the Forensic Analysis of Textile Fiber Dyes**; Amy Stefan[1], Brandi Clelland[1], Brittany Baguley[1], Stephen Morgan[1] [1]University of South Carolina

11:10 (219) **Elemental Analysis of Biological Matrices using LA-ICP-MS for Sourcing**; Waleska Castro[1], Tatiana Trejos[1], Benjamin Naes[1], José R. Almirall[1]; [1]Florida International University

11:30 (220) **Forensic Studies of Dye and Fiber Degradation during Environmental Exposure by Microspectrophotometry and Capillary Electrophoresis/Mass Spectrometry**; Anthony R. Trimboli[1], Allyson A. Wells[1], Jennifer J. Yiu[1], Heather M. Taylor[1], Amy R. Stefan[1], Brandi L. Clelland[1], Stephen L. Morgan[1]; [1]University of South Carolina

11:50 (221) **Detection of Drugs of Abuse using Ion Mobility Spectrometry**; Monica Joshi[1], Jose Almirall[1]; [1]Florida International University

12:10 (222) **Elemental Characterization of Automobile Body Fillers and Caulk by Laser Ablation-Inductively Coupled Plasma-Mass Spectrometry for Matching of Evidence**; Joshua Messerly[1], Stan Bajic[1], David Baldwin[1], R. S. Houk[1]; [1]Iowa State University - Ames Laboratory - USDOE

Tuesday Morning, Fantasia D
APPLICATIONS OF NIR SPECTROSCOPY – DIVERSITY IN ACTION
Organizer: Katherine A. Bakeev; Presider: Jessica Jarman

10:30 (223) **Evaluation of NIR Spectroscopy for Identification and Content Uniformity of Pharmaceutical Solid Dosage Forms**; Peter Larkin[1], Eileen Fruhling[1], Carl Longfellow[1]; [1]Wyeth Pharmaceuticals

10:50 (224) **Application of NIR Spectroscopy for Rapid Analysis of Barley as a Source of Ethanol**; Miryeong Sohn[1], David Himmelsbach[1], Franklin Barton, II[1], Kevin Hicks[2]; [1]USDA-ARS, R. B. Russell Research Center; [2]USDA-ARS, Eastern Regional Research Center

11:10 (225) **Scatter Correction and Spectral Resolution Aspects for NIR Diffuse-Reflection Spectroscopy of Solid Materials**; Heinz W. Siesler[1], Olga Kolomiets[1]; [1]Dept. of Phys. Chem., University of Duisburg-Essen

11:30 (226) **Measurement of Tissue Oxygen Saturation Using Single-Distance Multiwavelength Near Infrared Spectroscopy**; Olusola Soyemi[1], Babs Soller[1], Michelle Landry[1], Ye Yang[1]; [1]University of Massachusetts Medical School

11:50 (227) **Standoff Detection of High Explosives with Near Infrared Spectroscopy**; Greg Klunder[1]; [1]LLNL Forensic Science Center

12:10 (228) **Effect of Physical Properties and Water on the Identification of Pharmaceutical Excipients by Near-infrared Spectroscopy**; Kelly Palmer[1], Roger Jee[1], James Kraunsoe[2], Anthony Moffat[1]; [1]School of Pharmacy, University of London; [2]AstraZeneca R&D Charnwood UK

Tuesday Morning, Fantasia E/F
ANALYSIS OF DISSOLVED ORGANIC MATTER IN SEAWATER USING MASS SPECTROMETRY
Organizer and Presider: Aaron Timperman

10:30 (229) **Seawater Proteomics: Biopanning for Clues of the Mechanisms of Carbon Cycling**; Aaron Timperman[1], Carlos Del Castillo[2], Ting Zhao[1], Brent Reschke[1], Kathleen Kelly[1], Matthew Powell[1]; [1]West Virginia University, Department of Chemistry; [2]Johns Hopkins, Applied Physics Lab

11:10 (230) **Proteins at Sea: Tracing the Sources and Cycling of Organic Matter in Marine Systems**; Rodger Harvey[1], Angela Squier[1]; [1]University of Maryland/ CES

11:50 (231) **Detection and Identification of Biomolecules within Marine Dissolved Organic Matter: Use of Electrospray Ionization Fourier Transform Ion Cyclotron Resonance MS**; Elizabeth Kujawinski[1]; [1]Woods Hole Oceanographic Institution

Tuesday Morning, Fantasia K/L
CHEMOMETRICS IN SENSORS
Organizer and Presider: Frank Vogt

10:30 (232) **Optical Sectioning of Live Cells via Hyperspectral Confocal Fluorescence Imaging and Multivariate Curve Resolution**; David Haaland[1], Howland Jones[1], Michael Sinclair[1], Jerilyn Timlin[1], Linda Nieman[1], Roberto Rebeil[1], David Melgaard[1], Sawsan Hamad[2], Wim Vermaas[2]; [1]Sandia National Laboratories; [2]Arizona State University

11:10 (233) **Robust Multivariate Analysis for Problem Images**; Jeremy Shaver[1]; [1]Eigenvector Research, Inc.

11:30 (234) **Calibration of Fiber Optic Excitation Emission Matrix Spectroscopy for Environmental Pollutants**; Karl Booksh[1], James Jordan[1], Yoon-Chang Kim[1], Wei Peng[1]; [1]Arizona State University

11:50 (235) **Evaluation of the Precision of Chemometric-Based Quantification of Multidimensional Analytical Methods**; Sarah Rutan[1], Marc Cantwell[1], Sarah Porter[1], Peter Carr[2]; [1]Virginia Commonwealth University; [2]University of Minnesota

12:10 (236) **Incorporation of Practical Shape Constraints in the ALS Procedure for Analysis of Two-Way UV Resonance Raman spectra**; Renee JiJi[1], John Simpson[1], Gurusamy Balakrishan[2], Ying Hu[2], Janina Kneipp[2], Thomas Spiro[2]; [1]University of Missouri-Columbia; [2]Princeton University

Tuesday Morning, Fantasia M
SURFACE PLASMON RESONANCE I
Organizer and Presider: Karl Booksh

10:30 (237) **Optimization of Materials Parameters for Surface Plasmon Resonance Sensing on Conducting Metal Oxides**; Stefan Franzen, Crissy Rhodes, Alina Efremenko, Mark Losego, Jon-Paul Maria; [1]North Carolina State University

10:50 (238) **2-D Analysis of FT-SPR Spectra Acquired at Different Angles**; Eirc Jiang[1], Koichi Nishikida[1], Dennis Merril[1], Steve Lowry[1], Voula Kodoyianni[2], Steve Weibel[2]; [1]Thermo Electron Corp.; [2]GWC Technolgies

11:10 (239) **Enhanced Biosensing using Asymmetric Plasmonic Structures**; Alastair W Wark[1], Hye Jin Lee[1], Robert M Corn[1]; [1]University of Cailfornia-Irvine

11:30 (240) **Inhibition Assay for On-Chip Phosphorylation of Peptide by Surface Plasmon Resonance Imaging Technique**; Kazuki Inamori[1], Motoki Kyo[1], Kazuki Matsukawa[1], Yusuke Inoue[2], Tatsuhiko Sonoda[2], Eiji Kinoshita[3], Tohru Koike[3], Yoshiki Katayama[2]; [1]Biotechnology Frontier Project, Toyobo Co., Ltd.; [2]Department of Applied Chemistry Faculty; [3]Department of Functional Molecular Science

11:50 (241) **Swelling of Functionalized Colloidal poly-N-Isopropylacrylamide Particles: Applications to Optical Sensing and Bioconjugation**; Barry Lavine[1], Necati Kaval[1], David Westover[1], Leah Oxenford[1], Nikhil Mirjankar[1]; [1]Oklahoma State University

12:10 (242) **Molecularly Imprinted Polymerization based Surface Plasmon Resonance Sensing for Glucose Detection in Human Urine**; Wei Peng[1], Soame Banerji[1], Yoon-Chang Kim[1], Karl Booksh[1]; [1]ASU1

TECHNICAL PROGRAM – TUESDAY
Orals 10:30 AM – 12:30 PM and 3:15 – 5:15 PM

Tuesday Morning, Fantasia N
SEPARATION OF CARBON NANOTUBES I
Organizer: Wei Zhao and Stephen K. Doorn; Presider: Jie Liu

10:30 (243) **Studies of Redox Reactivity of Carbon Nanotubes**; Stephen Doorn[1], Satishkumar Chikkannanavar[1]; [1]Los Alamos National Laboratory

10:50 (244) **Using the Inherent Redox Differences of Single Wall Carbon Nanotubes to Fractionate Them According to Diameter and Metallicity**; Fotios Papadimitrakopoulos; [1]University of Connecticut

11:10 (245) **Understanding the Relationship between the Growth Conditions and the Diameter of Single Walled Carbon Nanotubes**; Jie Liu[1], Chenguang Lu[1]; [1]Duke University

11:30 (246) **"Super-Growth" Carbon Nanotubes -What can we do with this highly efficient synthesis?**; Don Futaba; [1]National Institute of Advanced Science and Technol

11:50 (247) **Reversible Cyclic Peptides and Other Designed Peptide Systems for Use in the Noncovalent Functionalization of Carbon Nanotubes**; Gregg Dieckmann[1,2], Ray Baughman[1,2], Alan Dalton[3], Rockford Draper[1,2], Inga Musselman[1,2], Paul Pantano[1,2]; [1]The University of Texas at Dallas; [2]NanoTech Institute, UTD; [3]University of Surrey

12:10 (248) **Dispersion and Separation of Single-Walled Carbon Nanotubes**; Takeshi Akasaka[1], Yutaka Maeda[2], Takatsugu Wakahara[2], Yongfu Lian[2], Takahiro Tsuchiya[2], Jing Lu[3], Shigeru Nagase[4]; [1]University of Tsukuba; [2]Tokyo Gakugei University; [3]Peking University; [4]Institute for Molecula Science

Tuesday Morning, Nutcracker 1
PHARMACEUTICAL RAMAN: PROCESS AND SCREENING APPLICATIONS
Organizer and Presider: Randy Bishop

10:30 (249) **Does Raman Microscopy play a significant role in the Pharmaceutical Chemical Imaging Toolbox?**; Fiona Clarke[1], Jordan Cheyne[1], Linda Jayes[1], Christina Pattoni[1]; [1]Pfizer

10:50 (250) **Sampling and Linearity Study for Raman Pharmaceutical Product Analysis Using Raman Mapping Spectroscopy**; Husheng Yang[1]; [1]AstraZeneca Pharmaceuticals

11:10 (251) **Raman Spectroscopy In Pharmaceutical Process Development**; Zhihao Lin; Merck & Co., Inc.

11:30 (252) **Raman Spectroscopy: A Technique for the Process Analytical Technology Toolbox**; Jonas Johansson[1], Matti Ahlqvist[1], Henric Brage[1], Anders Sparén[1], Staffan Folestad[1]; [1]AstraZeneca R&D Mölndal[4]

11:50 (253) **PAT for Measurement and Control in Continuous Processing of Solid Dosage Forms**; Manoharan Ramasamy[1], John Higgins[1], Gert Thurau[1], Stephen Heidel[1]; [1]Merck & Co, Inc.

12:10 (254) **The Use of a Revolutionary Raman System for Quantification of Low Dosage Solid Formulations**; Maryann Ehly[1], Ian Lewis[1], David Strachan[1], Mark Kemper[1]; [1]Kaiser Optical Systems, Inc.

Tuesday Morning, Nutcracker 3
ATOMIC SPECTROSCOPY IN THE CLINICAL LABORATORY
Organizer and Presider: Kathleen Caldwell

10:30 (255) **Assessing Laboratory Performance for Trace Element Analysis of Clinical Matrices: Experience of the New York State Proficiency Testing Program**; Patrick Parsons[1], Ciaran Geraghty[1], Michael Minnich[1], Christopher Palmer[1], Mary Fran Verostek[1]; [1]New York State Department of Health

10:50 (256) **CDC's Biomonitoring of Trace and Toxic Metal Exposures in the U.S. Population: Analytical Methods and Exposure Results**; Kathleen L. Caldwell[1], Robert L. Jones[1], Jeffery M. Jarrett[1], Carl Verdon[1]; [1]Centers for Disease Control and Prevention

11:30 (257) **Arsenic and Other Contaminants in New Hampshire Well Waters**; Brian Jackson[1], Margaret Karagas[2]; [1]Dartmouth College; [2]Dartmouth-Hitchcock Medical School

11:50 (258) **Contamination Issues During Sample Collection and Analysis of Clinical Samples**; Anastasia Skipor[1]; [1]Rush University Medical Center

12:10 (259) **Transferability of Serum Aluminum Determinations by Electrothermal Atomic Absorption Spectrometry and Continuum Background Correction**; Pamela Kruger[1], Shida Tang[2], Patrick Parsons[1,2]; [1]University at Albany; [2]New York State Department of Health

TUESDAY POSTER SESSION and DESSERT RECEPTION
1:45 – 3:15 PM, see page 48
FANTASIA J/H

Tuesday Afternoon, Fantasia C
RECENT ADVANCES IN FORENSICS SCIENCES II
Organizer and Presider: Bruce McCord

3:15 (260) **Microfluidic Detection of Amphetamines using Laser Induced Fluorescence Detection**; Carla Turner[1], Bruce McCord[1]; [1]Florida International University

3:35 (261) **Optimization of Non-Contact Human Scent Evidence Collection**; Paola Prada[1], Allison Curran[2], Kenneth Furton[1]; [1]Florida International University; [2]ORISE, FBI Academy

3:55 (262) **Optimized Analysis of Triacetone Triperoxide by GC-MS**; Doug Clark[1], Michael Sigman[1]; [1]National Center for Forensic Science at UCF

4:15 (263) **Analysis of Fatty Acids Ethyl Esters by Fast-Gas Chromatography-Mass Spectrometry**; Olivier L. Collin[1], Carolyn M. Zimmermann[1], Glen P. Jackson[1]; [1]Ohio University

4:35 (264) **The affect of PCR inhibitors on the amplification of low concentrations of template DNA using reduced-size STR primer sets**; Kerry Opel[1]; [1]Florida International University; [2]Center for Neurological Diseases

4:55 (265) **The Development of a Hierarchical SNP Typing System to Predict Ethnogeographic Ancestry using Pyrosequencing Technology**; Lynn Sims[1,2], Dennis Garvey[3], Jack Ballantyne[1,2]; [1]National Center for Forensic Science; [2]University of Central Florida; [3]Gonzaga University

TECHNICAL PROGRAM – TUESDAY
Orals 3:15 – 5:15 PM

Tuesday Afternoon, Fantasia D
INNOVATIONS IN NIR – ADVANCING THE FIELD
Organizer and Presider: Katherine A. Bakeev

3:15 (266) **Transferring Calibrations and Libraries for Pharmaceutical Analysis in Near-Infrared Spectroscopy**; Tony Moffat, The School of Pharmacy, London

3:55 (267) **Interferometers vs Imaging Spectrometers for NIR Applications**; Franklin Barton[1], James de Haseth[2], David Himmelsbach[1]; [1]USDA,ARS, Russell Research Center; [2]University of Georgia

4:15 (268) **Consistent Background Reference for NIR Reflectance Spectroscopy – How and Why it Aids in Model Transfer**; William Muller[1]; [1]FOSS NIRSystems, Inc.

4:35 (269) **Wavelength Selection with Applications to Molecular Spectroscopic Data**; Dongsheng Bu[1]; [1]Camo Software Inc.

4:55 (270) **Expanding the power of NIR by the Internet technology**; Ching-Hui Tseng[1], Nan Wang[1]; [1]Cognis/QTA

Tuesday Afternoon, Fantasia E/F
MICROCHIPS AND MASS SPECTROMETRY
Organizer and Presider: Kermit Murray

3:15 (271) **Chip-Based Nanoelectrospray Employed with Conventional Dimension LC/MS Analyses**; Jack Henion, Gary Schultz, Ellen Pace; [1]Advion BioSciences

3:55 (272) **Transforming nano-LC/MS using Microfluidics Technology**; Tom van de Goor[1]; [1]Agilent Technologies

4:15 (273) **Antibody- and Mass Spectrometry-Based Peptide Chip Technology for Clinical Diagnostic**; Christoph Borchers[1], Jian Jiang[1], Carol Parker[1], Tom Kawula[1]; [1]University of North Carolina at Chapel Hill

4:35 (274) **Matrix-Free Approach to Laser Desorption Ionization using Silicon Microcolumn Arrays**; Mazdak Taghioskoui[1], Yong Chen[1], Akos Vertes[1]; [1]The George Washington University

4:55 (275) **A Proteomics Chip for MALDI Mass Spectrometry**; Kermit Murray, Harrison Musyimi, Jeonghoon Lee, Hamed Shadpour, Steven Soper; [1]Louisiana State University

Tuesday Afternoon, Fantasia K/L
MULTIVARIATE IMAGING, WAVELETS, AND GENETIC ALGORITHMS FOR 21ST CENTURY APPLICATIONS
Organizer: Thomas Hancewicz; Presider: Frank Vogt

3:15 (276) **Introducing High-dimensional Hybrid Wavelet Transforms for Optimized Chemometric Analyses of Spectroscopic Imaging Data**; Frank Vogt[1], Robert Luttrell[1], Michael Gilbert[1]; [1]University of Tennessee

3:55 (277) **Multivariate Analysis of 3D Hyperspectral Confocal Fluorescent Biological Images**; Howland Jones[1], David Haaland[1], Michael Sinclair[1], Roberto Rebeil[1], Linda Nieman[1], David Melgaard[1]; [1]Sandia National Labs

4:15 (278) **An Integrated Graphical User Interface to Facilitate the Visualization and Analysis of Hyperspectral Images**; Christopher Stork[1], David Haaland[1], Howland Jones[1], David Melgaard[1]; [1]Sandia National Laboratories

4:35 (279) **Multivariate Curve Resolution and its Practical Use in Remote Sensing Applications**; Christine Wehlburg[1]; [1]MITRE Corporation

4:55 (280) **Genetic Algorithms and Wavelet Packet Transform for Spectral Pattern Recognition – Identification of Waxy Wheat by Near Infrared Reflectance Spectroscopy**; Barry Lavine[1], Nikhil Mirjankar[1], Stephen Delwiche[2]; [1]Oklahoma State University; [2]USDA-ARS, Beltsville Agriculture Research

Tuesday Afternoon, Fantasia M
SURFACE PLASMON RESONANCE II
Organizer: Karl Booksh; Presider Roger Terrill

3:15 (281) **SPR Measurements of Ion-Ion Repulsion Limited Self Assembly**; Roger Terrill[1], Shaowei Chen[2], Yong Nam Pak[3], Arthur Cheng[1]; [1]San Jose State University; [2]University of California at Santa Cruz; [3]Korean National University of Education

3:35 (282) **Characterization of In-Plane Laterally Varying Gradients of Polymer Films and Polymer Brushes by Surface Plasmon Resonance**; Xuejun Wang[1], Paul Bohn[1]; [1]University of Notre Dame

3:55 (283) **Microarray Analysis of Influenza Virus with SPR Imaging**; Quan Cheng[1], Guangyu Ma[1]; [1]University of California Riverside

4:15 (284) **Fiber optic SPR Sensor for Determining Salinity and Dissolved Organic Carbon in Coastal Waters**; Yoon-Chang Kim[1], Jeffrey Cramer[1], Hilairy Hartnett[1], Karl Booksh[1]; [1]ASU

4:35 (285) **Surface Plasmon Resonance Sensors for Analyses in Biological Fluids**; Karl Booksh[1], Michael Malone[1], Jean-Francois Masson[1], Tina Battaglia[1], Mergarette Barnhart[1]; [1]ASU

4:55 (286) **Sandwich SERS Substrates for Monitoring Germination of Bacillus Spores**; George Chumanov[1], Jacquitta Daniels[1], David Evanoff[1], Thomas Caldwell[1], Kenneth Christensen[1]; [1]Clemson University

Tuesday Afternoon, Fantasia N
SEPARATION OF CARBON NANOTUBES II
Organizer: Wei Zhao and Stephen K. Doorn
Presider Stephen K. Doorn

3:15 (287) **Near-infrared Fluorimetric Analysis of Single-Walled Carbon Nanotubes: Recent Progress**; R. Bruce Weisman; [1]Rice University

3:35 (288) **Combining DNA's Molecular Biology Tools with Single Walled Carbon Nanotubes for Purification & Assembly**; Jennifer Cha; [1]IBM Almaden Research Center

3:55 (289) **Towards Chiral Pure Nanotube Samples**; Michael Heben[1], Timothy McDonald[1,2], Chaiwat Engtrakul[1], Jeffrey Blackburn[1], Garry Rumbles[1]; [1]National Renewable Energy Lab; [2]Columbia University

4:15 (290) **Silica Functionalization of Carbon Nanotubes**; Stanislaus Wong[1, 2]; [1]SUNY Stony Brook; [2]Brookhaven National Laboratory

4:35 (291) **Understanding the Dispersion of Single-Wall Carbon Nanotubes for Effective Separations**; Kirk Ziegler[1]; [1]University of Florida

4:55 (292) **Biomimetic Polysoaps for SWNT Dispersion and Electric Force Microscopy Characterization of Individual SWNTs**; Liwei Chen[1], Zi-Chen Li[2], Dan Wang[1], Ru Zhang[3]; [1]Ohio University, Dept. of Chem and Biochem; [2]Peking University, China; [3]Ohio Univ., Dept. of Phy. and Astronomy

Tuesday Afternoon, Nutcracker 1
CHARLES MANN AWARD
Organizer and Presider: Bruce Chase

3:15 (293) **Quantitative Biological Raman Spectroscopy**; Michael Feld; MIT

3:55 (294) **Modelling, Testing and Improving the Depth Resolution of Confocal Raman Microscopy**; Neil Everall[1], Fran Adar[2], Andrew Whitley[2]; [1]ICI PLC; [2]Horiba Jobin Yvon

4:35 (295) **Protein and Peptide Structures at Solid/Liquid Interfaces Probed by Sum Frequency Generation Vibrational Spectroscopy**; Zhan Chen; [1]University of Michigan

Tuesday Afternoon, Nutcracker 3
FROM ELEMENTAL SPECIATION TO METALLOMICS
Organizer and Presider: Joseph Caruso

3:15 (296) **Metallomics - New Analytical Techniques for the Post-Genomic Era**; David W. Koppenaal[1], Charles J. Barinaga[1], Steven J. Ray[2], Duane A. Rogers[2], Gary M. Hieftje[2], Michelle Liberton[3], Jana Stockel[3], Himadri B. Pakrasi[3]; [1]Pacific Northwest National Laboratory; [2]Indiana University; [3]Washington University

3:35 (297) **Green Sample Preparation for Metallomics**; Anne Vonderheide; [1]University of Cincinnati

3:55 (298) **New Separation and Detection Schemes for Metal Speciation of Botanical Products**; R. Kenneth Marcus[1], Timothy M. Brewer[1], Joaudimir Castro[1], M. V. Balarama Krishna[1]; [1]Clemson University

4:15 (299) **Elemental Speciation - One Tool in the Fight Against Chemical Terrorism**; Douglas T. Heitkemper[1], Nohora V. Shockey[1], Barbara S. Barnes[1], John R. Urban[1], Catherine Dasenbrock[1], Kevin Kubachka[2], Joseph A. Caruso[2]; [1]Food and Drug Administration; [2]University of Cincinnati

4:35 (300) **Selenium Speciation - Implication for Cancer Chemoprevention**; Julian Tyson; [1]UMass Amherst

4:55 (301) **A Metallomics Approach to Metal Profiling in Clinical Samples**; Joseph Caruso; [1]University of Cincinnati

TECHNICAL PROGRAM – WEDNESDAY
Plenaries and Posters

William F. Meggers Award
8:00 AM Plenary Session, *Fantasia G*

Pavel Matousek

(302) **Subsurface Probing in Diffusely Scattering Media Using Spatially Offset Raman Spectroscopy**; Pavel Matousek[1], Ian P. Clark[1], Edward R.C. Draper[2], Michael D. Morris[3], Allen E. Goodship[2], Neil Everall[4], Michael Towrie[1], William F. Finney[3], Anthony W. Parker[1]; [1]Rutherford Appleton Laboratory; [2]Royal Veterinary College; [3]University of Michigan; [4]ICI PLC

Refer to page 16 for additional information

Lester W. Strock Award
8:30 AM Plenary Session, *Fantasia G*

Paul Farnsworth

(303) **Probing Plasmas with Photons**; Paul Farnsworth[1]; [1]Brigham Young University

Refer to page 18 for additional information

WEDNESDAY POSTER SESSIONS
9:00 – 10:30 AM and 1:45 – 3:15 PM
Fantasia H/J

All Wednesday posters should be put up in Fantasia H/J between 7:30 – 8:00 AM and removed between 5:00 – 6:00 PM. If your poster board is an odd number (1, 3, 5, etc.) , the presenting author must be present 9:00 – 9:45 AM and 1:45 – 2:30 PM on Wednesday. If your poster board number is an even number (2, 4, 6, etc.), the presenting author must be present 9:45 – 10:30 AM and 2:30 – 3:15 PM on Wednesday.

Atomic Mass Spectrometry

Board #

1 (304) **Application of Isotope Dilution for the Accurate Determination of Cr(III), Cr(VI) and Total Cr in Yeast**; Lu Yang[1]; [1]National Research Council Canada

2 (305) **Characterization Of Nuclear Materials Using Time-Of-Flight ICP-MS**; Stefan Bürger[1], Lee R. Riciputi[1], Debra A. Bostick[1], Douglas C. Duckworth[1]; [1]Oak Ridge National Laboratory

3 (306) **Low Level Boron Analysis in Plutonium Oxide**; Jeffrey Miller[1], David Gallimore[1], Frances Martin[1], Alexander Martinez[1], Joseph Rodriguez[1], Lawrence Drake[1]; [1]Los Alamos National Laboratory

4 (307) **Speciation of Plutonium Under Environmental Conditions**; Buda Razvan Aurel[3]; [1]Institut für Kernchemie, Universität Mainz; [2]Oak Ridge National Laboratory, USA; [3]TU Graz, Austria

5 (308) **A New Interference Management Solution for ICP-MS - The Unique Collision Reaction Interface (CRI)**; Doug Shrader[1], Shane Elliott[1], Xue Dong Wang[1], Iouri Kalinitchenko[1]; [1]Varian, Inc.

6 (309) **Elemental Speciation by Non-Aqueous Capillary Electrophoresis - Inductively Coupled Plasma Mass Spectrometry and Its Applictions in Pharmaceutical Process Reaseach**; Xiaodong Bu[1], Tiebang Wang[1], Xiujuan Jia[1], Qiang Tu[1], Gene Hall[2], Christopher Welch[1]; [1]Merck Research Lab; [2]Rutgers University

7 (310) **Observation of Plasma Jet in Interface Region for Microplasma Mass Spectrometer**; Hidekazu Miyahara[1], Taichi Kageyasu[2], Kazuyasu Takimoto[2], Wataru Kumagai[2], Eiki Hotta[2], Ryuichi Shimada[1], Akitoshi Okino[2]; [1]Laboratory for Nuclear Reactors, Tokyo Institute; [2]Department of Energy Sciences, Tokyo Institute

8 (311) **Long Term Exposure to Lead – Measuring Lead in Bones by ICP-MS**; Ela Bakowska[1], Anna Foror[1], Michael Kraky[1], Tatyana Kandova[1]; [1]National Medical Services

9 (312) **Examination of Coal Utilization Byproducts by Pulsed Glow Discharge Plasma Spectrometries**; Jennifer Robertson-Honecker[1], Alexandria Pavkovich[1]; [1]West Virginia University

10 (313) **Monitoring Metals Hypersensitivity by Measuring Chromium, Cobalt and Molybdenum in Whole Blood**; Ela Bakowska[1], Judy Vinosky[1], Michael Welsh[1]; [1]National Medical Services

11 (314) **Arsenic Speciation of Selected US Rice Samples**; Melanie N. Allen[1,2], Nohora V. Shockey[1], Douglas T. Heitkemper[1], [1]Food and Drug Administration; [2]Oak Ridge Associated Universities

12 (315) **A New Approach for Calibration in Trace Analysis of Ultrahigh Purity Materials by Glow Discharge Mass Spectrometry**; Ulrich Panne[1], Tamara Gusarova[1], Heinrich Kipphardt[1], Ralf Matschat[1], Joachim Hinrichs[2]; [1]Federal Institute for Materials Research BAM; [2]Thermo Electron Corporation

13 (316) **Speciation of Vanadium in Some Environmental Samples by ICP-OES and HR-ICP-MS Combined with Liquid Chromatography**; Jerzy Mierzwa[1]; [1]University of Central Florida

14 (317) **Determination of Burn-up Monitors for Use in Nuclear Forensics**; Jeffrey Giglio[1], Daniel Cummings[1], James Sommers[1], Kevin Carney[1]; [1]Idaho National Laboratory

15 (318) **Summing Multiple Internal Standards to Track Serum Calcium During Reference Analysis by Inductively Coupled Plasma-Mass Spectrometry**; Jonathan Good[1], John Butz[1]; [1]Mayo Clinic

16 (319) **Induction Heating ETV for ICP MS**; Eric Salin[1], Rebecca Lam[1]; [1]McGill University

17 (320) **Time-resolved ICP-MS Measurement of Part-Per-Trillion Level of Analyte Ions Adsorbed Onto Carbon Nanotubes**; Wing-Tat Chan[1], Michael H.P. Yau[1], Thomas K.O. Lui[1]; [1]The University of Hong Kong

18 (321) **Exploring the Analytical Utility of LA-ICP-TOFMS for the Provenancing of Archaeological Materials**; John Dudgeon[1,4], William Balsanek[2], Hector Neff[3,4], Andrew Saint[2]; [1]Department of Anthropology, University of Hawaii; [2]GBC Scientific Equipment, Hampshire, IL; [3]Department of Anthropology, California; [4]Institute for Integrated Research

19 (322) **Exploring the Benefits of ICP- oTOF (orthogonal time of flight) MS for a Variety of Multi-Element Applications**; William Balsanek[1], Andrew Saint[2],[1]GBC Scientific Equipment, Hampshire, IL 14060; [2]GBC Scientific Equipment, Dandenong, VI

20 (323) **Determination of Ultra-Trace Levels of Uranium, Thorium and Potassium in High Purity Materials by ICP-MS**; Patricia Grinberg[1,2], Ralph Sturgeon[1], Andreas Piepke[3], David; [1]National Research Council Canada; [2]Carleton University, Dep. of Physics; [3]University of Alabama, Dep. of Physics

21 (324) **High Repetition Rate Femtosecond Laser Ablation-ICP-MS**; Jhanis Gonzalez[1], Alberto Fernandez[2], Dayana Oropeza[1], Xianglei Mao[1], Richard Russo[1]; [1]Lawrence Berkeley National Laboratory; [2]Universidad Central de Venezuela

Atomic Spectroscopy

Board #

22 (325) **Depth Profile Analysis of Thin Film by using dc Voltage Modulation Glow Discharge Optical Emission Spectrometry (GD-OES)**; Hyunkook Park[1], Kazuaki Wagatsuma[1]; [1]Institute for materials research, Tohoku Univ

23 (326) **Single Event Spectroscopy with VSMS™ Spectrograph – Applications in Physical Chemistry**; Radek Sobczynski[1,2], H. Lange[3], Dr. Huczko[3], Markus Berger[4], Stephan Dietrich[4]; [1]Princeton Instruments; [2]Acton Research; [3]University of Warsaw; [4]Dipl. Phys. Group of Frau Priv. Doz. Dr. Ing. Ursel Fantz, Uni. Augsburg, Experimentelle Plasmaphsik

24 (327) **Four-Point Standardization Reduces Bias in Spectrometric Determinations**; James W. Anderson

25 (328) **A Dedicated, Interactive Tool for Multi-Line Selection in ICP-AES**; Albert Brennsteiner[1], Philippe Hunault[1], Agnès Cosnier[2], Yves Danthez[2], Cendrine Dubuisson[2], Emmanuel Fretel[2], Jean-Michel Mermet[3], Olivier Rogerieux[2]; [1]HORIBA Jobin Yvon, Inc; [2]HORIBA Jobin Yvon SAS; [3]Spectroscopy Forever

26 (329) **Determination of Total Cesium in Irradiated Samples by Inductively Coupled Plasma Atomic Emission Spectroscopy (ICP-AES)**; Jana Northam[1], Daniel Cummings[1], James Sommers[1], Jeffrey Giglio[1]; [1]Idaho National Laboratory

27 (330) **Determination of Lead and Arsenic by ICP-OES in Cosmetic Products**; Hee Yun Kim[1], Young Me Song[1], Myung Hee Kang, Sun Kun Hong[1], Soo Yeul Cho[1], Chul Joo Lim[1]; [1]Gyungin Regional Korea Food & Drug Administration

28 (331) **Exposure Assessment Considerations in Utilizing Conventional Chemical and Physiological Based Extraction Techniques Prior to Arsenic Speciation Analysis in Seafood Samples**; John T. Creed[1], Patricia A. Creed[1], Christina M. Gallawa[2], Andrea R. Young[2], Carol A. Schwegel[1]; [1]US EPA, NERL, MCEARD, Cincinnati, OH 45268; [2]Student Services Contract

29 (332) **Analysis of Environmental Samples Following US EPA Guidelines Utilizing a New Simultaneous CCD Detector ICP-OES System**; Doug Shrader[1], Vincent Calderon[1], Andrew Ryan[1]; [1]Varian, Inc.

30 (333) **Droplet Direct Injection System for Inductively Coupled Plasma Source**; Kazuyasu Takimoto[1], Hidekazu Miyahara[2], Taichi Kageyasu[1], Masato Watanabe[1], Eiki Hotta[1], Akitoshi Okino[1]; [1]Department of Energy Sciences,Tokyo Instutute of T; [2]Laboratory for Nuclear Reactors, Tokyo

31 (334) **Molecular Species in Glow Discharge Emission - a Connection with Matrix Effects?** Arne Bengtson[1], Thomas Björk[1]; [1]KIMAB

32 (335) **Efficient Determination of Phosphorus Levels – How to Handle Hundreds of Stool Samples**; Ela Bakowska[1], Joan Schemmer[1], Matthew McMullin[1], Cecelia White-Powell[1], Kirsten Trbovich[1]; [1]National Medical Services

33 (336) **The Determination of Mercury in Solids and Liquids: Bringing Together USEPA Methods 1631, 245.1, 245.7 and 7473**; David Pfeil[1], Peter Brown[1]; [1]Teledyne Leeman Labs

34 (337) **On the Use of Collisional Transfer in a Cesium Cell to Enhance its Application as a Resonance Fluorescence Detector**; Benoit Lauly[1], Benjamin W. Smith[1], Nicolo Omenetto[1], James D. Winefordner[1]; [1]University of Florida

35 (338) **The Determination of Halogens by Inductively Coupled Plasma Optical Emission Spectroscopy in the Ultralow Uv Wavelength Range**; David Pfeil[5]; [1]Teledyne Leeman Labs

36 (339) **Spectroscopic Diagnostics of a Thallium Glow Discharge Lamp by Absorption, Emission, and Laser-Induced Saturated Fluorescence Spectroscopy**; Nicholas Taylor, Nicolò Omenetto, Benjamin W. Smith, James D. Winefordner [1]University of Florida

37 (340) **Approaching a Universal Pneumatic Nebulizer – The Next Step**; Ronald Stux[1], Gerald Dulude[1], Vesna Dolic[1], Paul Neal[2]; [1]Glass Expansion, Inc; [2]Thermo Electron, Inc

38 (341) **Molecular Gas Interference in Diode Array Glow Discharge Optical Emission Analysis**; Kim Marshall[1], Kevin Brushwyler[1]; [1]Leco Corporation

39 (342) **Indicator and Novel Correction Methodology for Plasma-related Matrix Effects in Inductively Coupled Plasma-Atomic Emission Spectrometry; *SAS Graduate Student Award;*** George Chan[1], Gary Hieftje[1], [1]Department of Chemistry, Indiana University

40 (343) **Induction Heating-Electrothermal Vaporization for Direct Mercury Analysis of a Single Human Hair by Atomic Fluorescence and Atomic Absorption Spectrometry**; Eric D. Salin[1], David Duford[1], Josiane P. Lafleur[1], Rebecca Lam[1], Cameron D. Skinner[2]; [1]McGill University; [2]Concordia University

Board #

41 (344) **Tandem Calibration Methodology using a Dual Nebulizer Sample Introduction System for the Analysis of Micro Sample by ICP-OES**; Zully Benzo[1], Domingo Maldonado[2], José Chirinos[3], Eunice Marcano[1], Clara Gomez[1]; [1]Centro de Química. IVIC; [2]CICBa, Departamento de Química. UNEFM; [3]Centro de Química Analítica. UCV

42 (345) **A New Upstream Electrothermal Vaporization (Etv) Device - Properties and Understanding of Analyte Condensation and Transport**; Gerd Hermann, Alexander Trenin

43 (346) **Interferometric Droplet Imaging for In-situ Aerosol Characterization in an Inductively Coupled Plasma**; Ryan Brennan[1], Kaveh Jorabchi[1], Jonathan Levine[1], Maryam Farmand[1], Mazdak Taghioskouei[1], Akbar Montaser[1]; [1]The George Washington University

44 (347) **Micro Plasma Chips for Chemical Analysis**; Mazdak Taghioskoui[1], Kaveh Jorabchi[1], Mona Zaghloul[1], Akbar Montaser[1]; [1]The George Washington University

45 (348) **Statistical Determination of the Uncertainty Associated**; Ralph Obenauf[1], NImi Kocherlakota[11]SPEX CertiPrep, Inc.

46 (349) **A Simplified Approach for Absolute Qunatitation of Nucleic Acids using ICP-OES**; Myungsub Hahn[1], Euijin Hwang[1], Yong-Hyeon Yim[1], In-Chul Yang[1], Sang-Ryoul Park[1]; [1]Korea Research Institute of Standards and Science

47 (350) **Detection of Contaminated Metal Ion on Solid Surface Using Nano-Electrospray**; Deok-im Jean[1]; [1]Dankook University

Infrared Spectroscopy

Board #

48 (351) **FTIR Spectroscopy as a Function of Molecular Weight Distribution of Wood Coatings**; Richard Papez; [1]Armstrong World Ind

49 (352) **Imaging Studies of Phase Separation and Diffusion in Polymers by FTIR Transmission and ATR Spectroscopy**; Heinz W. Siesler[1], Christian Vogel[1], Elke Wessel[2]; [1]Dept. of Phys. Chem., University of Duisburg-Essen; [2]Beiersdorf AG, Hamburg, Germany

50 (353) **Detection of Explosives by Hyperspectral Imaging**; Diane Williams[1], Hina Ayub[2]; [1]Federal Bureau of Investigation; [2]Oak Ridge Institute of Science Education

51 (354) **Water Sorption Process into a Biocompatible Polymer Film: Time-Resolved In-Situ ATR-IR Observation**; Shigeaki Morita[1], Masaru Tanaka[2], Yukihiro Ozaki[1]; [1]Kwansei-Gakuin University; [2]Hokkaido University

52 (355) **Water Sorption Process into a Biocompatible Polymer Film: Effects of Small Molecules on Water, Studied by ATR-IR**; Akiko Tanabe[1], Shigeaki Morita[1], Masaru Tanaka[2], Yukihiro Ozaki[1]; [1]Kwansei-Gakuin University; [2]Hokkaido

53 (356) **Infrared Study of Degradation and Degradation Products of Poly(amides) and Poly(phthalamides)**; Katherine Robertson[1], Xiaodong Liu[1], Richard A. Nyquist[2],[1]Impact Analytical; [2]Nyquist Associates

54 (357) **Promoting Method Globalization Through Internal Infrared Reference Libraries**; Jessica Jarman[1]; [1]GE Industrial - Plastics

55 (358) **UV Radiation Effects on Reflectance FTIR Microscopy of Clean B. Subtilis Spores**; Heather Brooke[1], Barbara Setlow[2], Peter Setlow[2], Burt Bronk[3], Michael Myrick[1]; [1]University of South Carolina; [2]University of Connecticut Health Center; [3]Air Force Research Laboratory

56 (359) **Dipole Moment Derivatives of Benzene in the Liquid and Gas Phases: Evidence for Pseudo-Hydrogen Bonding**; Dale Keefe[1]; [1]Cape Breton University

57 (360) **Diffuse-Reflectance Mid-IR and NIR Spectroscopic Properties of Mycorrhizal and Non-mycorrhizal roots**; Francisco Calderon[1], Veronica Acosta-Martinez[2]; [1]USDA-ARS, Akron, CO; [2]USDA-ARS, Lubbock, TX; [3]; [4]

58 (361) **FT-Infrared Spectroscopic Studies of Lymphoid and Myeloid Leukaemia Cell Lines**; Jaspreet Babrah[1], Nicholas Stone[1], Richard Lush[2], Adam Rye[2], Keith McCarthy[3], Conrad Bessant[4]; [1]Biophotonics Research Group, Gloucestershire Royal; [2]Department of Haematology, Gloucestershi; [3]Department of Histopathology, Gloucester; [4]Cranfield University, UK.

59 (362) **Topographic Dependence of ATR-FTIR Signal and its Applications**; Dongmao Zhang[1], Olivier Guise[1]; [1]General Electric; [2]General Electric

60 (363) **An ATR/FT-IR Spectral Database to Identify Foreign Matter in Cotton**; David Himmelsbach[1], John Hellgeth[2], David McAlister[3]; [1]USDA-ARS, Russell Research Center, Athens, GA; [2]Hewlett Packard Company, Corvallis, OR; [3]Uster Technologies, Inc, Knoxville, TN

61 (364) **Thermal Behavior of Poly(beta-propiolactone) Studied by Infrared Spectroscopy and Wide Angle X-Ray Diffraction**; Yohei Ando[1], Harumi Sato[1], Tadahisa Iwata[2], Hiroshi Yamaguchi[1], Yukihiro Ozaki[1]; [1]Kwansei Gakuin University; [2]Riken

62 (365) **Dipole Directions of Low Frequency Vibrations in Biological Single Crystals Observed by Terahertz Time-Domain Spectroscopy**; Katsuhiro Ajito[1], Yuko Ueno[1], Isao Tomita[1], Rakchanok Rungsawang[1]; [1]NTT Basic Research Laboratories

63 (366) **Organogelation Kinetics of a C22 Tailed Bis-urea Organogelator Examined by FTIR**; Karla S. McCain[1], Andrew J. Carr[1], Aaron M. Pierce[1], Tatjana D. Talamentes[1], Jason M. Cohen[1]; [1]Austin College

64 (367) **Infrared Chemical Imaging with MCT, InGaAs, or InSb Detection and Synchrotron or Thermal Sources**; David Wetzel[1]; [1]Kansas State University

65 (368) **Nondestructive Testing for Sprout Resistance in Wheat via Chemical Imaging with InGaAs Focal Plane Array Spectroscopy**; David Wetzel[1], Hicran Koc[1], Virgil Smail[1]; [1]Kansas State University

66 (369) **Determining Drug Distribution in Hair Samples Utilizing ATR and IR Microscopy Techniques**; Ali Kocak[1], Ronald Birke[2], Sue Barrets[3]; [1]John Jay Coleege of Criminal Justice; [2]The City College of CUNY; [3]Harrick Scientific Products

67 (370) **Wheat Aleurone Fraction Purity via Diamond Internal Reflection Infrared Spectroscopy**; David Wetzel[1], Emily Bonwell[1], Scott Frazer[2], Steve Ellis[2]; [1]Kansas State University; [2]Horizon Milling

68 (371) **Integration of an IR Analyzer as an Intelligent Internet Appliance**; Bertrand Lanher[1], Alexander Seyfarth[1]; [1]Aspectrics, Inc.

TECHNICAL PROGRAM – WEDNESDAY
Posters 9:00 – 10:30 AM and 1:45 – 3:15 PM and Orals 10:30 AM – 12:30 PM

Board #

69 (372) **Plasma-assisted Deposition of Fluorocarbon Films for Molecular Recognition Layers in Mid-Infrared Attenuated Total Reflection Chemical Sensors**; Gary T. Dobbs[1], Balamurali Balu[1], Christina Young[1], Ashwini Sinha[1], Dennis W. Hess[1], Boris Mizaikoff[1]; [1]Georgia Institute of Technology

70 (373) **Advantages and Limitations of Searching FTIR Difference Spectra**; Kenneth Laughlin[1]; [1]Rohm and Haas Company

71 (374) **Mid-IR ATR Imaging Using a Linear Detector Array System**; Jerry Sellors[1], Tony Canas[1], Ralph Carter[1], Robert Hoult[1], Sharon Williams[1]; [1]PerkinElmer, Beaconsfield, UK

72 (375) **Resolution in Mid-IR ATR Microscopic Imaging: Measurement and Meaning**; Tony Canas[1], Ralph Carter[1], Robert Hoult[1], Jerry Sellors[1], Sharon Williams[1]; [1]Perkinelmer, Beaconsfield, UK

73 (376) **Viscosity and NIR Studies of Lithium Halides in Binary Solvent Systems**; Bobbie Hood[1], Alex Williamson[1]; [1]N. C. A&T State University

74 (376a) **Mid-Infrared Gas Sensors Using Hollow Waveguides For Sensing Volatile Organic Pollutants**; Christina Young[1], Boris Mizaikoff[1]; [1]Georgia Institute of Technology; [2]School of Chemistry and Biochemistry

Fluorescence

Board #

75 (377) **Comparison of Deep UV Lasers and LEDs for Fluorescence Detection of Organic Compounds in Water**; Anna Sharikova[1], Dennis Killinger[1]; [1]University of South Florida

76 (378) **Spectrophotometric and Spectrofluorophotometric Determinations of Iron with 4'-(2,2'-Bithienyl-5-yl)-2,2':6',2''-terpyridine**; Riichiro Nakajima[1], Kazuaki Mima[1], Kou Kyou[1], Keiich Noda[1], Yasuro Kawauchi[1], Takashi Tamura[1], Takeko Matsumura-Inoue[2], Kazuhiko Tsukagoshi[1];[1]Doshisha University; [2]Minerva Light Laboratory, L.L.C

77 (379) **Analytical Data: So Much to See - So Little Time**; Gene Hall[1], Michael Boruta[2]; [1]Rutgers University; [2]Advanced Chemistry Development, Inc.

78 (380) **Anomalous Fluorescence of an Amino-Substituted 4-nitropyridine N-oxide Prone to Intra- or Intermolecular Excited-State Proton Transfer**; Joost de Klerk[1], Anna Szemik-Hojniak[2], Freek Ariese[1], Cees Gooijer[1]; [1]Laser Centre Vrije Universiteit Amsterdam; [2]University of Wroclaw, Poland

79 (381) **Choosing the Right Solvent for the Analysis of Polycyclic Aromatic Hydrocarbons Metabolites via Laser-Excited Time-Resolved Shpol'skii Spectroscopy**; Shenjiang Yu[1], Huiyong Wang[1], Keerthika Vatsavai[1], Andres Campiglia[1]; [1]University of Central Florida

80 (382) **Getting It Right with Fluorescence: Where Do We Stand and What Do We Need?**; Ulrich Panne[1], Ute Resch-Genger[1], Dietmar Pfeifer[1], Katrin Hoffmann[1], Angelika Hoffmann[1]; [1]BAM

81 (383) **The Legacy Continues, Seventeen Years in the Wake of the Exxon Valdez Oil Spill**; James Jordan[1], Karl Booksh[1], Kristin Kirk[2], David Gort[2]; [1]Arizona State University; [2]Grand Canyon University

82 (384) **Designing Analytical Instrumentation for Use with Fluorescing Samples using TraceProTM Optical System Design Software**; Richard Hassler[1]; [1]Lambda Research Corporation

Wednesday Morning, Fantasia A/B
MICROCHIP-CE
Organizer and Presider: Carlos Garcia

10:30 (385) **Sensitive Quantification by Nested-RT-PCR to Detect Viable Spores of A. acidoterrestris After Inhibition Treatments by CE with LIF using Microchips**; Emanuel Carrilho[1], Maribel Funes Huacca[1], Juliana Alberice[1], Sheila B. Guterres[1]; [1]Instituto de Química de São Carlos – USP

10:50 (386) **Generation of Hydrophilic Poly(Dimethylsiloxane) Microfluidic Devices**; Charles Henry[1], Jonathon J. Vickers[1], Brian M. Murphy[1], Xinya He[1], David W. Grainger[1], David S. Dandy[1]; [1]Colorado State University

11:10 (387) **Progress Towards LC-based Microfluidic Devices for Medical Diagnostics**; Vincent Remcho[1], Carlos Gonzalez[1], Daniela Hutanu[1], Jack Rundel[1]; [1]Oregon State University

11:30 (388) **Synthesis, Characterization, and Testing of Novel Block Copolymers as Substrate Materials for the Fabrication of Microfluidic Devices**; Christopher Culbertson[1], Scott Klasner[1], Gregory Roman[1]; [1]Kansas State University

11:50 (389) **Multiple Tissues Occupying a Single Channel in a Microfluidic Device: Determination of Possible New Mechanisms of Drug Efficacy**; Nicole Villiere[1], Jamie Carroll[1], Teresa Oblak[1], Paul Root[1], Dana Spence[1]; [1]Wayne State University

12:10 (390) **Analysis of Phenolic Contaminants using Microchip-Capillary Electrophoresis and Electrochemical Detection**; Carlos D. Garcia[1], Maria Fernanda Mora[1], Yongsheng Ding[1], Eric Mejia[1]; [1]The University of Texas at San Antonio

Wednesday Morning, Fantasia C
SPECTROSCOPY AND MASS SPECTROMETRY IN FORENSIC SCIENCES I
Organizer and Presider: Jose Almirall

10:30 (391) **Stable isotopes of explosives provide additional forensic information**; James Ehleringer; IsoForensics Inc.

10:50 (392) **The Application of CE and Ion Chromatography to Explosives Residue Analysis**; Bruce McCord, Megan Bottegal; [1]Florida International University

11:10 (393) **Advances in Identification of Dyed Textile Fibers using Capillary Electrophoresis/Mass Spectrometry**; Stephen L Morgan[1], Amy R Stefan[1], Anthony R Trimboli[1], Edward G Bartick[2]; [1]University of South Carolina; [2]FBI Laboratory

11:30 (394) **UV-visible, Fluorescence, and Raman Microspectrophotometry for Identification of Dyed Textile Fibers**; Edward G Bartick[1], Stephen L Morgan[2], Suzanna H Hall[2], Anthony R Trimboli[2]; [1]FBI Laboratory; [2]University of South Carolina

11:50 (395) **Application of Laser Ablation Inductively Coupled Plasma Mass Spectrometry (LA-ICP-MS) to Solid Matrices of Forensic Interest**; Tatiana Trejos[1,2], Jose Almirall[1,2]; [1]Florida International University; [2]International Forensic Research Institut

12:10 (396) **Trace Chemical Detection using Laser Ablation Ion-Storage Time-of-Flight Mass Spectrometry**; Greg Klunder[1], Jason Holt[1]; [1]LLNL

TECHNICAL PROGRAM – WEDNESDAY
Orals 10:30 AM – 12:30 PM

Wednesday Morning, Fantasia D
RAMAN MICROSCOPY
Organizer and Presider: Richard Bormett

10:30 (397) **Simultaneous microRaman Spectroscopy and X-ray Microdiffraction**; Richard Davies[1], Manfred Burghammer[1], Christian Riekel[1]; [1]ESRF

11:10 (398) **A New Class of Substrates for Surface Enhanced Raman Micro-Spectroscopy**; Alexandre Brolo[1], Jason Anema[1], Reuven Gordon[2], Karen Kavanagh[3]; [1]University of Victoria, Dept. of Chemistry; [2]University of Victoria, Dept Elect. Eng; [3]Simon Fraser University, Dept Physics

11:30 (399) **The Critical Challenges Facing Surface-Enhanced Raman Spectroscopy for Trace Chemical Detection**; Nicholas Pieczonka[1], Ricardo Aroca[1]; [1]University of Windsor

11:50 (400) **Low Frequency Raman Measurements and Lattice Dynamic Calculations for Pharmaceutical Polymorph Characterisation**; Mike Claybourn[2], Graeme Day[1], Storey Richard[2]; [1]Cambridge University; [2]AstraZeneca

12:10 (401) **Hyphenated-Raman Microscopy for Materials Analysis**; Ken Williams; Renishaw PLC

Wednesday Morning, Fantasia E/F
FIELD DEPLOYABLE MASS SPECTROMETERS
Organizer and Presider: Tim Short

10:30 (402) **25 Years of On-Site Analysis with Mobile Mass Spectrometers**; Thomas Ludwig[1], Thomas Arthen-Engeland[1], Jochen Franzen[1], Joachim Stach[1]; [1]Bruker Daltonik GmbH

10:50 (403) **HAPSITE Portable GC/MS Chemical Identification System**; Bob Felty, Ben Shultes[1], Teresa Kristoff[1], [1]INFICON Inc.

11:10 (404) **Development of Field Applications for Mass Spectrometers**; Garth Patterson[1], John Grossenbacher[1], J. Mitchell Wells[1]; [1]Griffin Analytical Technologies

11:30 (405) **Quantitative Gas Analysis via Field Portable Mass Spectrometer System**; C Richard Arkin[1], J. Andres Diaz[2], Timothy Griffin[3], Elian Conejo[2], Kristel Heinrich[2], Carlomagno Soto[2], Guy Naylor[1], Charles Curley[1], David Floyd[1], Oliver Gomex[2]; [1]ASRC Aerospace; [2]Universidad de Costa Rica; [3]National Aeronautics and Space Administration

11:50 (406) **GC-MS System Based on a Miniature Toroidal Ion Trap Mass Spectrometer for Field Detection of Chemical Threats**; Milton L. Lee[1], Stephen A. Lammert[1], Samuel E. Tolley[2], Jesse A. Contreras[1], Jacolin A. Murray[1], James R. Oliphant[2], H. Dennis Tolley[1], Edgar D. Lee[2]; [1]Brigham Young University; [2]Palmar Technologies

12:10 (407) **In-Situ Mass Spectrometry for Field Chemical Analysis**; Ryan Bell[1], Tim Short[1], Strawn Toler[1], Pete Wenner[1], Friso van Ameron[1], Bob Byrne[1]; [1]Center for Ocean Technology /USF

Wednesday Morning, Fantasia K/L
PROCESS ANALYSIS: SPECTROSCOPIC MONITORING TOOLS
Organize: James W. Rydzak; Presider: Chris Hassell

10:15 Introduction

10:30 (408) **What is the Extent of the PAT Toolbox?** Martin Warman[1]; He Kong[1]; [1]Pfizer

11:10 (409) **Development of Mid-infrared Methods for Real World Process Analysis**; John Ryan[1], Brian Wittkamp[1]; [1]Mettler Toledo

11:30 (410) **Near-Infrared Chemical Imaging for In-Situ Monitoring of Pharmaceutical Blends**; Neil Lewis[1], Kenneth Haber[1], Fiona Clarke[2]; [1]Malvern Instruments; [2]Pfizer, Inc.

11:50 (411) **Isotope Selective Laser Ionization Spectrometry as a Process Analytical Technology**; Summer Randall[1], Bruce A. Bushaw[1]; [1]Pacific Northwest National Laboratory

12:10 (412) **Using AOTF-NIR Analyzers for "Real-time" Monitor and Control Blending and Drying Operations**; Igor Nazarov[1]; David Chong[1], [1]Brimrose Corporation

Wednesday Morning, Fantasia M
NANOTUBES AND NANOWIRES FOR SENSING
Organizer: Pehr E. Pehrsson; Presider: Jennifer N. Cha

10:30 (413) **Carbon Nanotube Networks as Detection Platform**; Christian Valcke[1], Jean-Christophe Gabriel[1], Ying-Lan Chang[1], Eugene Tu[1]; [1]Nanomix

11:10 (414) **One-dimensional Nanostructures as Spectroscopic Sensing Platforms,** *Tomas Hirschfeld Scholar*; Andrea Tao[1], Donald Sirbuly[1,2], Peidong Yang[1,2]; [1]UC Berkeley; [2]Lawrence-Berkeley National Laboratory

11:50 (415) **Multiwalled Carbon Nanotubes: Interconnecting Solid State Electronics with Biosystems**; Alan Cassell, Jun Li, T.D. Barbara Nguyen-Vu, Hua Chen, Jessica Koehne, Russell Andrews, M. Meyyappan; [1]NASA Ames Research Center

12:10 (416) **Integration of Metal Oxide Nanobelts with Microsystems for Nerve Agent Detection**; Li Shi[1]; [1]University of Texas at Austin

Wednesday Morning, Fantasia N
ADVANCES IN IR SPECTROSCOPY, sponsored by the Coblentz Society, a technical affiliate of SAS
Organizer and Presider: John Hellgeth

10:30 (417) **Dynamic Infrared Microspectroscopy Using a Prism Based Infrapid Spectrograph**; André Sommer[1], Zachary Keltner[1], Katherine Kayima[1], Luis Lavalle[1], Adam Lanzorotta[1], Marina Canepa[1], Curtis Marcott[2], Gloria Story[2], Anthony Dowrey[2]; [1]Molecular Microspectroscopy Laboratory; [2]The Procter & Gamble Company

10:50 (418) **Application of Planar Array IR (PA-IR) to Early Detection of Disease**; John Rabolt[1], Chris Snively[1], Bruce Chase[2], Andrea Persapane[1]; [1]University of Delaware; [2]DuPont CR&D

11:10 (419) **High Spatial Resolution Infrared Imaging with a Solid Immersion Lens and a Broadband Laser Source**; Chris Michaels[1]; [1]NIST, Surface and Microanalysis Science Division

11:30 (420) **Novel Search Algorithms for a Mid-IR Spectra Database of Cotton Contaminants**; J. Brian Loudermilk[1], David S. Himmelsbach[2], Franklin E. Barton, II[2], James A. de Haseth[1]; [1]The University of Georgia; [2]United States Department of Agriculture

11:50 (421) **Vibrational Spectroscopic Characterization of Poly(ethylene terephthalate) Nanotube Composites**; Vasilis Gregoriou[1], Spiros Tzavalas[1], Dieter Fischer[2], Dionysis Mouzakis[3], Vasilis Drakonakis[3]; [1]FORTH/ICE-HT; [2]IPF; [3]University of Patras

12:10 (422) **Attenuated Total Reflectance Infrared Imaging Using a Large Radius Internal Reflectance Element**; Brian Patterson[1], George Havrilla[1], Curt Marcott[2], Gloria Story[2]; [1]Los Alamos National Laboratory; [2]Procter and Gamble

Wednesday Morning, Nutcracker 1
WILLIAM F. MEGGERS AWARD: NEW APPROACHES IN RAMAN SPECTROSCOPY OF TURBID MEDIA
Organizer and Presider: Pavel Matousek

10:30 (423) **Non-invasive Raman Spectroscopy of Human and Animal Tissue**; Michael D. Morris; [1]University of Michigan

10:50 (424) **Time Resolved Raman Photon Migration for Depth Profiling Opaque Samples**; Neil Everall[1], Pavel Matousek[2], Mike Towrie[2], Tony Parker[2], Michael Morris[3]; [1]ICI PLC; [2]Rutherford Appleton Laboratory; [3]University of Michigan

11:10 (425) **Future Possibilities in Diagnosis of Breast Cancer by Subsurface Probing of Calcifications with Kerr-gated & Spatially Offset Raman Spectroscopy (SORS)**; Nicholas Stone[1], Pavel Matousek[2], Kate Ronayne[2], Rebecca Baker[1], Tony Parker[2], Keith Rogers[3]; [1]Gloucestershire Royal Hospital, UK; [2]CCLRC Rutherford Appleton Laboratory, UK; [3]Cranfield Health, Cranfield University

11:30 (426) **Subsurface Raman Spectroscopy of Pharmaceutical Tablets and Capsules**; Pavel Matousek[1], Anthony W. Parker[1]; [1]Rutherford Appleton Laboratory

11:50 (427) **Raman Kerr Gating in the Study of Street Drugs**; W. Ewen Smith[1], Rachael Littleford[1], Karen Faulds[1], Pavel Matousek[2], Mike Towrie[2], Antony Parker[2], Geoffrey Dent[3], Richard Lacey[4]; [1]Strathclyde University; [2]CLRC Rutherford Appleton Laboratory; [3]Avecia Ltd; [4]HOSDB

12:10 (428) **Kerr gated resonance Raman spectroscopic studies on the photochemistry of papers and prints**; Anna-Stiina Jaaskelainen[1], Katri Vikman[1], Anna-Maija Saariaho[1], Jouko Vyorykka[1], Tapani Vuorinen[1], Pavel Matousek[2], Anthony Parker[2]; [1]Helsinki University of Technology; [2]Rutherford Appleton Laboratory

Wednesday Morning, Nutcracker 3
ION PROCESSING, DETECTION AND LASER SAMPLING IN PLASMA SOURCE MS
Organizer and Presider: John Olesik

10:30 (429) **Some Remaining Issues in Plasma Source Mass Spectrometry**; John Olesik; [1]The Ohio State University

10:50 (430) **Experimental and Theoretical Studies of Energy and Mass in Laser Ablation Plumes**; Richard E Russo[1], Sy-Bor Wen[1], Xianglei Mao[1]; [1]Lawrence Berkeley National Laboratory

11:10 (431) **Diagnostic Measurements in Laser Induced Plasmas: A Critical Look**; Nicolo Omenetto[1], Galan Moore[1], Igor Gornushkin[1], Benjamin Smith[1], James Winefordner[1]; [1]University of Florida, Gainesville, FL

11:30 (432) **Matrix Effects in Laser Ablation Inductively Coupled Plasma Mass Spectrometry**; Detlef Günther[1], Zhongke Wang[2], Bodo Hattendorf[1], Kroslakova Ivana[1], Joachim Koch[1], Markus Wälle[1], Jorge Pisonero[1]; [1]ETH Zürich; [2]Laser Technology Lab., Japan

11:50 (433) **Ion Trap ICPMS - New Instrumentation and Methods**; Charles J. Barinaga[1], David W. Koppenaal[1]; [1]Pacific Northwest National Laboratory

12:10 (434) **A High-Performance Multichannel Mass Spectrometer for Elemental Analysis**; Gary M. Hieftje[1], Gregory D. Schilling[1], Francisco J. Andrade[1], M. Bonner Denton[2], Roger P. Sperline[2], David W. Koppenaal[3], Charles J. Barinaga[3]; [1]Department of Chemistry, Indiana University; [2]Dept. of Chem., University of Arizona; [3]Pacific Northwest National Laboratory

WEDNESDAY POSTER SESSION and DESSERT RECEPTION
1:45 – 3:15 PM, see page 56
FANTASIA J/H

Wednesday Afternoon, Fantasia A/B
STANDARD CE & HPLC OF BIOMOLECULES
Organizer and Presider: Charles S. Henry

3:15 (435) **Perchlorate, Wherefrom, Wherein and Where Do We go From Here?** Purnendu Dasgupta; [1]Texas Tech University

3:55 (436) **The Analysis of Club Drugs by CE and CE/MS**; Bruce McCord; [1]Florida International University

4:15 (437) **Determination of Biomarkers in Biological Fluids, Tissues, and Cells by Immunoaffinity Capillary Electrophoresis**; Norberto Guzman; [1]Johnson & Johnson Pharm. R&D

4:35 (438) **Protein Aggregate Separations by Capillary Electrophoresis**; Doug Gilman[1], Julia Moses[1], David Schrum[1], Ryan Picou[1]; [1]Louisiana State University

4:55 (439) **Predicting Physical Protein Stability by Self-Interaction Chromatography**; Charles Henry[1], Joseph Valente[1], Robert Payne[1], Beth Fryksdale[2], Douglas Dale[2], Alfred Gaertner[2], Mark Manning[3], William Wilson[4]; [1]Colorado State University; [2]Genencor International; [3]Legacy Biodesign; [4]Mississippi State University

Wednesday Afternoon, Fantasia C
SPECTROSCOPY AND MASS SPECTROMETRY IN FORENSIC SCIENCES II
Organizer and Presider: Jose Almirall

3:15 (440) **Isotopic and Elemental Analysis for Forensics and Attribution of Biological Agents**; Douglas C. Duckworth[1], Juske Horita Horita[1], Mark Lavelle[3], Stefan Bürger Bürger[1], Lee R. Riciputi[1], Brad Knippel[1], Debra A. Bostick[1], Craig C. Brandt[1], Helen Kreuzer[2]; [1]Oak Ridge National Laboratory, Chemical & Isotope; [2]Pacific Northwest National Laboratory, C; [3]New Scotland Yard, Broadway, London, UK

3:35 (441) **Classification of Two-way Data for Forensic Fingerprinting of Fuels by Gas Chromatography-Mass Spectrometry and Gas Chromatography-Differential Mobility Spectrometry**; Peter Harrington[1], Ping Chen[1], Yao Lu[1], Christopher Bunker[2], John Karnes[2]; [1]Ohio University; [2]Air Force Research Laboratory

3:55 (442) **Laser Ablation in LIBS and ICP-MS: Plasma and Aerosol Formation Processes**; Rick Russo[1], Sy-Bor Wen[1], Jhanis Gonzalez[1], Xianglei Mao[1]; [1]Lawrence Berkeley National Laboratory

4:15 (443) **Forensic provenancing by NITE**; Jurian Hoogewerff[4], Simon Kelly[1], Members NITECRIME Network[3], Members TRACE Consortium[4]; [1]Institute of Food Research; [2]NITECRIME Network; [3]TRACE Consortium

4:35 (444) **Improved Location of Forensic Traces through Optimized Biological and Instrumental Detection of Vapor Signatures**; Kenneth Furton[1], JoNell Aarons[1], Laura Conner[1], Robert Griffith[1], Michael Macias[1], Samantha Tolliver[1]; [1]Florida Int'l University

4:55 (445) **A Novel LIBS system for Forensic Analysis of Materials**; Jose Almirall[1], Benjamin Naes[1], Hanh Lai[1], Scott Ryland[2]; [1]Florida International University; [2]Florida Department of Law Enforcement

Wednesday Afternoon, Fantasia D
ILLUMINATING THE BIOLOGICAL WORLD WITH RAMAN MICROSCOPY
Organizer and Presider: Fred LaPlant

3:15 (446) **Raman Spectroscopy in the Female Reproductive System**; Elizabeth Kanter[1], Alanna Patsiokas[1], Amy Robichaux-iehoever[1], Anita Mahadevan-Jansen[1]; [1]Vanderbilt University

3:35 (447) **In Situ fs-Coherent anti-Stokes Raman Microscopy of Stem Cells**; Stanislav Konorov[1, 2], Michael Blades[1], Georg Schulze[2], Robin Turner[2]; [1]Chemistry Dept., UBC, Canada; [2]Michael Smith Laboratory, UBC, Canada

3:55 (448) **Raman Spectroscopy of Murine-derived Osteogenic Stem/Progenitor Cells**; Gurjit S. Mandair[1], Michael D. Morris[1], Pieter Steenhuis[2], Michael A. Ignelzi Jr[2]; [1]University of Michigan, Department of Chemistry; [2]University of Michigan, Dental School

4:15 (449) **Analysis of Plant Surfaces Using Raman Spectroscopy**; Marcia M.L. Yu[1], Stanislav Konorov[1], Georg Schulze[1], Reinhard Jetter[1], Michael W. Blades[1], Robin F.B. Turner[1]; [1]The University of British Columbia

4:35 (450) **MCR-ALS Analysis of Two-way UVRR Spectra of Biologically Relevant Compounds**; John Simpson[1], Gurusamy Balakrishan[2], Ying Hu[2], Janina Kneipp[2], Thomas Spiro[2], Renee Jiji[1]; [1]University of Missouri-Columbia; [2]Princeton University

4:55 (451) **Virus Assembly and Architecture Investigated by Raman Spectroscopy**; George J. Thomas[1], Edward H. Egelman[2], Stacy A. Overman[1]; [1]University of Missouri-Kansas City; [2]University of Virginia

Wednesday Afternoon, Fantasia E/F
APPLICATIONS IN ATOMIC SPECTROSCOPY
Organizer and Presider: Deborah Bradshaw

3:15 (452) **A Review of the Changing Needs for Measuring Trace Elements in Clinical Matrices: From Occupational Medicine to Environmental Biomonitoring**; Patrick Parsons[1 2]; [1]New York State Department of Health; [2]University at Albany

3:35 (453) **High-throughput Screening of Environmental Samples with Collision-Cell ICP-MS.**; Neal Julien[1]; [1]Midwest Research Institute, FL Division

3:55 (454) **Removing Some Analytical Limits using ETV-ICP(TOF)MS**; James Holcombe[1], Adam Rowland[1]; [1]Univ of Texas at Austin

4:15 (455) **Chemical Analysis for Forensic Attribution: Atomic Spectroscopy in Action**; Vahid Majidi, Lav Tandon, Elizabeth Hastings, James Barnes, David Gallimore, Cris Lewis, Robert Steiner; [1]Los Alamos National

4:35 (456) **ICPMS – Emerging Player in Organic Trace Analysis**; Joseph Caruso; [1]University of Cincinnati

4:55 (457) **Three-Dimensional Nonstationary Model of an ETV-ICP System**; Albert Gilmutdinov[1], Shamil Araslanov[2], Rinat Ibragimov[1], Mjakzjum Salakhov[1], Andrey Staroverov[1]; [1]Kazan State University; [2]Research Institute of Mechanics and Math

Wednesday Afternoon, Fantasia K/L
PROCESS ANALYSIS: INTERFACES FOR SPECTROSCOPIC MEASUREMENTS, sponsored by the Coblentz Society, a technical affiliate of SAS
Organizer and Presider: David Radspinner

3:15 (458) **Spectroscopic Interfacing Then and Now: Part 1: Interfacing to the Process; Part 2: Interfacing to the World**; Mike Doyle[1]; [1]Axiom Analytical, Inc.

3:55 (459) **Spectroscopic Sampling Interfaces used in Pharmaceutical Process Analysis**; Mary Jo Wojtuskik[1]; [1]Axsun Technologies

4:35 (460) **Interfacing Spectrometers: Beyond the Sample**; Zafar Kamal[1]; [1]Thermo Electron

Wednesday Afternoon, Fantasia M
ELECTRON TRANSFER CHEMISTRY OF NANOSTRUCTURED MATERIALS; acknowledgement is made to the donors of the American Chemical Society Petroleum Research Fund, for partial support of this symposium.
Organizer and Presider: Shaowei Chen

3:15 (461) **Barrier Properties of SAMs on Gold Nanoparticle Surfaces**; Bernadette Quinn[1], Serge Lemay[2]; [1] Helsinki University of Technology; [2]Delft University of Technology

3:35 (462) **Irreversibly Adsorbed Adatoms as in situ Surface Probe of Two-Dimensional Domains at Platinum Surfaces**; Enrique Herrero[1], Paramaconi Rodríguez[1], José Solla-Gulón[1], Antonio Aldaz[1], Juan M. Feliu[1]; [1]Universidad de Alicante

3:55 (463) **Room Temperature Ionic Liquid Based Hybrid Materials: Applications in Direct Electrochemistry and Biosensors**; Xianbo Lu[1], Jinghong Li[1]; [1]Department of Chemistry, Tsinghua University

4:15 (464) **Electronic Communication between Redox Centers in Hydrogen-Bonded Systems**; Angel Kaifer, Hao Sun; University of Miami

4:35 (465) **DNA and Carbon Nanotube Self-Assembled Monolayers on Metallic Surfaces: An Electrochemistry and Surface Analysis Study**; Carlos Cabrera[1]; [1]University of Puerto Rico

4:55 (466) **Single-molecule Electron Transport: from Photochemistry to Electrochemistry**; Ling Zang[1], Xiaomei Yang[1], Tammene Naddo[1], Aniket Datar[1], Kaushik Balakrishnan[1]; [1]Southern Illinois University, Dept of Chem

5:15 (467) **Discrete Charge Transfer in Nanoparticle Solids**; Shaowei Chen[1], Sulolit Pradhan[1]; [1]University of California, Santa Cruz

Wednesday Afternoon, Nutcracker 1
PROBES FOR SPECTROSCOPIC BIO-ANALYSIS, sponsored by the Royal Society of Chemistry
Organizer and Presider: John M. Chalmers

3:15 (468) **SERS Nanotags: Multiplexed Biodetection with a Raman-Based Readout**; Michael Natan[1]; [1]Oxonica, Inc.

3:55 (469) **Rapid Characterisation of Bacteria using SERS and Chemometrics**; Roy Goodacre[1], Roger Jarvis[1]; [1]University of Manchester

4:15 (470) **Novel Methods for Molecular Diagnostics by SERRS**; Duncan Graham, Karen Faulds, W. Ewen Smith, Karen McCarney, Alastair Ricketts, Jennifer Dougan, David Thompson, Camilla Karlsson; University of Strathclyde

4:55 (471) **Vibrational Spectroscopic Elucidation of the Gross Biochemistry Associated with Carcinogenesis**; Nicholas Stone[1], Catherine Kendall[1], Mike Sowa[2], Jon Aning[1], Consuelo Hart Prieto[1], Martin Isabelle[1], Geeta Shetty[1], Hugh Barr[1]; [1]Gloucestershire Royal Hospital, UK; [2]Institute for Biodiagnostics, Canada

Wednesday Afternoon, Nutcracker 3
LESTER W. STROCK AWARD: ION GENERATION, TRANSPORT AND DETECTION IN MS
Organizer and Presider: John Olesik

3:15 (472) **New Opportunities in Plasma Source Mass Spectrometry**; John Olesik; The Ohio State

3:35 (473) **New Plasma Based Ionization Sources for Organic Mass Spectrometry**; Francisco Andrade[1], Steven Ray[1], Gerardo Gamez[1], Michael Webb[1], William Wetzel[1], Gary Hieftje; [1]Department of Chemistry, Indiana University

3:55 (474) **Novel RF Ion Containment Strategies for Electron Ionization Mass Spectrometry**; Milton Lee[1], Bingfang Yue[1], Jesse Contreras[1], Alan Rockwood[1,2], Stephen Lammert[1,2], Samuel Tolley[1,2], Dennis Tolley[1], Edgar Lee[1,2]; [1]Brigham Young University; [2]Palmar Technologies

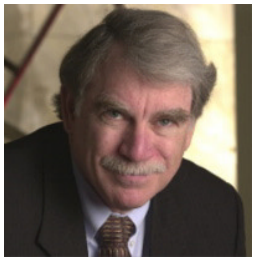
4:15 (475) **Atom and Ion Densities Immediately Upstream from the Sampling Cone of an ICP-MS.**; Jeff Macedone[1], Haibin Ma[1], Paul Farnsworth[1]; [1]Brigham Young University

4:35 (476) **A Comparison of Neutral Atom and Ion Behavior in the First Vacuum Stage of an ICP-MS**; Jordan Olsen[1], Paul Farnsworth[1]; [1]Brigham Young University

4:55 (477) **Gas Flow Simulations via Direct-Simulation Monte Carlo in the ICP-MS**; Ross Spencer, Paul Farnsworth, Jaron Krogel, Jamie Palmer, Adam Payne, Andrew Sampson, William Somers; [1]Brigham Young University

TECHNICAL PROGRAM – THURSDAY
Plenary and Posters

8:00 AM, Plenary Session, *Fantasia G*



Alan G. Marshall

(478) **Ultrahigh-resolution Mass Spectrometry for Separation and Identification of Complex Analytical, Biological, and Environmental Organic Mixtures**; Alan G. Marshall; Florida State University

Alan G. Marshall was born in Bluffton, Ohio in 1944, and grew up through high school in San Diego. He entered the then-new six-year medical program at Northwestern University in 1961, persisted through the first year of medical school, and then left to complete his B.A. degree with Honors in Chemistry in 1965. He completed his Ph.D. in Physical Chemistry from Stanford University in 1970, working with John Baldeschwieler on both NMR and ICR projects. He joined the Chemistry faculty at the University of British Columbia (Vancouver, Canada) in 1969, where he was joined two years later by Melvin Comisarow. In 1973, they collaborated on the invention of FT-ICR mass spectrometry. While in Canada, Alan was ace hitter for the 1978 Canadian Men's Open Volleyball National Champion team. He moved to Ohio State University in 1980 as Professor of Chemistry and Biochemistry and Director of the Campus Chemical Instrument Center. In 1993, he moved to Florida State University, where he is Kasha Professor of Chemistry and Director of the Ion Cyclotron Resonance Program, supported by NSF as a national user facility. Although he has published extensively in several areas of spectroscopy, he is best known for his co-invention (with M. B. Comisarow) and continuing leading development of Fourier transform ion cyclotron resonance (FT-ICR) mass spectrometry. His major recognitions include: Fellow of American Physical Society, Fellow of American Association for the Advancement of Science, Fellow of the Society for Applied Spectroscopy; three American Chemical Society national awards (Chemical Instrumentation, Field-Franklin Award, and Analytical Chemistry Award); two Spectroscopy Society of Pittsburgh Awards (Hasler Award and Spectroscopy Award); the ASMS Distinguished Contribution Award; the International Society for Mass Spectrometry Thomson Medal; and a 60th birthday Honor Issue of the International Journal of Mass Spectrometry. He is the current President of the American Society for Mass Spectrometry, and serves on several editorial boards. He has published three books, three patents, 419 refereed journal articles, and presented 1,250 talks/posters at conferences, universities, government labs, and industry. His papers have been cited more than 13,000 times. His current reseach spans FT-ICR instrumentation development, fossil fuels and environmental analysis, and mapping the primary and higher-order structures of biological macromolecules and their complexes.

THURSDAY POSTER SESSIONS
9:00 – 10:30 AM and 1:45 – 3:15 PM
Fantasia H/J

All Thursday posters should be put up in Fantasia H/J between 7:30 – 8:00 AM and removed between 5:00 – 6:00 PM. If your poster board is an odd number (1, 3, 5, etc.) , the presenting author must be present 9:00 – 9:45 AM and 1:45 – 2:30 PM on Thursday. If your poster board number is an even number (2, 4, 6, etc.), the presenting author must be present 9:45 – 10:30 AM and 2:30 – 3:15 PM on Thursday.

Molecular Mass Spectrometry

Board #

1 (479) **A Validated SPME-GC-MS Method for the Quantification of Four 'Club Drugs' in Human Urine**; Stacy Brown[1], Daniel Rhodes[1], Boyd Pritchard[1]; [1]The Citadel Chemistry Department

2 (480) **Simultaneous Analysis Method of 21 Pesticides using LC/ESI-MS**; Jae Chun Choi[1], Weun Sook Jung[1], Sang Bae Han[1], Chan Soon Kang[1], Hee Ju Choi; [1]Seoul Regional Food & Drug Administration; [2]Korea Health Supplement Association Sub.; [3]Seoul Regional Food & Drug Administratio; [4]Seoul Regional Food & Drug Administration

3 (481) **Analysis of Volatiles in Flavored Coffees by Head Space GC-Ion Trap MS and Liquid Chemical Ionization**; Evaldo DeArmas[1], Marisa Bonilla[1]; [1]Thermo Electron Corporation

4 (482) **Analysis of Volatiles in Flavored Coffees by Static Headspace GC/MS: Are They Really Different?**; Marisa Bonilla[1], Evaldo DeArmas[1]; [1]Thermo Electron Corporation

5 (483) **Electron Monochromator Mass Spectrometry Analysis of Nitro-Aromatic Compounds in Tobacco Smoke**; Kent J. Voorhees[1], A. John Dane[1], Crystal D. Havey[1], Christy Abbas-Hawks[1]; [1]Colorado School of Mines

6 (484) **Complete Electrostatic, Diffusion, and Air Flow Modeling for Ion Mobility: Case Study of Drift Tube Designs**; Jill Scott[1], David Dahl[1,2], Timothy McJunkin[1], Paul Tremblay[1]; [1]Idaho National Laboratory; [2]Retired

7 (485) **Biosignature Identification Using Laser Desorption Fourier Transform Mass Spectrometry and Infrared Spectroscopy**; Jill Scott[1], Beizhan Yan[2], Daphne Stoner[2], Michelle Kotler[3], Nancy Hinman[3], William Bauer[1]; [1]Idaho National Laboratory; [2]University of Idaho; [3]University of Montana

8 (486) **Photosensitized Dimerization of m-dinitrobenzene**; Pranav Trivedi[1], Umesh Chandra Pande[1]; [1]School of Sciences, Dept of Chemistry; [2]Guhjarat University

9 (487) **Why is Automating the Determination of Molecular Ions So Hard and How Might it be Used?**; Michel Hachey[1], Mark Bayliss[1], Vitaly Lashin[1]; [1]Advanced Chemistry Development

10 (488) **A Coaxially-Heated Hollow Fibre Membrane Introduction Mass Spectrometry Interface for Trace Volatile and Semi-volatile Molecules in Air and Water**; Chris Gill[1,2], Alexander Thompson[1,2], Skye Creba[1,2], Robyn Ferguson[1,2], Erik Krogh[1,2]; [1]Malaspina University College; [2]Applied Environ. Research Labs

11 (489) **Membrane Introduction Flame Ionization and Electron Capture Detection (MIFID/MIECD) as a Real Time Monitor for Drinking Water Dis-Infection By-Products**; Chris Gill[1,2], Jason Devlin[1,2], John Amaral[1]; [1]Malaspina University College; [2]Applied Environ. Research Labs

12 (490) **Mass Spectrometry and Biology Combined Tools for Biochemical Markers for Source Identification of Fecal Pollution in Surface Water**; Vesna Furtula[1], Heather Osachoff[1], May Chiu[2], Randy Englar[1], Al Colodey[1]; [1]Pacific Environmental Science Centre, Science and; [2]Commercial Chemicals Division, Environment

13 (491) **Fractal Lotus Leaf Surfaces to Improve Sensitivity of MALDI**; Melissa McLauchlin[1], Mark Hayes[1], Antonio Garcia[1], Tom Picraux[1,2,3], Devens Gust[1]; [1]Arizona State University; [2]Sandia National Laboratories; [3]Center for Integrated Nanotechnology

14 (492) **Clinical Proteomics: Validation of Global Chromatin Modifications as Biomarkers in Chronic Lymphocytic Leukemia (CLL)**; Michael A. Freitas[1], Xiaodan Su[1], David M. Lucas[1], Amy R. Sklenar[1], Mark R. Parthun[1], Michael R. Grever[1], John C. Byrd; [1]The Ohio State University

15 (493) **Differential Analysis of High Resolution Mass Spectrometric Data**; Jennifer Busby[1], Valerie Cavett[1], Jeremiah Tipton[1], Moyez Dharsee[2], Ian Stewart[2], Robert Ewing[2], Bruce Pascal[1]; [1]Scripps Florida; [2]Infochromics

16 (494) **Identifying Protein Nucleotide Binding Sites with Photoaffinity Nucleotide Analogues and High-Resolution Mass Spectrometry**; Jeremiah Tipton[1], Bruce Pascal[1], Jennifer Busby[1]; [1]Scripps Florida

17 (495) **Automated Identification of Multiply Digested Peptides by Comparison Of Theoretical to Observed Peptide Masses**; Bruce Pascal[1], Jennifer Caldwell Busby[1], Jerimiah Tipton[1]; [1]The Scripps Research Institute - Florida

18 (496) **Small Volume Analytical Technique of Affinity Capture IgG Subclass Proteins Separated by CIEF and Offline Couple to MALDI-TOF MS**; Nicole Zwick-Kozup[1], Mark Hayes[1]; [1]Arizona State University[4]

19 (497) **GC/MS Analysis of PAHs in Well Water Samples from the Niger Delta Region of Nigeria**; Chimezie Anyakora, Herbert Coker; [1]University of Lagos; [2]University of Lagos

20 (498) **Ion Distribution Profile in Atmospheric Pressure Photoionization (APPI) Source for LC-MS**; Mahmoud Tabrizchi[1, 2], Michael Blades[1], Damon Robb[1]; [1]The University of British Columbia; [2]Isfaha University of Technology

21 (499) **A Monolithic Phase Based On-line Extraction Approach for Determination of Pharmaceutical Components in Human Plasma by HPLC-MS/MS**; Raymond Xu[1], Leimin Fan[1], Grace Kim[1], Tawakol El-shourbagy[1]; [1]Abbott Laboratories

22 (500) **Novel nanospray emitter design with a custom interface for peptide/protein nanoLC/MS analysis**; Ananya Dubey[1], James Murphy[1], Jeffrey Finch[1], John Gebler[1]; [1]Waters Corporation

23 (501) **Simultaneous determination of Polycyclic Aromatic Hydrocarbons (PAHs) and Chlorinated Pesticides (OCPs) in Sewage Sludge using Gas Chromatography - Tandm Mass Spectrometry**; Zainab Al-Ballam, Murad Helaleh, Ali Al-Omair, Nisar Ahmed; Kuwait Institute for Scientific Research

24 (502) **On Charge Exchange IonizatiAgents for Dopant-Assisted Atmospheric Pressure Photoionization for Reverse-Phase LC/MS**; Michael Blades[1], Derek Smith[1], Damon Robb[1]; [1]University of British Columbia

25 (503) **Pyrolysis GC/MS Analysis of a Halophilic Bacterial Population in an Activated Sludge System**; John Glass Green[1]; [1]The Dow Chemical Company, Louisiana Operations

26 (504) **Direct analysis of drugs and their metabolites by infrared atmospheric pressure matrix-assisted laser desorption ionization mass spectrometry**; Bindesh Shreath[1], Yue Li[1], Akos Vertes[1]; [1]George Washington University

27 (505) **Levitated and dried droplet sample preparation strategies with ionic matrix compounds and common matrices applied to membrane protein sequence coverage**; Diem Ly Van[1], Teresita M. Cruz Sanchez[1], George Agnes[1]; [1]Simon Fraser University

28 (506) **Differential Protein Expression by MALDI-TOF-MS Following The Deposition of Organic Particulate Matter Mimics**; Alice Kardjaputri[1], George Agnes[1]; [1]Simon Fraser University

29 (507) **Evaluation of the Internal Temperature of Protein Cations Exposed to a Hot Dispenser Cathode Employed in Electron Capture Dissociation**; Yong-Hyeon Yim[1], Sunyoung Lee[2], Byungjoo Kim[1], Seonghee Ahn[1], Hun-Young So[1], Han Bin Oh[2]; [1]Korea Research Institute of Standards and Science; [2]Sogang University

Forensic Sciences

Board #

30 (508) **Conversion of Sertraline to N-methyl Sertraline in Embalming Fluid, a Forensic Implication**; Sai Prakash P.K[1], Suma Ramagiri[1]; [1]Osmania University,Department of Chemistry, India

31 (509) **Detection of Explosive Hexanitrohexaazaisowurtzitane (Cl-20) Residues by Surface Laser Photfragmentaion-Fragment Ionization Spectrometry**; R Sausa, J Cabalo [1]; [1]US Army Research Laboratory

32 (510) **Analysis of Forensic Adhesive Tapes by ATR Infrared Spectroscopy**; Hsiu-Hsien Shis[1], Liling Cho[2]; [1]Forensic Science Center, Taipei City Police Depart; [2]Department of Forensic Science, Central

33 (511) **Analysis of Photocopy and Laser Toners by ATR Microspectroscopy**; Liling Cho[1], Chih Chicung Cheng[2]; [1]Dept.of Forensic Sci., Central Police University; [2]Taipei County Government Police Bureau

34 (512) **Determination of Storage Effects on Human Scent using SPME-GC/MS**; Davia Hudson[1], Allison Curran[1], Adee Schoon[2,3], Kenneth Furton[1]; [1]Florida International University; [2]University of Leiden; [3]Canine Unit, Netherlands National Police

35 (513) **Analysis of Lipstick Smears by ATR Microspectroscopy**; Liling Cho[1], Kuo-Chao Hsui[2], Ming-Ju Chuang[3]; [1]Central Police University; [2]Keelung Police Department; [3]Taipei County Government Police Bureau

36 (514) **Laser Photofragmentation Mechanisms of Nitro-Based Explosives**; Maria-Pamela Monterola[1], Benjamin Smith[1], Nicolo Omenetto[1], James Winefordner[1]; [1]University of Florida

37 (515) **Development of Reliable, Contraband Mimics for Biological/Instrumental Training Aids/Calibration Standards using SPME/GC-MS**; Micahel S. Macias[1], Kenneth G. Furton[1]; [1]Florida International University

38 (516) **Characterizing Illicit Drug Residues and Drug Odor Chemicals in Paper Currency**; Jo Nell Aarons[1,2], Ya-Li Hsu[1,2], Kenneth Furton[1,2]; [1]International Forensic Research Institute; [2]Florida International University

39 (517) **Pulsed Glow Discharge Mass Spectrometry Detection for Gas Chromatography: Explosives Analysis**; Megan DeJesus[1], James H. Barnes IV[1], Elizabeth P. Hastings[1], Fred L. King[2], Crist L. Lewis[1]; [1]Los Alamos National Laboratory; [2]West Virginia University

40 (518) **Explosive Recovery Off of Solid Matrices Over Time**; Julie Bitter[2], Kristi George[1,2], C. Douglas Clark[1], Michael Sigman[1,2]; [1]National Center for Forensic Science; [2]University of Central Florida

Raman Spectroscopy

Board #

41 (519) **A Complete Set of Vibrational Assignment for 1,10-Phenanthroline-5,6-Dione**; Uche Udeochu[1], Toiya Jimerson[1], Charles Hosten[1], Alberto Vivoni[2]; [1]Howard University; [2]InterAmerican University

42 (520) **Raman Study of the Variability of the Cobalt Blue Pigment**; Danita de Waal; [1]University of Pretoria

43 (521) **Probing the Effects of Trehalose on Protein Structure in Food Materials using FTIR-ATR and FT-Raman Spectroscopy**; Douglas L. Elmore[1], Sean Smith[1], Carrie Lendon[1], Allen Muroski[1]; [1]Cargill

44 (522) **Comparative Performance of NIR Image Intensified Cameras and InGaAs Arrays for Raman Spectroscopy**; Leslie Tack[1], J. Bruce True[1], M. Bonner Denton[2]; [1]Intevac Corporation; [2]University of Arizona

45 (523) **Raman Spectroscopy – From Spectra to Knowledge**; Gene Hall[1], Michael Boruta[2]; [1]Rutgers University; [2]Advanced Chemistry Development, Inc.

46 (524) **Fluorescence Rejection in Resonance Raman Spectroscopy Using a Picosecond-Gated Intensified CCD Camera**; Freek Ariese[1], Evtim Efremov[1], Joost Buijs[1], Cees Gooijer[1]; [1]Laser Centre Vrije Univ. Amsterdam, Netherlands

47 (525) **UV resonance Raman Examination of Concentration-Dependent Conformational Distributions in the Fs Peptide**; Jonathan Scaffidi[1], Zeeshan Ahmed[1], Alexander Mikhonin[1], Sanford Asher[1]; [1]University of Pittsburgh

48 (526) **Considerations for Raw Material Inspection and Authentication Using Intelligent Portable Raman Systems**; Christopher D. Brown[1], Masud Azimi[1], Peili Chen[1], Kevin Knopp[1], Greg Vander Rhodes[1], Peidong Wang[1], Daryoosh Vakhshoori[1]; [1]Ahura Corporation

49 (527) **Development and Validation of Novel Raman Spectroscopic Methods for Assay of Polymorphic Content in Drug Products**; Xiaohua Zhang[1], Gregory Webster[1]; [1]Pfizer Inc.

50 (528) **Regarding Raman Spectral Intensity Calibration: (A) Cyclohexane Validation Measurements; (B) Treatment of Column-Summed CCD Data**; Wilbur Hurst[1], Steven Choquette[1], Edgar Etz[1]; [1]National Institute of Standards & Technology

51 (529) **Rapid Raman Microspectscopy and Imaging: The Role of the Electron-Multiplied CCD (EMCCD)**; Mayank Tripathi[1], William Finney[2], Kurtulus Golcuk[2], Tso-Ching Chen[2], Michael Morris[2]; [1]Andor Technology; [2]Univ of Michigan

52 (529a) **Enhanced Gas Phase Raman Scattering using Silver Coated Hollow Waveguides;** William F. Pearman[1], S. Michael Angel[1], J. Chance Carter[2]; [1]University of South Carolina; [2]Lawrence Livermore National Laboratory

Thursday Morning, Fantasia A/B
FRONTIERS IN ANALYTICAL SPECTROCHEMISTRY I HONORING GARY HORLICK

Organizers: Michael W. Blades, Ron Williams
Presider: Ron Williams

10:30 (530) **41 Years of Competition, Collegiality, and Collaboration**; Gary M. Hieftje[1]; [1]Department of Chemistry, Indiana University

11:00 (531) **Improving Chemical Analysis With Advanced Detector Technology**; M. Bonner Denton[1]; [1]University of Arizona

11:30 (532) **Application of Microfluidics for Elemental Analysis**; Eric Salin[1], Josiane Lafleur[1]; [1]McGill University

11:50 (533) **Membrane Introduction Mass Spectrometry - Recent Advances and Applications**; Chris Gill[1,2], Alexander Thompson[1,2], Skye Creba[1,2], Robyn Ferguson[1,2], Derek Van Pel[1,2], Owen Stechishin[1,2], Erik Krogh[1,2]; [1]Malaspina University-College; [2]Applied Environ. Research Labs

12:10 (534) **Laser Particle Spectrochemistry**; Nicolo Omenetto[1], Xihong Wu[1], Benjamin Smith[1], James Winefordner[1]; [1]University of Florida, Gainesville, FL

Thursday Morning, Fantasia C
HIGHLIGHTING DIVERSITY IN FORENSIC APPLICATIONS OF MASS SPECTROMETRY

Organizer and Presider: Ruth Waddell

10:30 (535) **Ambient Mass Spectrometry in Forensics and Biology**; Andre Venter[1], R. Graham Cooks[1], Robert J. Noll[1], Ismael Cotte-Rodriguez[1]; [1]Purdue University

10:50 (536) **Analysis of Explosives using Fast Separations and Fast Tandem Mass Spectrometry**; Glen P. Jackson[1], Matthias Beier[1], Olivier Collin[1], Unige A. Laskay[1], Carolyn M. Zimmerman[1]; [1]Ohio University

11:10 (537) **Latent-Print Detection by Macro-Raman Imaging - SERS Active Fingerprint Components and Degradation Products**; Linda Lewis[1], Samuel Lewis[1], Maggie Connatser[2], Ellyn Schuette[1]; [1]Oak Ridge Natioonal Laboratory; [2]University of Tennessee

11:30 (538) **Analysis of Inorganic Oxidizer Salts by ESI-MS**; Michael E. Sigman[1]; [1]University of Central Florida

11:50 (539) **Characterization of Depleted Uranium Oxides Fabricated Using Different Processing Methods to Identify Key Signatures for Nuclear Forensics**; Elizabeth Hastings[1], Cris Lewis[1], John FitzPatrick[1], Lav Tandon[1]; [1]Los Alamos National Laboratory

12:10 (540) **Characterization of Explosives Compounds Using High-Field Asymmetric-Waveform Ion Mobility Spectrometry**; Richard A. Yost[1], Christopher K. Hilton[1], Jared Boock[1]; [1]University of Florida, Department of Chemistry

Thursday Morning, Fantasia D
BIOELECTRONICS AND BIOSENSORS
Organizer and Presider: Erica Forzani

10:30 (541) **Electrical "Visualization" of Biomolecules to the Single Molecule Level with Silicon Nanowire Devices**; Ying Fang[1], Gengfeng Zheng[1], Fernando Patolsky[1], Charles M. Lieber[1]; [1]Harvard University

11:10 (542) **Single Conducting Polymer Nanowire Based Chemical and Biosensors**; Nosang Myung[1], Adam Wanakeya[1], Wilfred Chen[1], Ashok Mulchandani[1]; [1]University of California-Riverside

11:30 (543) **Localization and Detection of Oxidized LDL by MEMS Shear Stress Sensors and In_2O_3 Nanowire/Carbon Nanotube Based FETs**; Mahsa Rouhanizadeh[1], Hongyu Yu[1], Juliana Hwang[1], Eun Sok Kim[1], Chongwu Zhou[1], Tzung Hsiai[1]; [1]University of Southern California

11:50 (544) **Detection of DNA Oligonucleotides on Nanowire Array Electrodes**; Mahnaz El-Kouedi, Aja Andreu, Jon Merkert; [1]UNC-Charlotte

12:10 (545) **Tuning the Chemical Selectivity of SWNT-FET and Polymer Nanojunctions for Selective Heavy Metal Ion Detection**; Larry Nagahara[3], Alvaro Díaz Aguilar[1], Erica Forzani[1], Xiulan Li[1], Peiming Zhang[2], Ruth Zhang[3], Islamshah Amlani[3], Raymond Tsui[3], Nongjian Tao[1]; [1]Dep. of Electrical Engineering & CSSER, ASU; [2]Biodesign Institute, ASU; [3]ESPS, Motorola Labs, Tempe

Thursday Morning, Fantasia E/F
VAPOR GENERATION FOR ATOMIC SPECTROSCOPY
Organizer and Presider: Ralph Sturgeon

10:30 (546) **Fundamental Aspects of Chemical Vapor Generation by Aqueous Tetrahydroborate(III) Derivatization**; Alessandro D'Ulivo[1]; [1]C.N.R., Inst. Chem. & Phys. Processes, Pisa, Italy

11:10 (547) **Arsenic Speciation: an Evaluation of their Determination by Various Techniques**; Ian D. Brindle[1], Roger McLaughlin[1], April Conn[1]; [1]Brock University

11:30 (548) **Generation of Volatile Drivatives with Borohydride-form Anion-exchangers: Possibilities for Simultaneous Determinations by ICP-OES**; Julian Tyson[1], Yustina Rodriguez[1]; [1]UMass Amherst

11:50 (549) **Metal Vapor Generation - Radical Approaches to Mature Techniques**; Ralph Sturgeon[1], Scott Willie[1], Mariana Antunes Vieira[1], Anderson Schwingel Ribeiro[1]; [1]NRC-INMS, Ottawa

12:10 (550) **Investigations of Photochemical Vapor Generation Atomic Absorption Spectrometry**; Neil Fitzgerald; [1]Marist College

Thursday Morning, Fantasia K/L
PROCESS ANALYSIS: NEW SPECTROSCOPIC TECHNOLOGIES
Organizer and Presider: Mark Druy

10:30 (551) **Spectral Resolution Effects on Calibration Quality and Calibration Transfer in Multivariate Optical Computing**; Michael Myrick[1], Luisa Profeta[1]; [1]University of South Carolina

10:50 (552) **From Earth to Mars (and Back): Developing a Raman Analyzer Rugged Enough for Process Analysis**; Norman Wright[1], Robert Hegger[1], Bruce McIntosh[1]; [1]Hamilton Sundstrand

11:10 (553) **Optical Mass Flow Monitor for Pharmaceutical Freeze Drying**; Mark Druy[1], William Kessler[1], Mike Finson[1], Steve Davis[1], Phillip Mulhall[1], Henning Gieseler[2], Michael Pikal[3], David Debo[4], Vincent Bons[4]; [1]Physical Sciences Inc.; [2]University of Erlangen; [3]University of Connecticut; [4]BOC Edwards Pharmaceutical Systems

11:30 (554) **Application of NIR Spectroscopy to the Real Time Monitoring of Pharmaceutical Blend Uniformity: A Mass Balance Approach**; Kevin Bynum, Busolo Wabuyele, Joseph Zilenski, Rosario LoBrutto, Subash Patel, Richard Vivilecchia; [1]Novartis

11:50 (555) **The Application of Variable Filter Array (VFA) Mid Infrared Spectrometers in Process Monitoring**; Paul Wilks[1], Sandra Rintoul[1]; [1]Wilks Enterprise, Inc.

12:10 (556) **A Miniature Raman Spectrometer Engine and Its Industrial Applications**; Richard Crocombe[1], Bill Ahern[1], Dale Flanders[1], David Coppeta[1]; [1]Axsun Technologies

Thursday Morning, Pastoral 1
APPLICATIONS OF NOVEL MATERIALS FOR FLUORESCENCE SPECTROSCOPY
Organizer and Presider: Andres D. Campiglia

10:30 (557) **Linear, Nonlinear, and Excitation Anisotropy Spectroscopic Characterization of Efficient Multiphoton Absorbing Fluorine Derivatives**; Kevin Belfield[1], Mykhailo Bondar[2], Olga Przhonska[2], Sheng Yao[1]; [1]University of Central Florida; [2]Institute of Physics

11:10 (558) **Spectroscopic Investigations of Binary Guanosine Gels**; Elizabeth Morgan[1], Darren Nakamura[1], Yuehua Yu[1], Linda McGown[1]; [1]Rensselaer Polytechnic Institute

11:30 (559) **Application of Dendritic and Hyperbranched Polymers to Chemical Sensing**; Sheryl Tucker[1], Lisa Norton[1], Katrina Kline[1]; [1]University of Missouri

12:10 (560) **Fluorescence Lifetime Enhancement of Organic Chromophores Attached to Gold Nanoparticles**; Florencio E. Hernandez; UCF

TECHNICAL PROGRAM – THURSDAY
Orals 10:30 AM – 12:30 PM and 3:15 – 5:15 PM

Thursday Morning, Pastoral 2
GAS ANALYSIS BY IR SPECTROSCOPY, sponsored by the Coblentz Society, a technical affiliate of SAS
Organizer and Presider: Richard Crocombe

10:30 (561) **One Step Closer to the IR Spectral Nose**; John Coates[1]; [1]Coates Consulting

10:50 (562) **Highly Accurate Trace Gas Measurements Using Cavity Ring-Down Spectroscopy and a Precision Optical Wavemeter**; Chris Rella[1], Serguei Koulikov[1], Sze Tan[1], Edward Wahl[1]; [1]Picarro, Inc.

11:10 (563) **Trace Gas Analysis Using Cavity Ring-Down Spectroscopy**; Wen-Bin Yan[1]; [1]Tiger Optics, LLC

11:30 (564) **Designing a MEMS-scale Photoacoustic Sensor Using a Interband Quantum Cascade Laser**; David Heaps[1], Paul Pellegrino[1]; [1]Army Research Laboratory

11:50 (565) **Near-infrared Optical Sensor for Monitoring NH3 using Wavelength Modulation Spectroscopy**; Mohammadreza Gharavi[1], Steven G Buckley[1]; [1]University of California at San Diego

12:10 (566) **Trace Gas Analysis With Miniaturized Mid-Infrared Sensors: From Ft-Ir To Quantum Cascade Lasers;** B. Mizaikoff[1], C. Young[1], C. Charlton[1], B. Temelkuran[2], G. Dellemann[2], L. Mechold[3], J. Kunsch[3]; [1]Georgia Institute of Technology, School of Chemistry and Biochemistry, Atlanta; [2]OmniGuide Communications, [3]Laser Components GmbH

Thursday Morning, Nutcracker 1
IN SITU RAMAN ANALYSIS IN NON-TRADITIONAL ENVIRONMENTS
Organizer and Presider: Steve Choquette

10:30 (567) **Spectroscopic Monitoring of Polymerization in Microfluidic Channels**; Susan Barnes[1], Zuzanna Cygan[1], Jesse Yates[1], Kathryn Beers[1]; [1]Polymers Division, National Institute of Standards

10:50 (568) **Environmental Monitoring of Deep Sea Hydrothermal Vents using Raman Spectroscopy**; Michelle Meighan[1], Tina Battaglia[1], Karl Booksh[1]; [1]Arizona State University

11:10 (569) **Fluidic Devices Integrated with Uniquely Fabricated Nanocomposite SERS Features**; Michael Sepaniak, R. Maggie Connatser[1], Jenny Oran[1], Nahla AbuHatab[1], Marco DeJesus[2]; [1]University of Tennessee, Department of Chemistry; [2]University of Puerto Rico

11:30 (570) **Surface Enhanced Raman Spectroscopy of Dipicolinic Acid on Silver Colloids Generated by Flow Injection Analysis**; Joy Guingab[1], Young Seok Kim[2], Benoit Lauly[1], Benjamin Smith[1], Nicolo Omenetto[1], James Winefordner[1]; [1]Department of Chemistry, University of Florida; [2]Department of Chemical Engineering

11:50 (571) **Smart Combinatorial Operando Spectroscopy Catalytic System**; Fran Adar[1], Israel Wachs[2], Sukwon Choi[2], Nicholas Burke[1], Sergey Mamedov[1]; [1]Horiba Jobin Yvon; [2]Lehigh University

12:10 (572) **Evaluation of Raman Spectrometry for Monitoring Powder Blending**; Pamela Allan[1], David Littlejohn[1], Alison Nordon[1], Luke Bellamy[1]; [1]University of Strathclyde

THURSDAY POSTER SESSION and BREAK
1:45 – 3:15 PM, see page 64
FANTASIA H

Thursday Afternoon, FantasiaA/B
FRONTIERS IN ANALYTICAL SPECTROCHEMISTRY II HONORING GARY HORLICK
Organizer: Michael W. Blades; Presider: Ron Williams

3:15 (573) **Developing New Tools for Analytical Measurements - A Horlick Legacy**; Michael Blades, [1]University of British Columbia

3:35 (574) **Individual Particle and Correlation Based Measurements: Insight into Elemental Fractionation and Particle Composition**; John Olesik[1]; [1]Ohio State University

3:55 (575) **Speciation with Field-Flow Fractionation Inductively Coupled Plasma Mass Spectrometry**; Ramon Barnes[1], Atitaya Siripinyanond[2]; [1]University Research Institute for Analytical Chem; [2]Mahidol University

4:15 (576) **The Pro-inflammatory Potential of Ambient Particle Types**; George Agnes; [1]Simon Fraser University

4:35 (577) **Looking for Many Elements in Small Samples With a Complex Matrix: It Doesn't Have to be Painful**; James A. Holcombe[1]; [1]The University of Texas

4:55 (578) **Ideal Analytical Spectroscopy**; Gary Horlick[1]; [1]University of Alberta

Thursday Afternoon, Fantasia C
ELECTROPHORETIC SEPARATIONS
Organizer: S. Douglass Gilman; Presider: Mark A. Hayes

3:15 (579) **Microfluidic Bioanalysis Systems Formed Using Sacrificial Layer Methods**; Adam Woolley[1], Bridget Peeni[1], Milton Lee[1], Aaron Hawkins[1]; [1]Brigham Young University

3:35 (580) **Understanding the Utility of Fluorescent Dyes as Noncovalent Labels for Protein Assays by Capillary Electrophoresis with Laser-Induced Fluorescence Detection**; Christa Colyer[1], Weiying Yan[2], Amy Sloat[1], Anthony Gerardi[1], Jennifer Lubbeck[1]; [1]Department of Chemistry, Wake Forest University; [2]Dept of Physiology and Pharmacology, WFU

3:55 (581) **Non-SELEX Selection of Aptamers with Kinetic Capillary Electrophoresis**; Maxim Berezovski[1], Michael Musheev[1], Andrei Drabovich[1], Sergey Krylov[1]; [1]York University

4:15 (582) **Analysis of Environmentally Important Phenolic Compounds by Capillary Electrophoresis using Fused Silica Capillaries Coated with Montmorillonite,** *FACSS Student Honorable Mention*; Maria Fernanda Mora[1], Carlos Garcia[1]; [1]Univ. of Texas at San Antonio

4:35 (583) **Characterization of Selected Aptamer Binding Affinity towards Campylobacter Jejuni Employing Capillary Electrophoresis**; Sun McMasters[1], Dimitra Stratis-Cullum[1]; [1]US Army Research Laboratory

4:55 (584) **Study of Electroosmotic Flow and Electrophoretic Mobility in Discontinuous Solutions in Capillaries Using Periodic Photobleaching of Neutral and Negative Fluorophores**; Yohannes H. Rezenom[1], Gervas E. Assey[1], Funda Kizikaya[1], S. Douglass Gilman[1]; [1]Louisiana State University

TECHNICAL PROGRAM – THURSDAY
3:15 – 5:15 PM

Thursday Afternoon, Fantasia D
ADVANCES IN NEBULIZATION AND PLASMA SPECTROMETRY
Organizer and Presider: Akbar Montaser

3:15 (585) **Developments and Applications of Low and Medium Flow Nebulization for ICP-MS and ICP-AES**; Fred Smith; [1]CETAC Technologies

3:35 (586) **Nano-HPLC-Plasma Mass Spectrometry for Arsenic Speciation**; Ryan Brennan[1], Maryam Farmand[1], Jessica Gray[1], Kaveh Kahen[1], Sue-Ann O'Brien-Murdock[1], Akbar Montaser[1]; [1]The George Washington University

3:55 (587) **The Roles of Evaporation and Aerosol Charging in Approaching 100% Aerosol Utilization from Sub-Microliter Samples in Elemental Analysis and CE-ICP-MS**; Noel Casey[1], John W. Olesik[1]; [1]Ohio State University

4:15 (588) **Ion chemistry and Conformation Change with Spraying Modes in Electrosprays**; Peter Nemes[1], Ioan Marginean[1], Akos Vertes[1]; [1]George Washington University

4:35 (589) **A Dual-Source Inductively-Coupled Plasma/Electrospray Ionization Time-of-Flight Mass Spectrometer for Comprehensive Elemental Speciation**; Steven Ray[1], Gary Hieftje[1], Duane Rogers[1], David Koppenaal[2]; [1]Indiana University, Department of Chemistry; [2]Pacific Northwest National Laboratory

4:55 (590) **LIBS for Quantitative Aerosol Analysis: Plasma Interactions and Analyte Response**; David Hahn[1], Bret Windom[1], Prasoon Diwakar[1]; [1]University of Florida

Thursday Afternoon, Fantasia E/F
INNOVATIONS IN FOURIER TRANSFORM MASS SPECTROMETRY
Organizer and Presider: Richard Cole

3:15 (591) **Infrared Spectra of Gaseous Ions**; John Eyler[1]; [1]University of Florida

3:55 (592) **Development of nLC-dualESI-FT-ICR MS and it Applications in Cancer and Cardiovascular Plasma Proteomics**; David Muddiman[1], Adam Hawkridge[1], Yuko Ogata[2], William Cliby[3], John Burnett[3]; [1]North Carolina State University; [2]Seattle Biomedical Institute; [3]Mayo Clinic College of Medicine

4:15 (593) **Rapid de-novo Terminal Domain Assignment of CAD Fragments from Intact Proteins**; Paul Speir[1], Michael Easterling[1], Christian Berg[1]; [1]Bruker Daltonics

4:35 (594) **Mass Spectral Studies of Bioactive Chromium Peptides**; Carolyn Cassady, Jungie Gao; [1]The University of Alabama

4:55 (595) **Memory of Hydrophobic Component in Lipid-Peptide Binding as Observed by Nano-ES-FT-ICR**; Yan Li[1], Frédéric Heitz[2], Christian Le Grimellec[3], Richard Cole[1]; [1]University of New Orleans; [2]CRBM CNRS-FRE; [3]CBS INSERM

Thursday Afternoon, Pastoral 1
DEVELOPMENTS IN LUMINESCENCE SPECTROSCOPY AND INSTRUMENTATION
Organizer and Presider: Andres D. Campiglia

3:15 (596) **Single Molecule Detection and Spatial Multiplexing: Detection of Rare Events for Clinical Diagnostics**; Steven Soper; [1]Louisiana State University

3:55 (597) **High-Resolution, Low-Temperature Fluorescence Methods: What Can We Learn From Them?**; Freek Ariese[1], Arjen N. Bader[1], Joost de Klerk[1], Cees Gooijer[1]; [1]Laser Centre Vrije Univ. Amsterdam, Netherlands

4:35 (598) **Low-Temperature Luminescence Studies of Europium Complexes with Humic Acids and Well-Defined Model Ligands**; Michael Kumke[1], Bettina Bettina Marmodee[1], Freek Ariese[2], Joost de Klerk[2], Cees Gooijer[2]; [1]University of Potsdam; [2]Vrije Universiteit of Amsterdam

4:55 (599) **New Experimental and Instrumentation Measuring Fluorescence and Phosphorescence Quantum Yields at Liquid Nitrogen and Helium Temperature**; Andres Campiglia[1], Shenjiang Yu[1], Huiyong Wang[1]; [1]Dept. of Chemistry University of Central Florida

Thursday Afternoon, Pastoral 2
ADVANCES IN VIBRATIONAL SPECTROSCOPY, sponsored by the Coblentz Society, a technical affiliate of SAS
Organizer and Presider; Richard Crocombe

3:15 (602) **Terahertz Spectroscopic Imaging for Non-Destructive Pharmaceutical Film Coating Analysis**; Ryanne N. Forcht[1], Robert P. Cogdill[1], Richard Creekmore[2], James K. Drennen[1]; [1]Duquesne University; [2]AstraZeneca

3:35 (604) **Imaging-Based Algorithms for Determining the Uniformity of Drug Products and Blends**; Mazen L. Hamad[1], Christopher D. Ellison[1], Mansoor A. Khan[1], Robbe C. Lyon[1]; [1]Food and Drug Administration/CDER/OTR/DPQR

(600) **Withdrawn - Terahertz Attenuated Total Reflection Spectroscopy**; David Newnham[1], Axel Zeitler[1], Philip Taday[1]; [1]TeraView Limited; [2]University of Cambridge, England; [3]University of Otago, New Zealand

(601) **Withdrawn - Terahertz Attenuated Total Reflection Spectroscopy for Pharmaceutical Analysis**; J Axel Zeitler[1,2,3], Mike Claybourn[4], David A. Newnham[3], Philip F. Taday[3], Michael Pepper[2,3], Keith C. Gordon[5], Thomas Rades[1]; [1]School of Pharmacy, University of Otago, NZ; [2]Cavendish Lab, University of Cambridge; [3]TeraView Limited, Cambridge, UK; [4]AstraZeneca, Macclesfield, UK

(603) **Withdrawn - Hyperspectral Imaging of Obliterated Writing**; Diane Williams[1], Hina Ayub[2]; [1]Federal Bureau of Investigation; [2]ORISE

Thursday Afternoon, Nutcracker 1
COMBINING RAMAN AND SCANNING PROBE MICROSCOPY – ARE WE THERE YET?
Organizer and Presider: Andrew Whitley

3:15 (605) **Advances in Vibrational Spectroscopic Spatial Resolution and Measurement Speed Using Raman Microscopy and AFM Tip-Enhanced Raman Spectroscopy (TERS);** Andrew Whitley[1], Eunah Lee[1], Fran Adar[1], [1]Horiba Jobin Yvon, Inc.

3:35 (606) **Raman Microscopy and Raman NSOM: Chemical Imaging on the Nanometer Length Scale**; Alan Campion; The University of Texas at Austin

3:55 (607) **Scanning Nano-Raman Spectroscopy of Silicon and Other Semiconducting Materials**; Alexei Sokolov[1], Nam-Heui Lee[1], Ryan Hartschuh[1], Disha Mehtani[1], Alexander Kisliuk[1], Mark Foster[1], John Maguire[2]; [1]University of Akron; [2]AirForce Research Laboratory

4:15 (608) **Tip enhanced Raman Spectroscopy - Applications for Life Science**; Volker Deckert[1]; [1]ISAS - Institute for Analytical Sciences

4:35 (609) **Raman/AFM - TERS: Understanding and Optimizing Measurement Conditions to Obtain High Spectral Contrast**; Razvigor Ossikovski[1], Quang Nguyen[1], Joachim Schreiber[2]; [1]Ecole Polytechnique; [2]Horiba Jobin Yvon

4:55 (610) **Investigation of Apertureless NSOM for Measurement of Stress in Strained Silicon**; Robert Geer[1], Colin McDonough[1], Jacob Atesang[1]; [1]College of Nanoscale Sci & Eng, UAlbany

ABSTRACTS

(1) **Spectroscopy on the Red Planet: More than Meets the Eye**

Harry Y. McSween Jr.; University of Tennessee

Remote sensing of Mars is accomplished using a variety of spectroscopic instruments on orbiting and landed spacecraft. This presentation focuses on the Mars Exploration Rovers (MER), which have been operating on the Martian surface for more than two years. The landing sites for both rovers were selected to test the hypothesis that liquid water was once present. Spirit has explored Gusev Crater, thought to have contained an ancient lake, and Opportunity has examined Meridiani Planum, a site with abundant hematite thought to have formed by interaction with water. MER spectroscopic instruments are: Pancam, a digital imaging system of two CCD cameras and filter wheels capable of obtaining visible/near-infrared spectra using 11 filters ranging from 0.4 to 1.0 microns; Mini-TES, a Michelson interferometer that collects thermal infrared spectra from 5 to 29 microns; an Alpha Particle X-ray Spectrometer (APXS) that measures Rutherford backscattered alpha particles and characteristic X-rays using a silicon drift detector; and a Mössbauer Spectrometer, which counts recoilless emission and absorption of gamma rays by 57Fe nuclei. The rovers also carry a Microscopic Imager (a fixed-focus CCD camera acquiring images with a spatial resolution of 31 microns/pixel) and a Rock Abrasion Tool to brush off dust or grind away weathering rinds. Spirit found volcanic basaltic rocks with varying degrees of aqueous alteration, but not the expected lakebed sediments. Opportunity discovered outcrops of evaporates – salts (mostly sulfates and halides) formed by precipitation from evaporating brines. The hematite seen from orbital spectroscopy occurs as a lag deposit of concretions weathered out of the outcrops. The sample characterization afforded by these spectroscopic techniques is unprecedented, and demonstrates the utility of mineralogical and geochemical spectroscopy in robotic planetary exploration.

(2) **Self-Modeling Curve Resolution (SMCR) by Hybrid Genetic Algorithms (HGA)**

Hideyuki Shinzawa[1], Makio Iwahashi[2], Yukihiro Ozaki[1]; [1]Kwansei-Gakuin University, [2]Kitasato University

Hybrid Genetic Algorithms (HGA) is introduced for initial estimates in Self-Modeling Curve Resolution (SMCR). HGA aims to search the optimal initial estimate, such as concentration profile or pure spectra, in SMCR procedures. By generating multiple populations representing candidates for the optimal solutions and effects of GA operators, crossover and mutation, GA avoids getting stuck in the local minimum in a search space. In this study, Hybrid GA, connecting GA technique with Alternating Least Squares (ALS) is proposed. By connecting GA with ALS algorithms, these populations effectively search the optimal solutions which minimize the residuals between global phase angle of the original spectra and that of the reconstructed spectra. This error criterion effectively brings its result a firm link between a mathematical decomposition and a real physical model. The effects of SMCR with HGA are discussed with near-infrared (NIR) spectra of mixture solutions of oleic acid and ethanol. Its result is also compared with SMCR by Evolving Factor Analysis (EFA). HGA clearly shows the better resolution performances than that of EFA. It is also revealed a physical model in the solution. Namely, pure concentration profiles indicates that oleic acid tends to form a complex with sufficient ethanol. The results show that the SMCR with HGA is effective tool for the cure resolution. This may create a new dimension for the development of two-way resolution techniques.

(3) **Perturbation-Correlation Moving-Window Two-Dimensional Correlation Analysis Applied to Temperature-Dependent IR Spectra of Cellulose I beta**

Akihiko Watanabe[1,2], Shigeaki Morita[1], Yukihiro Ozaki[1]; [1]Kwansei Gakuin University, [2]Yasuma Co. LTD

Infrared (IR) spectra were measured for cellulose I beta prepared from the mantle of Halocynthia roretzi over a temperature range of 30-260 deg. C (at every 1 deg. C increments, total 231 spectra) to explore the temperature-dependent changes in OH---O(H) hydrogen bonds (H-bonds). Perturbation-correlation moving-window two-dimensional (PCMW2D) correlation spectroscopy (Morita, S. et al., Appl. Spectrosc. 2006, 60, 398.) was utilized to analyze the complicated spectral variations in the O-H stretching region where many bands arising from OH groups with various types of H-bonds overlap. The PCMW2D correlation analysis is characterized by synchronous and asynchronous PCMW2D correlation spectra spread on a plane between a spectral variable (e.g., wavenumber) axis and a perturbation variable (e.g., temperature) axis. This future of the PCMW2D correlation analysis made it possible to extract useful information about temperature-dependent changes in the OH---O(H) H-bonds in cellulose, which never be obtained from the raw spectra. It is revealed that the phase transition of cellulose I beta at 220 C, which was reported by Wada (Wada, M. J. Polym. Sci, Part B: Polym. Phys. 2002, 40, 1095.) is induced by the drastic disruption of the intrachain H-bonds. Thus, it has been demonstrated that the PCMW2D correlation spectroscopy is a powerful tool for the elucidation of the thermal behavior of OH---O(H) H-bonds in cellulose.

(4) **Biophysical Studies on Mutated Surfactant Protein C Using Infrared Spectroscopy and 2D Correlation Analysis**

Yu Zhu[1], Saratchandra Shanmukh[1], Shin-ichi Morita[1], John E Baatz[2], Richard A Dluhy[1]; [1]Chemistry Department, University of Georgia, [2]Dept Pediat, Div Neonatol,Med Univ S Ca

Surfactant protein C (SP-C) is a small (4.2kDa) unique hydrophobic protein presenting in pulmonary surfactant and has been shown to be important for normal lung breathing functionalities, such as reducing surfactant potential, promoting adsorption, spreading and stability of the lipid lining in lung. Amyloid fibril formation of mature SP-C has been detected under pathological conditions and is believed to contribute to the failure in proper lung functioning. The molecular structure of mature SP-C consists of 1) two palmitoylated Cysteine residues surrounded by two Prolines at the N-terminus, 2) a positively charged Lys-Arg pair, 3) a very hydrophobic poly-valine alpha-helix segment, and 4) a heptapeptide C-terminus. The poly-valine segment is metastable and has an intrinsic tendency to form beta-sheet. Palmitoylation at the N-terminus of mature SP-C appears to stabilize the alpha-helix from aggregating into beta-sheets. [1] Work done previously by our group has revealed a pH-dependent mechanism of amyloid fibril formation of deacylated SP-C (dSP-C). [2] However, the detailed molecular mechanism of amyloid fibril formation of SP-C remains unclear. We present here a further investigation of the pH-dependence of amyloid fibril formation of a mutated (V20/A20) recombinant of deacylated SP-C, using infrared spectroscopy (IR) at the air/water interface combined with 2D IR correlation analyses. The present results showed an alpha to beta conformational change with increasing pH, similar to the results of our study on dSP-C. [2]However, it is apparent that even a single mutation (V20/A20) in the hydrophobic polyvaline segment of dSP-C has resulted in significant changes in the secondary structure. Based on 2D IR analyses of the spectra, beta-turns have been assigned to be the major component of the secondary structures. Further studies on a series of mutants of SP-C will be undertaken and in the mimic biological membrane environment of phospholipids.

References:Johansson, J., Structure and properties of surfactant protein C. Biochimica Et Biophysica Acta-Molecular Basis of Disease, 1998. 1408(2-3): p. 161-172. 2. Dluhy, R.A., et al., Deacylated pulmonary surfactant protein SP-C transforms from alpha-helical to amyloid fibril structure via a pH-dependent mechanism: An infrared structural investigation. Biophysical Journal, 2003. 85(4): p. 2417-2429.

(5) **Moving Window Correlation Analysis of Photoluminescence Images of Biotinylated CdTe – Streptavidin Au Bioconjugates**

Alyssa Thomas[1], Hugh Richardson[1]; [1]Dept of Chemistry and Biochemistry Ohio University

The unique properties of quantum dots (size dependent optical properties1-2) and metal nanoparticles (thermooptical properties3-4) make them ideal candidates for biological applications. Surface modifications employing biological molecules allow for the formation of bioconjugates for diagnostic assays, cell labeling, and imaging5. Due to its high binding affinity and specificity6, streptavidin and biotin are often the receptor – ligand pair used to make bioconjugates. Characterization of the bioconjugates is essential prior to their incorporation into current applications, as well as the development of new assays. Raman and photoluminescence imaging were used to characterize bioconjugates of biotinylated CdTe quantum dots and commercially available streptavidin – Au nanoparticles that were 50 nm in diameter. Resulting photoluminescence images also show Raman peak contributions. A moving window correlation analysis of the images allows for the separation and characterization of the photoluminescence and Raman contributions for each species of the bioconjugates. [1] M. Bruchez Jr., M. Moronne, P. Gin, S. Weiss, A.P. Alivisatos, Science 281 (1998) 2013\r\n[2] W. C. W. Chan, S. Nie. Science 281 (1998) 2016 [3] H. H. Richardson, Z. N. Hickman, A. O. Govorov, A. C. Thomas, W. Zhang, M. E. Kordesch, Nano Letters 6 (2006) 783 [4] J. Lee, A. O. Govorov, N. A. Kotov, Agnew. Chem. 117 (2005) 7605 [5] See reviews R.C. Doty, D. G. Fernig, R. Lévy, Cell. Mol. Life Sci. 61 (2004) 1843; R. E. Bailey, A. M. Smith, S. Nie, Physica E 25 (2004) 1; and J. L. West, N. J. Halas, Curr. Opin. Biotechnol. 11 (2000) 215 [6] C. Yuan, A. Chen, P. Kolb, V. T. Moy, Biochemistry 39 (2000) 10219

(6) **2D Correlation Analysis of Thin Film Water on alpha-Al2O3 (0001): A Theoretical Comparison**

Alyssa Thomas[1], Hugh Richardson[1]; [1]Dept of Chemistry and Biochemistry Ohio University

The spectral characteristics of thin film water adsorbed onto alpha-Al2O3 (0001) were investigated using attenuated total reflection spectroscopy. Extinction spectra were collected as the water vapor was changed using a controlled temperature bath [1]. Isotherms for different temperatures were generated using relative humidity and coverage values determined by spectral heights and scaled using a BET analysis for appropriate surface area. The spectral heights were determined by comparing the experimental spectra to calculated spectra using bulk water optical constants [2]. The band shapes for the experimental spectra are noticeable different than those calculated using bulk water as a model. The extinction spectra also indicate three distinct regions: molecular (coverages that approach a monolayer), intermediate (coverages between 1 and 15 water layers), and bulk-like (coverages greater than 15 water layers). A 2D correlation analysis of the difference between the experimental spectra and the calculated spectra in each region allows for elucidation of areas with similar properties, as well as the correlation between modeling thin film water with bulk like water optical constants.

(7) **Characterization of Interaction in Weakly Interacting Block Copolymer by Two-Dimensional Hetero-Spectral Analysis of Wide Angle X-Ray Scattering and Infrared Spectroscopy**

Hye Jeong Kim[1,3], Young Mee Jung[2,4], Jin Kon Kim[1,3], Seung Bin Kim[2,3]; [1]Department of Chemical Engineering, [2]Department of Chemistry, [3]Pohang University of Science and Technol, [4]Kangwon National University

We investigated, via two-dimensional hetero-spectral correlation analysis of wide angle X-ray scattering (WAXS) and infrared (IR) spectroscopy, the specific chemical interaction existing in weakly interacting polystyrene-block-poly(n-pentyl methacrylate) copolymer (PS-PnPMA). PS-PnPMA was shown to exhibit a closed-loop type phase behavior, 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 specific interaction between PS and PnPMA block is mainly arising from the dipole in the benzene ring of PS and the induced dipole in the PnPMA due to the cluster formation with a size of 1~2 nm. We found that the synchronous 2D WAXS-IR hetero-spectral correlation spectrum of the ordered state was completely different from that in the two disordered states. The CH group of the main chains of PS and PnPMA did not contribute to the cluster formation in the two disordered states, indicating that the main chains of PS and PnPMA blocks were randomly distributed in the two disordered states. However, only the C=C group in the PS block contributed to the cluster at a disordered state below the LDOT, whereas both the C-C-O group in PnPMA and the phenyl ring as well as the C=C group in PS contributed to cluster formation at another disordered state above the UODT. Thus, the probability that PS (and PnPMA) chains were located at their own neighboring chains at one disordered state above the UODT is larger than that at another disordered state below the LDOT.

(8) **Detection of Fires Aboard Naval Vessels using Cermet Sensor Arrays**

Kirsten Kramer[1], Susan Rose-Pehrsson[1], Mark Hammond[1], Kevin Johnson[1], Daniel Gottuk[2], James Lynch[2], Duane Tillett[3], Holger Streckert ; [1]Naval Research Laboratory, [2]Hughes Associates, Inc., [3]General Atomics

The development of robust and reliable gas sensors would allow for a decrease in the manpower required to monitor and control fires or other hazards aboard naval vessels. Sensor arrays containing four cermet (ceramic-metallic) sensors are being developed to detect changes in the air quality of the ship's compartment and to alarm if the sensor response indicates the presence of a fire or a hazardous gaseous compound. Each of the four sensors is composed of a specific combination of either yttria stabilized zirconia (YSZ) or tungsten bismuth oxide (WBO) solid electrolytes sandwiched between Pt or Pt/Pd electrodes. Cyclic voltammetry is used to probe the four sensors, resulting in an oxidation/reduction response spectra for each analyte. The CV method along with the ability to flash heat the sensors provides continual renewal of the surface of the sensor for long term use. The raw data is processed by background subtraction of a clean air voltammogram from the response of each sensor and the four signals are concatenated to produce one high-resolution data vector containing many features. Chemometric techniques are used for data compression and analysis. Principal Component Analysis (PCA) and the wavelet transform are compared for their abilities to extract and compress the features of the data. Feature selection is carried out using analysis of variance (ANOVA), and a Probabilistic Neural Network (PNN) is used for classification. The main challenge in this analysis is distinguishing fire hazards from nuisance sources such as nearby welding or grinding activities. Data collected in both a laboratory

environment and aboard a naval vessel are used to train classifiers that are validated with an external set of prediction data. As many as five prototype sensor units are compared in order to evaluate sensor-to-sensor reproducibility. When compared to various commercial smoke detectors in terms of accuracy and response time, results indicate that the sensors are particularly useful for the early detection of slow-growing, smoldering fires. The gases and vapors generated by the smoldering fire are detected before the smoke can diffuse to the smoke detectors. Cermet sensors have the advantages of being low-cost, light-weight, and rugged, and are able to detect many harmful gaseous compounds in the parts-per-million to parts-per-billion range, potentially allowing them to serve as both fire detectors as well as air quality monitors.

(9) **Investigation of Bagged Kernel Partial Least Squares (KPLS) and Boosting KPLS**

Hideyuki Shinzawa[1], Jian-Hui Jiang[2], Pitiporn Ritthiruangdej[3], Yukihiro Ozaki[1]; [1]Kwansei-Gakuin University, [2]Hunan University, [3]Kasetsart University

The effects of ensemble learning methods, bagging and boosting, on kernel partial least squares (KPLS) regression are investigated. The proposed methods built regression models by ensembling a series of 'weak' hypothesis. For example, in bagging KPLS, several samples in a training set are picked out randomly and used to make a hypothesis. In this process, the overlapping of the picked samples is allowed. A hypothesis is made with these picked samples by KPLS. Finally, an ensemble prediction is made with numerous hypotheses by taking their average. In boosting KPLS, samples in a training set are picked out (with overlapped) with the probability which is obtained by the previous hypothesis. For example, if the prediction result of a specific sample with the previous hypothesis is poor, the probability of the sample is replaced by high probability to be trained more intensively. Finally, an ensemble prediction is made by weighted median of the collected numerous hypotheses. By combining these ensemble learning methods and kernel function, it enables to make a KPLS regression model less sensitive to over-fitting. The abilities of bagged KPLS and boosting KPLSR are investigated with two near-infrared (NIR) spectroscopic data sets by comparing with other methods, standard PLS, bagged PLS, boosting PLS and KPLS. The results reveal that bagged KPLS and boosting KPLS yield superior regression performances to standard PLS. Especially, boosting KPLS indicates clear improvements over to PLS, bagged PLS boosting PLS, KPLS and bagged KPLS.

(10) **Spectral Studies of Enantiodiscrimination with Chiral Ionic Liquids**

Jody Harvey[1], Marianna Busch[1], Kenneth Busch[1] ; [1]Baylor University

With the advent of single-enantiomer drugs, rapid screening methods of chiral analysis are urgently needed by the pharmaceutical community. For this purpose, spectroscopic methods are most desirable. Previous work by our group has successfully demonstrated that multivariate regression modeling (PLS-1) of spectral data can be used to determine the enantiomeric composition of an analyte in the presence of a chiral auxiliary. In our early studies, various cyclodextrins were used as auxiliaries. While CDs have been widely studied as chiral selectors, they have some major limitations when it comes to enantiodiscrimination. First of all, CDs have limited solubility in water so the concentration of diastereomeric adducts that form in solutions containing cyclodextrins is relatively low. Secondly, inclusion complexes formed with naturally occurring CDs have limited enantioselectivity because there is often limited interaction between the chiral centers of the cyclodextrin and those of the guest molecule. Finally, since inclusion complexation is needed to produce diastereomeric effects, different chiral guest molecules require CDs with different cavity sizes. These problems can potentially be overcome by using chiral ionic liquids (CILs) as solvents to produce a chiral environment without the need for inclusion complex formation. These novel solvents are ideal for chiral discrimination because they can interact with chiral solutes by a wide variety of intermolecular interactions, including hydrogen bonding, pi-pi and n-pi interactions, dipolar interactions, electrostatic interactions, and hydrophobic interactions. This paper will discuss our efforts to use CILs in conjunction with regression modeling of spectral data to provide mathematical models to predict enantiomeric composition of analytical samples.

(11) **A Practical Algorithm to Remove Cosmic Spikes in Raman Imaging Data for Pharmaceutical Applications**

Lin Zhang[1], Mark Henson[1]; [1]Pfizer Global R&D

Raman dispersive microscopic imaging techniques are finding ever-increasing applications in pharmaceutical research for their capability to provide spatial and spectral information about the sample. Multivariate data analysis methods are widely used to extract chemical information from the image cube. However, charge-coupled device detectors generate spikes arising from cosmic ray events, which are superimposed on chemically meaningful spectra. Some extremely challenging cosmic spikes are found to seriously interfere with multivariate data analysis for our application, e.g., spikes with greater bandwidth than the band of interest, spikes in neighboring pixels occurring at the same spectral channels, spikes right on top of the band of interest, etc. A practical algorithm is proposed in the presentation for cosmic spike removal. The algorithm is computationally efficient, conceptually simple and easy to implement. It eliminates the need for time-consuming repetitive measurements by taking advantage of the spatial characteristic of imaging techniques and existing knowledge from the formulation. The algorithm will be illustrated by the analysis of Raman imaging of pharmaceutical samples. The algorithm has been shown to generate recovered spectra with negligible spectral distortion.

(12) **The Harmony/Parsimony Tradeoff in Multivariate Calibration**

John Kalivas[1], Forrest Stout[1]; [1]Idaho State University

For multivariate calibration, it is often necessary to determine the degrees of freedom for parsimony consideration and for the error measure root mean square error of calibration (RMSEC). This presentation shows that this can be accomplished by effective rank (ER). This presentation also shows that when such a measure is used on the x-axis, simultaneous graphing of regression diagnostics is possible for ridge regression (RR), partial least squares (PLS), principal component regression (PCR), and others thereby allowing a fair comparison between all potential models. It is often noted that by selecting variables, more parsimonious models are obtained; typically by multiple linear regression (MLR). By using the ER, this is shown to not always be the case. Additionally, a harmony measure is discussed in this presentation that expresses the bias/variance tradeoff for a particular model. By plotting this new measure against the ER, a model with a proper harmony/parsimony tradeoff can be determined. That is, an important problem with many multivariate calibration methods, such as RR, PCR, and PLS, is selection of acceptable meta-parameter values as well as variable selection. The harmony/parsimony plot is shown to provide a mechanism to accomplish this. The presentation emphasizes that pluralistic criteria for characterizing and evaluating models is better than a dualistic or a single criterion approach which is the usual

method. Results are presented using spectral, industrial, and quantitative structure activity relationship data.

(13) **Water Sorption Process into a Biocompatible Polymer Film: Self-Modeling Curve Resolution Analysis of ATR-IR Spectra**

Akiko Tanabe[1], Shigeaki Morita[1], Masaru Tanaka[2], Yukihiro Ozaki[1]; [1]Kwansei-Gakuin University, [2]Hokkaido University

It has been said that highly biocompatible polymer materials have special hydration structures. Most tightly bound water is called "non-freezing water", which does not freeze until ca. –100 oC. Sorbed water that can freely move is called "freezing water", which freezes around 0 oC, same as bulk water. Besides these well-known hydrated waters, there exists another type of water, called "freezing bound water", which shows the cold crystallization and is unique to the biocompatible materials. Time-resolved in-situ ATR-IR spectra of water sorption process into a highly biocompatible polymer, poly(2-methyoxyethyl acrylate)(PMEA), allowed us to assign non-freezing water to 3600 cm-1, freezing bound water to 3400 cm-1, and freezing water to 3200 cm-1 (Morita, et al., submitted). In the original OH stretching region, these bands are heavily overlapped, but they were reasonably separated by the difference spectra of time-resolved series spectra. By using self-modeling curve resolution (SMCR) by means of alternating least squares (ALS), we investigated how much each water component was contained in the original broad OH stretching band. As a result, it was found that the freezing bound water was contained in the largest amount, and the relative amount of those three waters is consistent with another literature, determined by the gravimetric method and the differential scanning calorimetry (DSC) measurements (Tanaka, et al., J. Biomed. Mater. Res., 2004, 68A, 684-695). Changes of the fitted coefficients (i.e. amplitudes) with elapse of time described the kinetics of sorption processes of these waters very well; non-freezing water becomes saturation very quickly, and after that, freezing bound water appears, and finally, after some latency period, freezing water gets sorbed, and the amount slowly increases.

(14) **Application of Row-wise Constraints in Multivariate Curve Resolution for Spectral Un-mixing of Highly Overlapped Components***

David Melgaard; [1]Sandia National Laboratories

Instrument and environmental artifacts in addition to typical molecular interactions and spectral overlap can make spectral unmixing a daunting task. For some cases Multivariate Curve Resolution (MCR), offers the only choice for resolving pure component species for spectral data sets where limited concentration or spectral information renders traditional multivariate methods ineffective. However the rotational ambiguity of MCR requires the application of realistic constraints to coerce the alternating least squares algorithm to converge to a realistic solution. The proper application of constraints consistent with the knowledge of the true pure components of the data set continues to be active and important areas of development and understanding of MCR. One important aspect of spectral data is the realization of individual peaks within prescribed frequency regions which lends itself to the application of the row-wise monotonic and unimodality constraints. The row-wise constraints are differentiated from nonnegativity and equality constraints because they are applied over adjoining frequencies while the other constraints are unaffected by those values. In this presentation we will discuss the application of row-wise constraints and present results demonstrating their effectiveness in resolving highly overlapped peaks. Also by revealing the convergence pattern of the algorithm, we will show the importance of understanding the range of solutions within the prescribed convergence criteria and constraints. *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.

(15) **Chiral Analysis by Regression Modeling of Fluorescence Spectral Data Obtained with a CCD Fluorescence Spectrophotometer**

Selorm Modzabi[1], Marianna Busch[1], Kenneth Busch[1] ; [1]Baylor University

Rapid screening methods for determination of enantiomeric excess are urgently needed for catalyst evaluation in asymmetric synthesis. For this purpose, spectroscopic methods are most desirable. Previous work by our group has successfully demonstrated that chiral analysis by regression modeling of spectral data (CARMSD) can be used to develop regression models that can predict the enantiomeric composition of unknown chiral analytes solely on the basis of ordinary spectral data. In these early studies, individual samples with different enantiomeric compositions were prepared and the spectra were taken with standard commercial spectrometers, using standard spectrophotometer cells. This was time-consuming, and required relatively large amounts of sample, making the method less than satisfactory for high-throughput screening. In this paper, we explore various ways of making fluorescence measurements with a CCD fluorescence spectrophotometer to provide a rapid and sensitive means of determining the enantiomeric composition of small samples of chiral analytes. The basic instrumentation will be described and the chemometric models developed from the fluorescence spectral data will be discussed.

(16) **Whole Product Analysis by 1H NMR and Multivariate Statistics**

Laura H. Lucas[1], Molly P. Armstrong[1], Mike Rothgeb[1], Carrie Furnish[2], Charles D. Eads[2]; [1]Procter and Gamble, Household Care Analytical, [2]Procter and Gamble, Discovery Analytical

Solution-state 1H NMR spectroscopy was used to study the compositions of liquid cleaning products. Products were analyzed "as is," requiring only dilution with an appropriate NMR solvent mixture. Each product gives rise to a unique NMR fingerprint that serves as a basis for classification of products of different composition. Programs have been developed that batch process NMR spectra with the use of a single command in MatLab, thus greatly improving throughput. Multivariate analysis (principal components analysis or PCA) was used to group the products and model their classification based on composition. Additional software tools were developed to compare other products to those in the models to qualitatively assess product composition changes. The models were demonstrated to be sensitive and robust for detecting small changes in product composition. We have been able to discern and quantify analyst variability, instrument variability and manufacturing variability to ensure that such variability is small relative to real compositional changes. Additional validation was performed by comparing results obtained by NMR for a series of products relative to those obtained by traditional wet chemistry methods. The developed methods are directly applicable to analysis of liquid or solid-state samples by a variety of analytical techniques for routine monitoring and quality control of whole products.

(17) **Determination of the Enantiomeric Composition of High-Percentile Range Samples by Multivariate Regression Modeling of Spectral Data**

Jemima Ingle[1], Marianna Busch[1], Kenneth Busch[1]; [1]Baylor University

Rapid, high-throughput methods of chiral analysis are increasingly needed by the pharmaceutical industry to establish the purity of single-enantiomer drugs as required by regulatory agencies like the U.S. Food & Drug Administration. Previous work by our group has successfully demonstrated that multivariate regression modeling (PLS-1) of spectral data can be used to determine the enantiomeric excess (ee) of an analyte in the presence of chiral auxiliaries like cyclodextrins. In our previous studies, we developed regression models using calibration samples that spanned a wide range of possible mol fractions, typically from 0.05R:0.95S to 0.95R:0.05S. However, many potential applications for chiral analysis call for the determination of the enantiomeric composition of a sample that is mostly one enantiomer, contaminated with small amounts of its antipode. In this study, we investigate the accuracy of regression models developed with calibration samples that cover just the high-percentile range from 90 - 100 % of one enantiomer. In this study, we will compare the prediction results obtained for high-percentile (90%-100%) validation samples using regression models developed with calibration samples that span a wide range of enantiomeric compositions against the results obtained with regression models developed with calibration samples that span the limited range from 90%-100%. Both the absolute and percent relative errors will be compared with both sets of regression models.

(18) **Interactive Self-modeling Image Analysis**

Willem Windig[1], R. Scott Koch[1]; [1]Eigenvector Research, Inc.

Chemical imaging is of increasing importance. The amount of data generated is overwhelming. For example, secondary ion mass spectrometry (SIMS) image data contains hundreds of masses, each representing an image and thousands of spectra. Therefore tools are needed to reduce the data into a manageable amount. One such tool is self-modeling mixture analysis. Since this type of data is often noisy, iterative chemometric tools that facilitate the use of expert knowledge are desirable. We will here demonstrate PLS_Toolbox function purity, enhanced with image analysis capabilities. The purity program applied to a SIMS data set with, in the example used, 600 masses/images and 4032 spectra (63×64 pixels) , will express the data set in a limited number of chemically meaningful images, typically 3-5, and associated spectra, without loss of information. The approach is based on the purity concept. A pure mass is a mass that has contributions from only one of the components in the mixture data set. Pure masses can be used as the estimate of the contributions ('concentrations') of the component in the mixture spectra. With classical least squares the spectra of the pure components of the mixtures can now be resolved. Pure variables can be found by simple mathematical means. Similarly, one can determine pure spectra/pixels and resolve the mixture data. This poster will show the pure spectrum/pixel approach. The purity program shows an image representing the complete mixture data. When a pure pixel is selected the next image will eliminate the component represented by that pixel and the image will show the remaining components. The image will represent only noise after all the components have been selected. The use of pure spectra/pixels has the advantage of the image representation during the interactive process. However, the pure spectrum/pixel approach has the disadvantage that the pure(st) spectra selected do not necessarily represent chemically pure components. Therefore, the program has a second resolution step, converting the pure spectrum/pixel solution into a pure variable (mass) solution. Since the pure variable concept is valid for mass spectra, properly resolved images and spectra will result.

(19) **New Approach for Spectroscopic Analysis Applied to Infrared Spectroscopy**

Marie Scandone[1], Gregory Banik, Ph.D.[1], Ty Abshear[1], Omoshile Clement, Ph.D.[1]; [1]Bio-Rad Laboratories, Inc., Informatics Division

Methods such as Principal Component Analysis (PCA) to perform multivariate analyses on spectral and chromatographic data have been a mainstay of chemometrics for years. This presentation describes a new method that combines cheminformatics tools with chemometrics tools for PCA in an intuitive environment for performing such analyses. A new patent pending technology—Overlap Density Heatmaps—now allows the comparative visualization of heretofore unheard of numbers of spectra or chromatograms. Overlap Density Heatmaps are used for visual data mining and analysis to assess the similarities and dissimilarities in large amounts of spectral, chromatographic, and other graphical data. This new approach for spectroscopic analysis will be examined in specific case studies as applied to IR and Raman data. We will demonstrate the successful use of PCA and Overlap Density Heatmaps to analyze a query and the hit list resulting from an IR spectral search and perform an overall analysis of a database.

(20) **MCR Analysis of Spectral Data Files**

Jon Schoonover[1], Jennifer Butler[1], Cole Paffett[1], Jonathan Cox[1]; [1]Los Alamos National Laboratory

Multivariate curve resolution (MCR) analysis has been utilized to manipulate and understand matrices of spectra as a function of a perturbation. This approach allows the analysis of spectra that provides insight into the chemistry of the system understudy. The MCR approach is demonstrated to be an excellent chemometrics technique to reduce and analyze spectral data files.

(21) **Chemometric Analysis of Bio-Aerosol Agents Using a LIF Biological Agent Monitor**

Brian Dable[1], Geoff Wilson[1], Jim Brady[1], Mike Carrabba[1]; [1]Hach Homeland Security Technologies

This presentation will describe the performance of a bio-aerosol agent monitor developed to detect releases of pathogens at low concentrations while rejecting anomalous bursts of non-pathogenic particles. Through chemometric analysis using the fluorescence information about a particular agent material and the ambient air background sampled, a threshold may be computed that corresponds to a desired maximum level of detection of agent within the sampled air. Receiver Operating Characteristic (ROC) curves computed for the detection of agents in backgrounds collected in a variety of indoor and outdoor environments will be used to show the performance of a bio-aerosol agent monitor in minimizing false positives while maintaining high confidence that an agent may be detected at a desired concentration.

(22) **Performance of a NIR Multivariate Optical Computing Based Instrument on a Binary Organic Mixture**

Luisa T.M. Profeta[1], Michael L. Myrick[1]; [1]University of South Carolina

Multivariate Optical Computing (MOC) is a method by which an analyte characteristic of interest is predicted via optical regression using a specialized interference filter called a Multivariate Optical Element (MOE). Previous work in our laboratory has investigated the design and fabrication process of MOEs and their use in MOC systems in the UV-Visible region. More recent studies have probed into the consequences of spectral resolution on the theoretical design of MOEs for application work in the near-infrared (NIR)

region. The work presented here will examine the actual application of a MOC system designed for a spectrally dense open binary organic mixture of naphthalene and pyrene in the nominal 1675 to 2600 nm region. Details relating to compensation for non-linearity in the spectrum and how this affects the final instrument response will be explored.

(23) **PARAFAC-Based Estuarine Water Fingerprinting**

Gregory Hall[1], Jonathan Kenny[2]; [1]U.S. Coast Guard Academy, [2]Tufts University

Aquatic nuisance species invasion to the estuarine waters of many countries has prompted studies into methods for fingerprint natural waters with respect to their location of origin. This ability would be particularly useful in the enforcement of Ballast Water Exchange (BWE) regulations. Time Resolved Excitation Emission Matrix (TREEM) spectroscopy has been used by several groups to determine the characteristic fluorescence of Colored Dissolved Organic Matter (CDOM) in water samples and shows promise as a method for water fingerprinting. Ratios of fluorescent component compounds are the important, specific data for these determinations. A PARAFAC-SIMCA based classification method will be shown that successfully categorized samples to their ports of origin based on their fluorescent components as determined by PARAFAC. This method is particularly powerful, as it allows for classification based upon chemically interpretable spectral loadings, and allows for removal from consideration effects of interferants or contributions from unknown sources.

(24) **Classifications in Biospectroscopy using a Non-Generational Genetic Algorithm for Automated Preprocessing and Wavelength Selection**

Francis Esmonde-White[1], David Burns[1]; [1]McGill University

A novel non-generational genetic algorithm for automated preprocessing of spectral data will be presented. The complexity of data collected using biospectroscopic measurements requires tedious preprocessing which may not provide objective analysis parameters. Moreover, the preprocessing methodology must be optimized for each experiment. Thus, there is a need for a robust method that can consistently preprocess biospectroscopic data quickly and accurately. Many novel features will be illustrated and compared with existing genetic algorithms. These new features include a comparison of methods for determining parsimonious models, variable preprocessing ordering, a Bayesian probability measure to indicate the probability of correct classification, and a population member aging function. Indicators of parsimony lead the processing models developed to be biased towards a minimum complexity. Smaller models decrease the likelihood of calibrating for noise, and outline necessary components for the construction of simplified instruments. Variable preprocessing ordering allows many preprocessing options to self-order, subject to predefined validity constraints. A Bayesian probability measure is used when testing unknown samples to indicate the probability of assigning the correct class identification. An aging function can be used to avoid calculation of a full cross-validation for every population member, by performing a full cross-validation only when a model has survived a predefined number of iterations.

(25) **Eureka: An Online Research Data Archiving and Analysis Portal for Faculty**

Stuart Chalk[1]; [1]University of North Florida

Faculty are overwhelmed by the amount of research data their students and postdocs collect. Commercial LIMS software could address this need, but is expensive and not geared to faculty needs. Eureka is an online data archiving, analysis and dissemination software package that fits the needs of faculty. This presentation will address the technologies and features of the Eureka software as well as the data storage model.

(26) **Classification of Textiles by Diffuse Near-infrared Reflectance Spectroscopy**

Christopher Davis[1], Dennis Rabbe[1], Kenneth Busch[1], Marianna Busch[1], Alton Hassell[1], Judith Lusk[1]; [1]Baylor University

A wide variety of chemical treatments and finishes are applied to textiles to produce or enhance desired fabric characteristics. These treatments and finishes include: softening agents, hand-building agents, easy-care/durability agents, repellents, soil-release agents, flame-retardant agents, non-slip agents, antistatic agents, anti-pilling agents, elastomeric agents, color-fastness agents, UV-protection agents, and antimicrobial finishes. When finishing a textile or garment, the clothing manufacturer must know what is already on the fabric to avoid deleterious secondary effects that may result from combining two incompatible finishes. Previous work in this laboratory has shown the effectiveness of near-infrared (NIR) spectroscopy combined with chemometric modeling techniques like SIMCA (soft independent modeling of class analogies) in the spectroscopic classification of textile samples. In our previous studies, sub-classes were sometimes observed within different fiber groups, leading to the speculation that differences in fabric finishes and process residues were the cause. In this study, the effect of different finishing agents on the classification of textiles by NIR-SIMCA modeling techniques will be investigated.

(27) **Quantitative Crystal Form Determination by XRPD Partial Least Squares**

Michael Dotlich[1], John Mannin[1], Sharon Snorek[1]; [1]Eli Lilly and Company

Purpose: To develop and validate a XRPD model for quantifying three undesirable crystal forms and the amorphous level within the primary crystal form matrix. Methods: This method utilizes partial least square (PLS) modeling for determining four component form mixtures (Crystal Forms A, B, C and amorphous). The standard concentration ranges used to calibrate the models included 0 to 60 wt/wt% for Form B, Form C, and amorphous, and Form A from 40 to 100%. The crystal form mixtures were prepared by tumble mixing the dry solids and then measuring the dry mixtures by XRPD. The data was modeled by CAMO PLS software - The Unscrambler©. The models were then verified with prepared standards at ranges from 0 to 30 wt/wt% for Form B, Form C, and amorphous. Results: The PLS models demonstrated a limit of detection and quantitation of approximately 1% and 4%, respectively, for Form B, C and amorphous content. When validation samples containing Form B and C were compared against the models, the modeled results agreed to within ±5 wt/wt% of the prepared validation sample concentrations. Amorphous content at concentrations below 10 wt/wt% was predicted to ±2 wt/wt%.Conclusions: The models exhibited acceptable detection and quantitation limits. When compared to the validation sample sets, the models performed acceptably at the lower concentration ranges for Form B and Form C, however, a slight increase in accuracy was demonstrated for amorphous content.

(28) **Use of a Portable Electrochemical Sensor to Evaluate Packaging Container Effectiveness**

Gregory Webster[1], William Buttner[2], Joseph Stetter[2]; [1]Pfizer Global R&D, [2]Illinois Institute of Technology

A novel testing scheme to study packaging integrity for liquid products was developed at in our laboratory to ensure product integrity. The previous system developed for this application used a gas chromatograph/surface acoustic wave (GC/SAW) detection scheme to detect breaches in packaging integrity which results in a

release of trace amounts of the ethanol solvent. In the mode of "keeping it simple," the new process design relies on the application of electrochemical gas sensor technology to replace the GC-SAW detector. The selectivity of the electrochemical sensor eliminates the need for a separation column to ensure the integrity of the alcohol response and provides adequate detection capability for the analyte of interest. As configured, the portable electrochemical sensor detector not only presented no safety concerns, but also operated as an "environmentally green" instrument in that no mobile phase or detector gases needed to be supplied. Validation results will be illustrated and statistically compared in terms of detection performance and limits. The use of the electrochemical sensor in concert with vacuum chamber testing was fully characterized. It was the most feasible system that can operate inside the manufacturing work area. This conclusion stems from two points: (1) concerns regarding the use of a flame based detectors in the area due to volatile solvents and (2) the portable sensor fewer consumable parts to worry about and is inexpensive to operate. The development investigations supported the goal of having the vacuum chamber system as a diagnostic tool to provide assurance of adequate integrity in product market containers without the need for individual inspection.

(29) **Forensic Analysis of Micro-Particle Contaminant in Biopharmaceutical Manufacturing**

Guiyang Li[1], Zai-qing Wen[1], Gianni Torraca[1], Chanel Yee[1]; [1]Forensic Analysis Group, GCAR, Amgen Inc.

Over the last tow decades, the number of Biopharmaceutical products approved to treat patients with various diseases has dramatically increased. During the manufacturing process, micro-particle contamination in biopharmaceutical products or in manufacturing facilities can occur and result in Non-Conformance incidents. The contaminants could result from the materials, manufacturing equipment, manufacturing process or contract manufacturing deviation. All these potential sources could end up contributing to the presence of contaminants in the final product. The identification of unknown contaminants plays a key role in quality control for release of clinical or commercial products and validation of manufacturing equipment. The purpose of forensic analysis is to determine the composition of the contaminants by multiple microspectroscopic techniques and to help find the root cause and result in implementation of corrective and preventive actions. We have developed a systematic procedure to analyze the unknown materials in biopharmaceuticals, which differ significantly from traditional pharmaceutical products such as tablets or capsules. Initial analysis under the optical microscope can sometimes readily identify the particle based on morphology. However, most of the micro-particles cannot be identified by morphology alone. The best strategy is to combine multiple microspectroscopic techniques including the Scanning Electron Microscopy (SEM), Energy Dispersive Spectroscopy (EDS), FTIR microspectroscopy and Raman microscopy. Several forensic investigation cases will be presented to illustrate the special challenges in biopharmaceutical product manufacturing and quality control for forensic and microspectroscopic scientists.

(30) **Scatter Correction of Transmission NIR Spectra by Photon Migration Data for Analysis of Intact Pharmaceutical Samples**

Christoffer Abrahamsson[1], Tomas Svensson[1], Stefan Andersson-Engels[1], Sune Svanberg[1], Jonas Johansson[2], Staffan Folestad[2]; [1]Lund Institute of Technology, Sweden, [2]AstraZeneca R&D Mölndal, Sweden

The scope of this work is a new methodology to correct conventional NIR data for scattering effects. The technique aims at measuring the absorption coefficient of the samples rather than the total attenuation, measured in conventional NIR spectroscopy. The main advantage of this is that the absorption coefficient is independent of the path length of the light inside the sample, and therefore independent of the scattering effects. Two different instruments are used for the measurements, one conventional transmission NIR instrument and one time-resolved instrument. The unique broadband time-resolved spectroscopy system is based on a mode-locked Ti:Sapphire laser pumping a photonic crystal fibre (PCF) and a streak-camera for detection. The system covers a wavelength range spanning from 500 nm to 1200 nm. The streak camera allow recording of time-resolved data, in that wavelength range, with a time resolution of approximately 30 ps. The first step of the scattering correction scheme is to evaluate the recorded time-resolved data be means of diffusion theory. This provides an independent measure of the scattering properties of the samples in the wavelength range spanned by the time-resolved system. In the second step the extracted scattering coefficients is combined with the conventional NIR absorption data to calculate the absorption coefficients of the samples in the entire wavelength range spanned by the conventional NIR spectrometer. The calculated absorption coefficients are then used in a multivariate calibration scheme to extract quantitative information. The proposed scatter correction scheme have a clear advantage over other pre-processing techniques, where scattering effects are estimated and corrected for by using the shape of the measured spectrum only. PLS calibration models shows that, by using the proposed evaluation scheme, the predictive ability is improved by 50 % as compared to a model based on conventional NIR data only. The method also makes it possible to predict the concentration of active substance in samples with other physical properties than the samples included in the calibration model.

(31) **FT-IR Reflectance Imaging and Multivariate Analysis for Characterization of Defects in Pharmaceutical Tablet Modified Release Coatings**

Yang Liu[1], Mark Henson[1], Rafael Arguelles[2]; [1]Pfizer Inc, PGRD, [2]Pfizer Inc, PGM

Critical film coating defects such as breached membrane can jeopardize the release profile of controlled released tablets. When such defects occur, it is important to understand the root cause. Chemical imaging contains both rich chemical and physical location information, which can potentially provide more conclusive results than cosmetic examination through an optical microscope. In this work, FT-IR imaging was used to characterize defects in controlled released tablet coatings because of its rich chemical information and low penetration depth. A Partial Least Square – Discrimination Algorithm (PLS-DA) model was constructed and optimized on tablet cores and coated tablets. The model then was used to determine if the IR image of the damaged coating area contained core signal or not. Because the short wavelength range indirectly contained coating thickness information, a separated quantitative PLS model was constructed to estimate the thickness of the coating residue on the damage area. A false color 3-D image can then be generated based on the thickness estimation. Results showed that FT-IR imaging and multivariate analysis can effectively identify critical defected coating and provide semi-quantitative coating thickness information, which is valuable for further root cause analysis.

(32) **Non-invasive Characterization of Pharmaceutical Tablets using Gas in Scattering Media Absorption Spectroscopy (GASMAS)**

Tomas Svensson[1], Jonas Johansson[2], Stefan Andersson-Engels[1], Sune Svanberg[1], Staffan Folestad[2]; [1]Lund University, [2]Astra Zeneca R&D, Mölndal

Techniques for characterization of highly scattering pharmaceutical solids (e.g. tablets) are of great interest to the pharmaceutical industry. This work deals with the study of tablet porosity by employing a technique referred to as gas in scattering media absorption spectroscopy (GASMAS) to pharmaceutical tablets. High resolution diode laser spectroscopy allows detection of the narrow (~3 Ghz) but weak absorption features of, for example, free molecular oxygen (at 760 nm). The technological key is the contrast between narrow gas phase absorption and broadband bulk absorption. In contrast to common absorption spectroscopy, photon path lengths are in this case unknown due to massive light scattering in the bulk material. Quantitative interpretation of the absorption signal is therefore reached first after determination of the mean photon path length. Time- or frequency domain measurements are employed to extract these path lengths. Diode lasers (Fabry-Perot, VCSEL or DFB) emitting light in the range where oxygen absorbs (760-765 nm) are used as light sources. These are modulated and wavelength tuned over one of the narrow oxygen absorption lines. The light is guided into the tablets by fibre optics (single- or multimode), and transmitted or reflected ligth is detected using a PMT. Sensitive lock-in amplification is used to detect the absorption signal. The work includes GASMAS measurements on tablets with different particle size and density. The relation to mercury based porosity measurements are discussed. Technological issues are addressed, since detection of weak oxygen absorption often is a difficult matter.

(33) **Evaluation of Critical Experimental Parameter Settings for Tablet Content Uniformity Measurement Using Near Infrared Transmission Spectroscopy**

Dong Xiang[1], Paul Gargiulo[1], Jason Teelucksingh[1], Florian Battung[1], Rosario LoBrutto[1], James Pazdan[1], Busolo Wabuyele[1]; [1]Novartis Pharmaceuticals

Near-infrared (NIR) spectroscopy has been receiving an increased amount of attention in the pharmaceutical industry as the analytical technology that can be used to achieve rapid, real-time, non-destructive measurement with little or no sample preparation. One application of NIR spectroscopy is to determine the concentrations or content uniformity (CU) of active pharmaceutical ingredients in solid tablets. The procedure typically involves the generation of a multivariate calibration model based on a series of NIR spectra and their corresponding reference values. Initial studies have shown that CU measurements can be achieved either via reflectance or transmission mode that have been equipped with a properly designed tablet positioning apparatus. Compared to the reflectance mode, transmission mode is believed to provide information representative to the entire lot and to be less sensitive to inhomogeniety of the tablets because light penetrates a larger portion of the tablet in the transmission mode. A rule of thumb in NIR test methods is to incorporate any anticipated variation into the calibration model. These variations could originate from any spectroscopic sensitive parameters such as instrumental setting differences and chemical or physical properties of sample matrices. It is always important that those variations are evaluated in the stage of method development. Key sources of variability and parameter settings for diffuse reflectance measurement has been conducted and reported in the literature. However, few references in the literature have reported the investigation of those parameters in tablet CU measurement with NIR transmission mode. The goal of this study is to provide an experimental basis for future design and selection of critical parameter settings in method development for CU measurement with NIR transmission spectroscopy. Critical experimental parameter settings and variables are evaluated including scan number, stray light, resolution, hardness, etc. Their impact on the NIR spectra will be determined and characterized by various multivariate techniques.

(34) **Comparison of Transmission and Diffuse Reflectance Modes in Near-Infrared (NIR) Spectroscopic Measurements of Pharmaceutical Tablets**

Jason Teelucksingh[1], Dong Xiang[1], Rosario LoBrutto[1], Stephanie Metz[1], Paul Gargiulo[1], Richard Vivilecchia[1], Busolo Wa Wabuyele[1]; [1]Novartis Pharmaceuticals Corporation

In recent years the most innovative spectroscopic tools that has been widely used in the pharmaceutical industry is near-infrared (NIR) spectroscopy. Its sensitivity, selectivity and versatility allow NIR to analyze blend and tablet samples without any special preparation procedures. For example, the same spectra for tablets can be used to correlate tablet hardness, water content (bound and unbound), and assay determination thus minimizing analysis time. A fundamental question that commonly arises at the commencement of NIR method development is related to the selection of the appropriate modality to collect spectra, transmission or reflectance. We have a few choices when performing chemometric analysis for real time and offline implementation of PAT in pharmaceutical continuous process monitoring, control and end-product testing. The appropriate selection of modality also depends on evaluation of the critical factors that can impact the accuracy of the technique. Some of these considerations include the properties of the drug substance-drug product, drug content, thickness of the tablet, tablet coating materials, sensitivity of the instrumentation, surface imperfections such as embossment, and size of the tablet relative to the sampling area. In this proposal, two modes of measurement are evaluated. The goal is to derive a systematic decision diagram to guide the scientist in the selection of the proper modality. Spectral variances induced by certain physical properties in these two measurement modes are discussed, which include tablet hardness, moisture influences and surface imperfections.

(35) **Application of Vibrational Circular Dichroism Spectroscopy at BMS**

Ming-Hsing Huang[1], Linda Phillips[1], Yingru Zhang[1], Steve Gozo[1], Jack Gougoutas[1], Ming Huang[1], [1]Bristol-Myers Squibb

As an increasing number of pharmaceutical compounds are chiral, including synthetic intermediates, there is an increasing demand for determination of absolute configuration. VCD is an orthogonal method in our "tool box" that we use for this purpose. A ChiralIR Vibrational Circular Dichroism (VCD) spectrometer has been in our laboratory for about two years. This instrument employs a design of dual IR sources, dual Photoelastic Modulators (dualPEM), and two lock-in amplifiers to measure the IR and VCD spectra of samples in solution and solid-state. We have used VCD to study various pharmaceutical compounds, from rigid, small molecules to more flexible, larger molecules. VCD spectroscopy is used as an independent method to assign absolute configuration, or to complement X-ray crystallographic results when the X-ray studies are not definitive. VCD spectra can also be used as chiral "finger prints." That is, the observed VCD spectrum of a sample of known absolute configuration can be used to assign or confirm the absolute configuration of another sample. Additionally, we have been exploring the use of solid-state VCD in cases where only relative configuration is available from single crystal X-ray studies. The principles of VCD spectrometry and experimental

considerations for both solution and solid-state VCD will be presented and examples of our work will be discussed.

(36) **Multivariate Data Analysis of Near Infrared Chemical Imaging Measurements for Tablet Content Uniformity Study**

Wei Huang[1], Busolo Wa Wabuyele[1], Patrick Chen[1], Dong Xiang[1], Boyong Won[1], Yusuf Sulub[1], Joseph Etse[1], Richard Vivilecchia[1]; [1]Novartis Pharmaceutical Corporation

Near infrared (NIR) chemical imaging is gaining increasing attention in the pharmaceutical industry, especially with the advent of the process analytical initiative in 2004. The major advantages of NIR spectroscopy include nondestructiveness, no sample preparation, and fast analysis time. The NIR imaging technique captures chemical fingerprints in spectral dimension and visualizes the spatial distribution of the chemical species throughout the sample. These make it promising for noninvasive characterization of blend uniformity in a drug substance both during processing and in the final product. Implementing this technique is hampered by the question of how to efficiently extract quantitative chemical information from the large amount of data acquired during the analysis. Traditional univariate data analysis methods have been used in the past when enough selective information from a spectral channel is available. This approach, however, is restricted to distinct, nonoverlapping spectral data. For cases where such selective information is not available, established multivariate chemometric data analysis techniques such as principal component analysis (PCA) and partial least squares (PLS) can be used to extract relevant chemical information from the measured chemical imaging data. The goal of this study will be to investigate the viability of numerous chemometric data compression and feature extraction techniques such as PCA, PLS, wavelet transform, and Fourier transform on imaging data acquired from pharmaceutical samples. In addition, the performance of several multivariate calibration approaches will be evaluated based on content uniformity and table homogeneity.

(37) **High Throughput Raman Chemical Imaging Analysis of Pharmaceutical Products**

Matthew Nelson[1], Linda Batykefer[1], David Tuschel[1], Patrick Treado[1],; [1]ChemImage Corporation

Chemical imaging enhances the capabilities of more traditional molecular spectroscopy techniques. By combining molecular spectroscopy and digital imaging, morphology, composition, structure and concentration can be evaluated with a high degree of specificity and sensitivity at submicron spatial resolutions in a non-contact, non-invasive detection mode. Many practical applications of the technology rely heavily on speed of acquisition (i.e., second to sub-second timeframes) and throughput of sample analysis and to a lesser extent, the number of pixels present in the chemical image. This presentation will discuss high throughput / low image fidelity chemical imaging approaches and applications. Results will be shown from a polymorph mixture screening experiment using ChemImage's newly released POLLY Widefield Raman Polymorph Screener. POLLY's unique simultaneous full-well sampling and widefield illumination features provide significantly more robust sampling statistics than other polymorph screening techniques on the market today. This low-fidelity Raman chemical imaging platform provides the perfect tool for rapid scanning of 96 well plates in as little as 5 minutes. Finally, high fidelity Raman chemical imaging results from a pharmaceutical tablet obtained using a low fidelity Raman imaging platform will be discussed.

(38) **Estimation of Optical Constants from Diffuse Reflectance Measurements of Turbid Media Using Fractal Analysis**

Fabiano Pandozzi[1], Claudia E. W. Gributs[1], Dirk Bandilla[1], David H. Burns[1]; [1]McGill University

Pharmaceutical industries and researchers use particle sizing to monitor the characteristics and quality of products because it is important for sample properties to remain constant. Particle size and analyte concentration can be calculated from scattering and absorption coefficients, respectively. Currently, these coefficients of highly scattering samples are difficult to obtain due to the multiple scattering events which bias absorption estimates. Time series data, such as chromatograms and photon time-of-flight profiles, contain self repeating (fractal) characteristics. We hypothesize that by using a fractal analysis algorithm on time series data that we can determine analyte concentrations as well as scattering coefficients in a single experiment. To test our hypothesis we used a fractal analysis algorithm on photon time-of-flight data from scattering samples. After subsequent data processing, we were able to determine scattering coefficients and analyte concentrations. We validated our method using calibration and test sets in order to compare estimated values to those expected. We were able to estimate absorption and scattering coefficients which agreed well with theoretical values. Fractal analysis has been shown to be an effective data processing technique that can allow simultaneous estimation of particle size and analyte concentration in scattering samples.

(39) **Factors Affecting the Production of Broadband Acoustic Emission Signals and Their Use in Particle Characterisation**

Alison Nordon[1], Nichola Townshend[1]; [1]University of Strathclyde

Acoustic emission is of particular interest for the monitoring and control of particulate processes as the technique can be employed non-invasively, in situ, in real-time and is relatively inexpensive in comparison with the cost of optical techniques. Acoustic emission generally arises in particulate processes from the collision of particles with the inner wall of a vessel or pipe, and has been used to monitor, for example, granulation processes and the flow of powders through pipelines. In most cases, the signals were acquired over a narrow frequency range and/or converted to a DC signal. Although this methodology has been deployed successfully in a process environment, the information that can be derived from such signals is limited, as the signals do not contain any acoustic emission frequency information. In comparison, broadband acoustic emission signals contain both amplitude and frequency information. The amplitude and frequency of acoustic emission signals are not only affected by the physical properties of the particles, but also the properties of the vessel or pipe and the response characteristics of the transducer. Therefore, to understand the information content of such signals, it is important to assess the possible contributions. In this work, acoustic emission signals were acquired of particles impacting with a glass surface via attachment of a broadband piezoelectric transducer to the outer surface of the glass. The effects of a number of factors on the signals have been investigated including particle size, impact position with respect to the transducer and impact velocity. In addition, the effect of the shape and size of the vessel and the transducer response characteristics were considered. The effect of vessel size on the signals is particularly important if acoustic emission is to be used in process scale up. Broadband acoustic emission signals were then acquired for particles with different physical properties to investigate whether such particles could be characterised on the basis of their acoustic signals.

(40) **Monitoring Wood Composites Manufacture Using Near Infrared Spectroscopy**

Tim Rials[1], Nicolas Andre[1], Tim Young[1]; [1]The University of Tennessee

This paper reports on a preliminary study of on-line monitoring of the buffer capacity of particleboard furnish using near-infrared (NIR) spectroscopy and multivariate analysis models. The buffer capacity of wood furnish is known to affect the curing rates of urea-formaldehyde (UF) resins, which ultimately determines the mechanical properties of manufactured panel. In the initial phase of the study, multivariate calibration and validation models from NIR spectroscopy data were developed to predict the buffer capacity of particleboard furnish in a laboratory environment. During this phase, a spectrometer (Ocean Optics USB2000) operating in the 550-1100 nm spectral range was evaluated. The subsequent validation phase of the study took place at a North American particleboard plant over several weeks. Additional multivariate calibration models were constructed and tested on-line during a four-day test period. The on-line root mean square error of prediction (RMSEP) and the coefficient of variation (CV) for buffer capacity predictions ranged from 3.45 to 0.92 and 22.4% to 5.8%, respectively.

(41) **The Analytical Sciences Digital Library: A Growing Resource for Pedagogy in the Analytical Sciences**

Alexander Scheeline[1], Cynthia Larive[2]; [1]University of Illinois at Urbana-Champaign, [2]University of California at Riverside

The Analytical Sciences Digital Library is an open access online resource featuring peer-reviewed websites and original articles focused on teaching analytical chemistry, instrumentation, and related sciences. We report on the growing use of the Library, the range of topics covered, evaluation of the site's ease of use by students, and original publications in Undergraduate Research, Labware, Courseware, and Educational Practices. Discussion forums are linked to each original article. We report on usage of this feature, and on the possibilities opened by the availability of formats not easily employed in hard copy publishing.

(42) **An Undergraduate Lab for Lead in Ancient Bronze Coins by Atomic Absorption Spectrometry**

Mary Kate Donais[1], Ashley Dumas[1], Kathleen Golden[1], Abby Pelletier[1]; [1]Saint Anselm College

An experiment for undergraduates based on the analysis for lead in ancient bronze coins by atomic absorption spectrometry is presented. The coins used for the analyses were collected by students in Crete. Some information had already been obtained about the coins such as approximate terminus ante quem based on the context of finds. Chemical characterization of the coins was conducted post sample collection to aid in the determination of age and geographic area where the coins were originally minted. A simple method utilizing a block digestion system, acid matched standards, and atomic absorption analysis was successfully used by an archaeology class mostly composed of non-science majors. Through comparisons of the data to previously published data it was possible for the students to determine the approximate time and provenance from which the coins originated.

(43) **Spectroscopy Myth Busters: FTIR Spectra Collected with Diffuse Reflectance and Attenuated Total Reflectance Accessories can be Searched Against Transmission Libraries**

Eric J Bukowski[1], John A Monti[1], Shannon M Richard[1]; [1]Shimadzu Scientific Instruments

The recent increase in the popularity in FTIR spectroscopy across multiple industries, ranging from pharmaceuticals to forensics, can be partially attributed to the increased acceptance of reflectance based accessories. In particular, diffuse reflectance and attenuated total reflectance (ATR) have been particularly popular when compared to traditional KBr pellet techniques. A common practice for both the pharmaceutical industry and forensic science is to search acquired spectra against spectral libraries. In the case of the pharmaceutical industry they often compare the spectra of incoming raw materials against libraries of approved or accepted lots of the material. The scenario for forensic science can be much more complicated. They routinely search unknown powders against both multiple and extensive libraries hoping to uncover an identity. A large percentage of the existing spectral libraries contain transmission spectra, as it was the sole method used until the early 1960's. In theory, these huge transmission libraries can actually be used of for the identification of reflectance based spectra after the reflectance spectra have undergone mathematical correction factors. This poster compares and contrasts the quality of the search results obtained for spectra collected via reflectance accessories and searched against transmission libraries both before and after the appropriate mathematical corrections.

(44) **Brewing Beer to Teach Analytical Chemistry**

William Lammela[1]; [1]Nazareth College

There have been a variety of new approaches to teach analytical chemistry from using natural waters as model systems, various food and beverages and pharmaceutical preparation. This project involved having the students investigate beer: the ingredients, the variables in the preparation process, species measured as part of quality control and methods appropriate to such measurements. Students then make their own beer and quantify various constituents of their choosing throughout the beer-making process. The results have been a renewed interest in guided-inquiry projects, this one in particular, as well as development of the student into an independent investigator.

(45) **Nanoscale Antennae for Luminescent Lanthanide Cations Emitting in the Visible and Near-Infrared Domains**

Stephane Petoud[1]; [1]University of Pittsburgh

Luminescent lanthanide compounds have advantageous photophysical properties, such as sharp emission bands whose wavelengths are not affected by experimental conditions, long luminescence lifetimes (micro to milliseconds), a large energy gap between absorption and emission bands, and emission in the visible and/or in the near-infrared domains. For all these reasons, lanthanides could potentially be used in a broad range of bio-analytical assays and imagery applications. Nevertheless, few lanthanide compounds are currently used in practical applications, mainly because of their insufficient luminescence intensity. The reason for this limitation is doubly faceted: 1) lanthanide cations need to be sensitized with an "antenna" molecule. This has been done traditionally with small organic chromophoric molecules that need to be bound directly to the lanthanide cation. 2) the lanthanide cations need to be protected from the environment to prevent the loss of luminescence through non-radiative deactivation processes. Herein we will present our work based on an approach where lanthanide cations are sensitized using novel types of antennae. Examples will include the use of CdSe semi-conductor nanocrystals for the sensitization of lanthanide cations in doped CdSe:Ln nanocrystals. Other types of nanomaterials such as dendrimers will also be presented in this paper, which will demonstrate the flexibility and advantages provided by the nanoscale approach. Examples of applications of these compounds as sensors will be also presented in this paper.

(46) **Surface Second Harmonic Generation Imaging for the Detection of Biomolecule Adsorption to Patterned Ligand Arrays**

John Conboy[1], Trang Nguyen[1]; [1]University of Utah

Surface second harmonic generation (SHG) has long been used for the characterization of interfacial phenomena. In recent years, SHG has also been applied to the characterization of biological interfaces. We have recently employed SHG imaging for the detection of proteins and small molecules to patterned arrays on a surface, expanding the capabilities of SHG for the investigation of biomolecule adsorption to surfaces. The theoretical foundations of surface SHG imaging will be presented as well as experimental verification of the imaging method using the adsorption of bi-2-naphthol to a patterned planar supported lipid bilayer. SHG imaging is also capable of detecting submonolayer populations of proteins on a surface in a spatially resolved manner without the need for exogenous chemical labels or modifications of the protein. As a proof a principle, the adsorption of avidin and anti-biotin IgG to patterned biotin arrays has been measured. Equilibrium affinity constants of 1.3×0.5 ± 108 M-1 and 2.0×0.3 ± 109 M-1 were determined for avidin and anti-biotin IgG respectively. These affinity constants correlate well with conventional fluorescence measurements. The use of label-free optical methods also possesses certain problems with regards to elimination of background signals and nonspecific protein adsorption. Several of these key points, namely the influence of surface modification and the control of nonspecific adsorption will also be discussed.

(47) **Novel Phthalocyanine-Based Near-IR Fluorophores: Development and Bioanalytical Applications**

Steven Soper; Louisiana State University

Fluorescence detection in the near-infrared (near-IR) holds great promise for providing ultra-high sensitivity, even at the single molecule level, for bioanalyses even those performed in complex sample matrices. The technique has been demonstrated to provide overall better detection efficiencies compared to the UV or visible regions of the electromagnetic spectrum due in part to the limited number of compounds that show intrinsic fluorescence in the near-IR region. However, the full utilization of near-IR fluorescence in a variety of bioanalytical applications has been slow to develop due to the limited number of fluorochromes available and the rather poor photophysical properties they offer. Demands placed on readout modalities of bioassays that provide high degrees of multiplexing capabilities as well as high sensitivity require the development of new near-IR fluoropohores with a diverse range of photophysical properties and functional groups for labeling a vast range of targets. Here, we will present newly developed asymmetrical water-tolerant phthalocyanine (Pc) dyes that possess absorbance and fluorescence maxima in near-IR range. The dyes could be covalently attached to oligonucleotide probes with the conjugation conditions optimized to provide high labeling efficiencies (~85%). These Pc dye systems can be used as reporters of molecular association events using such readout formats as resonance energy transfer or fluorescence resonance energy transfer following a molecular beacon format.

(48) **Surface Enzymatic Processing of Nucleic Acid Microarrays for Enhanced SPR Imaging Biosensing**

Hye Jin Lee[1], Robert Corn[1]; [1]Univ. of California-Irvine, Dept. of Chemistry

Nucleic acid microarray biosensors are an indispensable tool for the rapid, multiplexed analysis of surface bioaffinity interactions such as DNA-DNA, DNA-RNA, RNA-protein, protein-peptide, and protein-protein complexes. These surface interactions can be detected using various surface-sensitive optical techniques including surface plasmon resonance imaging (SPRI), surface plasmon fluorescence spectroscopy (SPFS) and fluorescence imaging. Recently, we have demonstrated that the specificity and sensitivity of the SPRI bioaffinity sensing measurements can be greatly enhanced via surface enzymatic processing of nucleic acid microarrays. This talk will highlight a series of surface enzyme reactions of nucleic acid microarrays in conjunction with the use of various shapes and sizes of functionalized nanoparticles for ultra sensitive SPRI biosensing. Particularly, surface transformations utilizing T4 DNA ligase, Taq DNA ligase, T4 RNA ligase, T7 RNA polymerase and poly(A) polymerase will be discussed for the identification and detection of single nucleotide polymorphisms and various microRNAs.

(49) **Histology-guided Sampling Hyphenated with Capillary Electrophoresis and Laser Induced Fluorescence Detection**

Hossein Ahmadzadeh[1], LaDora Thompson[2], Edgar Arriaga[2]; [1]California State Polytechnic University, [2]University of Minnesota

Histology-guided sampling technique greatly enhances the chemical and biochemical analysis of spatially heterogeneous tissues. Here, we use histological ATPase reference maps to guide the single cell sampling device for direct mitochondrial sampling from individual fibers in muscle cross sections according to their energetic supply: oxidative versus glycolitic. The sampled mitochondria are separated by capillary electrophoresis and detected with laser-induced fluorescence (CE-LIF). Our results showed that Type I fibers (oxidative) display more mitochondrial events, less cardiolipin per event, and events with more negative electrophoretic mobilities than Type IIb fibers (glycolitic). Furthermore, this approach allows us to investigate the distributions of these mitochondrial properties within the same fiber despite the highly heterogeneous nature of muscle tissue.\r\nIn this presentation, we describe the principles of this technique. We show (i) how this technique is used for the analysis of individual mitochondria taken from individual muscle fibers with different cytochrome c oxidase activity and (ii) demonstrate the feasibility of correlating tissue properties in micrometer-size regions with the CE-LIF measurements. This report suggests how CE-LIF analysis of solid tissues can be used to investigate muscle aging and fiber typing.

(50) **Chiral Technology Toolboxes**

Oliver McConnell; Wyeth Research

Due to the rapid increase over the past decade in the pharmaceutical industry in potential drug candidates containing one or more asymmetric centers, the application of chiral technology, or the use of techniques or tools for the determination of absolute stereochemistry and the enantiomeric or chiral separation of racemic small molecule pharmaceutical lead compounds, has been critical to successfully discovering and developing single-enantiomer or chiral drugs. The current status of chiral technology toolboxes at Wyeth Research, including the implementation of known tools as well as the design, development and implementation of new chiral technology tools will be presented.

(51) **A Nanoscale Approach to Chiral Discrimination**

Regina Valluzzi[1]; [1]Evolved Nanomaterial Sciences

We have developed nanostructured materials that are highly chirally selective, with a high capacity for neat chiral oils and liquids. The chiral selectivity observed is not specific to the chemistry of the materials, aside from wetting and general chemical compatibility needed to get analyte into the material. These materials are comprised of an interpenetrating network of chiral polymer and chirally shaped channels. While the diameter of the channels is in all cases several nanometers or larger - much larger

than a typical small organic molecules - the materials exhibit extremely strong and general chiral selectivity. Characterization of these materials suggests that while chemistry and chemical interactions with the chiral polymer no doubt have a role in chiral discrimination, the symmetry and morphology of the chiral curved channels also play a very strong role. In some situations these physical characteristics may dominate chiral selectivity. Chiral columns can be readily packed with powdered forms of the materials. A significant number of chiral chromatographic separations have been demonstrated using these columns, now commercially available. In the process of developing and testing chiral chromatography columns some unusual features of the nanostructured materials have been observed, many of which may be advantageous to the separations scientist. A key feature is generality. In typical commercially available chiral columns, a combination of four or more stationary phases can address the majority of molecules. All of the separations we will present and list have been performed on the identical column and stationary phase, which has an unusually broad spectrum of selectivity. Other novel features observed for the nanostructured materials include a high capacity for many column analytes, the ability to separate molecules that do not have sites for strong H-bonding, electrostatic or pi-bond interactions, a strong selectivity for non-chiral isomers and structurally related compounds, and a wide range of usable mobile phases. In several cases reversal of elution order has been achieved through a change of mobile phase, on the same highly general column. Chromatograms, other chiral data and materials characterization data will be presented, and the possible selectivity mechanisms supported by the data will be discussed.

(52) **Application of VCD Spectroscopy to the Determination of the Structures of Natural Products, Pharmaceuticals, Peptides, Peptidomimetics, Supramolecules: Recent Developments.**

Philip Stephens; U. Southern California

The technique of Vibrational Circular Dichroism Spectroscopy provides an increasingly powerful method by which the structures of chiral molecules can be characterised. Its most important applications are the determination of Absolute Configuration and Conformational Analysis. These applications have been made possible by the implementation of the Stephens equation for vibrational rotational strengths using Density Functional Theory. We discuss recent developments in the computational methodology used to predict VCD spectra and recent applications to structure determination in the following classes of molecule: Natural Products, Pharmaceutically-relevant molecules, Peptides, Peptidomimetics and Supramolecular molecules.

(53) **Magneto-Optical Enantiomeric Detection**

Phillip Gibbs; Stheno Corporation

Chiral purity is a key factor in the efficacy of many agrochemicals, flavor & fragrance ingredients, and pharmaceuticals. Hence, the production of single enantiomers of chiral intermediates and final products has become increasingly important over the last several decades. However, the detection of these chiral analytes remains a daunting challenge especially in cases where a convenient UV chromophore is not present. While some progress in laser-based polarimetry and Circular Dichroism HPLC detectors has been achieved in the past decade, the current demands for rapid detection of enantiomeric purity on small volume and low concentration samples remains largely unresolved. To address these acute industry needs for novel chiral detection technologies, this work describes the development of a next-generation chiral analysis instrument that is suitable for non-contact, rapid, accurate, and highly sensitive screening of chiral samples. This instrumentation utilizes several experimentally simple, but scientifically sophisticated techniques from "state of the art" optics research first developed for nonlinear optical spectroscopy, but which is now applied to simple polarimetry. The method transforms the detection of optical rotation into a dual-beam double-modulation technique that utilizes the advantages of differential signals, heterodyne mixing, direct modulation of the sample Verdet constant via the Faraday effect, electronic noise cancellation, and phase sensitive detection for additional noise rejection and enantiomer identification. We call this set of techniques and the resulting system Magneto-Optical Enantiomeric Detection (MOPED™).

(54) **Solid State Vibrational Circular Dichroism and X-ray Crystallography: The Absolute Configuration of an α-Hydroxy-Betalactam**

Linda Phillips[1], Michael Galella[1], Ming Huang[1], Yingru Zhang[1], Stephen Gozo[2], Jack Gougoutas[1]; [1]Bristol-Myers Squibb PRI, Princeton, NJ, [2]Bristol-Myers Squibb PRI, Hopewell, NJ

Single crystal x-ray and solution VCD are two of several techniques by which the absolute configuration of molecules can be determined. Good results with solution VCD are dependent upon the identification of all important molecular conformations present in solution. This can be problematic when a molecule has more than four or five rotatable bonds. By contrast, if the single crystal structure (but not absolute stereochemistry) is known, the number of conformations needed for VCD calculations is reduced to the number of conformations in the unit cell - often a single conformation. In an earlier work, we described a dilemma which arose from x-ray crystallographic assignments of absolute configuration for a key drug intermediate. Solution VCD was used to clarify the results and confirm the absolute configuration. The VCD measurement was carried out in chloroform solutions, and it was found that a hydrogen bonded "dimer" model was necessary to achieve good agreement with the experimental data. Herein, we describe an alternate approach to solving the absolute configuration of this molecule. Solid state VCD measurements were carried out and calculations were conducted on a model constructed to mimic the molecular environment within the unit cell (multiple intermolecular H-bonds, but no "dimers"). Agreement between the experimental VCD spectrum and the predicted spectrum based on the crystal structure was sufficient to assign absolute configuration.

(55) **Pharmaceutical Applications of VCD: Reaction Monitoring and Solid-Phase Analysis of APIs and Excipients**

Laurence A. Nafie[1,2], Xiaolin Cao[1,2], Shengli Ma[1], Rosina Lombardi[1], Teresa B. Freedman[1], Rina K. Dukor[2]; [1]Syracuse University, [2]BioTools, Inc.

Within the past several years, VCD has become an accepted, and often a preferred, method for the determination of absolute configuration in chiral molecules that can be accomplished with only a solution-phase sample. Beyond this novel application, VCD has other areas of high promise for applications in the pharmaceutical industry that are both unique and important. Mid-infrared (mid-IR) and near-IR vibrational circular dichroism (VCD) spectroscopy can be used to determine simultaneously the mole fraction and percent enantiomeric excess (%EE) of multiple chiral species in solution as a function of time. We have also found that VCD can be used to characterize the chirality and structure of APIs and chiral excipients in the solid phase. In the first area, we have shown that VCD can be used to monitor the course of reactions involving chiral molecules. As a simple example, near-IR absorbance and VCD has been used to monitor the epimerization of (S)-(+)-2,2-dimethyl-1,3-dioxolane-4-methanol (S-DDM). The NIR-VCD spectra exhibit clear isolated VCD bands at the range of 5050-4700 cm-1 resulting from the O-H combination bands of S-DDM, which were found to decrease in intensity with reaction

time. NIR-VCD spectra of 10 reference samples obtained were subjected to partial least-squares (PLS) regression and the results were used to build predictive models for EE determination. The multivariate regression was carried out on three different sets of spectra for the DDM epimerization reaction in three different solvents, methylcyclohexane, carbon tetrachloride and tetrahydrofuran. The solvent effects in DDM epimerization will be discussed. The potential of NIR-VCD for stereochemistry reaction monitoring is highlighted. In the second area, examples will be given of different approaches to obtaining VCD spectra from solid phase chiral APIs and excipients. Approaches include KBr pellets, mulls in nujol oil, and spray-dried films. In some cases for films anomalously large VCD spectra are obtained. The potential of VCD to serve as a chiral diagnostics of formulated pharmaceutical products will be examined.

(56) **Advancing Spectroscopic Imaging to Time-Resolved Chemical Sensing in Three Spatial Dimensions**

Frank Vogt[1], Michael Gilbert[1], Robert Luttrell[1]; [1]University of Tennessee

Spectroscopic imaging is a recent advancement in analytical spectroscopy which combines spectroscopic sensing with imaging techniques. As spatial resolution in an X-Y plane is introduced, heterogeneous samples can be investigated. However, all (2D) imaging techniques inherently lose depth information. This imposes a severe limitation for studies of chemical processes ongoing in three spatial dimensions; prominent examples include investigations of tissue growth in biomedical studies and process analytical sensing of complex-shaped 3D structures. We propose to advance conventional spectroscopic imaging by introducing additional optical components that will allow the acquisition of depth information. Our approach is based on projecting a regularly shaped light pattern onto 3D samples. Due to 3D surface structures this regularly shaped pattern in the X-Y plane is distorted upon projection onto the samples. By knowing the original pattern and by measuring the distorted one, a 3D surface structure can be extracted. If this information is combined with the conventionally determined spectroscopic imaging data, complex-shaped surface structures can be determined along with spatially resolved spectroscopic information. Since such data sets can be acquired in seconds, a high time resolution can be achieved by a acquiring time series. Our goal is to gain time-dependent X-Y-Z distributions of chemical information. This allows us to study dynamic chemical processes occurring in three spatial dimensions. This technique provides new perspectives in high-resolution chemical sensing for a wide variety of applications. Our first examples focus on microscopic applications; this will open new analytical perspectives, such as in the studies of complex biological or biomedical systems.

(57) **Optical Spectroscopies for Biological Structure at Interfaces**

Kimberly Briggman; NIST

In situ linear and novel nonlinear optical spectroscopies based on infrared, Raman and vibrationally-resonant sum frequency generation (VR-SFG) spectroscopies are being used to study biological interfaces such as biological membrane mimics and incorporated membrane protein structures. These optical techniques can uniquely probe the structure of specific native functional groups of molecules without the need for fluorescent or radioisotope tagging. Moreover, the use of multiple techniques allows unambiguous determination of molecular structure and orientation of molecules at the interface. Presented results will include determination of the gel-fluid phase transition temperature of lipid layers in supported bilayer membranes, and the influence of membrane fluidity on the incorporation kinetics and secondary structure of transmembrane polypeptides and enzymes.

(58) **Inorganic Colloidal Nanocrystals for Biological Labeling**

Yunwei Charles Cao; University of Florida

Inorganic nanocrystals exhibit size- and shape-dependent properties that are of interest for applications ranging from biosensing and catalysis to optics and data storage. They are readily available in a wide variety of discrete compositions and sizes. Shape-selective synthesis strategies now also yield shapes other than nanospheres, such as anisotropic semiconductor and metal nanostructures with interesting optical properties. Herein we report a synthesis of high-quality lanthanide-oxide and II-VI semiconductor nanocrystals while controlling the nanocrystal's size and shape. The as-prepared nanocrystals are highly dispersible in non-polar organic solvents, and simultaneously form surperlattice structures via a self-organization process. In addition, these nanocrystals are highly fluorescent, and exhibit higher stability against chemical and photo-oxidation, which is very important to biological labeling studies.

(59) **Engineering the Selectivity of Nanopatterned Surfaces for Protein Assays by Combining AFM Characterization and Nanoscale Lithography**

Jayne C. Garno; Louisiana State University

The reliability and sensitivity of protein biosensors and biochips depend on the affinity and viability of surface-bound biological components. Nanostructured surfaces provide highly-controllable test environments for fundamental investigations of protein binding. Researchers have begun to combine atomic force microscopy (AFM) and nanoscale lithography to develop protein assays with molecular level sensitivity. Latex particle lithography and scanning probe lithography are versatile tools for fabricating well-defined surfaces. Particle lithography provides nanometer precision for controlling the placement of target molecules. The dimensions and spacing of protein nanostructures can be systematically varied by changing the diameters of the latex particles and by controlling protein-to-latex ratios. Particle lithography uses simple physical adsorption of proteins in mild environments at ambient temperatures, which should enhance the retention of the bioactivities of immobilized proteins. Commercial AFM instruments typically include software with capabilities to control the length, direction, speed, bias, pulse duration, residence time, and the applied force of the AFM tip. Automated scanning probe lithography (SPL) can be used to rapidly write arrays of nanopatterns of functionalized alkanethiols with designated terminal chemistries. Nanografting of self-assembled monolayers (SAMs) enables superb control of spatial parameters such as ligand density for elements of test arrays and offers advantages of speed and reproducibility. Nanopatterns of SAMs can be chosen to present reactive groups (such as aldehyde or carboxylate) for binding proteins. After incubating the nanopatterns with desired molecules, the changes in height and surface morphology provide details of surface reactions. Using in situ AFM characterizations, experiments can be accomplished in ambient buffered environments for directly detecting and visualizing the binding of biomolecules on nano-engineered surfaces, to evaluate the specificity and selectivity of immobilization chemistries. Series of AFM images will be presented which display protein arrays produced by nanoscale lithography (such as automated nanografting or latex particle lithography) before and after incubation with antibodies. In situ AFM experiments furnish information regarding the orientation of immobilized proteins and the selectivity of engineered surfaces for binding antibodies or peptides. Conceptually, by developing high-throughput approaches for arranging and orienting proteins at the nanometer scale, the

sensitivity and reliability of commercial biochip technologies could be substantially improved.

(60) **Exploring Nanostructured Surfaces for Novel Electrochemically Based Sensing Devices**

Diego Diaz; University of Central Florida

Electrochemistry based techniques have provided simple, cheap and reliable sensors. Our group has explored the integration of nanoscale structured surfaces in the preparation of novel sensing methodologies. Our recent efforts have included the preparation of nano-porous wide-bandgap semiconductors and their use as templates for Schottky based gas sensors. Such sensors are being developed and explored as high temperature, fast response sensors for the detection of hydrogen at low concentrations. We have also explored the utilization of ceria nano-particles as catalyst for the amperometric detection of reactive oxygen species and the development of in-situ sensing for non-invasive bio-devices. Reactive oxygen species, hydrogen peroxyse in particular has been associated as a stress response in plant systems. We are currently developing micro-needle sensors for the in-vivo monitoring of hydrogen peroxide levels in plants as way to monitor plant health. Both efforts are currently under study and I will present recent developments on the understanding and implementation of those novel sensing methodologies, both of them based on our ability of controlling surface modification at the nanoscale.

(61) **Liquid-Deposited Carbon Nanotube Networks: A New Electronic Material**

Marcus D Lay[1], Pornnipa Vichchulada[1], Tasaday E Lync[1];
[1]University of Georgia

Analytical studies of 2-dimensional networks of carbon nanotubes (CNTs) will be presented. A novel method of creating ordered arrays of purified CNTs has been exploited to attain a higher level of control over reproducibility in CNT-based applications. This method uses unidirectional air flow to order CNTs in aqueous suspension and deposit them on a hydrophobic SAM-modified surface (i.e. 3-aminopropyl-triethoxysilane on Si/SiOx). 2-dimensional networks of CNTs show potential as a method of circumventing the difficulties associates with lack of control over the physical and electrical properties of individual CNTs; for a random distribution of CNTs, density control is the major factor controlling device properties, as fluctuations in characteristics of individual CNTs are averaged. These ordered arrays of CNTs exhibit anisotropic electrical conductivity over macroscopic lengths (up to 3"), and have shown promise in electrochemical, as well as field-effect transistor (FET) applications. Several novel approaches to CNT devices will be demonstrated.

(62) **Imaging Mass Spectrometry: Principle and Applications**

Pierre Chaurand[1], D. Shannon Cornett[1], Richard M. Caprioli[1];
[1]Vanderbilt University

Imaging Mass Spectrometry (IMS) is a relatively new technology that takes advantage of the methodology and instrumentation of MALDI mass spectrometry. It can be used to locate specific molecules such as drugs, lipids, peptides and proteins directly from the surface of fresh frozen tissue sections. Frozen tissues specimens are cut in very thin (~10 um) sections and thaw-mounted on flat metallic target plates. Matrix can be manually or automatically deposited on the sections. The protein profiles recovered upon analysis typically contain from 300 to 500 distinct signals in the m/z range up to 200,000. When imaging proteins from a tissue section, the matrix is deposited in a homogeneous manner minimizing the lateral dispersion of the peptides and proteins. This can be achieved by automatically printing arrays of small droplets. Each microspot is then automatically analyzed generating a mass spectrum. When monitoring the intensity of a protein signal within the data array, a two-dimensional ion density map (or image) can be reconstructed giving information on the protein location and relative abundance. From the analysis of a single section, images at virtually every MW may be obtained. IMS is an effective discovery tool for the comparison of MW based protein patterns in unhealthy versus normal tissues and in helping identifying potential protein markers in lesions and in various stages of disease progression. In this regard, histology directed profiling permits higher sample throughput and reproducibility. The visual specificity of histology is combined with the positioning accuracy of the robotic microdispenser to direct placement of matrix drops onto specific cells with high placement accuracy. Processing digital images of the spotted plate provides relative locations of each matrix spot. These coordinates are transferred and registered to the mass spectrometer for automated data acquisition. Thousands of proteomic profiles can now be acquired from large sample sets in very short periods of time, improving analysis statistics. The IMS technology has also been applied to drug targeting and metabolic studies and the measurement of concomitant protein changes in specific tissues after systemic drug administration. The specific advantages and capabilities of the technique and its limitations will be addressed.

(63) **Applications of Advanced High Speed Laser Optics for Imaging Mass Spectrometry**

Stacy D. Sherrod[1], Edward T. Castellana[1], David H. Russell[1];
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The ability to image biological analytes is an important tool in many areas of life science research. Mass spectrometry utilizing matrix assisted laser desorption/ionization time-of-flight mass spectrometry (MALDI-TOFMS) has opened new avenues for imaging biomolecular expression profiles (e.g. genomic, proteomic, etc.) directly from complex sample types. Imaging MS has shown the ability to map pharmaceutical drugs in targeted tissue and spatially determine the expression profile of specific proteins in healthy vs. diseased tissue states. Light-based optical imaging techniques typically require the use of extrinsic molecular tags (e.g. fluorophores, etc.) whereas mass spectrometry provides native state analyte identification owing to the intrinsic mass of each molecule. However, there are several challenges in contemporary imaging MS, these include: poor spatial resolution due to laser probe spot size (~25-50 micrometers), invariable probe dimensions, long analysis times, and spatial position imprecision due to mechanical translation of the MALDI plate. To address these limitations, we have designed and implemented innovative optical strategies for improving spatial resolution in imaging MS methodologies. The new optical arrangement consists of four major components: the primary MALDI laser beam, beam conditioning optics, a digital micromirror array (DMA), and an imaging lens system. Briefly, the beam conditioning optics consists of beam expansion, homogenization and collimation. After conditioning, the beam is incident upon the DMA. Mirrors in the DMA are individually addressed by software to be either in an "on" or "off" state depending on the uploaded pattern. Laser light reflected from individual mirrors in the DMA is focused on the sample plate by an imaging lens system. This provides a rapidly adjustable ionizing beam for the MALDI experiment. By using this arrangement, the MALDI irradiation can be quickly (~16 microseconds) patterned into regular or complex shapes of variable dimensions. Optical laser beam translation alleviates the challenges associated with mechanical rastering by decreasing analysis times afforded by the fast switching times (5 kHz) of the DMA. These advances provide a novel and powerful tool to facilitate studies at the forefront of proteomics and biomedicine.

(64) **Imaging MALDI MS With an Orthogonal TOF Mass Spectrometer**

Werner Ens[1], Gamini Piyadasa[1], Oleg Krokhin[1], Hui Qiao[1], Victor Spicer[1], Kenneth Standing[1]; [1]University of Manitoba

An orthogonal-injection MALDI TOF instrument is well-suited for obtaining mass-selected 2d images from tissue sections because the source is decoupled from the mass measurement. The mass spectral quality is thus independent of variations in sample properties (such as thickness), and the target may be held at low voltage and in a modest vacuum. Moreover it allows greater flexibility for the incident laser optics and also allows the possibility to perform MS/MS measurements on selected peptides or proteins. A high-repetition rate Nd-Yag laser is coupled to a 10-µm optical fibre. The output is imaged on the sample and the sample is rastered at a uniform rate to obtain an image. A continuous data log of flight times is acquired along with real-time markers to coordinate the position of the laser spot. In the usual QqTOF geometry, the incident angle is 30º, and the spot size is approximately 35 µm. We have also constructed a new MALDI source for orthogonal TOF in which the ions are ejected perpendicular to the axis of the collisional cooling ion guide. This allows normal incidence for the desorbing laser, and much closer placement of the final focusing optic, both of which are essential for high-resolution imaging. In this geometry, effective spot size of about 5 µm has been achieved. Desorbed ions are drawn into the ion guide by gas flow. The source and software have been tested with a 500 lines-per-inch grid, coated with angiotensin and placed on a target coated with C60. Mass selected images for both species clearly show spatial resolution of 10 microns or better with the new source. We present preliminary images of small proteins from kidney and mouse brain tissues using both sources. With the 500 Hz repetition rate laser, mass-selected images for proteins up to 20 kDa can be acquired at the rate of 20 pixels per second. This represents at least an order of magnitude improvement in data rate compared to previously reported methods.

(65) **Mass Spectrometry in the Brain: From Single Cells to Imaging**

Jonathan Sweedler; University of Illinois

In order to understand cell to cell communication in the brain, knowledge is required of the specific neuromodulators used and their locations within the tissue. In nervous tissue, spatial resolution is critical due to the significant differences in the chemical profiles of even adjacent cells. We present a suite of MS-based profiling and imaging approaches for brain samples ranging from individual neurons to brain regions. The first approach is the "Stretched Sample Method" for massively parallel single-cell sized sample preparation. In this technique, thin tissue slices are adhered to a layer of cell-sized solid supports anchored to a hydrophobic, stretchable membrane. Subsequent membrane stretching divides the tissue into thousands of pieces, each of which is typically anchored to a single solid support centered in an otherwise hydrophobic region and is well separated from neighboring beads and their attached pieces of tissue. Once the sample is separated into isolated pieces, matrix is sprayed onto the tissue, the membrane is cooled to condense moisture onto the beads, and analyte is extracted from the tissue and crystallizes with the MALDI matrix. Using this approach, hundreds of putative peptide peaks are detected. Which peaks in a mass spectrum are worth further characterization efforts? In order to create a functional assay, we measure the molecules that are released from a neuron in an activity dependent manner using a method to monitor peptide release from spatially defined locations of living cells and tissue. We place single particle solid-phase extraction probes directly over the region of interest of a brain slice and collect peptides secreted from the sample. These are collected and assayed using MALDI-MS. Using this technique we are able to measure secretions from invertebrate ganglia, single invertebrate neurons, and of living vertebrate brain slices.

(66) **Comparison of UV and IR Atmospheric Pressure MALDI Mass Spectrometry in Biomolecular Imaging**

Akos Vertes[1], Yue Li[1]; [1]The George Washington University

Biomolecular imaging with mass spectrometry offers several advantages over other imaging methods (e.g., fluorescence). Among them are the detailed structural information offered by mass spectrometry and compared, for example, to immunostaining, the minimal need for method development. There are, however, special requirements for mass spectrometric imaging that partially offset these advantages. Chief among them are the need to place the sample into a vacuum environment and, in the case of UV-MALDI, to apply a light absorbing organic matrix overlayer. These requirements present obstacles because the vacuum of a mass spectrometer is not conducive for studying biological samples and the application of an organic matrix can distort or even obscure the native distribution of biomolecules. In this contribution we report on our efforts to keep the sample at atmospheric pressure (AP) and utilize AP-MALDI for (bio)molecular imaging. Furthermore, the need for the organic matrix can be eliminated by using IR laser radiation to produce the ions. Near IR-MALDI at ~2940 nm can take advantage of the water content native in most biological samples for the deposition of energy. We showed the feasibility of imaging AP-MALDI-MS using both UV and IR lasers. Images of mock targets were collected using a Q-TOF Premier MS with a custom-built laser desorption ionization source. The ions produced by a nitrogen laser (at 337 nm) or a Nd:YAG laser driven tunable optical parametric oscillator (at 2940 nm) were sampled by the MS. In addition to conventional matrixes water was also successfully used for sustained ion production. Although in the IR mode at this point the resulting images had crude spatial resolution, the mass resolution and the sensitivity of the system were similar to UV AP MALDI. Improving spatial resolution and exploring the figures of merit of this system are being pursued.

(67) **Multidimensional Identification and Structural Characterization of Peptides and Proteins – Imaging Ion Mobility-Mass Spectrometry**

John A. McLean[1], David H. Russell[2]; [1]Vanderbilt University, [2]Texas A&M University

Imaging MS techniques using MALDI ionization have demonstrated great potential for identification of pathological biomarkers or biomarker signatures, which are correlated with the histological regions from which the ions were produced. Biocomputational methods in combination with biomarker signature determinations can be used as a powerful tool for disease diagnosis, prognosis, and to facilitate appropriate treatment decisions [1]. To further improve the utility of imaging MS, this report focuses on post-ionization analyte separation strategies using MALDI-ion mobility (IM)-MS for (i) extending concentration dynamic range, (ii) reduction of chemical noise, and (iii) data-dependent validation of signals in complex mass spectra. Following spatially-resolved MALDI ionization, ion separations are performed in the IM-dimension on the basis of collision cross section, a structure-dependent property, with a neutral background gas. Upon elution from the IM drift cell, the ions are mass analyzed in the second-dimension by using TOFMS. Thus, imaging mode MALDI-IM-MS provides a two-dimensional separation based-on analyte structure and m/z, plotted as conformation-space, at each x,y-position on the sample. Importantly, the regions in which signals appear in conformation-space correspond with specific molecular class, i.e. the correlation of collision cross section with

m/z varies as nucleotides/carbohydrates < peptides/proteins < lipids/surfactants. Furthermore, deviations from the predicted correlation can provide additional analyte information, for the case of peptides and proteins, these can include: identification of sights of post-translational modification, characterization of anhydrous structural motifs, and determination of analyte-ligand intermolecular interactions. Separations of analytes in conformation-space provide three distinct advantages over contemporary imaging MS strategies. Concentration dynamic range is improved for low-abundance species, because ion suppression effects are mitigated by the temporal separation of high abundance species prior to extraction in the TOFMS. Chemical noise is reduced when isobaric concomitant species are separated to different regions of conformation-space than the analytes of interest. Data validation is provided by identification of m/z and confirmation of the molecular class from which the specific signal is derived. These and future applications such as the determination of structural biomarkers will be addressed in the context of imaging mode analyses. [1].\tR. M. Caprioli, Cancer Res. 65 (2005) 10642.

(68) **PhD Scientists for the 21st Century**

Thomas Isenhour; Old Dominion University

PhD Scientists for the 21st Century. The concept of science and scientific scholarship began with the ancient Greeks. Plato established the first institution dedicated to learning. The modern university emerged during the renaissance and Europe became the center of graduate education. Most of us can trace our academic origin to Europe. Yale started graduate education in the US and it evolved into a one-on-one process where the education of the student, while having to conform to a department or university curriculum and set of standards, depended principally on the direction of the professor. This was true when I directed Peter Jurs and remains true in most universities today. Although science has historically been global, scientists have not. Now, however, scientists cannot work alone within a sheltered environment. Scientists work more often in teams and commonly teams that are dispersed around the globe. The modern PhD must have addition skills such as cultural awareness, ethics training and even legal and business knowledge. Can we continue to produce PhD's directed by a single individual? I think not. In this paper, I will present some ideas for reforming the science PhD for the 21st century. And I will take a moment, to pay tribute to my own first PhD, Professor Peter. C. Jurs. Thomas L. Isenhour Provost and Vice President for Academic affairs Old Dominion University.

(69) **Multivariate Calibration Strategies for Near-Infrared Glucose Sensors**

Gary Small; University of Iowa

The determination of blood glucose levels by near-infrared spectroscopy offers the potential of noninvasive, continuous monitoring of this clinically important blood constituent. As a replacement for current invasive glucose home testing procedures, this measurement capability would provide significant benefits to diabetic patients, in terms of both better management of their disease and improved quality of life. The technology would also find use in hospital settings for applications such as patient bedside monitoring. Two issues that impede the successful development of near-infrared blood glucose measurements are the implementation of a successful and stable calibration model to relate the spectral measurements to the glucose level and the need to produce a simple, rugged instrument for the measurement that still possesses the required optical performance. These two issues are intertwined because the calibration requirements dictate the characteristics of the measurement platform. In this presentation, strategies to improve the stability of calibration models will be addressed in the context of glucose measurements made in model systems that are designed to simulate the pertinent characteristics of the physiological measurement. By collection of spectra over time, the effects of instrument variation on calibration model performance can be assessed. On the basis of this investigation, calibration protocols will be described that allow the effects of this instrumental variation to be minimized.

(70) **Is PLS a General Paradigm for Multivariate Data Analysis in Chemistry?**

Barry Lavine[1], Nikhil Mirjankar[1], Mehul Vora[1]; [1]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 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, which do not perform as well on prediction sets because of overfitting. Second, pattern recognition on data at a higher level can be performed, 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 a concern when using any variable selection technique, does not pose a problem because of the stringent criteria imposed on feature selection by the pattern recognition GA. Fourth, this approach to feature selection can be extended to include problems in multivariate calibration. The efficacy and efficiency of this procedure is demonstrated in a number of studies recently completed in our laboratory in classification and calibration of near-infrared data, IR library matching, and supervised learning from gene expression data.

(71) **Multi-sensory Approach to Improved Situational Awareness**

Susan Rose-Pehrsson[1], Christian Minor[2], Kevin Johnson[1], Jeff Owrutsky[1], Stephen Wales[1], Daniel Gottuk[3], Daniel Steinhurst[2]; [1]Naval Research Lab, [2]Nova Research, Inc, [3]Hughes Associates, Inc.

A multi-sensory approach is being used to develop new detection capabilities for improved damage assessment and real-time situational awareness. The new detection system was developed as part of the Advanced Damage Countermeasures program where the U.S. Navy seeks to develop and demonstrate improved, low cost damage control capabilities that will be incorporated into new ship designs. The detection system combines surveillance camera video images with selected spectral and acoustic signatures and image recognition technologies to provide a broad range of situational awareness. Various spectral and acoustic signatures, new video imaging techniques, and image recognition methods have been investigated and integrated into a multi-sensory prototype system. The prototype system is able to detect event signatures within the volume of a space (i.e., a "volume sensor") rather than relying on spot-type fire detectors. Two prototype systems were built and assessed in full-scale testing aboard the ex-USS Shadwell side-by-side with two commercial video image fire detection systems and several spot-type fire detection systems. Tests included a wide range of fire and nuisance sources, plus flooding and pipe rupture scenarios under actual shipboard background conditions. The prototype systems are shown to outperform the commercial fire

detection systems for flaming and smoldering fires with a high level of nuisance immunity. In addition, they successfully detected the pipe ruptures and flooding scenarios. The system can be adapted for homeland security.

(72) **Student-Designed Undergraduate Research Projects**

Debra Egolf[1]; [1]Marietta College

My graduate advisor, Peter C. Jurs, both encouraged and valued independent thinking among his research students; his example influences how I teach and mentor my students. Senior undergraduate chemistry and biochemistry majors that pursue research under my supervision are challenged with the opportunity to propose their own projects. They are limited only by time frame, budget, and their own creativity. While some students have developed projects closely related to my areas of interest, most select unrelated topics often associated with their individual experiences. By adapting to their project choices I enjoy the benefit of expanding my own knowledge base. This talk will describe such student-designed projects as the measurement of fructan levels in pasture grasses, by a horse owner; the analysis of nutritional supplements for anabolic steroids, by a football player; the determination of malathion levels in apples, by a farmer's son; and the investigation of the temperature-viscosity relationship in motor oils, by a car enthusiast.

(73) **Advances in Protein QSPR and Surface Analysis**

Curt Breneman[1]; [1]Rensselaer Polytechnic Institute

pH-dependent distributions of the electronic properties found on the solvent-accessible surfaces of proteins are key components of protein behavior. While full characterization of localized binding site environments are crucial to scoring small molecule binding, other exterior features of proteins are indicative of their ability to bind to chromatographic media and their propensity to bind with other proteins. Recent work in protein surface characterization and modeling will be discussed.

(74) **Chemometrics, Computational Chemistry, and Cheminformatics Over the Decades**

Peter C. Jurs; Penn State University

Powerful forces over the past forty years – the availability of ever more capable computers and ever better software coupled with a growing number of computational chemists – have led to dramatic advances in the fields of chemometrics, computational chemistry, QSPR, QSAR, and cheminformatics. Computer-aided chemistry has gone from a curiosity to an integral part of the science. This paper will chronicle one professor's journey through these exciting times. Research in the areas of pattern recognition, chemometics, quantitative structure-property relationships, quantitative structure-activity relationships, cheminformatics and related topics will be highlighted. Given ever more capable hardware and software, the types of applications that could be tackled have advanced dramatically, both qualitatively and quantitatively. The contributions of the many students and postdocs involved in the research will be pointed out.

(75) **2D Raman Correlation Spectroscopy Study of Emulsion Polymerization Reaction**

Isao Noda[1], William Allen[1], Seth Lindberg[1]; [1]The Procter & Gamble Company

Two-dimensional (2D) Raman correlation spectroscopy was used to investigate the emulsion copolymerization of styrene and 1,3-butadine to produce an ultra fine nano scale dispersion of styrene-butadiene rubber (SBR) particles. The reaction process was monitored in situ with a Raman spectroscopic probe directly coupled with a pressurized reactor. The resulting time-resolved Raman spectra were converted to 2D correlation spectra for further analysis. The existence of asynchronous 2D Raman cross peaks clearly indicated that the reaction rates of styrene and butadiene were not identical to each other in this system. It was found that butadiene was preferentially polymerized into SBR before styrene during the early stage of copolymerization reaction. By using the positions of asynchronous cross peaks as distinct markers for pure variables, the self modelling curve resolution (SMCR) analysis was carried out, and time-resolved concentration profiles of comonomers and SBR copolymer were estimated. The recently developed 2D correlation kernel analysis technique was applied to obtain the quantitative indices describing the synchronicity and asynchronicity of the reaction system constituents to further elucidate the details of the reaction process.

(76) **Noise Perturbation in Functional Principal Component Analysis Filtering for Two-Dimensional Correlation Spectroscopy: Its Theory and Application to Infrared Spectra**

Yukihiro Ozaki[1], Yun Hu[1], Boyan Li[1], Harumi Sato[1], Isao Noda[2]; [1]Kwansei Gakuin University, [2]The Procter & Gamble Company

Generalized two-dimensional correlation spectroscopy (2D-COS), introduced by Noda in 1993, has become a powerful and versatile tool for elucidating subtle spectral changes induced by an external perturbation. It is based on the correlation analysis of perturbation-induced variations of spectral intensities monitored by an electromagnetic probe, for instance, time series spectra produced by an infrared spectrometer from n measurements at m different frequencies. Despite its utility and popularity in recent decade, especially in vibrational spectroscopy, it has been recognized that there are certain limitations to the use of 2D-COS. Among them, noise is often a major obstacle to the interpretation of 2D correlation patterns, because it introduces artifact peaks, and sometimes even causes peaks to enhance or attenuate. Therefore, a method based on noise perturbation in functional principal component analysis (NPFPCA) is introduced to overcome the noise problem in 2D-COS. By the systematic addition of synthetic noise to the dynamic multivariate spectral data, the functional principal component analysis (FPCA) described in this report is able to accurately determine which eigenvectors are representing significant signals instead of noise in the original data. This feature is especially useful for the data reconstruction and noise filtering. Reconstructed data resulted from the smooth eigenvectors can produce much more reliable 2D correlation spectra by removing the correlation artifacts from noise, which in turn enable more accurate interpretation of the spectral variations. The usefulness of this method is demonstrated with a theoretical framework and applications to the 2D correlation analyses of both simulated data and temperature-dependent reflection-absorption infrared spectra of a poly(3-hydroxybutyrate) (PHB) thin film.

(77) **Moving Window Correlation Analysis of Photoluminescence Images of Single and Aggregated Gold Nanoparticles**

Hugh Richardson[1], Alyssa Thomas[1], Zachary Hickman[1], Alexander Govorov[1]; [1]Ohio University

Images of gold nanoparticles (NPs) on surfaces have been constructed from photoluminescence spectra collected with a Witec Raman Imaging near-field optical microscope. The integrated intensity from the plasmon emission is plotted against position on the surface. Moving window correlation analysis (MWCA) is applied to a cluster of photoluminescence spectra in the image. The cluster position is moved across the entire image to discriminate between single and aggregated gold NPs. MWCA is able to resolve and separate overlapping peaks from adjacent pixels

and the spatial resolution of images obtained after MWCA approaches the diffraction limit of the microscope.

(78) **Cross Spectra Correlation Analysis and Its Application to Time-Resolved FTIR Spectroscopy of Transient Radicals**

Hai-Lung Dai[1], William McNavage[1]; [1]Department of Chemistry, University of Pennsylvania

A spectral analysis method, based on the generalized two-dimensional vibrational spectra correlation analysis, is developed for deciphering the correlation among the spectral peaks of two different spectra. This 2D cross-spectral correlation (2DCSC) analysis is aimed at revealing the vibrational features associated with a common species in two spectra, each obtained from a system containing multiple species with at least one common species. The cross-spectral correlation is based on the premise that the spectral features of the same species should have the same time- and frequency-response toward similar perturbations. The effectiveness of the cross-spectral correlation analysis is first illustrated with model systems, with spectral peaks decaying linearly or exponentially with time, before being applied to analyzing time-resolved emission spectra obtained, by a Fourier transform IR spectrometer, for samples consisting of the vibrationally excited transient cyanooxomethyl radical (OCCN). 2DCSC among the three different sets of time-resolved spectra collected following the photodissociation of three different precursor molecules of OCCN, respectively, allows the identification of the CN and CO stretching modes of this radical.

(79) **Spectroscopic Studies of Gas Interactions with Carbon Nanotubes**

Christopher Matranga; NETL - U. S. Dept. of Energy

Fourier Transform Infrared Spectroscopy (FTIR) is used to study the vacuum thermolysis of acid purified single-walled carbon nanotube bundles (SWNT). Results show that the decomposition of oxygen-containing functional groups produces CO2 that becomes permanently trapped within the interstitial and endohedral spaces of the bundle. The linewidth and intensity of the asymmetric stretching mode (í3) for the trapped species varies with sample temperature. This temperature dependence was studied using two dimensional infrared correlation spectroscopy (2D IR). The 2D IR results suggest that 3 distinct features contribute to the lineshape for the trapped CO2 . The limited number of sites available to the trapped species is used to facilitate assignment of the vibrational peaks to specific sites in the nanotube bundles. Subsequent infrared studies of CO2 adsorption and its coadsorption with Xe and CO further confirm these peak assignments. The unambiguous assignment of these infrared features for CO2 has allowed us to use them in various competitive adsorption experiments to aid in the assignment of infrared bands for other adsorbate species

(80) **pH Unfolding of Apomyoglobin Studied with Two-Dimensional Hetero-Correlation Spectroscopy**

Maxwell Geng[1], Gufeng Wang[1]; [1]University of Iowa,

We demonstrate two-dimensional hetero-correlation analysis between spectrally-resolved and temporally-resolved fluorescence to investigate the decay dynamics of ANS-apomyoglobin complex. The dynamic changes of the lifetime components are disclosed across the emission spectrum with an external pH-perturbation. Two different fluorescence lifetime schemes of ANS-apomyoglobin complex are revealed. From pH 8.5 to 4.5, the transition of protein conformation from the native state to the folding intermediate, a short lifetime component is found to correlate with a short-wavelength emission whose population diminishes with decreasing pH. The lifetime components reflect the excited-state populations of the nascent and the charge-transfer species. From pH 4.2 to 1.0, the transition from folding intermediate to the acid-unfolded state, the short lifetime is responsible for a long-wavelength emission and the fraction of this component increases when the solution becomes more acidic. In this pH range, the decay components reflect the ground state populations of microenvironments. The relative decay dynamics across the emission spectrum are revealed without collecting decays at each wavelength. More importantly, these conclusions are reached without the necessity of statistical fitting of the decay data with an a priori decay model.

(81) **High Spatial Resolution Raman Spectral Imaging of Human Cells**

Max Diem[1], Christian Matthäus[1]; [1]Northeastern University

We have collected high spatial resolution confocal Raman spectral maps of individual human cells, using a WITec (Ulm, Germany) CRM200 microspectrometer. Typically, ca. 30 mW laser power at 488, 514.5 or 632.8 nm was used for excitation. The laser light was focused into the sample via a 100x air or a 60x water immersion objective. The spot size illuminated varies (depending on excitation wavelength) between ca. 350 and 400 nanometer. Using the piezo-electrically driven scan stage, Raman spectra were collected at a 500 nanometer grid, using between 0.5 and 3 sec dwell time for each data point. For large human cells, upwards of 10,000 data points were collected for X-Y scans, and ca. 5000 data points for depth profiling (X-Z) scans. Pseudo-color images were constructed from the spectral hypercubes using hierarchical cluster analysis, after suitable preprocessing (removal of cosmic ray signals and data normalization). Since the spatial resolution of these experiments approaches that of optical microscopy, the spectral pseudo-color maps reveal objects on the sub-micron size scale, identified by their specific biochemical composition. In particular, sub-cellular objects such as nucleoli, mitochondria or liposomes may be observed. Since cells can be kept in cell cuture medium, spectra of live cells can be collected with ease. This methodology opens new avenues to microscopic studies of live cells without the used of contrast agents or dyes.

(82) **In Situ Raman Microspectroscopic Detection of Focally Elevated Creatine in Transgenic APP Mouse Brain**

Kathleen Gough; Department of Chemistry, University of Manitoba

We have used Raman microspectroscopy to examine hippocampal, cortical and caudal tissue from brains of 21 to 89 week old transgenic mice expressing doubly mutant (K670N/M671L and V717F) amyloid precursor protein, and displaying robust pathology from an early age. Raman microspectroscopy combines spatial resolution of 1 micron with molecular fingerprint information, providing a unique tool for the study of plaques and associated changes in situ. Microcrystalline deposits of creatine, suggestive of perturbed energetic status, were detected by Raman microspectroscopy in all animals with advanced plaque pathology. The creatine/phosphocreatine system, regulated by creatine kinase, plays an important role in maintaining energy balance in the brain. Energy metabolism and the function of creatine kinase are known to be affected in Alzheimer diseased brain and in cells exposed to the â-amyloid peptide. With Raman microspectroscopy, we are now exploring possible location and compartmentalization of creatine.

(83) **Macro- and Micro-Investigation of Arterial Tissue by Optical Coherence Tomography and Raman Spectroscopy.**

Lin-P'ing Choo-Smith[1], Mark Hewko[1], Alex Ko[1], Jeffrey Werner[1], Elicia Kohlenberg[1], Sebastien Delorme[2], Rouwayda El-Ayoubi[2], Michael Sowa[1]; [1]NRC-Institute for Biodiagnostics, [2]NRC-Industrial Materials Institute

Coronary angioplasty is the clinical procedure used to clear blocked arteries and involves using small balloons guided into coronary arteries to widen the blocked area. This is incorporated with deploying a mesh stent in the artery to keep it from re-narrowing in the future. However, complications such as re-stenosis and thrombosis can occur due to arterial wall damage during the procedure. In order to reduce the likelihood of restenosis, it is beneficial to understand the interaction of the balloon, stent and arterial wall in order to minimize the vessel injury. We propose to characterize this interaction by using optical coherence tomography to obtain morphological images and Raman spectroscopy to gain biochemical information of these vessels. In preliminary studies, mechanical stretching and friction application were used as models for vessel stress to mimic the balloon inflation procedure. OCT images and Raman spectral maps were collected from control and mechanically stressed regions. Studies were focused on the intima layer of the vessel which most closely contacts the balloon during angioplasty. These results and their correlation with histological analyses to assess degree of tissue damage will be discussed.

(84) **Adventures in Wonderland: Through the Biofilm**

Truis Smith-Palmer[1], Christophe Sandt[1], Judith Pink[1], David Pink[1]; [1]St Francis Xavier University

Biofilms can be found on most moist surfaces – rocks, teeth, medical implants, underwater pipes. They consist of communities of microorganisms surrounded by a matrix of exopolymeric substances (EPS). Their presence has health and economic implications. In order to control them, we need to know more about them: the presence of the EPS makes the bacteria in the biofilm much more resistant to antibiotics, environmental stress, and the immune system of the host, than are free floating (planktonic) bacteria. We are using Raman microspectroscopy for analyzing the chemical composition and spatial organization of fully hydrated biofilms, in situ and in real time, non-destructively and non-invasively. Our system includes a Renishaw inVia confocal spectrometer, equipped with a 514.5nm laser, an 1800 l/mm holographic grating, a 63x immersion lens microscope objective, and a cold stage. Monospecies biofilms of the maritime isolate Pseudomonas aeruginosa PAO1 were grown in an artificial sea water minimal medium in a custom made flow cell. Raman spectra of the PAO1 biofilms and bacteria exhibited some of the characteristic peaks of microorganisms (nucleic acids, protein, polysaccharides, lipids). They were dominated by the contribution of water and also showed strong contributions from EPS. The chemical composition, spatial heterogeneity, and aging of the biofilms was followed over several days. The spatial heterogeneity was evaluated in the horizontal plane as well as in vertical depth profiles. Low resolution maps showed overall biofilm heterogeneity: foreign body inclusions, water channels, and microcolony heterogeneity. The water channels were not totally devoid of biomass and the microcolonies were often highly heterogeneous.\r\n Young colonies in the biofilm were thin and almost homogeneous, with very little EPS. Older colonies showed EPS at the top, edges and the base (at the glass surface) while yet older colonies had even more EPS.

(85) **Micro-Raman Studies of Dental Materials**

Richard Larsen[1], Tim Williams[1], Mark Latta[2]; [1]Jasco, Inc., [2]Creighton University

Dental science presents an exciting applications area for modern dispersive micro-Raman spectroscopy. In order to develop more effective treatments for teeth damaged by decay or physical injury, modern materials science methods are combined with surgery and with both laboratory testing and field trials (evaluation in patient's teeth). The adhesives, resins and tooth preparative treatments used must be bio-compatible, non-toxic and yet resistant to the constantly moist, corrosive environment of the mouth. These materials must cure rapidly and also be easy to use. Micro-Raman spectroscopy, including confocal full-spectral mapping, is a powerful method for development and evaluation of existing and future dental materials. Raman spectral data collected from some examples of these dental materials will be presented and discussed.

(86) **Cell and Tissue Imaging With SERS Nanotags: Surface Enhanced Raman Scattering Meets Medicine**

Michael Natan; Oxonica, Inc.

SERS nanotags are silica-encapsulated metal nanoparticles that give a characterstic Raman spectrum of molecules adsorbed to the metal nanoparticle cores. As such, they can be used as optical detection labels, with a variety of options to functionalize the silica surface with biorecognition elements (e.g. DNA, antibodies). This presentation will highlight three imaging appplications involving antibody-coated SERS nanotags: live animal in vivo imaging, histopathology of cancerous tissue, and cell surface imaging. All three applications highlight the benefits of SERS nanotags: near-IR excitation, high-level multiplexing, and excellent stability.

(87) **Weird Science: ICPMS without a Nebulizer!**

Frank Vanhaecke[1], Luc Moens[1], Martín Resano[1+2]; [1]Ghent University, Dept. of Analytical Chemistry, [2]University of Zaragoza

Self-evidently, acid digestion of solid materials and continuous nebulization of the aqueous solutions thus obtained into the ICP provides important advantages, since the sample solutions can be diluted adequately, problems with analyte heterogeneity can be avoided and calibration can be accomplished with relative ease. However, the ICPMS analyst should not be 'addicted' to the nebulizer, as some analytical problems can be tackled more adequately using alternative sample introduction approaches, e.g., those allowing the direct analysis of solids. With this approach, sample dilution (and thus a deterioration of the LODs) is avoided and the risk of analyte losses or contamination during sample prep reduced, while the sample throughput is increased considerably. Of course, the benefits of laser ablation (LA) in this context are widely recognized by the analytical community. This approach provides, among other, the possibility of quasi non-destructive multi-elemental analysis, an undeniable advantage when very precious materials (e.g., diamonds) have to be characterized or when only minute fragments of sample are available (e.g., forensic evidence). Moreover, also spatially resolved analysis (including depth profiling analysis) can be accomplished using LA-ICPMS. Despite efforts by many research groups however, accurate calibration remains somewhat troublesome when no matrix-matched solid standards are available. In contrast to LA, electrothermal vaporization (ETV) from a graphite furnace is often overlooked as a means of sample introduction in ICPMS. None of the major manufacturers, e.g., offers an ETV-system for combination with their ICPMS instrument and this is a pity, as there is no better way to tackle some niche applications. Moreover, usually calibration is more straightforward than with LA-ICPMS as in the majority of cases, aqueous standard solutions do the job. Real-life applications carried out at Ghent University will be used to illustrate the wide

application range of ETV-ICPMS and will include the determination of non-metals (e.g., Si, S or I) in various matrixes, the speciation of Hg in marine samples and the determination of B in biological materials using isotope dilution (ID) for quantification.

(88) **Electrothermal Vaporization Processes for Plasma Sample Introduction**

Greet de Loos; Delft University of Technology

Electrothermal vaporization (ETV) is one of the techniques studied and used over the years for solution and solid sample introduction in inductively coupled plasma mass spectrometry (ICP-MS) and optical emission spectrometry (OES). From various studies, it can be concluded that the transport efficiency for the analyte depends on the amount of vaporized substance, resulting in non-linear calibration curves with matrix-free standard solutions. If chemical modifiers co-vaporize with the analyte, their effect is manifested in increased transport efficiency for the analyte. This effect can be explained by considering that the vapor of the modifier nucleates to a higher extent than the analyte vapor and the latter can condense onto the modifier nuclei. In addition to this physical condensation, chemical condensation can often be the case with complex matrices, when a less volatile compound is formed by a chemical reaction in the vapor phase. The resulting aerosol carrier effect has been reported for several analytes with a mixture of Pd-nitrate and Mg-nitrate as the modifier. In this study, the ETV sample introduction for plasmas is compared with electrothermal atomization atomic absorption spectrometry (ETAAS), where chemical modifiers are traditionally used to provide better atomization conditions for the analyte and contribute to the reduction of background absorption. We as well as others have observed different behavior of pyrolysis curves in ETAAS and ETV-ICP-MS in experimental work, using the same graphite furnace and power supply in both techniques. Examples of pyrolysis curves obtained for aqueous solutions and slurry samples, with and without using palladium modifier, will be presented and discussed. Gaseous phase modifiers, such as CCl4 vapor, have been used successfully in graphite furnace-ETVs to convert heavy volatile analyte forms into volatile and medium volatile chlorides and also to produce aerosol carrier particles prior to transportation of the analyte to the plasma. ETV-ICP-MS has proven to be a useful tool in our laboratory for the study of vaporization and atom formation processes in the graphite furnace, e.g. the vaporization of Pb, As and Ga alone and in the presence of Pd modifier.

(89) **ETV-ICPMS: When Can it Solve Analytical Problems Better and Easier?**

James Holcombe[1], Adam Rowland[1], Thomas Kreschollek[1]; [1]University of Texas at Austin

Many samples need special care or extreme dilution to accommodate the nuances associated with conventional nebulizer-based sample introduction. This presentation will explore the advantages and disadvantages associated with electrothermal vaporization (ETV) as the introduction source. Many interferences are circumvented simply because the approach is inherently a “dry plasma” approach, i.e., minimal water is introduced to the plasma. Thus, for example, the transient 56Fe peak provides a significant S/N improvement over other the use of other Fe isotopes when using the ETV. While the ArO isobaric interference is still present, the ArO signal is greatly reduced in the dry plasma and the Fe transient signal is easily distinguishable from the steady-state ArO signal, thus simplifying background correction. The thermal program of the ETV virtually eliminates the isobaric overlap of As with ArCl at m/z=75, even in the presence of large amounts of Cl in the sample matrix. Other examples will be provided.

(90) **Benefits and Applications of On-Line Electrochemically-Modulated Separations for ICP-MS**

Douglas C. Duckworth[1], William J. Clark, Jr.[1], Gary J. Van Berkel[1], Debra A. Bostick[1]; [1]Oak Ridge National Laboratory

This presentation will address the varied benefits and applications of coupling electrochemically-modulated separations on-line with ICP-MS. Electrochemically-modulated separations are performed using a flow injection analysis approach and in most cases are similar to electrochemical stripping analysis. EMS-ICP-MS differs in that redox current is not measured, but instead, the analytes selectively accumulated from solution by potential control are released back to solution via step-wise potential control to the ICP-MS for elemental and isotopic analysis. The three-step process (i.e., accumulation, rinsing, and release to the ICP) typically occurs at the working electrode of a three-electrode electrochemical cell. Matrix elimination, analyte preconcentration, and redox- and mass-specificity are among the attributes of the hybrid approach. The development of this field will be reviewed, highlighting benefits, analytical characteristics, and various applications to date. Research sponsored by the Division of Chemical Sciences, Geosciences, and Biosciences, Office of Basic Energy Sciences, U.S. Department of Energy, under contract No. DE-AC05-00OR22725 with Oak Ridge National Laboratory, managed and operated by UT-Battelle, LLC.

(91) **Nanoparticulate Optical Labels Based on Surface Enhanced Raman Scattering: Progress and Opportunities**

Michael Natan; Oxonica, Inc.

Optical detection labels are widely used in life science to track and quantitate molecules, and also in brand security to authenticate and track goods across the supply chain. Interestingly, the shortcomings of fluorescence- and phosphorescence-based labels are apparent in both applications: inability to use near-IR excitation and detection, instability, and the lack of many spectrally distinct labels. We have developed a new type of optical detection tag based on surface enhanced Raman scattering (SERS), based on a core comprising one or more SERS-active nanoparticles, a reporter molecule, and a silica shell. These SERS nanotags yield spectra corresponding to the reporter molecule, and over two dozen different tags have been prepared and characterized. This presentation will describe the technology, and describe applications of the technology in anti-counterfeiting (via incorporation into ink), and in sensitive assays for proteins and DNA.

(92) **Nanoscale Plasmonics for Ultrasensitive Biosensor Development**

Amanda J. Haes; The University of Iowa

The development of new technologies based on nanoscale phenomenon is important and significant for many reasons. One of the most prominent reasons is for the development of biological sensors for the diagnosis of diseases, detection of environmental toxins, and drug discovery. In this talk, a silver nanoparticle-based optical sensor that utilizes localized surface plasmon resonance (LSPR) spectroscopy will be shown to detect a variety of ligands, including a biomarker for Alzheimer\'s disease. Studies on human brain tissue extract and cerebral spinal fluid reveal distinct differences between people who did and did not have Alzheimer\'s Disease. These results represent the first real-world application for the LSPR nanosensor for disease diagnosis.

(93) **Quantum dot FRET-based Sensors for Bioassays**

Zeev Rosenzweig[1], Georgeta Crivat[1], Darwin Reyes[2], Michael Giatan[2], Laurie ocascio[2], Nitsa Rosenzweig[1]; [1]Department of Chemistry-University of New Orleans, [2]Analytical Chemistry Division-NIST

Luminescent quantum dots have been used as alternative to organic fluorophores in bioimaging applications due to their high emission quantum yield, photostability, size dependent wavelength tunability in the visible range of the electromagnetic spectrum and narrow emission peaks, which enable simultaneous observation of multiple targets by using quantum dots of different emission wavelengths. Recently, the scope of use of luminescent quantum dots was expended through the development of quantum dot probes that are based on fluorescence resonance energy transfer (FRET) between quantum dots and organic fluorophores or gold nanocrystals immobilized on their surface. The quantum dot FRET based probes change their emission color when the organic fluorophores or gold nanocrystals are displaced from the quantum dots. Several research groups including ours have used this principle to carry out displacement assays or enzymatic assays and quantify the level of displacers, the level of enzymatic activity and potency of enzyme inhibitors and activators. In all these assays the quantum dot FRET-based probes were dispersed in aqueous solution. In this presentation we will describe for the first time the fabrication of a solid state sensor which is based on the FRET interactions between quantum dots and organic fluorophores. The quantum dots and organic fluorophores are immobilized to polymer layers that are deposited on a glass surface using a layer by layer deposition (LbL) method. The sensor is fabricated in a microfluidic system to precisely control the thickness of each polymer layer and the distance between the quantum dots and molecular acceptors. The presentation will focus on the fundamentals of this sensing geometry and demonstrate its use in various bioassays.

(94) **The Development of Quantum Dot Aptamer-based Biosensors for the Detection of Thrombin**

Marla Swain[1], Vivekanand Shete[1], Frank Hernandez[2], David Benson[1]; [1]Wayne State University, [2]Universitat Rovira i Virgili

The use of quantum dots for monitoring biological systems offer many advantages over organic fluorophores, such as increased photostability and higher quantum yield. These characteristics can be exploited for the real time detection of analytes when coupled with biological molecules that possess molecular recognition properties. Recent work has demonstrated the development of a modular nanoparticle-based system that provides selective, reagentless maltose biosensing. In this method, maltose binding protein (MBP) was attached to both a semiconducting nanoparticle and [Ru(1,10-phenanthroline-5-maleimide)(NH3)4][PF6]2 (1). Maltose-induced conformational changes in MBP influenced interactions between complex 1 and the nanoparticle surface that, in turn, gave rise to changes in nanoparticle emission. This methodology has been extended with the immobilization of CdSe@ZnS-based biosensors to the distal end of silane modified silica surface of an optical fiber for the detection of maltose. Also, a ruthenium(II) modified MBP mutant was adsorbed onto the surface a gold nanoparticle modified electrode and electrochemical responses were observed with the addition of maltose. Here, this approach will be expanded further using DNA aptamers, which are short oligonucleotides that selectively bind a broad range of targets with high affinities. Substrate binding to aptamers induces a change in oligonucleotide conformation, therefore suggesting the previous protein-based methodology can be translated to aptamers. As a pilot study, thrombin-binding aptamers were used. The aforementioned complex 1 has been attached to the 5'-thiol-modified thrombin binding aptamer. The ruthenated aptamer was then added to a partially complementary, 5'-thiol-modified DNA strand to form a double stranded DNA complex that was then attached to MHDA capped CdSe@ZnS nanoparticles. Upon the addition of thrombin, a 50% decrease in the fluorescence has been observed in this system. Non-specific protein adsorption was tested with lysozyme where only a 10% decrease in the fluorescence was observed. Only small changes in CdSe@ZnS nanoparticle emission intensity were observed with thrombin addition to non-ruthenated DNA. The potential for this approach to be utilized for the real time detection of analytes will be presented.

(95) **Monitoring Protease Kinetics with Quantum Dot Bioconjugates**

Igor L. Medintz[1], Aaron R. Clapp[2], Philip Dawson[3], Hedi Mattoussi[2]; [1]Center for BMSE - U.S. Naval Research Laboratory, [2]DOS - U.S. Naval Research Laboratory, [3]The Scripps Research Institute

Luminescent semiconductor nanocrystals or quantum dots (QDs) are finding increasing uses in bioassays due to their unique photophysical properties. We are exploring their use as active monitors of enzymatic proteolysis in fluorescence resonance energy transfer-based assays (FRET). The sensors we have developed consist of either dye-labeled proteins or peptides self-assembled onto the surface of QDs. The close proximity of the QD donor to the dye-acceptor(s) establishes an efficient rate of FRET. Addition of specific protease to the sensor solution results in digestion of the dye-labeled substrate which frees the dye from close proximity to the QD surface and disrupts FRET in a concentration dependent manner. Analysis of the assay data was carried out using Michaelis-Menten kinetic theory and quantitative measurements of enzymatic activity was demonstrated along with the derivation of standard Michaelis-Menten descriptors. These include the Michaelis constant Km, the maximal enzymatic velocity Vmax and the inhibition constant Ki when assays were carried out in the presence of inhibitor. The FRET efficiency data from these constructs can also be used to derive models of the QD-bioconjugate structures. These studies demonstrate that hybrid inorganic-biological materials such as these QD-peptide/protein conjugates can be successfully integrated into bioassays and may have properties which make them superior to the current generation of protease sensors.

(96) **Determination of "Free" Iron from Iron Metalloproteins via Liquid Chromatography- Particle Beam/Hollow Cathode and Inductively Coupled Plasma-Optical Emission Spectroscopy**

Tim Brewer[1], Kenneth Marcus[1]; [1]Clemson University

Iron in the ferrous state is a key element in mediating transformation from less to more reactive, and thus damaging oxygen species.1 Monitoring Fe levels in proteins provides information on oxidation and reduction reactions between red blood cells therefore, the quantitative determination of free iron from bound iron in the form of Fe-metalloproteins is desired. Previous work in this group has shown that Fe-metalloproteins can be determined using reversed phase liquid chromatography-particle beam/hollow cathode -optical emission spectroscopy (LC-PB/HC-OES).2 Presented here is a comparison between size exclusion chromatography SEC-PB/HC-OES and size exclusion chromatography-inductively couple plasma-optical emission spectroscopy (SEC-ICP-OES) for the quantitative determination of free iron from bound iron in metalloproteins. LC in combination with either technique allows for species specific information through monitoring both standard UV absorbance and atomic emission signals specific for Fe (I). ICP-OES is readily coupled to SEC and offers extremely low limits of detection, a wide linear

dynamic range and high sample throughput making it the benchmark for determination of metals. However, coupling of LC eluents into an ICP source can be cumbersome; therefore the coupling of LC eluent into PB/HC-OES was also studied. After separation and isolation of free iron from bound iron, the LC eluent passes into the particle beam interface, which includes a sequence of nebulization, solvent vapor removal and momentum separation steps. Ultimately, a beam of dry analyte particles is introduced into the hollow cathode glow discharge source for subsequent vaporization, atomization and excitation. It is envisioned that the ability of the techniques to provide complementary information will provide a powerful set of tools for biochemical researchers.U.A. Nilsson, M. Bassen, K. Savman and I. Kjellmer, Free Radical Research 2002, 36, 677-684. T.M. Brewer and R.K. Marcus, Analytical Chemistry, in press

(97) **LIBS in Extreme Environments: The Feasibility of Sequential-Pulse LIBS for Deep-Ocean Analysis**

Marion Lawrence-Snyder[1], S. Michael Angel[1], William F. Pearman[1]; [1]The University of South Carolina

Laser-Induced Breakdown Spectroscopy (LIBS) is one of the few techniques capable of non-contact and remote elemental analysis. Because of this, the technique is particularly useful for measuring in extreme or hazardous environments. We are currently investigating the feasibility of sequential-pulse LIBS for deep-ocean analysis, with the ultimate goal of using the technique to better understand the chemistry in hostile and unexplored environments, such as those surrounding deep-ocean hydrothermal vents. This paper describes the first investigations of LIBS for analysis of high-pressure aqueous solutions. The effect of elevated pressure on LIBS solution measurements has previously received little attention, with most published work performed at or below atmospheric pressure. Due to the lack of attention, the fundamental processes of laser-induced plasma evolution in high-pressure solution are poorly understood. Investigations are underway to understand the processes behind recently observed pressure effects on LIBS emission by using time-resolved imaging of laser-induced plasma and vapor bubble dynamics at ambient and elevated pressures. This paper will include LIBS solution measurements, as well as plasma and vapor bubble imaging results, at pressures up to 300 bar. We demonstrate that single-pulse LIBS (SP-LIBS) can be used for measurement of several dissolved elements, including both alkali and alkaline earth metals like Na, Li and Ca, and with less certainty, trace metals like Mn, at elevated pressures (exceeding 300 bar). Additionally, we observe only minor pressure effects on the SP-LIBS spectral features, specifically, emission intensity and line width, for all elements examined. Sequential-pulse excitation (also known as dual-pulse LIBS, DP-LIBS) is useful for measuring a range of elements that are difficult to detect using SP-LIBS. In contrast to SP-LIBS, we find that the magnitude of the DP-LIBS emission is highly pressure dependent, with little or no enhancement observed above approximately 75 bar. Preliminary results reveal that pressure has little effect on the early-stage plasma evolution, but as the plasma cools, solution pressure begins to play a major role. The results of these investigations have significant implications for applications of LIBS to in situ multi-elemental detection in deep-ocean environments, but also to the broader range of applications involving high-pressure liquids.

(98) **Host-Guest Properties of Novel, Self-Assembling, Hexameric Pyrogallol[4]Arene Nanocapsules**

Daniel B. Bassil[1], Sheryl A. Tucker[1], Scott J. Dalgarno[1], Jerry L. Atwood[1]; [1]University of Missouri – Columbia

Many researchers are working on understanding self-assembling macromolecules, in order to imitate and understand nature, especially after recognizing how many complex proteins and viruses are self-aggregating. Most instantaneously, self-assembling structures are based on noncovalent bonds, generally hydrogen bonds. In our case, hexameric nanocapsules are formed by six C-hexylpyrogallol[4]arenes (PgC6) held together by 72 hydrogen bonds, making the structure stable in solution, even in nonpolar solvents. Very few reports, have examined these new materials in solution or explored their viability as molecular transporters.\r\n\r\nAfter our success in encapsulating pyrene butyric acid (PBA) in PgC6, it is our desire to understand the encapsulation process so that it can be controlled and manipulated, for applications ranging from drug delivery to chemical separations. Here, we report the encapsulation of a self-quenching, fluorescent probe 1 (9-anthryl)-3-(4-dimethylaniline) propane or ADMA in PgC6. The ADMA molecule is composed of two rigid sections (anthracene and dimethylaniline, DMA) that have some degree of motion due to a flexible propyl linker. The ADMA anthryl moiety presents a relatively large ð-surface for potential adhesion to the inner capsule walls – observed in the PBA-containing nanocapsules. The polyaromatic nature of ADMA also might aid capsule in stability and guest retention. We found that ADMA encapsulation is not straightforward and appears to depend on its solution conformation prior to entrapment, which gives valuable insight into the capsules' ability to ensnare diverse molecules. Additionally, we discovered ADMA is capable of crystallizing in channels within the extended PgC6 supramolecular array, affording a means to control nanocapsule assemblage.

(99) **Coupling Depolarized RALS and MALS to Size-Exclusion Chromatography**

Andre Striegel, Florida State Univeristy

Study of the depolarization behavior of dilute polymer solutions can inform our understanding of polymer rigidity as a result of tacticity or heavy atom substitution as well as increase the accuracy of molar mass data derived from light scattering measurements. Coupling depolarized light scattering to a separation technique such as size-exclusion chromatography (SEC) allows for measuring the effects of depolarization as a continuous function of molecular size and, consequently, of molar mass. This coupling also facilitates measuring the depolarization of individual analytes in multi-component mixtures separated by SEC. When the light scattering detector on an SEC system is of the multi-angle variety, depolarization behavior may be studied at a multiplicity of angles as a continuous function of molar mass, simultaneously. Here, we present results of SEC coupled on-line to depolarized right-angle and multi-angle light scattering (RALS and MALS, respectively) detection. We compare the behavior of atactic and isotactic polymers, of polymers with and without heavy atom substituents, of highly extended helical polypeptides, and of contaminated industrial samples where the contaminant depolarizes light in a fashion quite different from that of the main sample component. We also show the effects on the molar mass distribution of light absorption by the analyzer in the optical train of our system and discuss a simple algorithm that may be used to empirically correct for this effect.

(100) **Detection of Biologically Relevant Phenolic Compounds using Ce and Microchip-Ce**

Carlos D. Garcia[1], Yongsheng Ding[1], Maria Fernanda Mora[1], Eric Mejia[1]; [1]The University of Texas at San Antonio

Most of the phenolic compounds are considered to have relevant biological activity. Depending on the particular group around the phenolic ring, these compounds could be considered contaminants, disinfectants, herbicides, pharmaceuticals, antioxidants, hormones, or neurotransmitters, just to name a few. Various methods have

been reported for the determination of phenolic compounds, including spectrophotometry, immunoassays, thin-layer, gas, and liquid chromatography, flow injection and biosensors. Many modes of capillary electrophoresis (CE) have also been used for the separation of phenols. CE provides high-speed, high-throughput, low waste generation, highly efficient and reliable separations, and offers a simple way to integrate different analysis steps into a single lab-on-a-chip device. Combined with electrochemical detection (ECD), CE microchips can provide inherent miniaturization, automation, and portability. In the present report, our most recent achievements regarding the analysis of phenolic compounds using CE microchips and electrochemical detection will be discussed. Results regarding the effect of the separation potential, buffer pH and composition, injection time, and detection parameters will be presented. Several examples of the potential of these devices to deal with real samples will be also discussed.

(101) **Microfluidic Hydrogels as an Alternative to Biomolecule Immobilization**

Gloria Thomas[1], Hui Chen[1], Bindu Nanduri[2], Shane Burgess[2]; [1]Mississippi State University, Chemistry Department, [2]MS State Univ, Center for Veterinary Med

In our work, microfluidic hydrogels have been developed for the immobilization of various probes in bioaffinity applications. These analyte-specific hydrogels are rapidly formed by photo-polymerizing a mixture of acrylamide and bisacrylamide monomers with biomolecules, including antibodies and acrydite-modified DNAs and streptavidin. The resulting biospecific hydrogels remain permeable to target analytes under electrophoretic conditions. The effectiveness of this technology has been demonstrated for the analysis of estradiol using antibody hydrogels and ssDNA using ssDNA hydrogels. Additionally, by grafting streptavidin into the hydrogel matrix, 'universal' microfluidic hydrogels allow the subsequent capture and robust immobilization of biotinylated probes. Characterization studies, cross-specificity, robustness and quantitative analysis will be discussed.

(102) **Glycoprotein Analysis for Vaccine Development**

Heather Desaire; University of Kansas

The discovery of an effective vaccine is the best hope to conquer the HIV virus. While current methods in HIV vaccine development span a variety of strategies, one common method is using the virus's own envelope glycoprotein as a vaccine candidate. This molecule is on the viral surface, and it provides the first contact between the virus and cells. Many glycoprotein vaccines are in development for the treatment of HIV, but none of them have passed the critical "efficacy" test in phase III clinical trials. My group hypothesizes that a major problem with the current candidates is the lack of design and control over the carbohydrate portion of these glycoprotein vaccines. This portion makes up 50% of the mass of the molecule, and very little is known about the "right" carbohydrates needed in the glycoprotein vaccine. We focus on analyzing these moieties using several mass spectrometric methods. Our key approach is to analyze glycoprotein vaccine candidates by digesting them with proteases, generating glycopeptides, then characterizing those glycopeptides using high resolution mass spectrometry and MS/MS techniques. Because of the complexity of the analyte, a significant amount of method development is required. By developing the appropriate methods to rapidly screen the carbohydrate content on glycoproteins, and applying these techniques to the glycoprotein on the surface of HIV, we hope to identify critical information needed that could help to generate an effective vaccine against the world's most illusive virus. This presentation will focus on our current successes and future goals in this endeavor.

(103) **Forensic Discrimination of Diesel Samples**

Ruth Waddell[1], Dahlia I. Campbell[2], Amber H. Hupp[2], Victoria L. McGuffin[2]; [1]Forensic Science Department, Michigan State University, [2]Department of Chemistry, Michigan State University

Arson investigation is often considered one of the most difficult and challenging forensic investigations. Potential evidence can be damaged, displaced, or destroyed, not only as the fire burns but also as the fire is extinguished. In potential arson cases, the forensic investigation is geared toward determining the presence of accelerants such as gasoline, kerosene, and diesel. Accelerant extracts from the arson debris are analyzed by gas chromatography, typically with mass spectrometric detection (GC-MS). Due to differences in the volatility of components in different types of accelerant, identification of the general class (*e.g.* gasoline or diesel) is possible based on the chromatogram. A preliminary investigation into the potential of associating an accelerant to a common manufacturer within a general class is presented. Ten diesel samples were collected from the East Lansing, MI area and analyzed by GC-MS. Compounds in the total ion chromatogram (TIC) were identified and extracted ion chromatograms were obtained for m/z 57, an ion characteristic of aliphatic compounds, and m/z 91, an ion characteristic of aromatic compounds. The extent of association between pairs of samples was determined for the TICs and the extracted ion chromatograms using Pearson's correlation co-efficient. Principle component analysis (PCA) was then applied to assess similarities and variation among all samples. Preliminary results indicated that, based on the TIC, diesel samples from different manufacturers were similar. However, greater discrimination of the samples is possible based on extracted ion chromatograms, particularly m/z 91, corresponding to aromatic compounds in the sample. This research indicates that differentiation of diesel samples according to manufacturer may be realized without significantly altering routine analytical procedures currently employed in forensic laboratories.

(104) **A Minimal Fragmentation Real Time Aerosol Mass Spectrometry**

Allan Bertram[1], Pedro Campuzano[1], Emily Simpson[1], Sarah Hanna[1], Damon Robb[1], Michael Blades[1], John Hepburn[1]; [1]University of British Columbia

Despite big advances in techniques to characterize the gaseous phase component, there is still a dearth of instruments capable of doing the same for the organic aerosol component. This is due in part to the type of the compounds present in the aerosol phase, which in general lend themselves less to classical analytical methods such as GC/MS. The most widely used approach is the aerosol mass spectrometer. Current aerosol mass spectrometer designs do a reasonably good job at delivering a representative probe of the aerosol phase to the detector while keeping track of the physical properties of the aerosol. However, the ionization step (multiphoton absorption or electron impact in most cases) still leads to massive fragmentation of all but the most stable organics, making it difficult to characterize individual compounds beyond establishing their functional groups. We have constructed a new real time aerosol mass spectrometer, based on the designs of Su et al & Smith et al, which incorporates a new, high-powered, fully tunable VUV source. This enables us to ionize quantitatively with little to no fragmentation almost all atmospherically relevant organic compounds. Coupled with an ion trap where the primary ions can be stored for further structural analysis, this instrument is both universal and sensitive enough to allow for detailed studies of SOA formation as well as the aging of mixed aerosols.

(105) **The Use of Process Analytical Technology (PAT) in Primary Pharmaceutical Manufacturing**

Jose Menezes[2], Licinia Rodrigues[1], Joao Lopes[2], Teresa Alves[1]; [1]CIPAN SA, [2]Center for Biological & Chemical Eng,

Within the PAT framework as presented in the Food and Drug Administration (FDA) guideline the aim is to design, develop and operate processes consistently to ensure a predefined quality at the end of the manufacturing process. Three PAT implementation scenarios can be envisaged. First, using PAT in its most modest version (almost non-PAT way) to simply replace an existing QC protocol (e.g., using NIR for an in-process quality control, such as moisture content). Second, the integrated use of in-process monitoring and process analysis to enhance process understanding and operation, for an existing industrial process. Third, the extensive and exclusive use of PAT throughout development, scale-up & full-scale production of a new product and process. Although type I implementations are well known, reports of type II and III are still scarce. Here we describe results obtained in PAT implementations of type II and III, in two industrial processes of bulk active pharmaceutical ingredients (API), showing the benefits in terms of increased process understanding and process control that can be obtained through PAT.

(106) **Process Induced Transformations of Erythromycin Dihydrate During Drying**

Meike Roemer[1], Jyrki Heinämäki[1], Inna Miroshnyk[1], Niklas Sandler[2], Jukka Rantanen[3], Jouko Yliruusi[1]; [1]University of Helsinki, [2]University of Otago, [3]University of Copenhagen

Process induced transformations (PITs) may have a great effect on the pharmaceutical and biopharmaceutical performance of the active therapeutical ingredient. Erythromycin(ERY) dihydrate may easily lose its two incorporated water molecules being necessary to satisfy hydrogen bond acceptor and donor groups.These cannot be satisfied simultaneously through intermolecular drug-drug hydrogen bonding leading to a highly reactive dehydrate form. The aim of the present study was to investigate and monitor the PITs of ERY during conventional tray drying at different temperatures using. Pellets were used as model particles, and they were produced by extrusion-spheronization technique using a 1:1 composition of Erythromycin dihydrate and microcrystalline cellulose (MCC). The drying process was performed at two different temperatures (30 C, 60 C). The at-line techniques used to monitor the drying, were FT-NIR spectroscopy, CCD Raman spectroscopy and variable temperature X-ray powder diffraction (VT-XRPD). The stage of the drying process was determined by measuring the water content with an IR-balance. The hot stage VT-XRPD measurements indicated various forms of ERY occuring over a temperature range of 25 C to 220 C. According to XRPD diffraction patterns the samples dried at 30 C did not show any changes in polymorphic composition of ERY. For the pellets dried at 60 C two forms (dihydrate and dehydrate) of ERY existed simulataneously in the end product. NIR confirmed the results of the VT-XRPD. The interpretation of Raman data was difficult due to fluorescence of MCC. Nonetheless, the best way to distinguish the various forms was in the fingerprint area where the fluorescence was the highest. According to the information from the IR balance there was a notable difference in water content between the final pellets dried at 30 and the ones dried at 60 C. The results indicate clearly PITs are occuring during the drying process studied. NIR and VT-XRPD results were both capable of indicating changes of ERY dihydrate in both amorphous and dehydrated dihydrate forms. The final product contained three solid state two forms of erythromycin.

(107) **Getting Value out of Your Process Analytical Results – Getting the Data to Where It Can Be Acted On**

Larry McDermott; Axsun Technologies

The PAT initiative has lead to a dramatic expansion in the use of sophisticated NIR, FTIR and UV spectrometers for on-line analysis of both batch and continuous processes. Much effort has been made in optimizing the hardware and analytical methods to achieve accurate and timely results. In order to optimize the utilization of and payback on these process analyzers, the data must be presented to the plant control systems, manufacturing engineers and operators in a reliable and clear fashion. Early control systems typically incorporated univariate data, such as the concentration of a component of interest into their user interfaces and control algorithms. Modern plant control systems allow for the incorporation of a wealth of information from process analyzers, ranging from the analytical values through diagnostic information for both the analyzer and the analytical method. A variety of "standard" interfaces widely used in industrial control systems including Modbus, OPC, Fieldbus, Profibus etc. allow access to data across an enterprise in standard formats. The use of additional information such as system diagnostics and model "outlier" diagnostics etc. greatly decrease the chance of "bad" data being used to make plant operating decisions, increasing the confidence in the use of sophisticated process analyzers. The capabilities and use of modern industrial interfaces will be discussed.

(108) **Comparison of Reaction Calorimetry and In-line Near Infrared Spectrometry for Monitoring of Esterification in a Novel Reactor**

Pamela Allan[1], David Littlejohn[1], Alison Nordon[1], Kathryn Hipkins[2]; [1]University of Strathclyde, [2]Powder Systems Limited (PSL)

During the scale-up of reactions, there is a need to understand in real-time and without manual sampling the effect of reaction conditions and when completion has been reached. Techniques that can be employed non-invasively and in situ are of particular interest as it is possible that manual sampling may not be representative and/or affect the dynamics of the process. Optical techniques such as near infrared spectrometry (NIRS) can be employed in-line. As chemical reactions either produce or absorb heat, on-line calorimetry can also be used for process monitoring. The esterification of acetic anhydride and 1-butanol was conducted in a 10 L ChemFlux reactor (Powder Systems Limited). The reactor uses a series of discrete independent jacket coils to regulate the temperature of the reactor contents. This method of temperature control, termed COFLUXTM, is superior to adjustment of the velocity or temperature of the heat transfer fluid (as with a conventional reactor) and gives more accurate calorimetric measurements. The reaction was monitored by in-line NIRS, off line gas chromatography (GC) and on-line calorimetry. The difference between manual and automated control of the reactor jacket coils was investigated. Better temperature control of the reaction occurred when the coils were controlled automatically. The NIR data was also easier to model and use with improved temperature control. The end-point of the reaction could be identified from the NIR, GC and enthalpy data. The NIR and enthalpy data showed good correlations with changes in the GC data.

(109) **Development and Transfer of a Near Infrared Identity Method for Polymorphic Form**

CJ Pommier[1], Shawn Yin[1], Anisha Patel[1]; [1]Bristol-Myers Squibb

Powder X-ray diffraction (PXRD) is normally the gold standard for polymorphic form identification. However, there are occasions where PXRD is not an acceptable method for form identity because

of a lack of sensitivity or lengthy analysis times, particularly for in-process tests. In such instances, secondary spectroscopic techniques may be developed in place of PXRD. This presentation will discuss the steps in development of a near infrared spectroscopic method for polymorph form identification and the lessons learned in the transfer of this method to a manufacturing site.

(110) **Chemometrics and Instrumentation: Where Have We Succeeded and Where Have We .. Not Succeeded?**

Garry Ritter; Thermo Electron Corporation

The early years of Chemometrics were filled with the hope of extracting unimagined information from chemical measurements. New techniques were applied to chemical data and we imagined problems that might be solved. Then came the time when we tried to move these techniques into the real, industrial world. We discovered that sometimes we succeeded, but that sometimes there were difficulties that we hadn't expected. That meant that we tried to select which industrial problems could be attempted. We are now in the time when we need to deploy solutions into the factory. That means that we need to make the methodology less obtuse, so that more people might be able to find solutions. We also need to make it easier to get and interpret the answers. People in Chemometrics and in instrumentation point to successes in all three of these areas. To be sure we have come a long way and our intentions have been good. But we need to build on these successes and listen to our customers about how we might improve. Let's look at what we've done well and let's discuss how we might make better Chemometrics.

(111) **A Successful Marriage between Chemometrics and Industry? I could tell you but then I\'d have to kill you.**

Barry M. Wise; Eigenvector Research, Inc.

On the surface, it appears that industry has been rather slow to adopt chemometric methods. But is this really true, and if so, why? It is argued here that certain companies that have been early adopters of the technology have realized significant benefits, and thus a real competitive advantage. This has made them very slow to allow examples of chemometrics successes to see the light of day. As chemometric consultants, we certainly know of many more projects, both successes and failures, than we are allowed to discuss. The lack of publicly available case studies has made it hard to sell chemometric technology to the later adopters. Only recently are the advantages of multivariate analysis in the process environment trickling down to many larger heavy industries. New interest is being seen in techniques originally demonstrated in the 1980s. This talk will include a survey of the status of our past consulting projects with some benefits derived, to the extent that our clients will share this information. Some examples of recent successes will also be included.

(112) **Chemometrics – What's it good for?**

Jerry Workman; Thermo Electron

This paper provides and overview of the most significant developments in problem solving in the field of chemometrics over the past 25 years. The current state of chemometrics pervades the disciplines of computer science, informatics, chemoinformatics, bioinformatics, environmetrics, psychometrics, econometrics, metabolomics, in silico methods, stochastic and deterministic statistical modeling and the like. A large number of review articles on chemometrics and applications of chemometrics to fields other than chemistry have been published. New frontiers such as diagnostic decisions in laboratory medicine and clinical chemistry are being addressed using chemometrics. The multivariate extraction of information from chemical data drives research in many areas of science and engineering including but not limited to, in-silico computational methods for drug discovery, biosensor data analysis, data preprocessing, genetic algorithms, hyperspectral image processing, advanced regression methods, calibration transfer between instrument systems and types, mapping approaches, signal processing, data compression and filtering, neural networks, proteomics, spectral searching and matching algorithms, and limit of detection testing. These will be important challenges for multivariate approaches as long as practitioners of chemometrics continue to solve problems that are important. One of the recent 'hot' topics for chemometrics includes the data mining theme as the new paradigm for scientific discovery. The New Paradigm is defined by a methodology where many experiments are performed under known experimental conditions followed by careful chemometric analysis. The analysis is performed using a rich toolbox of chemometric-like methods for analysis of the multidimensional inner relationships found between the variables within the measured or theoretical data. Examples of real-world problem solving approaches used in several fields will be presented.

(113) **Considerations and Applications of Chemometrics for On-line Classification and Prediction**

Dongsheng Bu[1], Scott Gordon[1], Ranga Vittala[2]; [1]Camo Software Inc., [2]Camo Software India Pvt. Ltd.

This paper discusses considerations in applying chemometrics for On-In-line classification and prediction practices in GMP environment, particularly the industrial real-time data management. Camo has endeavored in software development in compliance with 21 CFR Part 11 regarding security, traceability, and integrity of electronic records and electronic signatures. The Unscrambler On-Line Classifier (OLUC) and The Unscrambler On-Line Predictor (OLUP) are intermediary applications that allow models created in The Unscrambler. to be interfaced with instrument and third party software. This paper also discusses the software applications in quality control, process surveillance, and raw material control based on spectrometer or other multi-channel instrument, such as blending uniformity analysis, dissolution monitoring, API prediction and material ID identification. End-user version software which requires no programming knowledge will be presented.

(114) **Chemometrics and the FDA's PAT Initiative**

Howard Mark; [1]Mark Electronics

Roughly four years ago the U.S Food and Drug Administration (FDA) began a process that culminated with what is now familiarly known as "the PAT initiative". This talk will give an overview of what the PAT initiative is, what it's intended to accomplish, and how the science of Chemometrics fits into the schema.

(115) **Quantitative 2D IR Correlation Analysis of Dynamic Interfacial Reorganization - A Model-Based Approach**

Richard Dluhy[1], Saratchandra Shanmukh[1], Yu Zhu[1], Shin-ichi Morita[1]; [1]University of Georgia

We have recently introduced several new modified two-dimensional infrared correlation methods for quantitatively determining the degree of coherence between intensity variations in a discrete set of dynamic spectra. These methods perform a mathematical cross correlation between a set of spectra undergoing some dynamic variation against a specific mathematical function. The calculated correlation intensities are a function not only of the spectral frequency but also of a second parameter, such as the phase angle or a rate constant, which is characteristic of the function used. Correlation maxima and minima are observed at wavenumber values characteristic of the specific molecular groups involved in the dynamic process, while the intensity of the

correlation peaks indicates the relative magnitude of change. These methods are specific examples of a more general model-dependent standard that can be adapted within the theoretical framework of generalized 2D correlation spectroscopy. We have applied these model-dependent 2D IR correlation methods to the in-situ vibrational spectroscopy of bioanalytical systems and will present recent results in this presentation.

(116) **Two-way Multivariate Correlation as an Information Theoretic Tool for Measuring Analytical Orthogonality**

Peter Harrington; Ohio University

Hyphenated measurement methods abound in analytical chemistry. Typically a chromatographic stage is coupled with a multichannel detection stage. Each stage provides a way of data that may comprise hundreds or thousands of dimensions. Other popular variants are comprehensive gas chromatography (GC„eGC), multiway mass spectrometry (MSn), and ion mobility-mass spectrometry (IMMS). General tools for optimizing and evaluating the mutual information content of these multiway measurements do not exist. Furthermore, many of these hyphenated measurements exhibit trend lines (i.e., linear relationships between the two measurement stages), so they are not strictly orthogonal. Two-way correlation provides both time independent and dependent correlation spectra to visualize the quality of the measurement that can be used for optimizing signal processing or measurement parameters. However, in some cases the intricacies of the two-way correlation spectra are difficult to interpret, so the information content of these spectra has been quantified. These tools will be demonstrated for optimizing the signal processing conditions of gas chromatography-differential mobility spectrometric and gas chromatography-mass spectrometric measurements of jet fuels.

(117) **Rediscovering the Power of Conventional 2DCOS with Global Phase Correlation Analysis for Studying Phase and Sample Modulation Systems**

Eric Jiang[1], Alexander Grenov[1]; [1]Thermo Electron Corporation

Over the last decade, 2DCOS, particularly the generalized 2DCOS, has been widely applied to a variety of dynamic systems with arbitrary perturbations. The trend somehow had overshadowed the application of the conventional 2DCOS for sinusoidally modulated systems until recent rediscovery of the power of global phase correlation analysis. 2D global phase correlation map derived from synchronous and asynchronous 2D correction spectra, provides straightforward sequential information of spectral intensity variations of a spatially heterogeneous or a dynamic system, without being obscured by any amplitude influence. The recently developed software package (SpectraCorrTM) for 2D correlation spectroscopy allows global phase map to be generated with correlation profiles on both x- and y- axis readily available. The noise filtering capability of SpectraCorr interactively blanks areas that are contributed from lower amplitude noises, making 2D global phase clean and easy to read. Use of phase profiles extracted from 2D global phase map is an effective approach for quantitative and semi-quantitative analysis of heterogeneous and dynamic systems with highly overlapped bands and non-linear responses. This paper extends our recent 2D global phase analysis work on step-scan phase modulation photoacoustic depth profiling analysis of heterogeneous samples to step-scan sample modulation dynamic spectroscopy of polymeric samples. Polymer stretching data of both homogeneous polymer films and layered samples will be extensively studied by 2D global phase correlation spectroscopy.

(118) **Global Phase Angles for Specific Analytical Systems in Generalized Two-Dimensional Correlation Spectroscopy**

Shin-ichi Morita[1], Yu Zhu[1], Saratchandra Shanmukh[1], Richard Dluhy[1]; [1]University of Georgia

Generalized two-dimensional (2D) correlation spectroscopy has been applied to complex spectral intensity variations in infrared (IR), Raman, ultraviolet-visible, and any other optical signals having different waveforms [1]. In this presentation, we discuss further properties of 2D correlation spectroscopy using the global phase angle intensity normalization method [2]. The 2D global phase angle analysis method is shown to discriminate against arbitrary signal amplitude changes not related to real correlation intensities. We confirm that the positive or negative sign of a global phase angle 2D correlation peak is a direct expression of the sequential order of signal intensity changes. In addition, we derive analytical solutions of the global phase angles corresponding to sinusoidal, exponential, Lorentzian functions. For the each specific analytical case, the global phase angle is related only to the target parameters (i.e., phase angles for sinusoidal, rate constants for exponential, and peak positions for Lorentzian functions), and not influenced by the signal amplitude information. This feature indicates that determination of the global phase angle in actual spectroscopic measurements will allow us to estimate the quantitative relation of those target parameters. [1] I. Noda and Y. Ozaki, Two-Dimensional Correlation Spectroscopy: Applications in Vibrational and Optical Spectroscopy, John Wiley & Sons Inc., Chichester, UK (2004). [2] S. Morita, Y. Ozaki and I. Noda, Appl. Spectrsc. 55, 1618 (2001).

(119) **Investigation of Hydrogen Bonding Microenvironments in Methanol using Density Functional Calculations and Infrared Absorption Spectroscopy**

Daniel Besemann[1], Ryan Haws[1], Brody Anderson[1], Boyd Johnson[1]; [1]Hamline University

In mixtures of methanol and weakly interacting solvents, the amount of hydrogen bonding increases as the mole fraction of methanol increases. At high concentrations, it is clear that nearly all (if not all) methanol molecules simultaneously act as both a donor and an acceptor. There is, however, continued debate regarding the nature of these sequential H-bonds. Some researchers believe that the kinetic products—dynamic, winding chains—are present, while others believe the thermodynamic products—small cyclic n-mers—dominate the structure of liquid methanol. Neutron scattering experiments coupled with molecular dynamics (MD) simulations give results consistent with the formation of (branched) chains. However, the simulated infrared spectra from MD simulations tend to overestimate the size of the free O-H stretch peak that is caused by nondonating chain ends. Other experiments (infrared, nuclear magnetic resonance) have been interpreted using both chain and cyclic models. This work uses the results from density functional calculations on over forty different methanol clusters (monomer through octamer) to guide analysis of the observed one-dimensional (and when applicable, two-dimensional correlation) infrared absorption spectrum of the O-H stretch of methanol/carbon tetrachloride solutions. We observe seven likely infrared spectral features between 2800 cm-1 and 3700 cm-1, and are able to identify plausible hydrogen bonding microenvironments for five of the seven features. Our results indicate that branched and unbranched chains are a significant component of these methanol solutions; the presence of large amounts of cyclic structures is not supported by our analysis.

(120) **A Theory and Applications of Perturbation-Correlation Moving-Window Two-Dimensional Correlation Spectroscopy**

Shigeaki Morita[1], Akihiko Watanabe[1], Hideyuki Shinzawa[1], Isao Noda[2], Yukihiro Ozaki[1]; [1]Kwansei-Gakuin University, [2]The Procter & Gamble Company

A theory of perturbation-correlation moving-window two-dimensional (PCMW2D) correlation spectroscopy is introduced. For a set of spectral data collected under an external perturbation, PCMW2D correlation analysis provides a pair of synchronous and asynchronous 2D correlation spectra spread on a plane between a spectral variable (e.g., wavelength, wavenumber, etc.) axis and a perturbation variable (e.g., time, temperature, etc.) axis. It was demonstrated that synchronous and asynchronous PCMW2D correlation spectra are, respectively, proportional to positive first derivative (i.e., gradient) and negative second derivative (i.e., curvature) along the perturbation variable axis. Computational simulations revealed that each band position shift is directly visualized in a PCMW2D correlation spectrum, though they are highly overlapping each other. Several applications for practical data are also introduced. (1) Temperature-dependent IR spectra of following polymer samples were analyzed by the PCMW2D correlation spectroscopy; poly(vinyl alcohol) (PVA), poly(methyl methacrylate) (PMMA), cellulose, etc. Evidences of molecular structure changes induced by temperature were found in PCMW2D correlation spectra constructed form the temperature-dependent IR spectra. For example, the synchronous PCMW2D correlation peak at the crystalline phase C-O stretching band around the melting temperature of PVA demonstrates dissociation of OH--OH hydrogen bond around the temperature. (2) Time-resolved IR spectra of water sorption process into following biocompatible polymers were analyzed by the PCMW2D correlation spectroscopy; poly(2-methoxyethyl acrylate) (PMEA), poly(2-hydroxyethyl methacrylate) (PHEMA), etc. In the O-H stretching region, typical three different types of spectral feature were found. These results suggest existence of three different types of hydrated water. Respective hydration structures were discussed in detail from the results of the PCMW2D correlation analysis. [Ref.] S. Morita, et al., Appl. Spectrosc., 60, 398-406, (2006).

(121) **Orientation in LLDPE Blown Films by Polarized Raman Spectroscopy**

Amod Ogale[1], Giriprasath Gururajan[1], Srinivas Cherukupalli[1]; [1]Clemnson University

Online Raman spectroscopy was used in this study to measure the orientation development during blown film extrusion of linear low density polyethylene (LLDPE). The work was based on the theory developed by Bower (1976), which was later extended by Pigeon (1991) and Citra (1995) for polyethylene. It assumes uniaxial symmetry of the structural units with the chain axis. The trans C-C stretching vibration of PE at 1130 cm-1, whose Raman tensor is coincident with c-axis of the orthorhombic crystal, was used to solve a set of five intensity equations.\r\nPrior to online measurements, offline Raman spectra were obtained in backscattering and right-angle scattering geometries. The offline results were used to obtain instrument correction factors (compensation of power and focus differences) and also depolarization ratios (fÑ11/ fÑ33 and fÑ22/ fÑ33) as described by Lesko (2000). Online Raman measurements were carried out in the backscattering mode for a film subjected to a particular take-up ratio (TUR) and blow-up ratio (BUR). A set of three equations involving IZZ 180 (0), IYY 180 (0) and IYZ 180 (0) were solved to obtain second (P2) and fourth coefficients (P4) of orientation distribution function. Results indicated a gradual increase of crystalline orientation factor P2 along the axial distance in the film line. The value was close to zero (random) near FLH and developed a distinct sigmoidal trend before reaching equilibrium at certain distance in the film line. The P2 value obtained near the nip-roller were comparable with that estimated for the final film (offline Raman measurements). However, the orientation factor (P2) of the final film from Raman measurements was considerably different from the P2 value obtained from wide-angle x-ray diffraction (WAXD). The differences in Raman and WAXD measurements likely arise from the lack of uniaxial symmetry of the blown film, which is typically assumed in many analyses.

(122) **Raman of Structural Modifications of Silica Glass**

Carl W. Ponader; Corning Incorporated

We discuss the application of Raman spectroscopy to two systems and show how it has been used to understand the way both purposeful and unintended processes affect the structure of silica glass. Residual stress in optical fiber impacts several fiber properties, including reliability and geometry. One aspect of the effect of stress on geometry is the development of a permanent, large-radius bend in the fiber. The stress profile arises from an interaction between the thermal expansion mismatch of the constituent materials, tension applied during forming, and the thermal profile across the fiber during formation. The thermal profile of the fiber can be determined by measuring the fictive temperature of the fiber using the intensities of various bands in the Raman spectrum of silica glass. The fictive temperature profiles can be used to model the residual stress in the fiber and can be related to thermal non-uniformity during fiber cooling. The results show that stresses due to fictive temperature gradients account for only a portion of the total stress across a fiber that causes permanent bending. Techniques are also being developed to produce optical waveguides in silica glass by modifying the glass structure with femtosecond laser pulses which produce a micron-sized area with an increased refractive index. The mechanism that produces the refractive index change is not well understood. Using confocal Raman spectroscopy, we measured changes in the structure of the silica glass in the exposed spots. By monitoring the intensity and the position of various bands, we were able to show that the refractive index increase is correlated with an increase in glass density. The intensity of the 490 cm-1band shows that fictive temperature is not increased while the shift of the 1060 cm-1 band to lower wavenumbers indicates an increase in the density of the glass.

(123) **Raman Spectroscopic Analysis of Release Mechanism in Drug Delivery Systems**

Shaw Hsu; University of Massachusetts (Amherst)

Release kinetics in many drug delivery systems is dependent on the phase separated structures of multi-component systems, involving various polymers and low molecular weight drugs. The formation of these structures is not well understood. Vibrational spectroscopy, especially high resolution Raman microscopy, has proven to be invaluable to follow the kinetics of structural evolution, local chemical composition attained, and their changes as a function of time and temperature. It has also proven to be possible to characterize the sample heterogeneity associated with the active coatings of various implants. This type of structural information obtained directly contributes to better design of various drug delivery systems.

(124) **Advanced Automated Spectroscopic Data Analysis for High Throughput Materials Research**

Tzu-Chi Kuo[1], Harry H. Luo[2], Shao-Ching Hung[1], M. Anne Leugers[1]; [1]The Dow Chemical Company, [2]Symyx Technologies, Inc.

High Throughput Research (HTR) has commonly been applied in the agricultural and pharmaceutical fields to rapidly screen vast libraries of compounds for biological activity. Within the last five years, high throughput catalyst and materials research has become a major thrust in academic, government, and industrial R&D labs. With the emergence of new robotic tools for synthesis, formulation, and process research, new screening methods are necessary to adequately characterize the performance and composition of the materials. Many HTR characterization tools focus on screening against physical properties; however, chemical identification and quantification are extremely important when manipulations of chemical micro-environments or structures are involved. Vibrational spectroscopic characterizations, i.e. Raman and IR, could meet those needs with speed and accuracy, but there is also a greater need to convert the intensity-wavenumber curves automatically into data, information, and knowledge for end users, and ultimately transfer and organize both information and knowledge into searchable databases. For this purpose, we investigated advanced spectroscopic data analysis, including PCA/PLS, integrated with Symyx Renaissance software and database to automatically process and analyze spectra collected from high throughput Raman and Infrared instruments. The presentation of data and information generated in this manner can be easily utilized by researchers depending on their needs (simple screening or detail characterizations). Several examples will be shown to depict the integrated HTR spectroscopic analytical capabilities including: quantitative analysis of polymer and polymer blends, automated spectral subtraction and polymorph identification of pharmaceutical and agricultural actives, drug dissolution, and oxidation ranking of antioxidant packages for polymers.

(125) **Adsorption on Nanosurfaces: A Raman Spectroscopy Investigation**

Maher Amer; Wright State University

Raman spectroscopy has been successfully utilized to investigate material systems on the micro and the meso-scales. Recently, the technique has proven its ability to exploring systems on the nano-scale. In this talk, our recent work on Raman investigation of molecular adsorption on surfaces of single-walled carbon nanotubes and fullerene nanospheres will be presented emphasizing two major research findings. First, the development of Raman based nano-sensors capable of sensing local chemical interactions on the molecular level. Secondly, the agreement between experimental Raman results and the results of semi-empirical molecular calculations for adsorption on fullerene nanospheres. Our studies revealed that interaction between carbon nanotubes and nano-spheres is crucial from the viewpoint of meso-structure formation. The current findings represent a major new thrust for the development of new materials with superior adsorption capabilities and unique applications.

(126) **Raman Spectroscopy as a Probe of the Structure & Configuration**

Bruce Chase[1], John Rabolt[2], Meghana Kahade[2]; [1]DuPont, [2]University of Delaware

Raman scattering has found many significant applications in chemical analysis. The ability of Raman scattering to provide an in-situ probe for qualitative and quantitative chemical analysis is quite well established. It is equally powerful for the determination of structure and orientation in polymers, where the chemical structure is already known. Polymeric macroscopic properties such as tenacity, modulus, elasticity, etc. are determined by molecular level effects such as conformational state populations, orientation, and intermolecular interactions. Significant changes occur at the molecular level as a molten or solution phase polymer is spun into fiber form. The polymer goes from an unoriented, amorphous state to an oriented, semi-crystalline material via the deformations imposed by spinning and drawing. Raman spectroscopy can potentially provide information on both structure and orientation. Changes in band intensities can be related to conformational populations and to formation of crystalline regions. Changes in relative intensities as a function of incident and scattered polarization yields information on chain orientation. Electro-spinning, currently undergoing a renaissance, is a solution process whereby small diameter fibers (100s of nanometers) can be produced. With such small diameter fibers, small stresses during the spinning process can potentially have a very large effect of the mechanical properties of the final product. The issues of shear and tensile deformation in electro spinning are still largely unaddressed. Electro spinning of nylons and polyethylene oxide fibers provide examples where both conformational state populations and chain orientation can be perturbed by the process itself. The basics of electro-spinning and the use of vibrational spectroscopy to probe structure and orientation in such materials will be discussed.

(127) **Solids Sampled Directly: ICPMS Analysis with Laser Ablation Introduction**

Lawrence Neufeld; New Wave Research, Inc.

Direct solid sampling has many advantages over traditional acid digestion techniques. This is especially true if the solid sample matrix is highly refractory, difficult to digest or the sample to be analyzed is dimensionally restrictive; i.e. sub-micrograms of material embedded in a chemically uninteresting matrix. Using lasers with beam diameters as small as 2-3μm it is possible to extract picograms of analytical material for direct analysis. Losses of volatile elements or contamination during sample processing more common with aqueous digestion techniques are limited or eliminated with laser ablation. With laser ablation the sample surface is irradiated with a high intensity laser. The laser energy is transferred directly into the sample lattice causing explosive vaporization and aerosol formation. If connected to an Inductively Coupled Mass Spectrometry (ICP-MS) the laser aerosol is carried along an inert gas stream (argon or helium) and injected directly into the plasma. The aerosol, made up of micron and sub-micron particles, are then vaporized, atomized and ionized before entering the mass spectrometer. Lasers have been used as a direct solid sampling tool for over 20 years. Laser Ablation ICP Mass Spectrometry (LA-ICP-MS) has been slow to replace aqueous sample introduction, with a few key exceptions, due to its historically inferior limits of detection and accuracy. Over the last 10 years however and in particular in the past 5 years much progress has been made toward understanding the fundamentals of laser material interaction and how that interaction effects the laser generated aerosol to be analyzed. This has led to a new breed of laser systems with enhanced user interfaces, sample platforms and lasers designed for efficient energy coupling of laser energy to the sample without altering the stoichiometric relationship with the parent material. We will discuss lasers, laser wavelength, laser pulse width and the progress made toward an accurate and precise in-situ solid sampling technique suitable for the analysis of all materials.

(128) **Novel Strategies for Sample Introduction into and by Glow Discharges**

Gary M. Hieftje[1], Francisco J. Andrade[1], Michael R. Webb[1], Gerardo Gamez[1], Steven J. Ray[1]; [1]Department of Chemistry, Indiana University

Glow discharges are among the most widely used sources for the multi-element analysis of conductive solid samples, especially those that require depth-resolved information. It is less common for them to be applied to non-conductive solids or to liquid or gaseous samples, although those applications, too, have been explored. Even fewer examples have appeared in which glow discharges are used with biological samples or for generating molecular information. In this presentation, several new kinds of glow discharge sources will be introduced and evaluated which expand the sphere of applications of this versatile device. One is intended for determining the elemental composition of proteins separated on a two-dimensional gel substrate. All protein-containing spots are examined at once, by means of an optical imaging spectrometer. Although the instrument is currently limited to measuring a single element at a time, plans are to expand the concept to multi-element determinations. Other new glow discharges, unlike traditional systems, are operated at atmospheric pressure. One can produce emission spectra directly from elements in solution, another accepts aerosol samples, and a third can be used with solids, liquids, or gases with equal ease. The latter unit can be operated in a mode in which principally molecular ions or protonated molecular ions are generated, so mass spectra are greatly simplified.

(129) **Panel Discussion - Fact or Fiction? Looks Good On Paper, But How Is It In The Real World?**

Panel Discussion lead by Jim Holcombe; University of Texas, Austin

Nebulizers are certainly the dominant introduction source for ICPMS, but a number of alternatives exist in the literature and have been presented at this conference. It seems like literature articles and talks suggest these alternatives are “excellent” ways of circumventing problems typically encountered with nebulizers. For example, in some cases sample prep is greatly minimized. HOWEVER… are these claims reality or are there hidden problems that never really get discussed? In fact, the literature often presents conflicting views on the analytical utility of these “alternate techniques”. In reality are they as good (or as problematic?) as the claims? We hope to thrash out differences between CLAIMS and REALITY during the discussion using both “panel users” and “audience users”. Do you have problem samples? Do you have good/bad experiences with nebulizers or “and alternate introduction” approaches? Did you invest hundreds or thousands of dollars in a new approach and concluded that it was a waste of money… or money well spent? Information and frank discussions are the objectives of this discussion. Oh, yeah… it should be fun also!

(131) **From Exploding Wires to Rapid Chromatography: The Legacy of a High Speed Scientist and Gentle Mentor**

Presented by James A. Holcombe; University of Texas

Richard Sacks leaves a legacy of students and colleagues who have been enriched by exposure to and mentoring by this man. His mental flexibility and imagination fostered successful research expeditions into fields as diverse as atomic spectroscopy and high speed chromatography. He was affectionately referred to as "Boom boom" Sacks during his early years as a consequence of his novel attempts at using shock tubes and exploding wires for spectrochemical excitation. For those of us entering academia, he also provided elevated targets to shoot at. His fluid, efficient and clear delivery of material in class and at conferences remains elusive to many of us in spite of the desire for emulation. However, his upbeat and optimistic outlook on science... and life!... was more easily acquired by his students and can be seen today in his academic progeny.

(132) **Growing, Walking And Falling. The Role of Raman Spectroscopy in The Study of Musculoskeletal Tissue**

Michael D. Morris; University of Michigan

We will discuss the role of Raman spectroscopy and Raman imaging in the study of musculosketal tissue structure and function. Raman spectra contain signatures for bone mineral phosphate and carbonate. Both bone and cartilage collagen bands report secondary structure. These signatures report on the age of the tissue its health and its and response to mechanical loading. Uniquely among the high information content spectroscopies, Raman spectroscopy can be performed on tissue sections under culture in Petri dishes, in mechanical engineering test instruments and even transcutaneously on live animals. These powerful properties enable a wide-ranging set of investigation. These include probing the earliest stages of skeletal development, understanding how bone and cartilage respond to normal and traumatic mechanical loading and how tissue is damaged by metabolic disease and genetic defect. Because changes in the spectra can be correlated with tissue health or disease, Raman spectroscopy offers the potential for rapid, non-invasive and minimally invasive disease diagnosis.We will review these topics and discuss how they are enabled by advances in Raman instrumentation that have culminated in development of compact Raman spectrographs capable of subsecond spectroscopy and of fiber optic probes that enable subsurface Raman spectroscopy and mapping in highly scattering media such as human and animal tissues. Progress in this area requires close collaboration between investigators in the chemical sciences and the biomedical sciences and equally close collaboration between the academic investigators and industrial scientists and engineers.

(133) **Adsorption of Pyrazolone[HPMS],Calix[4]-arene,**

Mehdi Vadi, Anne Boos, Zouhair Asfari

The adsorption of pyrazolone(HPMSP), Calix[4]-arene,Cu and Cs.with carbon nanotube(CNT) at room temperature has been investigated using spectroscopy. Uv spectroscopy indicated that pyrazolone molecules adsorbed on carbon nanotube at room temperature in compared calix[4]- arene molecules adsorbed approximately same.The amount of pyrazolone(HPMSP) adsorb $3.8x10^{-5}$ mol/g and amount calix[4]-arene adsorbed $1.3x10^{-5}$mol/g.The physisorption of such an organic molecules is an example of nano covalent functionalization involving π-stacking interactions and corresponding to weak binding energy.The most favourable adsorption site is one type C-C bond. Atomic adsorption shown carbon nanotube has capability and a high adsorption efficiency for adsorption of Cu(II) and Cs from of water.

(134) **Dispersion And Functionalization of Single-Walled Carbon Nanotubes**

Dan Wang[1], Liwei Chen[1]; [1]Ohio University

Highly efficient dispersion of single-walled-carbon nanotubes has been achieved by wrapping with designed “polysoaps”, which contain aromatic pyrene side chains and anionic main chain. The solubility of SWNT in 1mg/ml polysoap solutions ranges from 0.7 to 1.3 mg/ml depending on the content of pyrene groups. AFM images and height measurements show that the SWNTs are individually dispersed. The polysoap-SWNT complexes are characterizes by UV-vis, fluorescene and raman specta. The anionic backbone of the polysoap is exploited for further assembly

of metal nanoparticles via electrostatic interactions and lone pair electrons donor-acceptor interactions. Pt, Pd and Au nanoparticles are attached to the sidewall of SWNTs. The AFM and TEM images show that the metal nanoparticles bind to the PSMA/polysoap-CNT complex and indicate the formation of PSMA/polysoap-CNT-Pt/Pd/Au nanocomposite.

(135) **In Situ AFM Investigation of The Effects of Concentration And Writing Parameters when Nanografting Functionalized N-Alkanethiol Sams on Au(111)**

Algernon Kelley[1], Johnpeter Ngunjiri[1], Jayne Garno[1]; [1]Louisiana State University

For methyl-terminated alkanethiols, a well-ordered dense monolayer is produced over a wide range of experimental conditions (e.g. concentration, immersion intervals). However, for alkanethiols with reactive headgroups such as carboxylates, dithiols and hydroxyl moieties, the situation is more complicated. According to AFM measurements, high concentrations and lengthy immersion intervals are observed to produce double layers for self-assembled monolayers (SAMs) with reactive headgroups. Under certain conditions, carboxylate-terminated n-alkanethiols consistently produce double layers of molecules when writing nanopatterns on Au(111) using AFM-based lithography (nanografting). Strong head-to-head interactions can direct the solution self-assembly of molecules to form double layers. Thus, the height of nanopatterns can be controlled by carefully evaluating the concentration parameters for writing nanopatterns. At low concentration (on the order of 10-100 micromolar) nanopatterns of 16-mercaptohexadecanoic acid exhibit the expected monolayer thickness; whereas at higher concentrations, nanografted patterns form multilayers. In contrast, methyl-terminated SAMs uniformly generate nanopatterns with heights corresponding to a monolayer, regardless of experimental parameters. In addition, we have also observed that lithography parameters can affect pattern heights. Nanografting is accomplished by scanning an area of a matrix SAM using high force while the AFM tip is immersed in a solution containing a molecule chosen for writing. By repeatedly writing over areas several times, nanopatterns of 16-MHA are observed to form multilayer structures. In contrast, multiple writing scans with methyl-terminated alkanethiols exhibit heights corresponding to the thickness of a monolayer. After writing is completed, the newly inscribed nanopatterns can be characterized using the same tip with low force. By using automated nanografting, arrays of patterns can rapidly be written, enabling exquisite nanometer-level control of the writing speed, force and geometry parameters. It has become evident that depending on experimental conditions, strong head-to-head interactions of ù-functionalized alkanethiols can direct the self-assembly of molecules such as 16-mercaptohexadecanoic acid (16-MHA) into double layers. Images of arrays of nanografted patterns written with designed systematic changes in writing parameters and concentrations will be presented to illustrate the effects of n-alkanethiol SAM head groups on solution-based self-assembly of n-alkanethiols. These results provide critical insight for optimizing conditions for sensor or test platforms which incorporate SAM surfaces in their design.

(136) **Studying Biomolecular Reactions at the Nanoscale: In Situ Studies of Proteins Patterned by Nanografting and Surface Activation Chemistry**

Johnpeter Ngunjiri[1], Brian Lewandowski[1], Jayne Garno[1]; [1]Louisiana State University

The tools of nanografting and chemical activation provide a new route investigating reactions at the nanometer scale. The demand for higher throughput, decreased sample consumption and analysis of complex samples has lead towards ever-increasing miniaturization in biochip platforms. High-resolution atomic force microscopy (AFM) characterization and in situ AFM-based nanolithography can be combined to achieve the ultimate miniaturization for surface-bound protein assays. Highly-ordered, nanometer-sized patterns of n-alkanethiols can be used to engineer the selectivity of surfaces for protein adsorption. Nanografting can produce nanostructures ranging in size from 10-100 nm by translating the AFM tip at designated speed, direction, and force. Nanografting is accomplished by exerting a high local force on an AFM tip, pushing through the matrix self-assembled monolayer (SAM) to contact the underlying gold surface. As matrix molecules are removed, new thiol molecules from solution immediately adsorb onto the uncovered areas of the substrate to form nanopatterns, following the scanning track of the tip. This enables the reproducible fabrication of arrays of SAM nanopatterns with superb control of parameters such as ligand density, pattern spacing and the size of array elements. By choosing the appropriate terminal groups, SAM surfaces are engineered to avoid non-specific protein adsorption, yet make specific interactions with targeted proteins to be assayed. Molecules with terminal moieties (carboxylate, aldehyde or amine groups) that are reactive to specific functional groups on proteins are inscribed within a resistive matrix SAM (methyl or hydroxyl) to impart selectivity for protein adsorption. After writing nanopatterns, the terminal moieties of SAM nanopatterns can be activated using N-ethyl-N'(dimethylaminopropyl)-carbodiimide (EDC) and N-hydroxysuccinimide (NHS) to mediate covalent interaction with amino groups of lysine residues on the outer surfaces of proteins. In situ AFM experiments are accomplished under ambient physiological conditions in aqueous buffered environments, to minimize the loss of activity and to preserve the native tertiary structure of immobilized proteins. High-resolution AFM images acquired in situ will be presented, which visualize successive changes on surfaces after proteins bind to arrays of SAM nanopatterns. In essence, local protein-binding events can be detected at the nanoscale without entities such as radiolabels or fluorescent tags.

(137) **Mapping Magnetic Nanomaterials on Surfaces Using Selective Modulation**

Brian Lewandowski[1], Johnpeter Ngunjiri[1], Jayne Garno[1]; [1]Louisiana State University

We have developed a new mode for AFM, magnetic sample modulation (MSM) that enables magnetic domains to be selectively imaged by inducing physical movement of nanomaterials by an oscillating magnetic field. Ferromagnetic domains can be induced to vibrate by applying a changing periodic magnetic field to the sample surface. This motion can be sensitively detected by a standard uncoated AFM tip as it scans across the sample in contact mode. Images exhibit distinct contrast enhancement of magnetic domains for friction, amplitude, and phase channels when a gradient of magnetic actuation is applied to samples. A MAC Mode® sample plate is used for modulation of magnetic domains. An AC voltage is applied to a solenoid located underneath the sample plate. This produces an oscillating magnetic field near the sample, which causes the selective vibration of magnetic domains. As the tip is raster scanned across the sample, the vibrational movement of the sample is used to map the location of magnetic domains. A standard soft commercial AFM tip is suitable for MSM, since the tip is not used to sense the magnetic field. Rather, the uncoated AFM tip is used to detect the vibration of materials which respond to the flux of the modulated magnetic field. Proof-of-concept images will be presented for samples of nanoparticles. The contrast in phase and amplitude images is more sensitive to differences in surface chemistry than topography images, so these

modes provide greater sensitivity for mapping magnetic domains, potentially to achieve nanometer scale lateral resolution. There are several advantages of this new MSM imaging mode compared to magnetic force microscopy. Magnetic sample modulation does not require the expense of tips that are coated with magnetic materials and only requires the simple modification of an AC-powered sample plate. Magnetic sample modulation has the potential for providing more sensitive measurements and characterizations of nanometer-sized magnetic materials than magnetic force microscopy. In nanometer-scale structures, size effects give rise to novel electronic, magnetic, optical, and structural properties. Development of a highly sensitive magnetic imaging technique may provide insight into size-dependent magnetic properties which occur at length scales between 1 and 15 nm.

(138) **In Situ AFM Studies of The Assembly of Porphyrins on Flat Surfaces**

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Porphyrin and metalloporphyrin systems are excellent materials for molecular electronics, due to their diverse structural motifs and associated electrical, optical and chemical properties. Porphyrins have very practical application in molecular electronics and LCD displays, due to their characteristic photophysical properties. The function and efficiency of these molecules in devices largely depends on how the molecules are organized on surfaces. Although considerable research has been published regarding the self-assembly of thiol self-assembled monolayers (SAMs), there are few investigations of the solution-phase assembly of porphyrins on different substrates. Unlike thiol SAMs, which have strong interactions between alkane chains to drive the self-assembly of monolayers, the architecture of porphyrins consists of a macrocyclic tetrapyrrole structure, which may be functionalized with various substituents. Strong pi-pi interactions between the porphyrin macrocycles result in a stacked assembly, analogous to a stack of coins. By changing the lengths and composition of the peripheral groups, the assembly of porphyrins on surfaces can be directed into either a side-on assembly or into a co-planar, stacked orientation. The resulting surface structures dictate the photonic and electronic properties of porphyrin films. Modifications of the macrocycle, peripheral groups or chelated metal ions can generate a range of electrical, photoelectrical or magnetic properties. Depending on the substituents attached to the core, molecules may adapt either side-on or co-planar arrangements on surfaces. In situ AFM was used to directly observe the adsorption of porphyrins on flat surfaces such as Au(111), mica(0001) and graphite(111). High resolution images of the substrates were first taken in ethanol, and flat areas with steps or defects were selected as landmarks for real-time monitoring of the successive stages of molecular adsorption. An ethanolic solution of porphyrin was introduced to the liquid cell and left to stabilize for ~ 3 minutes. A time lapse experiment was conducted by continuously imaging the surface at various times until the surface was fully covered with a layer of porphyrins. After the layers have formed, the thickness of the films can be measured using AFM-based nanolithography. Understanding the self-organization and assembly of porphyrins on surfaces is critical for maximizing the attributes (stability, robustness) of these molecules in device applications.

(139) **Application of Arrays of Protein Nanostructures Produced Using Particle Lithography for Investigation of Biomolecular Reactions on Surfaces**

Jie-Ren Li[1], Zorabel M. LeJeuene[1], Jayne C. Garno[1]; [1]Louisiana State University

Protein nanoarrays provide a valuable new tool for investigations of biomolecular reactions on surfaces. Periodic arrays of protein nanostructures can be fabricated using particle lithography. The self-assembly of monodisperse latex nanoparticles provide a structural template to organize the arrangement of proteins for nanopatterned surfaces. To fabricate arrays of protein nanostructures, latex nanospheres are first mixed with aqueous solutions of the desired proteins, such as bovine serum albumin (BSA) or staphylococcal protein A (SpA). During drying, the nanospheres self-assemble into organized crystalline layers on flat surfaces such as mica(0001) or Au(111). The proteins fill-in the void spaces on the surface surrounding and between spheres. The latex layer is efficiently and selectively removed by rinsing the surface with deionized water; however the protein layers persist and are not washed from the surface. A well-organized monolayer of the immobilized proteins remains attached to the surface with an imprinted hexagonal pattern of circular nanostructures covering micron-sized areas. The dimension, morphology and spacing of protein nanoarrays can be systematically varied by changing the diameters of the latex particles and by controlling the protein-to-latex ratios. Protein nanoarrays produced by particle lithography offer nanometer precision to improve surface-based protein assays by controlling the placement of target molecules. Atomic force microscopy (AFM) can be used to test the activity of surface-bound proteins for retaining their biological function. In situ AFM experiments enable the visualization of protein binding interactions in ambient non-denaturing conditions. Binding of secondary antibodies or other biomolecules to nanopatterns can be detected by viewing the successive changes in the morphology and height of protein patterns with time-lapse AFM images. Particle lithography offers advantages of reproducibility and high-throughput to controllably generate a single layer of defined protein nanostructures. Particle lithography enables investigations to transpire using simple physical adsorption of proteins in mild environments at ambient temperatures, which should enhance the retention of the bioactivities of immobilized proteins. The reliability and sensitivity of protein biosensors and biochips depend on the affinity and viability of surface-bound biological components. Conceptually, by developing high-throughput approaches for arranging and orienting proteins at the nanometer scale, the sensitivity and reliability of commercial biochip technologies could be substantially improved.

(140) **Electrochemistry of 2-Dimensional Carbon Nanotube Networks**

Pornnipa Vichchulada[1], Tasaday E Lynch[1], Marcus D Lay[1]; [1]University of Georgia

Electrochemical studies of 2-dimensional networks of carbon nanotubes (CNTs) will be presented. A new method of creating electrically continuous arrays of CNTs has been used to investigate electrodeposition of nanostructures at highly oriented nano-scale templates. Unidirectional air flow was used to order CNTs in aqueous suspension and deposit them on a hydrophobic SAM-modified surface (i.e. 3-aminopropyl-triethoxysilane on Si/SiOx). These 2-dimensional networks of CNTs show potential as a method of circumventing the difficulties associates with lack of control over the electrochemical properties of individual CNTs. For a random distribution of CNTs, density control is the major factor controlling device properties, as fluctuations in characteristics of individual CNTs are averaged. These ordered arrays of CNTs

exhibited anisotropic electrical conductivity over macroscopic lengths (up to 3"), and have shown promise in a wide variety of electrochemical applications. Electrochemical reduction of water-soluble diazonium salts will be discussed.

(141) **Near-Field Spectroscopy for the Investigation of Various Materials**

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Conventional optical microscopy involves using a system of lenses which focus light from the sample into a magnified image of the specimen. Unfortunately, this introduces diffraction effects and places a limit on the spatial resolution of the microscopy technique. Near-field spectroscopy, which can optically image a sample with spatial resolution beyond the optical diffraction limit, has enormous potential for optical probing and characterization of materials, surfaces, and thin films on the nanometer scale. The combination of a near-field probe and a spectrograph in near-field scanning optical microscopy (NSOM) can be used for spectroscopy with a spatial resolution well below 1 micron (visible) and 10 micron (infra-red). Multiple spectra can be collected and assembled into "3-D" maps providing powerful nano-scale characterization of the sample surface. By this method, images with spatial resolution far beyond what is possible with traditional microscopy can be recorded. This paper demonstrates the capability to provide topographic and spectroscopic data of various samples including semiconductors, quantum dots and carbon nanotubes among other types of samples. This paper also reviews the basic principles of near-field optics, the NSOM related instrumentation is introduced, and the benefits and limitations of NSOM will be discussed in reference to the sample data presented.

(142) **Thermal Behavior of J-Aggregates in Mixed Langmuir-Blodgett (LB) Films of Merocyanine Dye Investigated by UV-Visible and IR Absorption Spectroscopy**

Tateno Shinsuke[1], Hirano Yoshiaki[1], Ozaki Yukihiro[1]; [1]Kwansei Gakuin University

There has been a growing trend of applying thin films containing synthetic dyes to various devices including photovoltaic cells, optical waveguides and ultrafast optical switches. In particular, J- and H-aggregates with head-to-tail and side-by-side alignment of transition dipole moments, being two limiting types of dye aggregates, are candidates for the application to the above devices because of their sharp and narrow absorptions. In recent years, guidelines for the usefulness of J- and H-aggregates have been found according to their aggregation states. Consequently, one of the crucial subjects is to control the dye aggregation states in the thin films in a desired manner. We have been engaged in this research subject using J-aggregates in mixed Langmuir-Blodgett (LB) films of the merocyanine dye (MS)-deuterated arachidic acid (C20-d) binary system. As the first step, our study aims at exploring the possibility of the control of the MS aggregation states by annealing. In this presentation, we report the results of the thermal behavior of the mixed LB films with J-aggregates in the range from 25 to 250 degrees centigrade by means of UV-visible and IR absorption spectroscopy. When the mixed LB films of the MS-C20-d binary system are fabricated under aqueous subphase containing cadmium ions, a red-shifted J-band with sharp absorption is observed at 590 nm, which is red-shifted from an MS monomer peak at 530-540 nm. From 25 to 95 degrees centigrade, the intensity of the J-band decreases gradually with annealing. From 95 to 165 degrees centigrade, a blue-shifted band appears near 520 nm. From 165 to 250 degrees centigrade, moreover, a blue-shifted band is located near 470 nm. In addition, the intensity of these bands tends to decrease gradually during annealing from 25 to 250 degrees centigrade. It is also noted that the baseline of UV-visible absorption spectra gradually decreases with increasing temperature, suggesting a decrease in amount of Rayleigh scattering associated with a diminution in domain size of dye aggregates. We will discuss the correlation between the aggregation states, the intramolecular charge transfer and the conformation and orientation of alkyl chains substituted to MS.

(143) **Thermal Behavior of H-aggregates in Mixed Langmuir-Blodgett (LB) Films with Merocyanine Dye Investigated by UV-visible and IR Absorption**

Yoshiaki Hirano[1], Shinsuke Tateno[1], Yukihiro Ozaki[1]; [1]Kwansei Gakuin University

A great deal of attention has been paid to potential applications of thin films with dyes to various molecular devices such as photovoltaic cells, optical waveguides and ultrafast optical switches. The dye aggregates, which are called J- and H-aggregates, have been recently reported to possess the usefulness according to their respective aggregation states for the above device applications. Therefore, one of the attracting subjects is to control the dye aggregation states in the thin films in a desired manner. In recent years, we have examined the thermal behavior of H-aggregates formed in mixed Langmuir-Blodgett (LB) films of the merocyanine dye (MS)-arachidic acid (C20)-n-octadecane (AL18) ternary system in the range from 25 to 250 degrees centigrade by means of UV-visible and IR absorption spectroscopy to explore the possibility of the control of the MS aggregation states by annealing. In this presentation, we discuss the relationships between the MS aggregation state, the MS intramolecular charge transfer, and the orientation, conformation and thermal mobility of the MS hydrocarbon chains.\r\nAs is well known, the mixed LB films of the MS-C20 binary system exhibit a sharp red-shifted J-band at 590 nm. On the other hand, we have already found that a blue-shifted H-band at 505 nm appears by adding AL18 to the MS-C20 binary system. The thermal behavior of the MS H-aggregates in UV-visible region is as follows: From 25 to 50 degrees centigrade, the intensity of the H-band decreases drastically with annealing, and then a broad band with the absorption maxima at 537 nm is formed at 50 degrees centigrade. From 50 to 100 degrees centigrade, the absorption maxima of the broad bands gradually shift to shorter wavelengths. Then, a blue-shifted band at 512 nm appears at 110 degrees centigrade. The intensity of the 512-nm band decreases in the temperature range up to 150 degrees centigrade. Above 160 degrees centigrade, furthermore, the band intensity decreases with the absorption maxima shifting to shorter wavelengths than 500 nm. Finally, the absorption disappears at 250 degrees centigrade. Besides the correlation between each structure in MS, we also compare the individual structures of C20 and AL18.

(144) **Towards Quantitative Simulation of Two Photon Absorption Profiles for Multi-Photon Imaging Applications**

Sergio Tafur[1], Artem Masunov[1]; [1]University of Central Florida

Two-photon absorption (TPA) is an electronic excitation process involving the simultaneous absorption of two photons. Its probability is quadratically dependent on the intensity of incident light. As a result, each photon carries less energy and may be localized in space with a tightly focused laser beam. These properties can greatly increase penetration depth and resolution in fluorescent microscopy of living tissues. In-vivo imaging applications require organic chromophores with large TPA cross-sections to minimize laser intensity requirements and prevent overheating of targets. Accurate predictions of TPA profiles would assist in design of more effective TPA chromophores and eliminate poor candidates. The improved agreement between theoretical and experimental studies may also help in the identification of novel

structure/activity relationships of TPA chromophores that would assist in their design. We report theoretical studies of (7-benzothiazol-2-yl-9, 9-didecylfluoren-2-yl)diphenylamine, successfully used in multi-photon imaging, along with four other chromophores, all experimentally shown to have a large TPA cross-section. Time Dependent Density Functional Theory (TD-DFT) descriptions of excited states for large conjugated molecules were found to be both accurate and computationally efficient. A third order response formalism within TD-DFT was applied to calculate frequency-dependent third-order polarizability tensors. Thermal broadening was simulated implicitly via an empirical constant. In this contribution we report the results and compare them to experimental measurements, and find a qualitative agreement. We also discuss future plans, aimed to achieve the quantitative agreement between theory and experiment. These include the explicit simulation of thermal broadening and solvent effects by implementation of molecular dynamics, as well as reduction of computational costs by use of semi-empirical Hamiltonians and few-state models.

(145) **Molecular Spectroscopy of Acoustically Levitated Samples**

Jork Leiterer[1], Andreas F. Thünemann[1], Stefan Florek[2], Michael Okruss[2], Ute Resch-Genger[1], Knut Rurack[1], Markus Grabolle[1], Ulrich Panne[1]; [1]Federal Institute for Materials Research and Testing, [2]Institute for Analytical Sciences (ISAS), [3]to Institution 1: ng (BAM)

Many of today's analytical problems are characterized by small sample volumes and can only be solved through a corresponding miniaturization of the analytical instrumentation. Analytical methods, based on spectroscopic techniques, are sufficiently sensitive for analysis of trace elements. But handling of small sample volumes is inherently difficult due to contamination and sorption processes on the walls of containers. Often, the substance of sample containers by itself causes effects which are not negligible. Acoustic levitation is a powerful tool for contact-free sample handling of solid, liquid, and selected gaseous samples. In addition, levitation permits a chemical pre-treatment such as enrichment and extraction as well as combination with different analytical techniques such as optical spectroscopy. Acoustically levitated liquid and solid samples are typically in a range between 5 nl - 5 µl (diameter 0.2 - 2 mm respectively) and are suspended in a gaseous environment by a stationary ultrasonic field. This avoids sample contamination and sorption processes by container walls, but suffers from evaporation and loss of solvents. Levitation is a good possibility to characterize the initial conditions of crystallization and polymerization. Even for spectroscopic methods, the correct information on shape, size, and concentration of samples are indispensable. To determine the size and volume of levitated samples, different methods of contactless droplet size monitoring were developed in this work and compared in detail. In addition, for balancing evaporation and condensation on levitated drops during the experiments, non-contact techniques of solvent and reagent supply have been employed. Here, novel results of acoustic levitation are presented for on-line analysis of crystallization in a levitated droplet. Furthermore, the occurrence of polymorphic modifications depending on different conditions can be detected in-situ under controlled conditions. The analytical figures of merit for Raman and fluorescence spectroscopy of levitated droplets are reported. In preliminary experiments, the spectral properties of nanocrystals (so-called quantum dot systems) in a droplet were studied. The average distances of initially dispersed nanocrystals decrease due to evaporation of the solvent and change the fluorescence signal. This dependence allows a simple adjustment of the concentration, i.e. distance.

(146) **Nanometer Scale Center of Gravity Analysis of Single Quantum Dot Fluorescence. A New Tool for Study of Local Variation of Bone Tissue Biomechanical Properties**

Kurtulus Golcuk[1], Thomas M. Vanasse[2], Michael D. Morris[1], Steve A. Goldstein[2]; [1]Department of Chemistry, University of Michigan, [2]ORL, Orthopaedic Surgery, U.of Michigan

We are exploring the use of spatial arrays of single quantum dots (QD) as fluorescent probes to quantify local small deformations and displacements and mobility of bone tissue constituents at the ultrastructural level under mechanical load. Quantum dots are nanometer diameter semiconductor particles that fluoresce in the visible or near-infrared range. They are robust against photodecomposition and they have narrow (about 40-50 nm FWHH) emission spectra. Localization and motion tracking of an individual QD with nanometer resolution depends on its bright emission, so that the center of gravity (COG) of the laser-induced fluorescence diffraction is easily measured and tracked as the tissue is loaded in tension or compression, using a standard widefield epifluorescence microscope and an electron-multiplying CCD camera (EMCCD). We use coupons of canine cortical bone micro-milled to standard "dogbone" shapes and loaded in a purpose-built dynamic mechanical test system that fits on the microscope stage. The experiment has been validated by comparison of average values of Young's modulus obtained in incremental tensile loading by the Qdot/COG method against measurements made with an attached micro-strain gage and a calibrated load cell that is part of the dynamic mechanical test system. For these experiments streptavidin-conjugated 705 nm Qdot probes were used. Wash-off experiments showed that the Q-dots were preferentially bound to bone mineral, a carbonated apatite. Young's modulus was found to be 14.6 GPa (spatially averaged value) by the Qdot/COG method and 15.9 GPa by the strain gage method. The agreement is excellent because strain gage attachment is expected to increase the local modulus. The Qdot/COG method was also able to detect local variations in modulus. The optical technique is directly extensible to the measurement of relative motion of bone tissue components (e.g. collagen and carbonated apatite) as well as to the measurement of small out-of-plane motions that cannot otherwise be detected.

(147) **Laser Desorption Mass Spectrometry and Atomistic Modeling of Hydrogen Physisorption for Alloy-Doped Carbon Nanostructures**

Michael Miller[1, 2], Grant Merrill[2]; [1]Southwest Research Institute, [2]University of Texas at San Antonio

The storage and delivery of hydrogen under practical and safe conditions of temperature and pressure is arguably one of the greatest challenges facing the acceptance of hydrogen as an alternative fuel source for automotive propulsion of the future. Employment of a material in the solid state as a means of absorbing hydrogen reversibly may well become a practical venue for low-pressure, high-capacity storage, and for regeneration (desorption) into the gas phase at practical temperatures. Remarkable gains in solid-state storage capacities may be within our grasp with the advent of high surface area nano-architectures such as single wall carbon nanotubes (SWNTs) and, more recently, metal organic framework (MOF) compounds. In the case of SWNTs, high intrinsic hydrogen storage capacities approaching a theoretical limit of approximately 8 wt % could be realized for chemisorption uptake and, perhaps, even higher uptake at cryogenic temperatures (77 K) for molecular physisorption. Of particular interest in realizing these gains is the catalytic doping of purified forms of SWNTs with a transition metal or transition metal alloy. A plausible mechanism that may explain enhanced hydrogen uptake in catalyzed SWNTs is atomic hydrogen spillover from the metal

cluster to the SWNT support through a process of surface interphase migration. However, the mechanism still remains to be properly elucidated. The present work is concerned with elucidating the stable binding sites of hydrogen in alloy-doped SWNTs using laser desorption mass spectrometry in the low and moderate temperature regime (77 – 500 K) with high energy resolution. Efficient photon coupling to SWNT lattice vibrations are achieved with an ytterbium fiber laser (1080 nm). In the low temperature regime of hydrogen desorption, acousto-optic modulation is used to control power and to afford the thermal resolution required to differentiate the manifold of binding energies associated with stable interactions between alloy-doped SWNTs and atomic or molecular hydrogen (0-4 eV). Hydrogen yields are determined with a quadrupole mass spectrometer and a 90º off-axis SEM detector. Hydrogen yields and corresponding thermal desorption energies are correlated with those predicted from pseudo-potential molecular dynamics (MD) simulations, which take into consideration the phonon lattice dynamics over the configurational space of SWNTs.

(148) **Confocal Micro X-ray Fluorescence: 3 Dimensional Elemental Mapping**

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Confocal micro X-ray fluorescence is a new instrumental method for materials characterization. In a confocal geometry, the excitation and detection regions are bound by the same foci and therefore, share the same focal spot. The spatial resolution of the confocal approach is improved by only analyzing the confocal region which excludes the surrounding material. This confocal arrangement is achieved by using two monolithic polycapillaries; one focuses the x-rays to a focal spot and the second optic is oriented on the detector side for emission collection from the focal spot. An advantage of the confocal geometry is the capability of scanning the sampling volume in the x, y, and z directions and subsequently producing a 3D elemental distribution of a sample. Scanning in either the x or y direction generates a line scan while sampling along the z-axis produces a depth profile. 3D representation of an elemental distribution is obtained by mapping an x,y area at various z-position depths within the sample. Since this is nondestructive this technique can be applied to a variety of samples including semiconductors, forensics, and art. In this study, the performance of the confocal micro x-ray fluorescence microscope and its application capabilities are demonstrated. Instrumental parameters such as beam size, step size resolution, and data acquisition (i.e., point, line, depth, 2D, and 3D) are examined. Applications to be presented include 3-dimensional elemental images of a paint chip, cobalt precipitated onto a marble substrate, polymer foam density distribution and a nickel foam substrate coated with cobalt nanowires.

(149) **Microchannel Device Filled with Fluorescence Standards for The Characterization of Spectral Scanning Fluorescence Microscopes**

Ulrich Panne[1], Ute Resch-Genger[1], Katrin Hoffmann[1], Roland Nitschke[2]; [1]BAM, [2]Albert-Ludwigs-Universität Freiburg

Confocal and wide-field fluorescence microscopy have developed from being only imaging techniques and matured to a stage where quantification is desired. There is an increasing demand for reliable and comparable data especially in strongly regulated areas like e.g. medical diagnostics. In fluorescence microscopy, similarly to other fluorescence techniques, the measured signals contain not only sample-related but also instrument-specific contributions. These instrument-specific effects limit the direct comparison of fluorescence data obtained e.g. on different microscopes and at different times. To rule out instrumentation as major source of variability of emission data, fluorescence standards and procedures for control of instrument specification and long-term performances are required. As a first step towards an improved comparability of data in fluorescence microscopy, we discuss a calibration procedure based on liquid fluorescence standards measured within the micro channels of advanced slides, which allows the determination of spectral responsitivity of fluorescence microscopes. The applicability of these easy-to-operate liquid as well as the ready-for-use solid materials has been evaluated on several confocal microscopes to compare the instrument performance and the reproducibility of measurements in spectral scanning fluorescence microscopy as a first step towards standardized measurements in fluorescence microscopy.

(150) **Photoactivated Self-Assembly of TiO2 Nanoparticles on Sidewalls of Single-Walled Carbon Nanotubes**

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Titanium oxide nanoparticles (TiO2 NPs) are selectively coated on sidewalls of single-walled carbon nanotubes (SWNTs) upon UV light irradiation in an aqueous media. When UV light is irradiated, TiO2 NPs pre-adsorbed on a Si wafer are desorbed to self-assemble on the sidewalls of nearby SWNTs. Surface charge of TiO2 NPs and doping type of Si wafers turn out to be crucial for the selective self-assembly of TiO2 NPs on SWNTs. Two important photoactivated processes seem to enable such phenomena: 1) desorption of TiO2 NPs from Si surface due to electrostatic repulsion and 2) self-assembly of the desorbed TiO2 NPs on the sidewalls of SWNTs by electrostatic attraction. The photodesorption of TiO2 NPs from a p-type Si wafer is feasible due to electrostatic repulsion between negative-charged p-type Si substrate by photoactivation and negative-charged TiO2 NPs at higher pH than isoelectric point. Since the surface of semiconductors are highly populated with minority charge carriers on light irradiation, negative charges is substantially increased on p-type Si surface on UV irradiation. The desorbed TiO2 NPs are then attracted to nearby SWNTs via electrostatic interaction because the surface charge of SWNTs becomes positive as induced by negative surface charges of p-type Si wafer on UV irradiation. The self-assembly is successful for SiO2 NPs, which are not semiconductors like TiO2 NPs, indicating that the mechanism of the self-assembly is reasonable. Furthermore, a SWNT has been cut to generate a few nm gap at which TiO2 NPs catalyze the generation of highly reactive oxygen and hydroxyl radicals that eventually cut the SWNT. This facile photoactivated self-assembly of TiO2 NPs is believed to accelerate the development of highly efficient photo-harvesting nanocomposite materials as well as nanoelectronic devices for small molecule based electronics.

(151) **Multimodal Multiplex Raman Spectroscopy**

Mike Fuller[1], Prasant Potuluri[1], Mike Sullivan[1]; [1]Centice

Commercial Raman spectrometers are generally equipped with lasers that produce 10-70mW total power at the sample with a focused illumination spot of 10µm-100µm. This small spot size is well matched with fiber and slit based spectrometers where the entrance aperture is approximately the same size as the source image at the sample. In practice using a tightly focused, small illumination cross section at the sample causes a several problems. First, the power density of the laser at the sample is very high and samples are frequently degraded by the high intensity light resulting in an erroneous spectrum and a damaged sample. In addition, many samples are not uniform at a microscopic level and the spectrum resulting from a 10µm-100µm spot may not be

representative of the bulk of the sample. Recently a commercial Multimodal Multiplex Spectroscopy MMS™ Raman spectrometer has been introduced. In contrast to traditional slit spectrometers a MMS-based spectrometer samples several thousand optical channels simultaneously through a wide area encoded aperture instead of a slit then proprietary mathematical algorithms are used to precisely reconstruct the spectral content of a source. Light enters the system through the coded aperture and is collimated onto the grating by a collimating lens. The grating spectrally disperses the light which is then mapped to a 2-D detector array such as a CCD. The most dramatic MMS performance advantage is realized when making difficult low light measurements from diffuse or large sample areas. This presentation will detail the performance advantages of the MMS Raman system over conventional slit based spectrometers for the analysis of inhomogeneous samples such as pharmaceutical tablets and will also describe Surface Enhanced Raman Spectroscopy (SERS) measurements made on gold nanoparticle substrates.

(152) **Observation of Optical Coupling between Surface-Enhanced Raman Scattering and Localized Surface Plasmon Resonance from Single Ag Nanoaggregates**

Kenichi Yoshida[1], Tamitake Itoh[2], Yasuo Kikkawa[1], Vasudevan Biju[2], Mitsuru Ishikawa[2], Yukihiro Ozaki[1]; [1]Kwansei-Gakuin University, [2]AIST

Surface-enhanced Raman scattering (SERS) recently has attracted great interest for applications in analytical sciences because of enormous enhancement by a factor of 10 10-15. The electromagnetic enhancement model of SERS predicts that SERS light radiation is mediated by localized surface plasmon resonance (LSPR). However it has not experimentally been clarified because inhomogeneous broadening obscures optical correlations of Raman-LSPR scatterings in ensemble measurements. Here we investigated anti-Stokes plus Stokes SERS and LSPR from single Ag nanoaggregates adsorbed with Rhodamine 123 (R123). Samples for SERS and LSPR measurements were prepared by incubating aqueous solutions containing sub-micromolar concentrations of R123, millimolar concentrations of NaCl and sub-nanomolar concentrations of Ag colloids (diameter ~67nm) at room temperature. Ag nanoaggregates in the sample were dispersed on a glass plate by spin coating. LSPR was excited with white light through a field condenser. SERS was excited with 568 nm and 648 nm lasers respectively. We selected different SERS active Ag nanoaggregates, and then SERS and LSPR spectra were measured with micro spectroscopic systems. [1-4] Anti-Stokes plus Stokes SERS spectral shape changed according to the peak position of LSPR band. We found that anti-Stokes to Stokes ratios increased remarkably when the peak top wavelength of LSPR was at higher energy (shorter wavelength) sides. This increment directly indicated that SERS light radiation was mediated by LSPR. Reference [1] T. Itoh, K. Hashimoto, and Y. Ozaki, Appl. Phys. Lett. 2003, 83, 2274. [2] T. Itoh, K. Hashimoto, A. Ikehata, and Y. Ozaki, Chem. Phys. Lett. 2004, 83, 2274. [3] T. Itoh, K. Hashimoto, A. Ikehata, and Y. Ozaki, Appl. Phys. Lett. 2003, 83, 5557. [4] T. Itoh, V. Biju, M. Ishikawa, Y. Kikkawa, K. Hashimoto, A. Ikehata, and Y. Ozaki, J. Chem. Phys. 2006, 124, 134708.

(153) **Structural Characterization of J- and H-Aggregates in Mixed LB Films with Merocyanine Dye Investigated by Raman Scattering Spectroscopy**

Ari Maio[1], Yoshiaki Hirano[1], Kenichi Yoshida[1], Luhei Lu[1], Atsuko Kobayashi[2], Keiko Tawa[2], Yukihiro Ozaki[1]; [1]Kwansei Gakuin University, [2]AIST

As is well known, the mixed Langmuir-Blodgett (LB) film of merocyanine (3-carboxmethyl-5-[2-(3-octadecyl-benzothiazolin-2-ylidene)-ethylidene]rhodanine, MS)-arachidic acid (C20) binary system exhibits a sharp red-shifted J-band at 590 nm. On the other hand, we so far found that a blue-shifted H-band at 505 nm appears by adding n-octadecane (AL18) to the MS-C20 binary system. The structures of the J- and H-aggregates in the mixed LB films containing MS have been mainly investigated by UV-visible absorption spectroscopy, IR absorption spectroscopy and X-ray diffraction method towards the elucidation of the mechanism of the H-aggregation. As far as we know, the report as to the structural characterization of the MS LB films by means of Raman scattering spectroscopy is only one example. In the present study, we try to measure Raman scattering spectra of the J- and H-aggregates in the MS LB films, and discuss the structures in both aggregates based on the results of Raman scattering spectra. The MS LB films with the J-band at 595 nm and the H-band at 505 nm were prepared. For comparison, the MS spin coat film, exhibiting a broad absorption at 510-550 nm without J- and H-bands, was also fabricated. For the results of the 488 nm excited resonance Raman scattering (RRS) spectra of the J- and H-aggregates, shifts could be recognized for the bands at around 1555, 1500, 1470, 1290 and 1200 cm-1. Thus, the 488 nm excited RRS spectra of J- and H-bands were different from each other. However, the shape and peak position of the 488 nm excited RRS spectrum of J-band were fairly similar to those of the MS spin coat film without the J-band. Therefore, the 488 nm excited RRS spectra of J-band may mainly originate from the dimeric and monomeric components at around 540 nm rather than the J-aggregates at 590 nm. For the 514 and 568 nm excited RRS spectra of the J-aggregates, their spectral sensitivity became weak due to the increase in strong fluorescence characteristic of the J-aggregates. Moreover, we attempt to obtain Raman scattering spectrum inherent in the J-aggregates by means of surface enhanced resonance Raman scattering (SERRS) spectroscopy.

(154) **Surface-Enhanced Raman Spectroscopy: from Research Tool to A Routine Analytical Technique**

Caterina Netti[1], Helen Stanford[1], Pushwinder Kaur[1], David Reece[1], Stephen Allen[1]; [1]Mesophotonics Ltd.

During the past 5 years, the SERS technique has undergone a revolution in substrate design leading to a brand new arena of detection capabilities. However, previous SERS substrates have been limited to use as a research tool because of their poor reproducibility. Klarite is a new substrate comprising a gold-coated nanostructured surface, developed using photonic crystal technology and semiconductor fabrication processes. Its intrinsic reproducibility provides the potential to transform SERS into a powerful and unique analytical technique. SERS can provide high sensitivity: signals can be amplified one million-fold when looking at trace materials at ppb levels. This combination of sensitivity and specificity, now with high levels of reproducibility, means that SERS can be used to develop routine analytical methods for any application where detailed molecular information is required at low concentrations. Examples will be shown of applications in: pharmaceutical, chemical, medical diagnostics, forensics and hazardous materials detection.

(155) **Discrimination of Biologically Revelant Threat Materials via Surface Enhanced Raman Spectroscopy**

Jason Guicheteau[1], Darren Emge[1], Aaron Hyre[1], Leanne Argue[1], Steven Christesen[1]; [1]US Army ECBC

The adsorption of colloidal silver to biological material suppresses native biofluorescence while increasing the normal Raman signal via the surface-enhanced Raman effect. Surface-enhanced Raman spectroscopy (SERS) takes advantage of the localized enhancement of the electromagnetic field that occurs at metal surfaces offering enhancements of the normal Raman signal by several orders of magnitude. Furthermore, SER offers high sensitivity, large informational content, and is amenable to the aqueous environments typical of biological systems due to the relatively small Raman scattering cross section of water. This work presents the application of surface-enhanced Raman as a viable classification technique for biological materials when coupled with principal component analysis (PCA). PCA is a data reduction and analysis technique that allows spectral similarities or differences to be easily seen. The PC scores associated with similar SER spectra cluster, showing successful discrimination of a sample-specific SERS signature. In this study we present the discrimination of four spore forming Bacillus strains including Bacillus anthracis sterne, Bacillus anthracis ames, Bacillus thuringensis, and Bacillus globigii along with the three other bacteria: Brucella neotomae, Pantoea agglomerans, and Yersinia rhodei.

(155A) **Surface enhanced Raman Detection of Pathogenic Bacteria with Antibody Functionalized Raman Nanoprobes**

Li-Lin Tay[1], Shannon Ryan[1], Jamshid Tanha[1]; [1]National Research Council Canada

The detection of pathogenic bacteria bares important implication in public health and security. Raman micro-spectroscopy has been utilized to detect and classify different classes of bacteria based on their unique vibrational signatures. However, bulk Raman detections, inevitably, are plagued by sensitivity issues associated with the nature of low scattering cross-sections. Surface enhanced Raman spectroscopy (SERS) is known to boost the Raman scattering cross section through the intense, localized surface plasmon resonance near suitable nanostructure assemblies. In this study, we present the SERS based optical detection scheme for a well known human pathogen, staphylococci aureus. The surface of S. aureus is decorated with protein A. We rely on the binding specificity between protein A and antibody to achieve the pathogen selectivity. A human single domain antibody (sdAb) which contains only heavy chain antibody variable domain is conjugated to colloidal silver nanoparticles (NPs) through exposed lysine or cystine residue. The conjugated sdAb-Ag NPs bares unique recognition site for protein A of S. aureus. The aggregation of Ag-NP on the surface of the bacteria as well as the SdAb-Ag-NPs triggers agglutination response of S. aureus showed very prominent amide III vibration. Agglutinated bacteria cells can be detected through this strong SERS signature (amide III vibration) from either cells dried and desiccated on suitable substrates or in the buffer solution. In this presentation, we demonstrate the detection of S. aureus bacteria using SERS and compare this detection limit with the standard agglutination test and bulk Raman microspectroscopy.

(156) **Characterization and Application of Silver Nanorod SERS Substrates as Viral Biosensors**

Sarat Shanmukh[1], Les Jones[3], Rene Alvarez[3], Yiping Zhao[2], Ralph Tripp[3], Richard Dluhy[1]; [1]Department of Chemistry, University Of Georgia, [2]Department of Physics, University Of G, [3]Department of Infectious Diseases, UGA

Surface Enhanced Raman Scattering (SERS) spectroscopy is being increasingly utilized in the sensing, detection and identification of biomolecules and biological agents, such as bacteria and viruses, which are present in extremely low concentrations. In this study we report the capability to detect extremely low quantities of viruses with sensitivity and specificity. The prerequisite to such detection is the fabrication of SERS substrates that can provide high enhancement factors so as to enable the detection of extremely small quantities of the afore mentioned specimens. We have previously shown that silver nanorod substrates prepared using the glancing angle vapor deposition (GLAD) technique are capable of providing extremely high enhancement factors (~10E8) at Near Infra Red wavelengths (785 nm) for a standard reporter molecule 1,2 trans-(bis)pyridyl-ethene (BPE). The physical characteristics of the substrate such as the size and shape of the nanorods, orientation and the spacing between the nanorods can be modified using the GLAD technique. In addition, the polarization dependence of the SERS enhancement of the silver nanorod substrate has been studied by measuring the SERS response as a function of the angle between the nanorods and the direction of the polarization vector.The applicability of this substrate to the detection of viruses has been investigated by looking at extremely low quantities (~0.5uL) of different respiratory viruses such as Adenovirus, Rhinovirus and different stratins of Respiratory Syncytial Virus (RSV) in the presence of different media, different states of activity and concentrations.

(157) **Multilayer Enhanced Gold Film Over Nano-structured SERS Substrates for Extended Shelf-life and Sensitivity**

Brian Cullum[1], Honggang Li[1], Caitlin Baum[1], Jian Sun[1]; [1]U. of MD-Baltimore County

Development of surface enhanced Raman scattering (SERS) substrates with large enhancement factors, good reproducibility and long term stability has long been a goal of the SERS community. Typically to achieve the largest SERS enhancements with non-colloidal particles, silver is the metal of choice, as it generally provides significantly (i.e., ~ 2 orders of magnitude) better enhancement factors than comparable gold substrates. Unfortunately, silver oxidizes rapidly causing its enhancement to decay and making gold the better metal for substrates that need to have long usable SERS active lifetimes. To overcome this tradeoff between sensitivty and shelf-life, we have developed a novel class of gold multi-layer substrates that are capable of enhancing SERS signals by 1.5 orders of magnitude over conventional gold film over nanostructured substrates (GFONS), making them comparable in sensitivity to optimized silver film over nanostructured substrates. They are fabricated by depositing 1 nm thick silver oxide islands on a conventional GFON substrate followed by deposition of a second gold layer. This silver oxide layer acts as a dielectric spacer between the two gold films, producing two separate electric fields in the different gold layers that are capable of reinforcing each other and providing the multi-layer SERS enhancement. In addition to the enhanced sensitivity of these multi-layer substrates, they also exhibit long SERS active shelf-lives (i.e., greater than months), with no measurable degradation in SERS enhancement, and relative standard deviations in SERS enhancement of less than 6% across the substrate's surface. This presentation will describe the fabrication and characterization of

these novel multi-layer gold substrates as well as discuss their application to long-term field studies.

(158) **Development of a Surface-Enhanced Raman Spectroscopy Protocol for Identification of Potential Osteoarthritis Biomarkers**

Karen Dehring[1,4], Gurjit Mandair[3,4], Blake Roessler[2,4], Michael Morris[3,4]; [1]Department of Biomedical Engineering, [2]Department of Internal Medicine, [3]Department of Chemistry, [4]University of Michigan

We demonstrate a novel application of surface-enhanced Raman spectroscopy (SERS) for the identification of a potential osteoarthritis biomarker. Hyaluronic acid (HA) levels in synovial fluid have been previously correlated with joint space narrowing, a key predictor of osteoarthritis. Current immunoassay and chromatographic methods of detecting HA in synovial fluid involves complicated sample preparation and lengthy analysis times. HA is a polysaccharide of alternating N-acetyl-glucosamine and D-glucuronic acid units. Earlier Raman spectroscopic studies of the weakly scattering HA required concentrations of 40-50 mg/ml, a value that exceeds clinically relevant levels by 1000X. Surface-enhanced Raman spectroscopy lowers the detection limit of HA to below the clinical range; availability of commercial SERS substrates in a solid convenient format improves enhancement reproducibility. We report SERS identification of HA in aqueous solutions ranging from 0.25-6 mg/ml using short signal integration times and low laser power. A simple drop evaporation protocol separates HA from solution impurities, such as buffer salts, and also localizes HA into a concentric ring on the SERS substrate. Initial SERS examination of model synthetic synovial fluid and canine synovial fluid specimens indicated that Raman signal from proteins interfered with HA identification. Droplet evaporation and other coarse separation methods, such as filtration, do not adequately segregate HA from proteins because HA binds non specifically to synovial fluid proteins such as albumin or globulin. A three-step validated protocol, trichloroacetic acid precipitation of biofluid proteins, overnight cold storage, and ultracentrifugation, was used to reduce the protein content. The residual protein Raman signal did not interfere with identification of hyaluronic acid in artificial synovial fluid at concentrations ~0.5 mg/ml. We present the proof of principle results for incorporation of the protein removal protocol with drop evaporation to allow SERS identification of HA at clinically relevant concentrations. Strategies to quantify HA concentration in aqueous solutions and synthetic synovial fluid models are also presented.

(159) **SERS and DFT Of 4''-Trimethylsilylethylsulfanyl-4,4'-Bis-(Phenyleneethynylene)Benzenethiol On Ag Nanospheres**

Melissa Fletcher, Alberto Vivoni[2], Orest Glembocki[3], Sharka Prokes[3], James Lui[3], Joshua Caldwell[3], Martin Moore[3], Stephen Choquette[4], Charles Hosten[1]; [1]Howard University, [2]Inter American University, [3]Naval Research Laboratory, [4]National Institute of Standards and Tech

Monolayers of alpha, omega-dithiol oligo(phenyleneethynlene) molecules are critical to the field of molecular electronics because of their abilities to form bonds with many metallic surfaces and to rectify current. FT-Raman and surface-enhanced Raman scattering (SERS) were used to characterize a selectively oriented self-assembled monolayer of 4''-trimethylsilylethylsulfanyl-4,4'-bis-(phenyleneethynylene)benzenethiol (OPE') on silver coated nanospheres. Selective orientation was achieved by synthesizing 4''-trimethylsilylethylsulfanyl-4,4'-bis-(phenyleneethynylene)benzene disulfide, which undergoes oxidative dissociation and covalently bonds to the surface. The Ag coated nanosphere surfaces were characterized by scanning electron microscopy (SEM), which showed a large area of surface charging. The SERS spectrum shows a reduced number of peaks when compared to the FT-Raman spectrum. The =C–S peaks at 1087 and 1132 cm-1 exhibit a red shift when adsorbed on the Ag surface. Assignments of vibrational bands were based on DFT calculations performed at the B3LYP level with good agreement between theoretical and experimental values. An average percent difference of 2.93 was obtained.

(160) **Glass Sample Discrimination by Laser Induced Breakdown Spectroscopy (LIBS)**

Candice Bridge[1], Micheal Sigman[1], Joseph Powell[2], Katie Steele[1], Jean MacInnis[1], Mary Williams[1]; [1]National Center for Forensic Science at UCF, [2]South Carolina Law Enforcement Dept.

Results from a study of LIBS and refractive index (RI) for the comparative analysis of evidentiary glasses will be presented. Automobile float glasses, side mirror glasses, headlamp glasses and brown container glasses were analyzed using LIBS with and without the addition of RI. The emission ratios were evaluated by ANOVA to determine a set of ratios having significant F-statistic values to allow for discrimination between the glass samples comprising the set. The emission ratios were further analyzed by constructing a Pearson product moment correlation coefficient matrix and selecting those ratios displaying the lowest correlations, thereby maximizing the information content in the data set. The selected set of ratios were used to make pairwise comparison of the glass samples by means of a Tukey Honestly Significant Difference ANOVA post-hoc test to maintain prescribed data-wide significance levels at 0.10 and 0.01. LIBS coupled with RI allowed more than 90% discrimination for all of the sample sets except for side mirror glasses.

(161) **The Analysis of Commercial Blasting Agents by Laser Induced Breakdown Spectroscopy (LIBS), with Emphasis on Methods for Heterogeneous Samples.**

Katie Steele[1], Michael Sigman[1], Candice Bridge[1], Jean MacInnis[1], Zach Parker[1]; [1]National Center for Forensic Science, UCF

The objective of this presentation is to demonstrate the importance of sampling techniques that should be considered when analyzing heterogeneous samples using Laser Induced Breakdown Spectroscopy (LIBS). The twenty-two (22) heterogeneous blasting agents used in this study are comprised of slurries, watergels, and emulsions. These materials often contain glass microballoons, metal particles (i.e. Aluminum), ammonium nitrate prills, and other homogeneously distributed organic and inorganic components. Spectra were averaged from locations across the sample and the number of spectra averaged were varied. Spectra were compared by techniques including full spectral correlation, selected line correlations and spectral line ratioing. Air was found to be the optimal atmosphere for data collection, yielding coefficients of determination (R2) much higher than those obtained form samples purged with argon gas or with continuous argon flow. Spectral data collected back-to-back yielded much higher R2 values than the spectral data collected with several days in between data collections.

(162) **LIBS Analysis of Blood Samples in Clinical Applications**

Dale LeCaptain[1], Kishore Singirikonda[1]; [1]Central Michigan University

The analytical ability to perform in situ and multi element analysis without direct sample contact is desired to monitor clinical samples. The LIBS technique uses a ND:YAG laser beam to strike the blood sample and completely ionize the sample by creating a micro-plasma, which causes atomic emission that is detected by an Andor Mechelle spectrophotometer. The sample preparation

needed makes this LIBS application demonstration a potentially useful tool for analysis in clinical settings. The work presented here utilizes LIBS for quantification of calcium, sodium, and other biologically significant metals in blood sample specimens.

(163) **A Critical Assessment of Different Analytical Approaches to The Direct Determination of Carbon in Soil by LIBS**

Lydia Edwards[1], Benjamin W Smith[1], Nicolo Omenetto[1], Igor Gornushkin[1], Joda C Wormhoudt[2], Andrew Freedman[2], James D Winefordner[1]; [1]University of Florida, [2]Aerodyne Research, Inc.

Laser-induced breakdown spectrometry (LIBS) has been evaluated as a technique to monitor the total carbon content in soil, which can provide information about terrestrial carbon sequestration. LIBS has the advantage of little-to-no sample preparation and potential portability, which makes it an ideal in-situ carbon monitor. However, LIBS is susceptible to matrix effects and carbon signal strength can be affected by slight differences in soil compositions. For this reason, a comprehensive analysis of the LIBS soil spectra was performed for different standard soil samples of varying composition. This allowed the production of a single calibration curve that is applicable to a wide range of soils pertinent to the carbon sequestration. LIBS signal intensities also vary widely with soil moisture content. Previous drying techniques, including oven drying, are not compatible with an in-situ carbon monitor. Several efficient drying techniques that can be performed in the field were investigated. These include laser heating and a heated sample press. By combining laser heating of soil samples and comprehensive spectral analysis, acceptable absolute accuracy limits of total carbon content can be achieved.

(164) **Forensic Glass Identification by Laser Induced Breakdown Spectroscopy (Libs)**

Esperanza Rodriguez[1], Uwe Heitmann[2], J. R. Almirall[3], Igor Gornushkin[1], Ben Smtith[1], Nico Omenetto[1], James Winefordner[1]; [1]University of Florida, Department of Chemistry, [2]Institute for Analytical Sciences, Berl, [3]Florida International University, Miami

Fragments of broken glass collected in a crime scene might associate a suspect with the perpetration of a particular crime. These small fragments can be found on the perpetrators clothes or shoes and can later be compared to those found in the crime scene1. The chosen method of analysis should, therefore, be capable of dealing with small sample fragments while the results should provide a high level of confidence. This study assesses the potential of laser induced breakdown spectroscopy (LIBS) as a tool for fast and reliable glass analysis. The experimental set-up includes a 50 mJ Nd:YAG operating at 1064 nm and a high resolution echelle spectrometer equipped with a 2-dimensional CCD detector and a chopper wheel. This combination provides information-reach spectra consisting of 38565 simultaneously recorded data points (pixels). In our method, spectra from known glass samples are obtained and then stored in a computer in the form of a spectral library. Identification of the unknown glass is achieved by correlating its individual spectrum against all spectra stored in the library and finding the closest match. A thorough statistical procedure is developed based on the linear and rank correlation approaches. First, a narrow spectral gate is scanned across the spectrum to define regions of high and low correlations with the library. Second, the mask is imposed on the spectrum to select only highly correlating spectral regions. Third, a background correction and data smoothing routines are applied to improve a confidence of the correlation. All this together allows one to reliably differentiate between glasses of similar composition. 1. J.R. Almirall, in Forensic Examination of Glass and Paint, p. 65-80, B. Caddy, Ed. (Taylor and Francis, London, 2001).

(165) **Multi-Element Analysis of Cast Iron by Laser Induced Breakdown Spectroscopy using Ortogonal Pre-Ablation Spark and High-Resolution Echelle Spectrometer**

Igor Gornushkin[1], Uwe Heitmann[2], Nico Omenetto[1], Ben Smith[1], James Winefordner[1], M. Mueller[3]; [1]University of Florida, Department of Chemistry, [2]ISAS - Inst for Analytical Sciences, [3]BAM - Federal Inst Materials Res Testing

Dual-pulse laser induced breakdown spectroscopy (LIBS) gained its popularity due to a superior performance compared to single-pulse LIBS. There are two dual-pulse configurations commonly used in LIBS, collinear and orthogonal. We investigate the orthogonal configuration in which the first (horizontal) laser pulse induces a plasma in the air above the target while the second (vertical) pulse removes the target material into the rarefied environment. The experimental set-up includes a 300 mJ pre-ablating and a 50 mJ ablating Nd:YAG laser, both operating at 1064 nm. A high-resolution echelle spectrometer equipped with a 2-dimensional CCD detector is used for recording the spectra. A set of cast iron standards is used to obtain spectra at different time delays between pre-ablating and ablating lasers. The optimal orthogonal geometry and delay time are found for obtaining the maximal emission enhancement (compared to single-pulse LIBS) for a number of elements: Si, Mn, V, Mo, etc. The enhancement is then related to changes in spectroscopic characteristics of the plasma.

(166) **Standard-Free Quantitative Analysis in Laser-Induced Breakdown Spectroscopy: Experimental Evaluation of Existing Algorithms and Theoretical Modeling Approaches**

Kathleen Herrera[1], Igor B. Gornushkin[1], Elisabetta Tognoni[2], Benjamin W. Smith[1], Nicolo Omenetto[1], James D. Winefordner[1], M. Mueller[3]; [1]Department of Chemistry, University of Florida; [2]Applied Laser Spectroscopy Lab, Institute for Chemical Physical Processes Research Area of National Research Council, Pisa, Italy; [3]Federal Inst Materials Res and Testing

The laser-induced breakdown spectra obtained from different aluminum and iron standards are evaluated using two standard-free methods, the calibration-free laser-induced breakdown spectroscopy (CF-LIBS)1 and conventional LIBS in vacuum followed by Monte Carlo simulated annealing optimization2. The CF-LIBS1, which is based on the Boltzmann method, is used to directly evaluate the plasma temperature, electron number density and relative concentrations of species present in a given sample without the need of reference standards. In the second approach2, the initial value problem is solved based on the model of radiative plasma expanding into vacuum. Here, the prediction of the initial plasma conditions (i.e. temperature and species number densities) is achieved by a step-wise Monte Carlo optimization of calculated synthetic spectra in order to show a close correlation with experimentally measured ones. The results obtained from both methods are carefully investigated and compared. A. Ciucci, M. Corsi, V. Palleschi, S. Rastelli, A. Salvetti and E. Tognoni, Appl. Spectrosc., 53, 960 (1999). 2, I.B. Gornushkin, A.Ya. Kazakov, N. Omenetto, B.W. Smith and J.D. Winefordner, Spectrochim. Acta B, 60, 215, (2005).

(167) **Evaluation of Optical Thickness of Laser Induced Plasma by Duplication Factor Approach**

Igor Gornushkin[2], Uwe Heitmann[1], Galan Moore[2], M. Mueller[3], Ben Smith[2], James Winefordner[2], Nico Omenetto[2]; [1]ISAS- Institute for Analytical Sciences, Berlin, [2]University of Florida, Dept of Chemistry, [3]BAM - Federal Inst for Res and Testing

Quantitative LIBS strongly relies on proportionality between the elemental concentration and the corresponding emission signal. For many emission lines, this proportionality is broken due to strong self-absorption in the plasma plume. The traditional duplication

curve method is proposed to rapidly evaluate the optical thickness of a laser induced plasma at multiplicity of wavelengths and to select emission lines suitable for quantitative analysis. Duplication curves which relate the duplication factor to the atomic density are obtained by doubling the plasma absorption length using a spherical mirror. A high resolution echelle spectrometer equipped with a 2-dimensional CCD detector monitors simultaneously a 200 nm - wide spectral region. A series of cast iron standards are used to construct the duplication curves for Mn, Si, Mo, Ni, V, etc. The measurements are supplemented by theoretical simulations of duplication factors. The plasma damping parameters and line broadening mechanisms are evaluated.

(168) **Laser Ablation ICP Optical Emission Spectrometry Analysis of Semiconductor Components as Specified by WEEE and RoHS Compliance**

Craig Seeley[1], David Pfeil[1], Garry Kunselman[1]; [1]Teledyne Leeman Labs

Starting in August 2005, companies selling a broad range of electrical goods in Europe will need to conform to WEEE (Waste Electrical and Electronic Equipment Directive) and as of July 2006, those same companies will also need to conform to RoHS (Restriction of Use of certain Hazardous Substances Directive). The WEEE and RoHS Directive 2002/95/EC are having an enormous impact on anyone who produces or distributes electronic or electrical goods. Manufacturers of products from computers to IT equipment to clock radios to toasters could find themselves banned from selling their product in the European market if they do not comply to these new directives by the specific dates. From 1 July 2006, new electrical and electronic products that contain more than the agreed levels of lead, cadmium, mercury, hexavalent chromium (or chromium VI), polybrominated biphenyl (PBB) and polybrominated diphenyl ether (PBDE) flame retardants will be banned from the EU. A wide range of goods is affected, from computers and telecommunications equipment, to domestic appliances and electronic tools, toys and automatic dispensers. Recent improvements in both optical spectrometer technology and laser ablation system design has helped to improve accuracy and precision. We will be presenting data describing a Laser Ablation ICP Optical Emission Spectrometry (LA-ICP-OES) technique for the analysis of Pb, Cd, Hg and Cr in various semiconductor components integrating a large spot, ultraviolet, Nd:YAG laser ablation system with a simultaneous ICP-OES, incorporating a large format detector. This solid sampling technique has a number advantages over traditional dissolution techniques. These include, but are not limited to, high sample throughput and the elimination of additional mixed waste typically generated by aqueous analysis methods. Both bulk and microstructure chemical analysis will be performed and the data presented.

(169) **Double pulse Laser Induced Breakdown Spectroscopy (DP-LIBS) in Metallic Alloys. Matrix Influence Studies.**

Mauro Alberto Martinez L.[1], Vincent Piscitelli S.[1], Alberto Jose Fernandez C.[1], Jhanis Jose Gonzalez Ch.[2], Richard E. Russo[2]; [1]Universidad Central de Venezuela, [2]Lawrence Berkeley Laboratory

Different metals alloys were studied by means of Double-Pulse Laser Induced Breakdown Spectroscopy in collinear configuration. The plasma emission was produced by two Nd:YAG laser (Surelite I and II, 8ns, 10 Hz) operated at different wavelength (1064, 532, 355 nm). The two lasers were directed perpendicular to the sample surface and focused using achromatic lens. The focal point was located at 1 mm above the sample surface. The plasma was imaged by quartz cylindrical lens onto the entrance slit of a medium-resolution spectrograph (Spex 500M). The detector used is CCD (Hamamatsu C7041) using 20 ms integration time. Independent firing of the two laser pulse is achieved by using externally controlling by home made delay generator based on passive RC circuit, allowing variation on time between pulses from 0 to 200 µs. Different SMRs metals alloys series (NIST) were investigated: Zn-Al, Zn-Base Die-Casting, Al Base and Brass. The influence of the laser wavelength, laser energy, and delay time between pulses were studied. It is found a significant increase in atomic lines intensities for different elements in different matrix using DP-LIBS compared to a single pulse of equal energy. A maximum enhancement factor of 3-10 is attained with a delay time range 7-9 µs. No variation on optimum delay time between the lasers pulses were observed for the different studies matrix and for different elements. The emission signal enhancement is strongly dependent on sample matrix. For a specific matrix no dependence on the element is observed for the signal enhancement.

(170) **Laser Induced Breakdown Spectroscopy in The VUV Range**

Ulrich Panne[1], Maike Mueller[1], Saara Kaski[1], Helmut Becker-Ross[2], Stefan Florek[2]; [1]Federal Institute of Materials Research BAM, [2]ISAS Berlin

Laser-induced breakdown spectroscopy (LIBS) is a powerful tool for the multi-element analysis of a huge variety of solid, liquid, and gaseous samples of industrial relevance. For LIBS an intense, pulsed laser beam (typically a Nd:YAG or excimer laser) is focused on the sample of interest, resulting in an evaporation, atomization, and partial ionization of the sample in an expanding plasma cloud. After a delay of some hundred nanoseconds to discriminate against the recombination background, the elemental composition of the sample can be determined via the spectrally and temporally resolved detection of the characteristic atomic and ionic emissions. Due to the minimum sample preparation, the low cost for a single measurement, and the potential for an extensive automation, LIBS is an attractive approach to process analysis. The objective of this work was to extend the range of elements, which can be analyzed by LIBS, via observation of atomic emission in the VUV range. This permits not only a multielement analysis of metals, but also access to emission lines of metalloids such as S, P, N,O, C, As. Two experimental set-ups for VUV-LIBS are presented: a set-up for bulk analysis based on conventional Czerny-Turner monochromator and a new echelle spectrograph for high spectral resolution (> 10 000) in the spectral range 150-300 nm. In addition, this system allows a microanalysis with a spatial resolution in the order of 10 µm. Besides the special characteristics of the new echelle system, details of the sample cell and optical system will be discussed. General figures of merit (elemental detection limits, sensitivity, etc.) for both systems will be presented for geochemical samples as well as experimental techniques for compensating matrix interferences. In addition, results from the analysis of phophorylated proteins from blot membranes will be presented, which is highly relevant for determination of posttranslational protein modifications.

(171) **To Gate Or Not To Gate in Laser Induced Breakdown Spectroscopy (LIBS)**

Ulrich Panne[1], Maike Mueller[1], Igor Gornushkin[2]; [1]Federal Institute of Materials Research BAM, [2]Dept. of Chemistry, Univ. Florida

For spectrochemical analysis with LIBS, the choice of the spectrometer and detector is often limiting the envisioned application, e.g. covered wavelength region, spectral resolution, dynamic range, readout time, and cost. The aim of this work was to study a new approach to LIBS detection. Through a direct comparison of two detectors an ICCD and a non-intensified CCD

in combination with a high-resolution echelle spectrograph, we could demonstrate a comparable sensitivity of both systems. The detectors were coupled to the identical set-up and spectrometer to ensure comparable measurement conditions. While some authors reported already comparative detector/spectrometer studies in the past, none of these studies were comparing identical systems with intensified and non-intensified detectors. Compared to a CCD the ICCD which is conventionally used in LIBS, enables time-resolved measurements, whereas the CCD is less expensive and offers a higher quantum efficiency over a broad spectral range. The new echelle-spectrometer ARYELLE (LTB Berlin, Germany) provides high resolution combined with a wide spectral range. To employ a non-intensified CCD, the ARYELLE features a mechanical chopper to discriminate the unspecific early plasma emissions from the atomic and ionic emissions used for analytical purposes. We observed an excellent performance of the non-intensified system in terms of analytical figures of merit for several matrices. The results were further strengthened through comparisons with modelling of the plasma expansion and emission.

(172) **NMR Spectroscopy of Solid Lead Materials**

Cecil Dybowski[1], Alicia Glatfelter[1], Shi Bai[1], Dale L. Perry[2]; [1]University of Delawre, [2]Lawrence Berkeley National Laboratory

We report Pb-207 NMR chemical shielding and relaxation for solid lead materials, including the halides and complexes of the lead halides with 1,10-phenanthroline. The NMR parameters are correlated with structure. Changes in the chemical shielding with composition are compared to other measures such as electronegativity and local geometry. The substantial variation of chemical shielding with structure indicates that NMR spectroscopy will be useful in probing the structure of lead-containing materials in chemical analysis accompanying processes such as environmental clean-up and materials fabrication.

(173) **Thin Films Characterization Using Several Complementary Spectrometric Techniques**

Albert Brennsteiner[1], Julien Malherbe[2], Olivier Donard[2], Hervé Martinez[2], Sébastien Mazan[3], Franck Niveau[4], Célia Tauziede[1], Coralie Naudin[1], Céline Eypert[1], Jean-Paul Gaston[1]; [1]Horiba Jobin Yvon, [2]University of Pau, [3]PSA Peugeot Citroën, [4]Renault SA

Glow Discharge Optical Emission Spectrometry, Raman Spectrometry and Optical Ellipsometry have been complementary used to characterise various thin films. GD-OES is capable of Ultra Fast Depth Profiling of layers down to the nm level, Ellipsometry is the recognised technique for thin films measurement and µ Raman using multiple lasers could do mapping and in depth investigation of many layers. Cr conversion coatings used for corrosion protection of automotive vehicles with an attempt to differentiate the Cr species (Cr3 and Cr6), OLED (Organic Light Emitting Diodes) used for mobile phone displays and strained Si layers used in electronics to obtain faster chips have been characterized using the 3 techniques. With layers being metals, glasses and organics, this complementary approach reveals the relative strengths of the techniques and provides more in depth information on thin films.

(174) **Kinetic and Characterization Studies of The Formation of Barium Monomolybdate in Equimolar Powder Mixture of Baco3 and Moo3**

Latifa Alhajji; Kuwait Institute Sci. Research

The formation of BaMoO4 in equimolar powder mixtures of BaCO3 and MoO3 was examined under isothermal and non-isothermal conditions upon heating in air at 25-1200ºC, using thermogravimetry. Concurrence of the observed mass loss due to release of CO2 to the occurrence of the formation reaction was evidenced. Accordingly, the extent of reaction (x) was determined as a function of time (t) or Temperature (T). The x-t and x-T data obtained were processed using well established mathematical apparatus and methods, in order to characterize nature of reaction rate determining step, and derive isothermal and non-isothermal kinetics parameters (rate constant, frequency factor, reaction order and activation energy). Moreover, the reaction mixture quenched at various temperatures (450-575ºC) in the reaction course was analyzed by various spectroscopic (X-ray Diffractometry, infrared and laser Raman spectroscopy and microscopic (scanning electron microscopy and x-ray energy dispersive spectroscopy) techniques, for material characterization. The results obtained indicated that the reaction rate may by controlled by unidirectional diffusion of MoO3 species through the product layer (BaMoO4), which was implied to form on the barium carbonate particles. The non-isothermally determined activation energy (156 kJ/mol) was found to be close to the isothermally determined one (164-166 kJ/mol)

(175) **Evaluation of a Standardized Micro-Vacuum Sampling Method for Collection of Surface Dust**

Kevin Ashley[1], Gregory Applegate[1, 2], Tamara Wise[1], Joseph Fernback[1], Michael Goldcamp[2]; [1]CDC/NIOSH, Cincinnati, OH, [2]Wilmington College, Wilmington, OH

A standardized procedure for collecting dust samples from surfaces using a micro-vacuum sampling technique was evaluated. Experiments were carried out to investigate the collection efficiency of the vacuum sampling method described in American Society for Testing and Materials (ASTM) International Standard D7144, "Standard Practice for Collection of Surface Dust by Micro-Vacuum Sampling for Subsequent Metals Determination." Weighed masses (5, 10 and 25 mg) of three National Institute of Standards and Technology (NIST) Standard Reference Materials® (SRMs) were spiked onto surfaces of various substrates. The SRMs used were: (1) No. 1579, Powdered Lead-Based Paint; (2) No. 1648, Urban Particulate Matter; and (3) No. 2583, Trace Elements in Indoor Dust. Twelve different substrate materials, which were chosen to be representative of surfaces commonly encountered in occupational and/or indoor settings, were selected for investigation. These consisted of: (1) wood; (2) tile; (3) linoleum; (4) vinyl; (5) industrial carpet; (6) plush carpet; (7,8) concrete block (painted and unpainted); (9) car seat material; (10) denim; (11) steel; and (12) glass. Samples of SRMs originally spiked onto these surfaces were collected using the standardized micro-vacuum sampling procedure. Gravimetric analysis of material collected within pre-weighed inserts (housed within the samplers) was used to measure SRM recoveries. Recoveries ranged from ≈20% for SRM 1579 from industrial carpet to ≈60% for SRM 1579 from glass. For most SRM/substrate combinations, recoveries ranged from ≈25% to ≈50%; variabilities differed appreciably. In general, SRM recoveries were higher from smooth and hard surfaces and lower from rough and porous surfaces. Material captured within collection nozzles attached to the sampler inlets was also weighed. A significant fraction of SRM originally spiked onto substrate surfaces was captured within collection nozzles. Percentages of SRMs captured within collection nozzles ranged from ≈13% for SRMs 1579 and 2583 from industrial carpet to ≈45% for SRM 1648 from glass, tile and steel. For some substrates, loose material from the substrate itself was sometimes collected along with the SRM. Co-collection of substrate material can bias results and contribute to sampling variability. The results of this work have provided performance data on the standardized micro-vacuum sampling procedure.

(176) **Characterization of Hyperaccumulating Plants Employed for Phytoremediation of Arsenic and Lead**

David Butcher[1], James Bolick[1], Youngsoo Cho[1]; [1]Western Carolina University

Lead and arsenic are toxic elements found in a number of locations in contaminated soil. Compared to traditional methods of soil remediation, phytoremediation (the use of plants to concentrate elements from soil) offers reduced cost and widespread public acceptance. A commercially available brake fern (Pteris vittata) was evaluated to determine its suitability for phytoextraction of arsenic at Barber Orchard. Greenhouse studies were performed in which mature ferns were planted in contaminated soil and allowed to grow for several months before shoots were harvested. The uptake of various forms of arsenic were evaluated by the use of a hydroponics system to which various arsenic species were added. There was no significant difference in the uptake of arsenic when exposed to inorganic arsenic(III) and arsenic(V) compounds. The arsenic species present in the plants were evaluated by X-ray absorption spectroscopy.

(177) **Handheld Field Sensors For Indoor Air Pollutants**

Claire Robertson[1], Lorraine Gibson[1], Amy Cheung[1], Walter Johnstone[1], Claire Watt[1]; [1]University of Strathclyde

A portable, inexpensive sensor for the quantification of formaldehyde vapour in air has been developed. The vapour is trapped by a solution containing 0.07 mM pararosaniline, 2 mM sulphite and 0.02 M hydrochloric acid (Schiff's reagent). Reaction mechanisms were explored to explain the reduction of pararosaniline by sulphite and/or dilute hydrochloric acid, and to understand how the coloured alkyl sulphonic acid product forms. The optimized trapping reagent was doped into a transparent, robust, porous glass, (1 cm2, approximately 1 mm thick), prepared by the sol–gel method. The absorbance of the glass sensor was measured at 620 nm. When formaldehyde vapour (3–22 parts per million by volume (ppmv) was passively sampled for 6 h in the laboratory, a linear correlation was achieved between absorbance and concentration. The sensors were also exposed to lower concentrations of formaldehyde vapour (sub-ppmv) for 1–6 days. Initial results indicate linear responses to increasing vapour phase concentrations, and exposure times. To allow on-site measurements, a hand-held spectrophotometer has been designed to measure the intensity of transmitted light passing through the sensor. It employs an eight-bit microcontroller to modulate two light emitting diodes, one that emits light at a reference wavelength (lamda r) the other at the absorbing wavelength (lamda max) of the derivatized product. After the light has passed through the absorbing media it is detected by a photodiode. The net intensity of the transmitted light is measured as the difference between the intensity of light measured at lamda max and the intensity of light measured at lamda r. The data obtained are processed by a microcontroller and the absorbance measurements are output to a liquid crystal display. The accuracy and precision of the hand-held device were assessed by comparing absorbance measurements with those obtained from a bench top ultraviolet spectrometer.

(178) **Kinetics and Catalytic Reactions as Applied to Trace Analysis**

Surendra Prasad[1]; [1]The Univ. of the South Pacific

An ever increasing awareness of the important and critical role of extremely small concentration of some chemical species when present in chemical, physical and environmental samples has greatly stimulated interest in research aimed at determination of such species in trace level in a variety of complex matrices. The refinement and extension of analytical requirements imposed by the presence of trace amount of elements or compounds led to the development of same new micro-analytical techniques of chemical analysis. One of them is ¡§Kinetic Methods of Analysis¡¨, which is now emerging as a young area of research in the field of analytical chemistry. This is a ¡¥rate-based technique¡¦ rather than equilibrium based one. The ¡¥Kinetic Catalytic Methods (KCM)¡¦ continued to be the most popular method in the literature of kinetic methods of analysis. Their growing popularity and gradual acceptance is due to high specificity, sensitivity and precision combined with simple procedure and economy compared to the other methods of comparable analytical merit. Several reactions such as redox reactions, ligand substitution reactions and metalloporphyrin formation have been utilised as indicator reactions for the development of kinetic catalytic methods of trace analysis. Potassium hexacyanoferrate(II) is known to be among the least labile cyano-complexes of transition metal ions. Exchange of labeled cyanide between [Fe(CN)6]4- and free cyanide or aminopyridine is extremely slow, but under the action of u.v. light reversible aquation takes place with the formation of [Fe(CN)5H2O]3- and CN-. The aquapentacyanoferrate(II) produced has been reported to react with nitrogen heterocycles giving intensely coloured products. In line with an earlier investigation of a reaction of hexacyanoferrate(II) with nitrosobenzene, hexacyanoferrate(II) may react with n-methyl pyrazinium ion (Mpz+) Mercury is a potent environmental pollutant and we were looking for a kinetic method for its determination in trace concentrations. The search has resulted in an investigation of the kinetics and mechanistic anatomy of the mercury(II)-catalyzed reaction between hexacyanoferrate(II) and Mpz+ which gives an intense blue product, [Fe(CN)5Mpz]2-. The further search has resulted in an investigation of the kinetics and mechanistic anatomy of mercury(II) catalyzed reaction between hexacyanoferrate(II) and alpha-Nitroso-beta-Naphthol [*f*ÑN*f*ÒN] followed by its application for the determination of Hg(II). The kinetic behavior of these reactions have been thoroughly studied and plausible mechanisms have been proposed, and are utilised for development of methods for trace determination of Hg(II). This presentation describes how to design catalytic kinetic methods of analysis. The mechanisms of the reactions are particularly important in establishing the methods, and will be briefly discussed for two specific cases in the present talk.

(179) **Analysis of Nerve Agent Degradation Compounds Using the Vanadomolybdate Reagent**

Stuart Chalk[1], Tanya Alvers[1]; [1]University of North Florida

In order to remotely detect the prescence of chemical nerve agents (VX,Sarin,etc) a colorimetric analysis of the degradation products methylphosphonic acid (MPA), ethylmethylphosphonic acid (EMPA), and dimethyl methylphosphonic acid (DMMP) was investigated. Conversion of these products to phosphate and detection by use of the vanadomolybdate reagent was initially the focus of this research, but it was found that direct reaction with vanadomolybdate was also a possibility. This paper presents the analytical options of detection of MPA, EMPA, and DMMP with vanadomolybdate and current work to incorporate this chemistry in a remote flow based analyzer.

(180) **Flow Based Inkjet Reagent System for Cyanide Analysis**

Stuart Chalk[1], David Cacace[1], Heidi Ashbaugh[1], Sara Bledsoe[1], Naomi Kouri[1]; [1]University of North Florida

A small reverse flow injection analysis (FIA) system has been developed for remote monitoring applications. The traditional injection valve has been replaced with two electrically actuated inkjet valves that can deliver 200 - 2000 nL drops directly into a sample flow stream. This paper will discuss the setup and operation of the analysis system, characterizing the inkjet reagent

valves in terms of performance, and describe their application to the analysis of cyanide by the phenolphthalin/copper(II) method. Our experience with the remote operation of the instrument will be discussed in the context of homeland security.

(181) **Flow Analysis of Mixtures of Arsenite, Arsenate, Phosphate and Methylphosphonic Acid Using Vanadomolybdate**

Stuart Chalk[1], Doris Kosova[1], Leah Reed[1]; [1]University of North Florida

The vanadomolybdate reagent has been used extensively in the determination of phosphate with great success. We have applied the same reagent to the analysis of arsenate/arsenite and methylphosphonic acid and have shown that each gives linear calibrations with each of these analytes. In order to apply this reaction chemistry to the real world monitoring of chemical warfare agents an online separation is necessary as the spectra of the reaction products of these analytes with vanadomolybdate overlap. This paper will discuss the application of a small anion exchange column to afford the separation of these analytes prior to detection in a remote system.

(182) **Novel Focused Semi Open Microwave Instrument for Elemental Speciation Studies**

Greg Barlow[1], David Barclay[1], Elaine Hasty[1]; [1]CEM Corporation

Focused microwave technology has taken a lead in microwave instrumentation in the field of synthesis due to its advantages of fine control of power application. This translates into better control of the synthetic reaction process. This paper introduces instrumentation based on focused semi-open microwave technology to extractions for elemental speciation studies. Speciation studies suffer somewhat traditionally from the difficulty of consistently extracting the species from the matrix while preserving its native state and consequently methodology for sample preparation varies widely. Novel focused, semi-open microwave instrumentation is presented with an inbuilt optimization wizard allowing the same sample to be automatically run through an optimization series of parameter changes which can quickly identify the maximal extraction of elemental species. This paper will outline the incorporation of automated, focused microwave instrumentation to the semi open extraction of elemental species with inbuilt optimization wizards allowing easy parameter manipulation for method development. In addition, results will be presented demonstrating the use of the equipment for a total content, or mass balance for the element of interest utilizing the instrument for pressurized microwave dissolution.

(183) **A Field-Portable GC with Multi-stage Preconcentration, Dual-Column Separation, and Chemiresistor-Array Detection for VOC Analysis**

Qiongyan Zhong[1], William Steinecker[1], Rebecca Veeneman[1], Edward Zellers[1]; [1]University of Michigan

The goal of this project is to develop a field-portable GC for determination of complex VOC mixtures at concentrations relevant for indoor air quality (IAQ) investigations. The key features of the instrument are a miniature multi-stage adsorbent preconcentrator/focuser (PCF), series-coupled capillary columns with pressure- and temperature-tunable retention, and a detector consisting of an integrated array of chemiresistor (CR) sensors that use Au-thiolate monolayer-protected nanoparticle (MPN) interface layers whose collective responses provide crude spectra of eluting vapors. Scrubbed ambient is used as carrier gas. The current instrument is a second-generation prototype. Advancements over the first-generation prototype include aspects of hardware (e.g., a new sensor technology), fluidic layout (reduced dead volume), and software control (Labview implementation). The instrument has been characterized with respect to the performance of individual components, flow rate and sensor temperature effect on system sensitivity and limits of detection (LOD), sensor response patterns, and trade-offs associated with split-flow PCF injection. Different applications of the instrument are being explored, including the rapid determination of the environmental tobacco smoke (ETS) markers, 2,5-dimethylfuran (2,5-DMF) and 3-vinylpyridine (3-EP). For this application, a front-end adsorbent trap is added to remove semi-volatiles from the sample stream and conditions were established to quantitatively capture the markers and to separate them from the 34 most prominent co-contaminants present in ETS. A sample volume of 1 L is sufficient to achieve LODs of 0.58 and 0.08 ppb for DMF and 3-EP, respectively, which are below concentrations of these markers reported in typical smoking-permit environments. A complete analysis can be performed every 13 minutes.

(184) **Instrument Gain for a 24ml Ozone-Nitric Oxide Reaction Cell**

Ronald Whiddon[1], Igor Gornushkin[1], Benjamin Smith[1], Nicoló Omenetto[1], James D. Winefordner[1]; [1]University of Florida

The kinetic foundations of the chemiluminescence ozone-nitric oxide (O3, NO) reaction involve four important reactions: 1. NO and O3 yielding ground state nitrous oxide (NO2); k1, 2. NO and O3 yielding electronically excited NO2 (NO2*); k2, 3. radiative relaxation of (NO2)* ;k3, 4. collisional quenching of (NO2)*; k4. When considering the reaction in a flowing system, two additional terms are necessary: the instrument gain factor (G) and the reaction efficiency factor (1-e(-tcell/tNO)). The emission for a given cell can be determined by the formula: I=G*fNO*(k2/(k1+k2))*(k3/k4[M])*(1-e(-tcell/tNO)) For a 24ml cell at 1 Torr, 10 ppm NO, and 2300 ppm O3; the instrument gain was determined to be in the range of 1.2*10-6 to 6.7*10-6. The variation in instrument gain shows a relationship with the NO flow rate.

(185) **Effect of a Temperature Gradient on Retention Time and Efficiency for Solvating Gas Chromatography**

Steven Goates[1], John-David McElderry[1], Marisa Stark; [1]Brigham Young University

The compressibility of mobile phase fluids in techniques such as gas chromatography, supercritical fluid chromatography, and solvating gas chromatography has a marked effect of the flow behavior of the mobile phase through the column. We have used Raman spectroscopy and laser-induced fluorescence to investigate variations in density of the mobile phase and the elution rates of test compounds along the length of packed capillary columns. Our studies of solvating gas chromatography (SGC), a high-speed variant of supercritical fluid chromatography in which a large pressure drop is employed, have suggested that a temperature gradient applied to the length of the column would produce improvements in elution rate, efficiency, and range of compounds that can be separated by this technique. We will present results our investigations of the effect of various temperature gradients on separations by SGC.

(186) **Guanosine Gels for Sequence Dependent DNA Separations in Capillary Electrophoresis**

William Case[1], Keren Glinert[2], Linda McGown[1]; [1]Rensselaer Polytechnic Institute, [2]Princeton University

The separation of DNA using capillary gel electrophoresis (CGE) has become a common practice in fields ranging from forensics to medicine. A myriad of separation matrices have been developed as mobile phases for achieving size-dependent separations of DNA in

CE. These matrices have ranged from viscous permanent gels such as cross-linked polyacrylamide to polymeric solutions whose porous structure is determined by concentration and polymer chain length. While such matrices have been utilized in applications ranging from the sequencing of single-stranded DNA (ssDNA) to the separation of digested double-stranded DNA (dsDNA), their usefulness is confined to separations of DNA fragments with different lengths. The development of a gel matrix that could separate similarly sized DNA fragments exhibiting differences in base sequence would find great use in such fields as forensic human identity typing, microbial genome analysis, and detection of molecular disease. We present here the use of guanosine gels (G-gels) as mobile phases for sequence-dependent separations of both ssDNA oligonucleotides and dsDNA in CE. G-gels are self-assembled, hydrogen-bonded networks of guanine tetrads formed by guanosine nucleotides and their derivatives. Their degree of structural organization can be manipulated through changes in pH, concentration and temperature, thus providing a means of controlling parameters that are crucial in optimizing DNA separations. The separation of similarly sized oligonucleotides using G-gels as mobile phases is compared with separations performed using traditional sieving gel media. Studies of the sequence-dependent interactions between G-gels and DNA sequences using circular dichroism and fluorescence spectroscopic techniques will be discussed.

(187) **Novel label-free method for real-time flow rate monitoring in a capillary based on liquid core optical ring resonators**

Hongying Zhu[1], Ian M. White[1], Jonathan Suter[1], Hesam Oveys[1], Xudong Fan[1]; [1]Biological Engineering Dept, Univ. of Missouri

Flow-rate is important to the mixing of reagents in a microchannel, which is a critical step in realizing lab-on-a-chip analysis systems. Precisely measuring the flow-rate in a microchannel is critical for the implementation of lab-on-a-chip devices. We have developed a label-free method based on the liquid-core optical ring resonator (LCORR) sensing architecture to monitor the flow-rate in real time with high precision. The LCORR is formed by the circular wall of a quartz capillary with an outer diameter of 50-100 ìm and wall thickness of 3-5 ìm. The light circulates around the LCORR cross-section in the form of the whispering-gallery modes (WGMs). The WGM has an evanescent field extending into the capillary core and responds to the refractive index change in the core due to the conduction of analytes through the capillary. Despite the small diameter of the LCORR, the effective interaction length can be a few tens of centimeters, leading to a sensitivity of 16nm/RIU (refractive index units) and detection limit better than 10-5 RIU. Using refractive index detection enables us to perform in-situ real-time process monitoring without fluorescent labels, thus eliminating the need for the laborious labeling process and sophisticated measurement equipment. In our experiment, to detect the flow-rate in the capillary, two optical tapers 5 mm apart are brought in contact with the LCORR to launch the WGMs. These tapers also define the detection location along the LCORR. An ethanol/water solution is passed through the LCORR after a measurement baseline is established with water. When the flow front of the ethanol reaches each fiber taper, causing the refractive index change, an abrupt WGM shift is observed. Average flow rate can be calculated precisely from the time delay between the WGM shift at the two locations. Assuming 10 ìm inaccuracy in taper distance measurement, our system can measure a flow-rate with precision of 0.2%. The maximum detectable speed is 2.5 cm/s, limited by the computer data acquisition speed (5Hz) and the distance between the tapers. This demonstration verifies that the LCORR system can be utilized for flow rate measurements in microchannels. The technique can be applied to pressure- or electro-osmosis-driven systems.

(188) **Separation of Uranyl Species by Capillary Electrophoresis**

Greg Klunder[1], Julie Herberg[1]; [1]LLNL

Understanding uranium speciation in solids and solutions is important for environmental, toxicological, and radiological purposes. Uranium solution chemistry is notoriously complex due to the number of different species that are formed and the sensitivity to pH. Capillary electrophoresis (CE) is a simple rapid separation method that can be used to identify species in solution. The most common method of detection for metal species by CE is to use complexing agents and background electrolytes for indirect UV absorbance detection. However, this can drastically perturb the original distribution of species in the sample. Alternatively, time resolved fluorescence of uranyl species has been used to monitor species in solution. Nuclear magnetic resonance (NMR) has also been used to directly identify uranyl species that are coordinated with F, P, or C in aqueous solutions. Previous investigators have demonstrated coupling NMR to CE using small hand-wound coils around the capillary. LLNL is developing patterned microfabricated coils directly on the capillary that should provide adequate resolution to identify uranyl species. We are developing separation protocols to determine the speciation of uranyl complexes in solutions with minimal perturbation to the original sample equilibrium. Initially, we have demonstrated separation capabilities with UV absorption using a background electrolyte. Thermodynamic models have been employed to predict species concentrations under varying experimental conditions. These models are being used to determine the distribution profile for different CE operating conditions. The goal is to develop on-line NMR measurements for uranyl separations. Experimental results and detection capabilities will be presented.

(189) **De-Noising and Baseline Drifting Correction of Electropherograms on Real-Time Bases**

Alejandro Solis[1], Matthew Rex[1], Andres Campiglia[1], Pedro Sojo[2]; [1]Dept. of Chemistry, University of Central Florida, [2]Fac. de Ciens., Univ. Cent. de Venezuela

A new signal processing method is presented here with the purpose to correct baseline noise in Capillary Electrophoresis (CE). High frequency noise filtering and baseline drifting correction is achieved with a novel algorithm specifically developed to processing highly noise signals on real-time bases. Noise and baseline drifting correction of experimental and simulated (theoretical) data is performed by applying “accelerated” multiple-pass moving averages with small size windows and time delays. We present improvements close to two at various levels of signal-to-noise.

(190) **Cavity Ring-Down Spectroscopy Coupled to Liquid Chromatography: Extension to Tunable Sources and UV Wavelengths**

Freek Ariese[1], Lineke van der Sneppen[1], Arjan E. Wiskerke[1], Cees Gooijer[1], Wim Ubachs[1]; [1]Laser Centre Vrije Univ. Amsterdam, Netherlands

In earlier studies, it was demonstrated that the sensitivity of absorbance detection in liquid chromatography (LC) can be improved significantly by using cavity ring-down spectroscopy (CRDS). Thus far the CRDS experiments were performed using visible laser light at fixed standard wavelengths, such as 532 nm. However, since by far most compounds of analytical interest absorb in the UV, it would be important to develop UV-CRDS. In this study, as a first step towards the deep-UV region, LC

separations with CRDS detection (using a previously described liquid-only cavity flow cell) at 457 and 355 nm are reported for standard mixtures of dyes and nitro-polyaromatic hydrocarbons (nitro-PAHs), respectively. For the measurements in the blue range we used a home-built optical parametric oscillator (OPO) system, tunable between 425 and 478 nm. With this system we achieved a baseline noise corresponding to 2.7 x 10-6 A.U. at 457 nm, a major improvement in sensitivity in comparison with conventional absorbance detection (typically around 10-4 A.U.). A somewhat more modest improvement in sensitivity (baseline noise 1.3 x 10-5 A.U.) was also achieved at 355 nm. A limiting factor is the quality of the UV-CRDS mirrors that are currently available: whereas the ring-down times as obtained at 457 nm are 70 - 80 ns for the blank eluent, at 355 nm they are only 20 - 25 ns. Critical laser characteristics for LC-CRDS measurements, such as pulse length and mode structure, are given and prospects for moving to shorter wavelengths are discussed.

(191) **Separation of Gold Nanorods with Capillary Electrophoresis to Achieve Better Limits of Detection for Mercury in Water**

Matthew Rex[1], Florencio Hernandez[1], Andres Campiglia[1]; [1]University of Central Florida

Gold nanorods have been shown in the past to detect ultralow levels of mercury in water (6.6 x 10-13 g L-1). This was achieved by monitoring the absorption spectral shift in the plasmon resonance band when mercury amalgamates with gold1. The ultimate goal in the synthesis of nanorods is to obtain a population of nanoparticles with a single aspect ratio. Unfortunately, most synthetic approaches provide nanorod populations with mixed aspect ratio sizes. The work presented here provides methodology to separating nanorods according to aspect ratios. The methodology is based on Capillary Electrophoresis. The advantage of using narrower size distributions is demonstrated for the analysis of mercury in water samples. Rex, M.; Hernandez, F.E.; Campgilia, A. Anal. Chem. 2006, 78, 445-451

(192) **Simultaneous Estimation of Glimepiride and Pioglitazone in Bulk and in Pharmaceutical Formulation by HPLC and HPTLC Methods.**

Bhavesh Shah

This paper describes a validated Reversed Phase HPLC and HPTLC methods for simultaneous estimation of Glimepiride and Pioglitazone in bulk and in tablet formulations. In RP-HPLC method separation was achieved on Phenomenex C18 column (250mm x 4.6mm i.d., 5µm), using 0.01M 6.75pH phosphate buffer: Methanol (30:70 v/v, pH 6.75) as the mobile phase at a flow rate of 1.0 ml min-1 at ambient temperature. In HPTLC method separation was achieved on aluminum sheet of silica gel 60F254 using Toluene: Ethyl acetate: Methanol (50:45:05 v/v/v) as mobile phase. Quantification was achieved with UV detection at 230nm over concentration range of 100-1000 ng ml-1and 750-7500 ng ml-1with mean recovery of 99.35±1.2 and 99.08±0.935 for glimepiride and pioglitazone respectively in HPLC method. Quantification was achieved with UV detection at 230nm over concentration range of 200-700 ng/spot and 1500-5250 ng/spot with mean recovery of 98.40±0.675 and 98.75±1.140 for glimepiride and pioglitazone respectively in HPTLC method. These methods are simple, precise and sensitive and applicable for the simultaneous determination of glimepiride and pioglitazone in bulk and in tablets. Key words: Glimepiride, Pioglitazone, developed & validated methods, simultaneous, RP-HPLC and HPTLC methods.

(193) **Assessment of Anabolic Compounds**

Nisar Ahmed; [1]Kuwait Institute scie. Research

The main objective was Optimization of a multiresidue method, for assessing the levels of anabolic compounds in Kuwait meat industry. At present there is no control on the residues of anabolic agents in meat products. The present study was carried out for the detection of hormones at levels of 1mg/kg as proposed by van Ginkle (employing enzymatic digestion, immunoaffinity clean up after defating and detection by gas - chromatography- mass spectrometry, selected ion monitoring) was optimized for multiresidue analysis of large number of samples in shortest time. Six Steroids compounds were investigated. None of the 262 samples analyzed contained detectable levels of anabolic agents.

(197) **System for Studying Enzyme Kinetics in a Levitated Drop Reactor**

Alexander Scheeline[1], Christopher Field[1], Zakiah Robinson[1], Haylee Trout[1], [1]University of Illinois at Urbana-Champaign

Microfluidics are essential for studying kinetics of all but the most abundant enzymes. To ensure that concentrations are not reduced by adsorption onto flow system or reactor walls, flow system surfaces can be coated with polyethylene glycol or an innocuous protein such as bovine serum albumin. However, when these passivating species are themselves reactive toward substrates, products, or reaction intermediates, it becomes difficult to use a microfluidic system to study reaction mechanisms. Additionally, if gases are reactants or products, transport of such species in quartz or polymer microfluidic systems is either difficult or complicated. We have been developing an alternative approach: use of a microliter-scale, ultrasonically-levitated, and mixed drop reactor. Developments include quantitative understanding of levitator engineering parameters, design and characterization of optical diagnostics, and assembly of capillary-based fluid transport into and out of the drop. We report our initial kinetics experiments, using common enzymes as examples.

(198) **Fabrication and Characterization of a Superoxide Sensor for In Vivo and In Situ Studies**

Alexander Scheeline[1], Rebekah Wilson; [1]University of Illinois at Urbana-Champaign

Amperometric sensors for reactive oxygen species (ROS) are in common use in laboratory settings. We are developing two such sensors for use in vivo and in experiments where spatial resolution of ROS is critical to problem solving. Both sensors are assembled using gold films on Kapton &reg:. One style of sensor employs a three electrode setup, with Ir/IrOx, pseudo-reference electrode, polypyrrole counter electrode and superoxide dismutase (SOD) or peroxidases on the working electrode (with the enzyme anchored to the substrate via a thiol linker). The other style is a two electrode setup where both sensors are coated with SOD via a thiol linker. While initially targeted at studying oxidative stress in the inner ear of gerbils during exposure to intense sound, the same geometry will be used for studies of redox species in ultrasonic-levitated microliter drops and in sessile drops on photo-oxidation catalysts. We report sensitivity, repeatability, and interference studies where both sensors are 200 ƒÝm wide, 600 ƒÝm long sensor heads on ~ 2 cm substrates, and discuss the progress towards understanding the small spatial scale processes for which the sensors were designed.

(199) **Bis(carbocyanine) Near-Infrared Dyes as an Analytical Tool**

Gabor Patonay[1], Jun Seok Kim[1], Maged Henary[1], Lucjan Strekowski[1]; [1]Georgia State University

Fluorescent spectroscopy in the near-infrared (NIR) spectral range has proved to be a valuable tool in analytical chemistry. The

literature has a large number of publications reporting analytical use of NIR dyes including the rapidly increasing bioanalytical use of NIR labels. The application of NIR dyes is advantageous due to their high molar absorptivities and the relatively low background interference of the long wavelength spectral region. The use of semiconductor lasers further strengthens the analytical utility. New NIR bis(carbocyanine) chromophores synthesized in our laboratory make possible the more efficient use of NIR fluorophores. These dyes form intramolecular H-aggregates in polar solvents, even at very low concentrations. Spectral properties and the folding constant of the dimeric form greatly depend on the heterocyclic moieties and the length or flexibility of the connecting chain. The intramolecular dimeric form of the dye can be described as a clamshell complex with two interacting hydrophobic carbocyanine moieties. In this intramolecular H-aggregate, the chromophore has a low extinction coefficient and low fluorescence quantum yield. Upon addition of analytes or biomolecules the H- and D-bands are decreased and the monomeric band is increased, with concomitant increase in fluorescence intensity, suggesting that clamshell H-aggregates open up. One of the main advantages of this bis(carbocyanine) dye is that the free dye (i.e., not complexed to an analyte) has negligible fluorescence. Hence, the excess dye does not contribute to the NIR fluorescence signal. The studies presented here give representative examples of the wide variety of analytical, bioanalytical, and clinical applications of these new NIR bis(carbocyanine) probes. These dyes can be utilized as microenvironmental probes to map hydrophobic regions of large biomolecules or as simple non-covalent labels. Examples will be given for different analytical applications. These dyes can be used as effective non-covalent labels in complex CE separations of biomolecules, or just simply as reporters for the presence of biological materials including whole cells on solid surfaces or in solutions. For example, these are suitable for visualizing latent fingerprints or bacterial contamination on surfaces with virtually no interference from the background.

(200) **Application of Bipolar Semiconductor Microchip System to DNA Chip**

Joon Myong Song[1], Min-Sung Yang[2], Ho Taik Kwan[2]; [1]College of Pharmacy, Seoul National University, [2]Celltek Co. Ltd, Ansan-si, South Korea

An integrated circuit photodiode array (PDA) chip system has been applied to a DNA chip. The PDA chip system, constructed using a conventional bipolar semiconductor technology, can act as a solid transducer surface as well as a two-dimensional photodetector. A layer of silicon nitride on photodiodes gives extra protection to the PDA surface against damages that may occur during the on-chip bioassay. The DNA hybridization was performed directly on the PDA chip. The target DNA, the Bacillus subtilis sspE gene, was amplified by a polymerase chain reaction (PCR). The 340 bp PCR products were labeled using dioxigenin (DIG). Silicon nitride layer on the photodiode was treated with poly-l-lysine to immobilize probe DNA on the surface of the photodiode detection elements. Anti-DIG-alkaline phosphatase conjugate was reacted with hybridized DIG-labeled DNA. A coloring reaction was performed based on the enzymatic reaction between an NBT/BCIP staining solution and a DNA complex containing antibodies, and blue-stained precipitates were formed on the surface of the photodiode detection elements. Successful quantitative analysis of hybridized PCR products can be achieved from the light absorption properties of the blue-stained enzymatic reaction products that are produced after a series of reaction processes. The bipolar microchip system is appropriate for a high performance analog process with a low noise level. Our DNA chip system avoids the complicated optical alignments and light-collecting optical components that are usually required for an optical DNA chip device. As a result, a compact, simple, portable, and low-cost DNA chip is accomplished. This system demonstrates great potential as an alternative system to a conventional DNA reader.

(201) **Synchrotron Infrared Microspectroscopy Determines Secondary Protein Structure of Wheat Endosperm in situ Relative to Protein Quality**

David Wetzel[1], Tiffany Fisher[1], Virgil Smail[1], Hicran Koc[1], Emily Bonwell[1]; [1]Kansas State University

Mapping of cross sections of wheat endosperm in frozen sections allows accumulation of data for a number of pixels. Many of these pixels are filled with spectra of large starch granules and in those the starch spectrum predominates. What is observed for a few pixels is primarily interstitial, the spectrum of the protein in interstitial areas between the numerous large starch granules. From a map of 90-120 pixels, spectral differences permit sorting out the pixels that are predominantly protein from those that are predominantly starch. Although spectral interference is not an issue, the very serious scattering produced by the starch granules is detrimental to obtaining good signal-to-noise ratio for the spectrum of the protein that is being analyzed. With single image plane masking, a pin-hole mask is used that allows illumination of a 5.5 µm spot and with duel-pass single mask operation a 7 µm x 7 µm image is used. The alpha helix to beta sheet ratio of secondary protein structure is used as a way of assessing the hardness characteristic of hard winter wheats grown in Kansas. With information about the secondary protein structure, Kansas Agricultural Experiment Station wheat breeders can use this information in selection of breeding lines to carry forward in the process of producing a particular wheat with the desirable end-use characteristics (in this case, breadmaking).

(202) **Imaging of Tissue Phantoms Constructed of Biological Fluorophores Embedded in Mesoporous Particles.**

Yulia Skvortsova[1], Maxwell Geng[1]; [1]The University of Iowa

Rapidly increasing population of cancer patients demands the development of noninvasive real time detection of pre-cancerous formations in human tissues. Extensive research and clinical studies have shown the capability of fluorescence spectroscopy to provide highly sensitive, specific and minimally invasive diagnosis of cancers. Due to the patient-to-patient differences and complexity of the biochemical environment spectral characteristics of cancerous tissues vary significantly. The use of tissue phantoms with controlled boundaries of optical features can assist in the development of optical biopsy methods. This approach allows the overcoming of environmental as well as patient-to-patient variations. In this study the construction and imaging of the solid tissue phantoms are discussed. The phantoms are composed of endogenous tissue fluorophores, reduced nicotinamide adenine dinucleotide (NADH) and flavin adenine dinucleotide (FAD), enclosed in C18 silica beads. To simulate a real tissue matrix the beads are embedded in 1% agar gel. Highly uniform in shape 10-ƒÝm-diameter silica beads serve as perfect imaging objects when soaked in FAD or NADH solution, providing the features of known dimensions and shapes. Straightforward preparation procedure and non-toxicity of the materials allow fast and easy production of the samples in standard laboratory setting. The use of spherical beads as vesicles for the tissue chromophores allows the simulation of the sample inhomogeneities and localization of the areas with different composition of the fluorophores, which corresponds to different clinical conditions of the tissue. Constructed phantoms were imaged with confocal fluorescence microscopy with 454 nm laser excitation. Phantoms are used as a model for the analysis of the

effects of tissue optical properties, sample composition and structure, and the optical geometry of diagnostic imaging.

(203) **Probing Folding Pathways: Apomyoglobin Folding at High Salt Conditions**

Yi Gao[1], Lei Geng[1]; [1]The University of Iowa

Apomyoglobin has been studied for years for its folding and unfolding properties. This protein has all-helical structure and adopts several intermediates at different unfolding conditions. It has been found that addition of sodium chloride into acid-unfolded apomyoglobin induces the formation of a compact intermediate which has comparable topology of the AGH hydrophobic core to the native structure and acid-induced intermediate. In our research we use correlation analysis to reveal the folding process of apomyoglobin at high salt condition and compare the folding trajectory with its low-salt acid-induced folding pathway. 8-anilino-1-naphthalenesulfonate (ANS) is chosen as the fluorescence probe to report the hydrophobicity of probe binding site in the apomyoglobin because of its microenvironment-sensitive emission maximum. Correlation curve is obtained between the hydrophobicity of the probe-binding site as disclosed by ANS fluorescence and the folding extent of apomyoglobin as indicated by tryptophan fluorescence. The correlation trajectory of salt induced folding suggests a different folding pathway from low-salt acid-unfolding pathway.

(204) **Ratiometric Fluorescence Imaging of Water Transport in Subcellular Organelles of Live Cells Using D2O as A Contrast Agent**

Adriana Chaurra[1], Kenneth Christensen[1]; [1]Clemson University

Water transport across cell membranes has been measured using a wide array of morphological and spectroscopic techniques. Unfortunately, most of these methods provide only an indirect measurement of water transport. We identified Lucifer yellow as having a two-fold intensity increase in D2O while Alexa fluor 546 showed virtually no intensity change in D2O. Together these dyes are a quantitative ratiometric sensor of D2O that is independent of pH (4-7) and physiological ionic strength and can be easily localized to endosomal compartments when covalently coupled to high molecular weight dextrans. In addition, commonly available filters and beamsplitters are used to make ratiometric measurements with this dye-pair. We have used these probes to quantitatively measure water transport across subcellular organelle membranes using D2O as a contrast agent. Pinosomes, phagosomes, and lysosomes were labeled with a 1:1 molar ratio of Lucifer Yellow dextran (10,000 MW) and Alexa 546 dextran (10,000 MW). Using alternating rapid perfusion of H2O and D2O based buffers; we have directly determined the membrane permeability of these subcellular organelles. These measurements provide new insight and tools to quantitatively study water transport in these organelles.

(205) **Monitoring Conformational Rearrangements in Bacillus Anthracis Protective Antigen Using FRET Microscopy**

Kenneth Christensen[1], Nathaniel Smith[1], Thomas Caldwell[1]; [1]Clemson University

The binary anthrax toxin is a major virulence factor during infection with Bacillus anthracis. Intoxication proceeds initially through the high affinity interaction of monomeric protective antigen (PA) and cell-surface expressed anthrax toxin receptors tumor endothelial factor protein 8 (TEM8) and capillary morphogenesis gene protein 2 (CMG2). Following binding to either receptor, PA is cleaved by an endogenous furin protease which allows self-association to a heptameric ring-shaped prepore structure. Oligomeric PA is capable of binding the toxin A-moieties, lethal factor and edema factor, to form non-covalent toxic complexes on the cell surface. These complexes enter the cell via endocytosis. During endosomal acidification through normal host processes, PA prepore undergoes a conformational rearrangement to form a *f*Ò-barrel conduit (PA pore) which allows translocation of the toxin A-moieties and ultimately cell death. In the absence of structural data about the conformational rearrangement in the domains of PA during the prepore-to-pore transition, we have used fluorescence resonance energy transfer (FRET) microscopy of living cells to estimate relative changes in inter-domain distances between the prepore and pore conformations. Four single cysteine PA mutants (one in each domain) were constructed using site-directed mutagenesis and each mutant was labeled with the acceptor (Alexa fluor 546) or donor (Alexa fluor 488) fluorophores. Mixtures of labeled PA mutant pairs (e.g. a 1:1 mixture of domain 2 and domain 3 mutants) were oligomerized in vitro. The resulting heptamer was bound to CHO ATR-1 cells which overexpress TEM8. FRET efficiency was measured for both membrane-bound (prepore) and endosomal (pore) PA to estimate relative inter-domain distance changes between the prepore and pore state. Our observed changes in FRET efficiency shifts showed a pronounced increase in energy transfer between domains 3 and 4 indicating a structural contraction. In contrast, the FRET efficiency increased only slightly between domains 2 and 3 indicating little positional change between the two conformations. These data were compared to a proposed model and show significant differences. Together these measurements form the basis for construction of a new low-resolution structural model based on FRET imaging of live cells.

(206) **Comparison of Fluorescent Probes and Probe Technologies for Visualizing mRNAs in Brain Tissue**

Linda Nieman[1], Rachel Rohde[1], John Guzowski[2], Jerilyn Timlin[1]; [1]Sandia National Labs, [2]University of California, Irvine

The recent popularity of multispectral and hyperspectral microscopes have challenged the current fluorescent probe technology. It is now possible to resolve fluorescent emission spectra with high degrees of spectral overlap, permitting the biologist to use combinations of labels previously impractical and prompting the development of additional labels for biological microscopy. In addition, the potential for increased sensitivity of these spectral imaging instruments when coupled with advanced multivariate analysis is amenable to using lower concentrations of fluorescent dyes and following weaker signals. Using a line-scanning hyperspectral fluorescence imaging system and multivariate curve resolution algorithms, we will explore combinations of several fluorescent dyes and quantum dots for visualizing mRNAs in brain tissue and assess their suitability for use in future, highly multiplexed experiments based on spectral shape, emission intensity, and specificity. mRNAs are typically located by a hybridization reaction with ahapten-labeled (e.g., biotin, digoxigenin, etc.) complimentary RNA sequence. Following hybridization the signal is detected using tyramide signal amplification route, which deposits many fluorophores at the site of the probe. Without this amplification, direct detection of fluorophore labeled probes (especially for low abundance mRNAs) is often below the detection limits of traditional confocal microscopes. We will present results from hyperspectral imaging experiments on tissue labeled with and without the amplification step. The results of this study show the potential for hyperspectral imaging with multivariate analysis to extend the capabilities of biological microscopy for visualizing gene expression in tissue and cells both by increasing the degree of multiplexing and lowering the detection limit.

(207) **PCR-Free Nucleic Acid-Based Biosensing Using Magnetic Microparticle Carriers with a Fluorescent Polymer Hybridization Transducer**

Denis Boudreau[1], Sebastien Dubus[1], Boris Le Drogoff[2], Jean-François Gravel[1], Benoît Voisin[1], Teodor Veres[2]; [1]Dept. Chemistry and COPL, Laval University, [2]Industrial Materials institute, NRC

Novel DNA-based biosensor technologies for rapid, sensitive and affordable identification of genetic material hold great potential for various applications, such as identification of viral epidemic at points-of-entry into a country and early detection of biological germ warfare agents. Furthermore, great interest exists for fast and sensitive diagnostic screening tests usable directly in the field by staff with no laboratory training, since critical situations such as those listed above require near-instantaneous answers, which invalidates complex sample preparation procedures, including most PCR techniques. We report herein the latest results from the development of an approach based on the rapid and selective capture and pre-concentration of target nucleic acids by probe-functionalized magnetic microbeads followed by real-time optical detection using a cationic biochromic polymer acting as transducer of the probe-target hybridization event[1]. In this approach, the microbeads are used both as probe carriers and optical transducers, so that both target preconcentration and detection can be performed on the same support. Classic and confocal fluorescence microscopy were used to measure the fluorescence signal from analytes captured onto microbeads of varying diameter and surface chemistry suspended in homogeneous media and collected onto solid substrates by miniature electromagnetic traps. Ultimately, this detection approach will be implemented onto a microfluidics platform where all analysis steps (i.e. extraction, purification, identification and detection of the target DNA sequence) will be performed. This novel and simple technology should therefore enable on-site, rapid detection and identification of harmful pathogens and potential bioweapons for first responders and public health providers. 1. Dubus, S.; Gravel, J.-F.; Le Drogoff, B.; Nobert, P.; Veres, T.; Boudreau, D., Anal. Chem. (2006), 78, 4457-4464.

(208) **Gene Expression for Pro-Inflammatory Proteins Following the Deposition of Particles onto A549 Cell Culture**

George Agnes[1], Danielle Balik[1], Allen Haddrell[1], Stephan van Eeden[2]; [1]Simon Fraser University, [2]James Hogg iCAPTURE Centre

Inhalation of particles in the less than 10 micrometer diameter range that are suspended in the troposphere (PM10) results in local to systemic inflammation, and this is being shown to be relevant to the pathogenesis of respiratory and cardiovascular diseases. What is not characterized is how the chemical composition of ambient particles initiate varied biological responses. To address this we have developed a methodology to deposit particles of known composition onto lung cell cultures in vitro. In previous publications, we have suggested that endotoxin, lipopolysaccharide from gram negative bacterial cell membranes, and carbon act synergistically to initiate an inflammatory response. In our studies, the downstream biological response of the cultured lung cells has been measured using immunocytochemistry assays for a single protein only, intercellular adhesion molecule 1 (ICAM-1). ICAM-1 is a membrane protein expressed in response to tissue injury, and its expression is involved in an organism's inflammatory response. To complement on the previous measurements, we are now using quantitative real-time reverse transcription polymerase chain reaction (RT-PCR) to monitor the expression levels of multiple other proteins, such as tumor necrosis factor alpha (TNF-á) and interleukin 1 beta (IL-1â), that are involved in the initial cellular response following incubation with varied particle types. Currently, we are able to deposit less than 100 particles on a lung cell culture in vitro and observe changes in mRNA levels of specific proteins within the cell population.

(209) **Rapid Small Volume Analysis of Serum Myoglobin via Modulated Supraparticle Fluoroimmunoassays.**

Matthew Petkus[1], Mark Hayes[1], Antonio Garcia[1]; [1]Arizona State University

A new method using micro liter serum samples for the rapid diagnosis of acute myocardial infarction (AMI) has been developed utilizing solid phase fluoroimmunoassays magnetically modulated via paramagnetic particle structures. This new method involves the performance of a modulated competitive assay for initial diagnosis of AMI and a modulated sandwich assay for the monitoring of cardiac myoglobin released after hospital admission. Using a cut-off value of 5.0 nM (85 ng/ml) for AMI induced myoglobin, the modulated competitive assay was able to diagnose AMI-like conditions using serum doped with myoglobin after an incubation time of only 10 min. The standard curve developed for the modulated sandwich assay was linear from a range of 0-1nM (17 ng/ml) with a lower limit of detection at 50 pM (0.85ng/ml). Both assays required only 15 ìL of serum per analysis and were superior when compared to static aggregate methods, where particle structures were collected and analyzed for fluorescence intensity without particle modulation.

(210) **Fiber Optic Surface Plasmon Resonance Biosensors for Clinical Monitoring of Acute Myocardial Infraction Biomarker**

Michael R Malone, Karl Booksh; [1]Arizona State University

Fiber optic surface plasmon resonance (SPR) biosensors allow for the rapid detection and quantification of sub-ng/mL levels of molecular biomarkers. Cardiac troponin I (cTnI) is one of the clinically used biomarkers for acute myocardial infarctions. The concentration of cTnI will rise from basal concentrations to a range of a few ng/mL up to 30ng/mL after an infarction. Clinically, cTnI levels are batched sampled over a 12hr time course and the samples are analyzed in hospital labs with instrumentation using fluorescent or chemoluminescent immunoassay methodologies. A cross correlation study between fiber optic SPR biosensors and a clinical chemoluminescent based instrument was performed at a Phoenix area hospital. The SPR biosensors were calibrated by spiking human serum with relevant levels of recombinant cTnI.

(211) **Sacks-cess in Science: an Optical Elution**

Alexander Scheeline[1]; [1]University of Illinois at Urbana-Champaign

Richard Sacks ran the gamut from pioneer, to inspiration, to colleague, to friend, to prankster, and, at times most gratifyingly, to audience. He had more energy than his imploding thin films or exploding Z-pinches, and had the courage to adapt his technology to high speed gas chromatography when the funding gnomes refused to back his elemental ingenuity. This talk draws parallels between the author\'s career in and out of atomic spectroscopy and that of Prof. Sacks. After a quick refresher on very high current, very high voltage discharges, the path through chaos, complexity, and oscillating reactions to studies of oxidative stress is traversed. We end up doing opto-mechanical design with spatio-temporal resolution for the purpose of studying the redox chemistry of myeloperoxidase and (eventually) organelles.

(212) **Following in Grandfather's Footsteps: Research in High Speed Gas Chromatography Performed by Atomic Spectroscopists**

Frank Dorman[1], Richard Sacks[2], Rebecca Wittrig[1], Christopher English[1], Tincutta Veriotti[2]; [1]Restek Corporation, [2]University of Michigan

Gas chromatography has been referred to as a mature science for many years. What this has led to is a decline in fundamental research in improving separations, as most researchers view the gas chromatograph as a tool to be used, not improved. Ultimately most research chromatographers investigate method-based projects, not instrumental, and as a result gas chromatographic instrumentation has remained virtually unchanged for 25 years. This presentation will focus on instrumental developments resulting from the collaboration between many multidisciplinary scientists focusing on improving separation and analysis times. Specifically, stop-flow GC as both a stand-alone technique, as well as coupled to silicon-wafer based GC columns will be discussed. These techniques can improve the separation, and speed, as well as decrease the size and power consumption of gas chromatographic instruments, and offer the analytical chemist a number of options for chemical analysis which are not possible with existing instrumentation. Several examples will be shown to demonstrate the benefit of using these techniques relative to conventional GC systems.

(213) **Taming the Pulsed Plasma: Lessons Learned From a Fearless Mentor**

Joel Goldberg; University of Vermont

When even a small amount of current strays from a parent discharge, even at a high potential, the dangers associated with a short to ground are considerable. We report here on the the path taken by one such stray, landing in Vermont after ejection from the high-energy environment of Richard Sacks' laboratory in Michigan. The path taken from imploding high-energy plasmas to magnetically-modified laser plasmas to an inductively-coupled imploding plasma will be described and traced to the training, inspiration and guidance of Richard Sacks.

(214) **Sacks Lab Chemistry at the Engineering Interface: Gas Chromatography for the WIMS and MACE Projects**

Megan McGuigan[1,2], Richard Sacks[1], Cory Fix[1], Gordon Lambertus[1], Mark Libardoni[1,2], Amy Payeur[1], Peter Stevens[1], Shaelah Reidy[1]; [1]University of Michigan, [2]LECO Corporation

Professor Richard Sacks was an outstanding research mentor who gave his students every opportunity to take classical analytical chemistry techniques and apply them to the most complicated applications. Recent collaborations have provided for exciting projects including the miniaturization and micro-fabrication of GC systems for future terrestrial and space-based applications. Prof. Sacks' excitement for research continues today in his laboratory at the University of Michigan. This presentation will focus on the work being done by the recent and current Sacks lab group members. The development of low-resource GC and GCxGC systems will be discussed. In addition, applications studies on complex samples such as meteorites and tholins will be shown.

(215) **Richard Sacks and the Path to a Micro-GC**

Ted Zellers, Kensall Wise, Gordon Lambertus, Shaelah Reidy, Massoud Agah[4], Joseph Potkay, Qiongyan Zhong, Chia-Jung Lu[2], Joshua Whiting[3], Hanseup Kim; [1]University of Michigan, [2]Fu Jen Catholic University, Taiwan, [3]Sandia National Laboratories, [4]Virginia Polytechnic University

About 10 years ago, I had the good fortune to start a collaboration with Richard Sacks that would lead eventually to the first gas chromatographic analyses achieved with entirely microfabricated components (including the pump!). Along the way we have pushed, pulled, split, bled, tuned, programmed, accelerated, shrunk, shrunk some more, and wound our way to better, smaller, and faster separations, all due to his ingenuity and inspiration. This talk will highlight Richard's leadership in developing portable, and more recently, micro-scale GC separation systems from the perspectives of several of his colleagues and students.

(216) **Short Reflections by Friends and Colleagues**

David M. Coleman; Wayne State University

Friends and colleagues of the late Richard D. Sacks will have an opportunity at this point for brief commentary and reflections. Included will be Prof. David Coleman (Wayne State University), Prof. Steve Brewer (Eastern Michigan University, Retired), Mike Morris (University of Michigan), and others.

(217) **Single Fiber Dye Analysis by Liquid Chromatography Mass Spectrometry (LC-MS) with SWGMAT Dye Extraction Protocol.**

Derek Dorrien[1], Michael E. Sigman[1]; [1]University of Central Florida

The dye from a single fiber can be extracted following the SWGMAT protocol and then subsequently analyzed by liquid chromatography mass spectrometry (LC-MS) with an electrospray interface in series with a single wavelength UV/VIS absorbance detector, monitoring at a wavelength previously determined by microspectrophotometry. Textile fibers are encountered frequently in forensic casework and comparison of questioned and known fibers occurs regularly. A single fiber represents the smallest evidentiary unit for which robust analytical methods must be available. There are several non-destructive techniques (e.g. polarized light microscopy, fluorescence microscopy and microspectrophotmetry) which are currently employed to discriminate between questioned and known single fibers. When these methods fail to discriminate, alternative techniques such as dye extraction, UV/VIS spectroscopy and LC-MS offer a different, yet destructive approach. LC-MS offers advantages over other separation techniques such as thin layer chromatography (TLC) because LC-MS will not only provide separation, but also mass fragmentation unique to the dye. An LC-MS can also be coupled in series with a UV/VIS detector to aid in the detection of conjugated compounds. Previous work has shown that fiber dyes can be extracted using methanol as a solvent and then analyzed by LC-MS (1); however, methanol extraction does not offer the dye classification information afforded by the SWGMAT protocols. Fiber samples previously analyzed by methanol extraction (1) were reanalyzed following the SWGMAT dye extraction protocol. All separations were performed on a C18 reverse phase column and the instrumentation used was an Agilent 1100 Series LC-MS with an electrospray ionization source and a variable wavelength UV/Visible absorbance detector. Control blank samples consisting of the extraction solvent(s) were analyzed in each case. Overall, LC-MS proves to be a convenient yet sensitive technique for the analysis of single fiber dye extracts, and is compatible with SWGMAT dye extraction protocols. All single fiber extracts were detected using both the single wavelength detector and the mass selective detector. Single fiber analysis would benefit by incorporating this technique into the investigative routine due to the techniques high discriminating power. References (1) Huang, M. PhD, Yinon, J. PhD, Sigman, M. PhD (2004) Forensic Identification of Dyes Extracted from Textile Fibers by Liquid Chromatography Mass Spectrometry (LC-MS). J. Forensic Sci., 49(2): 1-12.

(218) **Microextraction/Capillary Electrophoresis/Mass Spectrometry for the Forensic Analysis of Textile Fiber Dyes**

Amy Stefan[1], Brandi Clelland[1], Brittany Baguley[1], Stephen Morgan[1]; [1]University of South Carolina

Fiber evidence is frequently used in forensic science to associate a suspect to a victim or crime scene. The fibers are found as trace evidence in crimes of personal contact such as homicide, assault, sexual offenses, and hit-and-run accidents. In forensic fiber comparison, fibers are screened by visual inspection using optical microscopic techniques such as polarized light microscopy (PLM) and by spectroscopic methods such as UV-Vis and fluorescence microspectrophotometry. If spectra of the known and questioned fibers are consistent, the hypothesis that the fibers originate from a common source should not be rejected. The premise of our current research is that additional discrimination may be achieved by extraction of the dye from the fiber, followed by trace analysis by a high resolution separation technique. A sensitive and selective technique such as capillary electrophoresis/mass spectrometry (CE/MS) is needed to analyze the small amount of dye (2-200 ng) present on forensically relevant fiber samples (as little as 2 mm). CE/MS can separate extracted dye components and provide semi-quantitative estimates of dye amounts as well as qualitative information to identify the dye present via molecular weight and mass spectral information. This presentation will report the use of an automated workstation to extract dyes from fibers, followed by analysis by CE/MS. Although this approach is destructive to the sample, automated micro-extractions offer the forensic analyst the potential of reproducible and complete removal of dyes from small quantities of a questioned fiber. The combined extraction CE/MS approach is capable of achieving both highly discriminating and highly sensitive identification of fiber dyes.

(219) **Elemental Analysis of Biological Matrices Using LA-ICP-MS for Sourcing**

Waleska Castro[1], Tatiana Trejos[1], Benjamin Naes[1], José R. Almirall[1]; [1]Florida International University

Elemental composition of biological matrices can provide essential isotopic information that could lead to very good discrimination between different sources of these materials. Several techniques have been used to create elemental profiles of different matrices but they require significant sample consumption (~ mg quantities) and labor intensive sample preparation steps. Laser ablation inductively coupled plasma mass spectrometry (LA-ICP-MS) has been implemented for the elemental analyses of glass and paint fragments reducing these difficulties. LA-ICP-MS has been shown to accurately discriminate between different sources of glass and paint and to associate samples originating from the same source. These LA-ICP-MS methods have been validated through intra-laboratory and inter-laboratory trials, published in the scientific literature and used in actual criminal prosecution proceedings in the US and in Europe. The elemental profiling of bone may be used to associate buried remains to a particular burial site, to associate remains to a geographic region where the person previously resided and/or to discriminate between sets of bones that have been co-mingled in a burial site. A technique has been developed to measure the trace elemental geochemical markers found in the bone to evaluate discrimination. Similarly, the elemental profile in marijuana could be used to associate samples collected during a crime to the source of origin and for provenance purposes. An analytical protocol for the determination of trace elemental profiles on the matrices of bone and plant material by LA-SF-ICP-MS has been developed and is presented. The SF-ICP-MS can resolve most of the polyatomic interferences present in such complicated matrices. A high resolution sector field instrument SF-ICP-MS from Thermo Finnigan coupled to a New Wave UP-213 LA system operating at 213 nm was used to determine the elemental menu for each of each standard reference material (NIST 1400 Bone Ash, NIST 1486 Bone Meal, NIST 15151 Apple Leaves) and samples of femur, humorous and marijuana ashed leaves samples. Future work includes the use of this method using LA-SF-ICP-MS for population studies of these biological matrices.

(220) **Forensic Studies of Dye and Fiber Degradation During Environmental Exposure by Microspectrophotometry and Capillary Electrophoresis/Mass Spectrometry**

Anthony R. Trimboli[1], Allyson A. Wells[1], Jennifer J. Yiu[1], Heather M. Taylor[1], Amy R. Stefan[1], Brandi L. Clelland[1], Stephen L. Morgan[1]; [1]University of South Carolina

Textile fibers found at crime scenes are rarely found in pristine condition. The degradation of fibers and dyes can complicate the forensic comparison between questioned (evidence) and known (suspect) fibers. The objective of this research is to characterize changes that occur in textile fibers as a result exposure to environmental conditions including laundering and outdoor exposure to sunlight, heat, and moisture. Fabric samples of the most commonly used fiber types (cotton, polyester, nylon and acrylic) have been dyed with the most commonly used dyes (reactive, disperse, acid and basic) and were subjected to a variety of environmental conditions (washing, bleaching, sunlight, heat, accelerated weathering, and natural weathering) and subsequently analyzed to determine the effects of these treatments. Fabric samples are being exposed to outdoor weathering (Arizona and Florida) and accelerated outdoor weathering (EMMA and EMMAQUA equivalent to 3, 6, 9 and 12-mos. in hot-dry and hot-wet environments). Samples are being laundered with Tide®, Gain® and Wisk®, each alone, with Clorox® (chlorine bleach), and with Clorox® 2 (peroxide bleach). Fabric samples were retired from exposure at predetermined time intervals of exposure and analyzed by UV/visible and fluorescence microspectrophotometry. Visual inspection of the changes in the dyed fiber spectra as a function of the number of wash/dry cycles is supplemented by analysis of selected samples using capillary electrophoresis/mass spectrometry. Information from this work will enable trace evidence examiners to understand these physical and chemical changes, account for these effects in laboratory comparisons of fibers, and thus more accurately describe such changes in court testimony.

(221) **Detection of Drugs of Abuse using Ion Mobility Spectrometry**

Monica Joshi[1], Jose Almirall[1]; [1]Florida International University

The poster discusses the use and sensitivity of both the Bench top and Portal Ion Mobility Spectrometer instruments for the detection of drugs. IMS is a good tool for narcotics detection because of its field portability , ease of use, simple data interpretation, low limits of detection and cost effectiveness. Data obtained from the analysis of various classes of drugs and their detection in the presence of interferences is presented. Studies performed to validate these instruments including detection limit studies are also presented. A portal IMS system (GE Entry Scan3) has been used to sample particles and a bench top system (Iontrack2) has been used to sample particles and also successfully coupled by an interface to allow for SPME sampling of the odor signature compounds that characterize drugs of abuse. The detection of Methyl Benzoate to characterize the presence of cocaine is an example of the use of the SPME-IMS system for drug detection.

(222) **Elemental Characterization of Automobile Body Fillers and Caulk by Laser Ablation-Inductively Coupled Plasma-Mass Spectrometry for Matching of Evidence**

Joshua Messerly[1], Stan Bajic[1], David Baldwin[1], R. S. Houk[1]; [1]Iowa State University - Ames Laboratory - USDOE

Two commonly used synthetic materials, automotive body filler and household caulk, were investigated for potential use in forensics. Filler is commonly used in the painting of new automobiles and in the repair of damaged automobiles. This material could be valuable in matching a vehicle to a crime scene, such as a hit and run accident. Caulk is used in many construction applications in homes, businesses, and boats. If caulk is found with a suspect, such as on their clothes from breaking into business, then it can help to show that the suspect was at the crime scene.\r\nThough mostly organic in nature, these materials contain inorganic elements which may allow for sample discrimination between similar materials. Elemental profiles of filler and caulk were obtained by Laser Ablation-Inductively Coupled Plasma-Mass Spectrometry (LA-ICP-MS). The samples were prepared according to the manufacturers instructions, and changes in sample profiles were measured during the curing process. Samples from several manufacturers and different lot numbers were evaluated using Principal Components Analysis (PCA). Scores plots were generated using PCA software. These plots show the similarity or dissimilarity of the samples analyzed between the different lots and manufacturers. For example, visually indistinguishable samples of white caulk from two different manufacturers are clearly distinguishable using the PCA scores plot of their inorganic elemental profile.

(223) **Evaluation of NIR Spectroscopy for Identification and Content Uniformity of Pharmaceutical Solid Dosage Forms**

Peter Larkin[1], Eileen Fruhling[1], Carl Longfellow[1]; [1]Wyeth Pharmaceuticals

Near-IR spectroscopy is a versatile technique for rapid analysis of samples with C-H, N-H, or O H bonds with an analyte composition of 0.1% or greater. Recent NIR work has demonstrated the potential of NIR spectroscopy for pharmaceutical analyses such as the noninvasive and nondestructive analysis of solid dosage forms. When used with appropriate standards and chemometric multivariate analyses, NIR spectroscopy can be used to simultaneously measure a variety of tablet properties. Once a chemometric method is developed, accurate qualitative and quantitative information can be obtained. Both an ID and quantitation method employing chemometric software has been developed to identify the tablet type as well as quantitate the concentration of the API and the excipients in the tablets. The present study evaluates this analysis using an FT-NIR (Bruker MPA) and a dispersive NIR (Foss-XDS). Tablet measurements using both reflectance and transmission spectral collection are compared. Fifteen different formulated uncoated tablets were prepared as calibration standards for this method. The standards are formulated tablets of 50, 100 and 200 mg API tablet cores with varying relative concentrations of both excipients and API. NIR spectra were measured of five tablets from each of the fifteen formulated calibration standards for a total of 75 tablets for the chemometric model development. The tablet calibration standards were generated using a process identical to that used for the registration batches and subsequent production batches of the tablets. The accuracy, intermediate precision, repeatability, specificity and robustness of the method are evaluated.

(224) **Application of NIR Spectroscopy for Rapid Analysis of Barley as a Source of Ethanol**

Miryeong Sohn[1], David Himmelsbach[1], Franklin Barton, II[1], Kevin Hicks[2]; [1]USDA-ARS, R. B. Russell Research Center, [2]USDA-ARS, Eastern Regional Research Cent.

Developing renewable fuels is receiving increased emphasis due to the current energy situation. Farm-based corps, other plant materials and agricultural wastes have been considered as renewable energy sources to produce ethanol. Barley is one of the potential ethanol sources. For efficient ethanol production, it is important to know the amount of fermentable and other components in barley. Also, it is important to develop a non-destructive and rapid method to analyze for these components. This study was conducted to investigate the potential of NIR spectroscopy as a rapid and non-destructive analytical technique. A total of 142 barley samples with various varieties, growing locations, types were collected and samples were prepared as flour and kernel types. Moisture, starch, and protein were analyzed as major components. NIR data were collected on FT-NIR and dispersive NIR, and the results compared. Principal component analysis and partial least squares (PLS) regression were performed using Matlab (ver 7.01) with PLS_Toolbox (ver. 3.5). PLS models using the kernel samples resulted in acceptable error levels, giving prediction errors: 0.5%, 1.7%, and 0.5% for moisture, starch, and protein (respectively), even though the accuracy was slightly lower than that by flour samples. Model performance between instruments was comparable.

(225) **Scatter Correction and Spectral Resolution Aspects for NIR Diffuse-Reflection Spectroscopy of Solid Materials**

Heinz W. Siesler[1], Olga Kolomiets[1]; [1]Dept. of Phys. Chem., University of Duisburg-Essen

For the qualitative and quantitative NIR spectroscopic characterization of solid materials scatter correction and spectral resolution are important issues. On the one hand for many applications the influence of scattering on the diffuse-reflection spectra has to be eliminated in order to focus exclusively on the chemical composition of the investigated material and on the other hand for the quantification of a crystalline active material in amorphous excipients, for example, the spectral resolution may have an important influence on the prediction accuracy of NIR-spectroscopic calibration models. In detailed investigations of materials with different particle size we could show that the multiplicative scatter correction (MSC) applied over many years obviously does not completely eliminate the influence of morphology on the corresponding diffuse-reflection spectra. Furthermore, we have shown, that the prediction accuracy for crystalline materials with sharp absorption bands in their diffuse-reflection spectra does not significantly depend on the spectral resolution of the NIR spectra used for the development of quantitative calibration models for these substances.

(226) **Measurement of Tissue Oxygen Saturation Using Single-Distance Multiwavelength Near Infrared Spectroscopy**

Olusola Soyemi[1], Babs Soller[1], Michelle Landry[1], Ye Yang[1]; [1]University of Massachusetts Medical School

The measurement of tissue oxygen saturation using near infrared spectroscopy is complicated by the complex interaction between near infrared light and tissue. The key challenge is the separation of tissue scattering and tissue absorption. We have developed a simple but novel method that uses the basic Beer's law model to calculate a residual spectrum that combines wavelength-dependent tissue scattering and background ("non-hemoglobin") absorption. This isolates the contribution of heme absorption from the measured tissue spectrum, permitting the calculation of hemoglobin

saturation. Unlike conventional tissue oximeters, this approach requires full spectrum or multi-wavelength tissue measurements at a fixed source-detector spacing that not only simplifies the design of the measurement device, but enables the calculation of additional variables that might prove useful in future physiologic monitors. This method has been tested on tissue near infrared spectra acquired from healthy volunteer subjects during (a) arterial occlusion (N = 5), and (b) rhythmic hand-grip exercise (N = 7). From the arterial occlusion study, we show that the measured percent tissue saturation at baseline (pre-occlusion), during ischemia, and during hyperemia (61.2 ± 4.9, 37.1 ± 3.0 and 69.9 ± 6.7) compare favorably with similar measurements from a frequency-domain multi-distance tissue oximeter. In addition to the response of the saturation measurements to cuff ischemia, we also show that tissue saturation measurements derived from our method respond to different levels of exercise intensity during rhythmic hand-grip exercise.

(227) **Standoff Detection of High Explosives with Near Infrared Spectroscopy**

Greg Klunder, LLNL

Detection of explosives has become a major priority for homeland security, first responders, and the military. Although there are numerous technologies available for detection and identification of explosives, there are few technologies that can detect explosives at a safe distance. Raman spectroscopy has recently been demonstrated detection of explosives at a distance of 50m. However, this requires putting energy into the material that could result in heating and possibly ignition of the explosive material. Terahertz spectroscopy also has the potential for standoff detection and has the ability to 'see' thru the some materials that might be used to conceal the explosives. Development of more powerful sources and atmospheric absorption primarily from water vapor are the primary obstacles for THz spectroscopy. Near infrared (NIR) spectroscopy has been used for many applications including remote measurements. Since the NIR spectra are primarily due to CH, OH, NH overtone and combination bands, explosives that contain these bonds and will have unique spectra in this range. We have measured the NIR reflectance spectra for many explosive materials and formulations and the materials are readily identified using principal component analysis. Since standoff detection of explosives will necessarily involve reflectance rather than transmission measurements, these results indicate that NIR spectroscopy offers great promise. In the lab measurements, have been made at a standoff of 20' using tungsten halogen light source. However, the solar spectral irradiance provides an adequate source for NIR reflectance measurements. Absorption bands due to water vapor lie outside the primary absorption bands for most explosives. Passive standoff detection of explosives has been demonstrated outside under solar illumination. The feasibility of using NIR spectroscopy for standoff detection of explosives and formulations will be discussed.

(228) **Effect of Physical Properties and Water on the Identification of Pharmaceutical Excipients by Near-infrared Spectroscopy**

Kelly Palmer[1], Roger Jee[1], James Kraunsoe[2], Anthony Moffat[1]; [1]School of Pharmacy, University of London, [2]AstraZeneca R&D Charnwood UK

Changes in the physical properties and water of materials affect the ability of near-infrared spectroscopy (NIRS) to identify pharmaceutical excipients. In this study the effects of moisture, powder compaction and particle size were investigated for 16 common excipients. Samples with different moisture contents were prepared by storing different batches of each excipient at relative humidities of 22, 32, 75 and 95% for 0, 2 and 3 weeks. Powder compaction was investigated by pressing discs at 5, 10 and 15 tonne/cm2. Particle size distributions for the samples stored at different humidities were also measured after drying. NIR reflectance spectra were measured for all samples. Absorbance at the water regions (1350 – 1450 and 1880 – 1930 nm) increased the longer and greater the humidity under which the samples were stored. Even after removing these spectral regions Principle Component Analysis score plots (on second-derivative spectra) still clearly showed the effect of increasing moisture content indicating that moisture affects other properties of the material such as particle size. The particle size measurements showed an increase in particle size for croscarmellose sodium, lactose and maize starch with an increase in moisture content. Compaction had little effect on the spectra except for maize starch which produced a new peak (1475 – 1600 nm) at high pressures. The physical properties had a large effect on the ability of NIRS to correctly identify the excipients. When using Correlation in Wavelength Space as the identification algorithm (criteria: $r > 0.90$ with Δr for nearest neighbour > 0.1) misidentifications occurred for the following groups of excipients: a)croscarmellose sodium/maize starch/sodium starch glycollate, b) microcrystalline cellulose PH101/PH102, c) Eudragit L100/S100, and d) Eudragit RLPO/PSPO grades. Moisture content was particularly important with r values reducing from 0.99 to 0.72 dry and moist samples of the same material. Physical and chemical properties are consequently very important and must be built into any spectral library used for identification and qualification purposes.

(229) **Seawater Proteomics: Biopanning for Clues of the Mechanisms of Carbon Cycling**

Aaron Timperman[1], Carlos Del Castillo[2], Ting Zhao[1], Brent Reschke[1], Kathleen Kelly[1], Matthew Powell[1]; [1]West Virginia University, Department of Chemistry, [2]Johns Hopkins, Applied Physics Lab.

The enormous complexity of marine high molecular weight dissolved organic matter (HMW DOM) has largely prevented its analysis at the molecular level. Recent advances in analytical methods for protein analysis have made molecular level analysis of the protein component of HMW DOM feasible. It is hypothesized that structural characterization of dissolved proteins will help reveal clues into the mechanisms that control cycling of dissolved organic matter. Bottom-up or peptide level proteomic methods can provide accurate identification and sequence tags from de novo sequencing, to determine what classes of proteins escape degradation. Top-down or whole protein methods are excellent for characterizing protein heterogeneity and elucidation of protein modifications. Dissolved protein from seawater is concentrated using tangential flow ultrafiltration and methanol/chloroform/water precipitation. Two methods are employed for bottom-up characterization of the proteins using electrospray ionization-mass spectrometry (ESI-MS). In the traditional protein identification method, intact proteins are separated by SDS-PAGE and digested enzymatically in-gel. The other approach utilizes MuDPIT or shot-gun sequencing in which the peptides resulting from a solution proteolytic digest of the whole protein pellet mixture are separated by capillary HPLC. In both methods, the final chromatographic separation was coupled on-line with a mass spectrometer using an electrospray interface, and peptide CID spectra were collected using tandem mass spectrometry. De novo sequencing of the peptide tandem mass spectra generated short amino acid sequences (peptide tags) that were used to search databases for protein class and source information. For whole protein analysis the proteins are recovered, and electroextracted from the gels. The intact proteins are analyzed using on-line RP-HPLC-MS. Trends of conserved

sequences for two specific classes of proteins were observed: membrane/envelope proteins and enzymes. Similarity searching of peptide tags produced identification of conserved sequences from several protein homologues originating from many different species, including: long chain fatty acyl CoA synthetase, anthranilate synthase, ribulose bisphosphate carboxylase, tubulin beta chain, adhesin, transport system protease, ATP synthase alpha chain, and luminal binding protein.

(230) **Proteins at Sea: Tracing the Sources and Cycling of Organic Matter in Marine Systems**

Rodger Harvey[1], Angela Squier[1]; [1]University of Maryland CES

The oceans represent the largest reservoir of reduced carbon on the planet and thus the cycling of organic carbon in marine systems is a key part of the global carbon cycle. Comp[rising a range of molecular sizes from dissolved individual molecules to macromolecular aggregates, the oceans contributing an estimated 44-50 Pg/yr of new production; roughly equal to the terrestrial system in terms of new organic carbon to the biosphere. Nevertheless, only about 1% of this material is ultimately buried and preserved in the geological record, with a smaller fraction leading to fossil fuels. Detailing the interaction of biological, chemical and physical processes which mediate these reactions and the fate of degradation products in the ocean presents a number of analytical challenges. These include highly complex distributions of analytes present at typically low concentrations, the possibility of unknown modifications driven by both biotic and abiotic catalysis, and the complex medium which interferes with many analytical techniques. The latter is a particularly important issue for marine samples where significant concentrations of inorganic species are the rule. It is well recognized that given the complexity of aquatic systems, it is impractical (if not impossible) to identify all of the constituents. An alternative approach to understanding these systems is to examine the processes that operate and govern organic carbon composition. In the case of proteins, potentially vast numbers of individual components, all comprising the same fundamental structures as amino acids, contribute to a substantial but largely unidentified pool. A mechanistic approach has the potential to reveal those factors that govern protein recycling or its preservation as intact or modified products. Advances in protein identification methods, in particular mass spectrometric methods and ion searching software, now permit much more detailed examinations of protein degradation, including the potential to follow the fate of individual proteins. Using both environmental samples and experimental systems, proteins and their transformation products were analyzed by a range of analytical techniques used in conventional proteomics including 2D-PAGE, GC-MS of hydrolyzed amino acids and LC-MS and LC-MS/MS of intact and trypsin-digested proteins. The results of these analyses and the role of proteins in the ocean carbon cycle will be used to provide examples of accomplishments and hurdles for future environmental analysis.

(231) **Detection and Identification of Biomolecules within Marine Dissolved Organic Matter: Use of Electrospray Ionization Fourier Transform Ion Cyclotron Resonance MS**

Elizabeth Kujawinsk; Woods Hole Oceanographic Institution

The structure and composition of organic matter (OM) plays a critical role in a number of geochemical processes such as cycles of redox-sensitive metals, contaminant transport and microbial growth and community structure. Since these processes all contain rate-limiting steps that comprise a reaction between two molecules, e.g., binding of a redox-sensitive metal by an organic ligand, understanding the reaction pathways within critical geochemical processes depends on elucidation of the structures of the pertinent components within each system. However, in spite of the centrality of organic matter in aquatic biogeochemical processes, its composition, sources and fates are often obscure. For example, although the importance of the microbial web is well-established in both freshwater and marine environments, the related changes in OM have not been studied on a molecular level. Very little information is available on the selectivity of heterotrophic bacteria for the suite of available OM compounds in dissolved or particulate organic material. We know even less about the molecular-level composition of OM excreted by autotrophic organisms in the water column. The amazing spatial heterogeneity and vast metabolic potential of the microbial community observed through genomic analyses could be due to chemical heterogeneity and a variety of responses of specific microbes to different OM compositions and concentrations. To test this hypothesis, molecular-level elucidation of OM in both laboratory incubations and field experiments will be required. The advent of electrospray ionization coupled with ultrahigh resolution mass spectrometers has opened the door to molecular-level analysis of polar mixtures such as natural organic matter. In this presentation, we focus on the application of ESI coupled to a 9.4 T Fourier transform ion cyclotron resonance mass spectrometer (FT-ICR MS) to marine dissolved organic matter (DOM) In particular, we examine the role of heterotrophic bacteria and protozoa in the modification and remineralization of marine DOM in both laboratory and field-based experiments. Our experiments show that ESI FT-ICR MS can be used to detect compounds selectively utilized by different bacterial species and to assign elemental formulae to compounds produced by both bacteria and protozoa during growth.

(232) **Optical Sectioning of Live Cells via Hyperspectral Confocal Fluorescence Imaging and Multivariate Curve Resolution**

David Haaland[1], Howland Jones[1], Michael Sinclair[1], Jerilyn Timlin[1], Linda Nieman[1], Roberto Rebeil[1], David Melgaard[1], Sawsan Hamad[2], Wim Vermaas[2]; [1]Sandia National Laboratories, [2]Arizona State University

We have developed a 3D hyperspectral confocal fluorescence microscope that can optically section live cells at diffraction-limited spatial resolutions. The design and operation of the microscope will be discussed along with its advantages over current commercial confocal microscopes. When coupled with multivariate curve resolution (MCR), the new microscope can resolve multiple spatially and spectrally overlapped emission components in the cells. These methods will be demonstrated with hyperspectral images of live Synechocystis cells and cells of interest in studying host-pathogen interactions. Synechocystis is a cyanobacterium, and is a member of a class of organisms responsible for a large fraction of carbon sequestration from the atmosphere. In these experiments, cells from wild type and from mutants lacking a photosystem or a step in chlorophyll biosynthesis were imaged to monitor the relative concentrations and spatial distributions of photosynthetic pigments in these bacteria, providing a way to directly localize specific pigments in a cell with sub-fÝm spatial resolution. The kinetics of photobleaching of these photosynthetic pigments in the wild type and mutant bacteria will be presented along with interesting spatial behavior of the pigments during the photobleaching process. Hyperspectral imaging experiments investigating events related to host-pathogen interactions will also be discussed. The new microscope and associated multivariate analyses constitute an enabling new technology for cell imaging and for understanding a variety of molecular and physical processes occurring in live cells. *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. This work was funded in part by the US Dep't of Energy's Genomics: GTL program (www.doegenomestolife.org) under project, ¡§Carbon Sequestration in Synechococcus Sp.: From Molecular Machines to Hierarchical Modeling¡¨ (www.genomes-to-life.org)

(233) **Robust Multivariate Analysis for Problem Images**

Jeremy Shaver; Eigenvector Research, Inc.

Real industrial applications seldom provide data which can be easily modeled without significant pre-treatment. Outliers and non-linear responses often complicate the use of standard multivariate modeling methods. Image analysis further challenges the modeling process because of the large volume of data and decreased control over data collection. In this paper we will discuss the development of automatic hierarchical and robust modeling techniques their application to difficult data analysis tasks. Automatic outlier detection through standard statistical tests or rapid clustering techniques can be used isolate problem data. This data can then be treated, excluded, or set aside for inclusion in a separate sub-model. Similarly, non-linear responses can be isolated and handled separately. These methods will be demonstrated on image data from several different analytical techniques.

(234) **Calibration of Fiber Optic Excitation Emission Matrix Spectroscopy for Environmental Pollutants**

Karl Booksh[1], James Jordan[1], Yoon-Chang Kim[1], Wei Peng[1]; [1]Arizona State University

A field portable fiber optic excitation-emission matrix fluorometer has been developed for field analyses. The ubiquitous fluorescence background and broad nature of fluorescence spectra require hyphenated instrumentation (such as EEM fluoremetry) and second order calibration methods (such as PARAFAC) to perform accurate analyses in natural waters. Presented here will be the calibration and application of the EEM fluorometer for two classes of analytes: natively fluorescent polycyclic aromatic hydrocarbons and non-fluorescent DDT type analytes that interact with fluorescent dyes.

(235) **Evaluation of The Precision of Chemometric-Based Quantification of Multidimensional Analytical Methods**

Sarah Rutan[1], Marc Cantwell[1], Sarah Porter[1], Peter Carr[2]; [1]Virginia Commonwealth University, [2]University of Minnesota

Multidimensional analytical techniques, either tandem or parallel, have dramatically increased the amount of information available from traditional analytical methods. Examples of multidimensional techniques include liquid chromatography with diode array detection (LC-DAD), LC with mass spectrometric detection (LC-MS), and comprehensive two dimensional LC with various detectors (2D-LC-DAD and 2D-LC-MS). Chemometric methods including parallel factor analysis (PARAFAC) and multivariate curve resolution-alternating least squares (MCR-ALS) are often used to obtain quantitative results from these methods. In this work, we quantify the improvement in the precision available upon the addition of a data dimension to a particular method. Measures of precision and resolving power used here include the use of information theory and analyte signal theory. These measures of precision have been validated using Monte Carlo simulations. Applications to forensic drug analysis and metabolism studies will be discussed.

(236) **Incorporation of Practical Shape Constraints in The ALS Procedure for Analysis of Two-Way UV Resonance Raman Spectra**

Renee JiJi[1], John Simpson[1], Gurusamy Balakrishan[2], Ying Hu[2], Janina Kneipp[2], Thomas Spiro[2]; [1]University of Missouri-Columbia, [2]Princeton University

Deep-UV resonance Raman (UVRR) is finding wider applications in equilibrium and kinetic studies of protein structure. The UVRR spectra of proteins are dominated by the amide and aromatic (tryptophan, tyrosine and phenylalanine) modes, which are sensitive to the local secondary structure of the peptide and the hydrophobicity of the individual amino acid residue's environment, respectively. Select Raman bands often contain a plethora of information about the structure and movement of the protein, but in order to glean the maximum amount of information, these bands must first be resolved from their counterparts. The most common method being a nonlinear least squares optimization of a series of peak descriptors (position, height, width, shape), which minimize the difference between a fitted spectrum and the data. Not surprisingly, inevitable minor fluctuations in the spectral background, signal intensity and instrument calibration within the time-course of a series of measurements often lead to significantly different estimations of peak profile and position for the same spectral components in different spectra. However, potentially two-way UVRR data produced by studies of protein dynamics in the time domain or multi-excitation measurements of proteins in the steady state may allow for more robust (multi-way) spectral deconvolution strategies. A promising method for achieving a more reliable estimation of the individual Raman bands is multivariate curve resolution - alternating least squares (MCR-ALS). However, the amide regions of the seemingly simpler resonance enhanced Raman spectra remain highly congested and overlapped with the aromatic modes. Preliminary studies indicate that non-negativity and unimodal constraints are wholly insufficient to facilitate convergence when analyzing highly congested regions of two-way UVRR spectra. Yet, when combined with the application of a Gaussian/Lorentzian shape constraint on the individual peak profiles, ALS optimization has begun to show promising results for resolution of these informative, but highly congested regions of the UVRR Raman spectra.

(237) **Optimization of Materials Parameters for Surface Plasmon Resonance Sensing on Conducting Metal Oxides**

Stefan Franzen[1], Crissy Rhodes[1], Alina Efremenko[1], Mark Losego[1], Jon-Paul Maria[1]; [1]North Carolina State University

The development of surface plasmon resonance (SPR) spectroscopy on novel conducting substrates involves the study of materials properties and optics in the near-infrared region of the electromagnetic spectrum. We have systematically studied the preparation of indium tin oxide (ITO) thin layers using characterization by X-ray diffraction, atomic force microscopy, electrochemistry, contact angle and conductivity. The ordering of adlayers has been studied by X-ray photoelectron spectroscopy, Near Edge X-ray Absorption Fine Structure (NEXAFS) and infrared spectroscopies. Extension of these methods to aluminum-doped zinc oxide (AZO) demonstrates that SPR can be successfully carried out on novel substrates. We recently established that SPR coupled in the Kretschmann configuration can be used as a detectiong method on a variety of conducting metal oxides. The materials properties are correlated both to the ordering of adlayers on the surface and surface plasmon resonance as measured using a theta-2theta stage with near-infrared radiation in the Kretschmann configuration. By tuning the materials properties the magnitude of the SPR signals has been further optimized and an understanding of the underlying physical parameters has been obtained. Extension

of the results to new sensing modes using thin layers and gas phase sensing will be discussed.

(238) **2-D Analysis of FT-SPR Spectra Acquired at Different Angles**

Eirc Jiang[1], Koichi Nishikida[1], Dennis Merril[1], Steve Lowry[1], Voula Kodoyianni[2], Steve Weibel[2]; [1]Thermo Electron Corp., [2]GWC Technolgies

A number of recent papers have described the use of wavelength scanning for Surface Plasmon Resonance (SPR) spectroscopy. Several researchers have described the advantages of using of FTIR spectroscopy in the near infrared region to take advantage of the wavelength precision, narrower line shapes and sensitivity of this technique in the spectral region between 1,000 nm and 2,500nm. While wavelength scanning instruments provide a great deal of flexibility, there are situations where changing the angle is also useful. In this paper we describe the interfacing of an automated high precision angle tuning device to the FT-SPR system. This combination of wavelength and angle tuning provides the incremental information required to determine both the dielectric constant and thickness of a biolayer. In this presentation we will describe some results obtained by analyzing a series of wavelength spectra acquired while varying the angle of the SPR chip as well as examples of binding studies. We will also describe the results of some studies that we performed to improve the accuracy of the FT-SPR measurement.

(239) **Enhanced Biosensing using Asymmetric Plasmonic Structures**

Alastair W Wark[1], Hye Jin Lee[1], Robert M Corn[1]; [1]University of Cailfornia-Irvine

Asymmetric plasmonic structures offer new opportunities for enhanced biosensing compared to conventional surface plasmon resonance (SPR) measurements using planar gold films. The highly localized, intense electric fields associated with coupled surface plasmon modes are particularly interesting and of importance to a wide range of spectroscopic bioanalytical techniques such as surface plasmon fluorescence spectroscopy, surface enhanced raman spectroscopy, nanoparticle-enhanced SPR imaging, and colorimetric analysis of colloidal solutions. Initial results using these methods in combination with metallic nanorods and nanoparticle networks will be discussed. Further insight into the optical properties of these plasmonic structures is also obtained via the use of femtosecond transient absorption pump-probe spectroscopy.

(240) **Inhibition Assay for On-Chip Phosphorylation of Peptide by Surface Plasmon Resonance Imaging Technique**

Kazuki Inamori[1], Motoki Kyo[1], Kazuki Matsukawa[1], Yusuke Inoue[2], Tatsuhiko Sonoda[2], Eiji Kinoshita[3], Tohru Koike[3], Yoshiki Katayama[2]; [1]Biotechnology Frontier Project, Toyobo Co., Ltd., [2]Department of Applied Chemistry Faculty, [3]Department of Functional Molecular Science

We have developed the comprehensive analysis technology for the on-chip phosphorylation using the peptide array. We previously reported a detection and quantification system for on-chip phosphorylation of peptides by surface plasmon resonance (SPR) imaging using a novel phosphate capture molecule, biotinylated zinc(II) complex. In this study, we examined the inhibition assay using this system. Autoradiography was also examined using the same peptide array. PKA reaction was mainly studied as the model experiment. The covalently immobilized peptide array was obtained using SSMCC as the crosslinker. The peptide arrays were reacted with PKA solution containing ATP. Then, PKA inhbitor was coexisted at various concentrations. In SPR analysis, the array which was incubated by biotynylated zinc(II) complex solution in advance was placed to the SPR instrument, and exposed with streptavidin (SA) and anti-SA antibody solution. By Both SPR imaging and autoradiography analysis, we found the inhibition effect for on-chip phosphorylation of PKA substrate peptide by coexistence of the inhibitor. The inhibition effect was enhanced with the concentration of PKA inhibitors. About the other kind of protein kinases, on-chip inhibition assay was also achieved. We propose that our system for the on-chip phosphorylation assay is very valuable for the screening of drug especially.

(241) **Swelling of Functionalized Colloidal Poly-N-Isopropylacrylamide Particles: Applications to Optical Sensing and Bioconjugation**

Barry Lavine[1], Necati Kaval[1], David Westover[1], Leah Oxenford[1], Nikhil Mirjankar[1]; [1]Oklahoma State University

Microgels based on N-isopropylacrylamide (NIPA) have attracted considerable attention as “smart” materials because of their ability to undergo a reversible volume phase transition at near physiological temperature. These gels which are often prepared as monodisperse colloidal particles undergo dramatic changes in size and water content over a narrow temperature range. This thermal sensitivity has led to their applications in drug delivery, biomedical devices, and controlled biomolecule recovery. More recent work has focused on attempts to incorporate functional groups into these gels. Of particular interest is the functionalization of polyNIPA particles by carboxylic acid groups at or near the particle surface which would be readily accessible for subsequent chemical reactions. Currently, methacrylic acid functionalized polyNIPA particles that are sensitized to pH (through photopolymerization) or theophylline (through molecular imprinting) have been prepared by dispersion polymerization. These particles possess unusual swelling properties which makes them suitable for optical sensing or as bioconjugates for proteins. The swelling properties of these particles have been investigated using surface plasmon resonance spectroscopy.

(242) **Molecularly Imprinted Polymerization based Surface Plasmon Resonance Sensing for Glucose Detection in Human Urine**

Wei Peng[1], Soame Banerji[1], Yoon-Chang Kim[1], Karl Booksh[1]; [1]ASU

Surface Plasmon Resonance (SPR) has been traditionally used as a probe for surface interaction of large molecules like proteins and peptides but harder to measure small molecules since the effective change in the SPR condition (thickness change of the layer bound to the gold) becomes smaller. The accurate measurement of glucose in complex physiological fluids like urine is particularly challenging since the constituents of these fluids vary significantly from person to person and even throughout the day for a particular individual. A novel SPR sensor to detect glucose using molecularly imprinted polymer will be presented in this paper. The polymer was prepared by crosslinking poly (allyl amine) in the presence of Glucose Phosphate, monobarium salt (GPS-Ba) and attached to a thin film of gold (50 nm) which had been sputtered on top of a glass slide, via amide coupling. Upon removal of the template, this sensor was used to detect glucose in human urine in physiologically significant levels (1-20 mg/ml). Enhancement of the glucose sensor was made possible by incorporating gold nanoparticles which improved the signal. This study has demonstrated the specific detection of glucose in a complex physiological fluid using SPR spectroscopy. The association of glucose to the imprinted polymer results in the swelling of the polymer that can be tracked by the minima in SPR spectra. The sensitivity of this method, while lower than protein based detection schemes, is sufficient for quantitative measurement of glucose in urine at physiologically significant

levels without extensive pre-treatment of the sample. Lower detection limits can be achieved by the incorporation of gold nanoparticles in the polymer matrix, which have been shown to increase the sensitivity of SPR signal significantly. Given the nature of the weak non-covalent binding of glucose to the amine functional groups, the scheme used here can be adapted to detect a number of different molecular species of sizes comparable to that of glucose without the need for extensive sample preparation or use of chemicals with limited shelf life.

(243) **Studies of Redox Reactivity of Carbon Nanotubes**

Stephen Doorn[1], Satishkumar Chikkannanavar[1]; [1]Los Alamos National Laboratory

We have previously demonstrated chiral selectivity in the redox reactions between SDS suspended carbon nanotubes and small organic electron acceptors (1). We present a more detailed study of this redox chemistry. Studies of the dependence of reaction kinetics on driving force are presented with discussion on implications for surfactant structure. We also present results for additional chiral selective reaction chemistry with discussion of possible mechanisms. (1) O'Connell, M.J.; Ebergen, E.E.; Doorn, S.K.; "Chiral Selectivity in the Charge-Transfer Bleaching of Single-Walled Carbon Nanotube Spectra", Nature Materials, 4, 412 (2005).

(244) **Using the Inherent Redox Differences of Single Wall Carbon Nanotubes to Fractionate Them According to Diameter and Metallicity**

Fotios Papadimitrakopoulos; University of Connecticut

Using the Inherent Redox Differences of Single Wall Carbon Nanotubes to Fractionate Them According to Diameter and Metallicity Fotios Papadimitrakopoulos Nanomaterials Optoelectronics Laboratory, Department of Chemistry, Polymer Program, Institute of Materials Science, University of Connecticut, Storrs, Connecticut 06269-3136 Precise control of single wall carbon nanotubes (SWNTs) over length, diameter, type (or otherwise termed metallicity (metallic vs. semiconducting)) and chirality are of pivotal importance for their future involvement in high-end electronic and optoelectronic devices as well as in biosensory applications. From an electronics perspective, separation of SWNTs according to type and diameter (the latter of which controls the band-gap for semiconducting SWNTs) is of extreme importance. During the past three years a number of separation methodologies have been debuted and although large-scale enrichment remains a challenge, considerable progress have been achieved in this frontier. Our initial report on the preferential interaction of surfactant amines with sem-SWNTs, as opposed to met-SWNT fraction, provided the means to alter their respective solubility characteristics and afford separation.1 Until recently, very little was known on the underlying nature of this separation. In this contribution, the differential dedoping characteristics of SWNTs according to diameter and metallicity will be described as the fundamental cause that triggers this separation.2 This was deduced with the help of resonance Raman spectroscopy in conjunction with modeling of the Gibbs free energy and charge-loss as it pertains to the (n,m)-dependent SWNT integrated density of states (IDOS) across a redox jump. 1. D. Chattopadhyay; I. Galeska; F. Papadimitrakopoulos, J. Am. Chem. Soc. 2003, 125(11), 3370-3375. 2. S. N. Kim; Z. Luo; F. Papadimitrakopoulos, Nano Letters, 2005, 5(12), 2500-2504. Financial support from ARO and AFOSR is kindly appreciated.

(245) **Understanding the Relationship between the Growth Conditions and the Diameter of Single Walled Carbon Nanotubes**

Jie Liu[1], Chenguang Lu[1]; [1]Duke University

Chemical Vapor Deposition (CVD), which allows versatile fabrication control and possibility of scaling-up, is the most promising way of producing single-walled carbon nanotubes. Many efforts have been made on unveiling the mechanism of SWNTs growth in CVD process in order to produce SWNTs with high productivity and desired atomic structures. A "seeded growth" model, supported by most lab results indicates that SWNTs grow from carbon-metal alloy particles. Most times one seed nucleate the growth of one SWNT and therefore the diameter of the SWNT is closely related to the size of its nucleating particle. Based on that model, researchers have been able to controllably grow SWNTs with narrow diameter distributions by using the narrowly distributed7,12-18 or identical nanoparticles19 for CVD growth of SWNTs. However, it is often found that a significant amount of particles were not nucleating the growth. Additionally, the nanotubes grown from the nanoparticles with the same starting size but at different growth conditions often produce nanotubes with different sizes. In this talk, we try to developed a theory that can explain most of the reported results by showing that carbon feeding rate during growth plays a key role in determining which catalyst particle is activated and which is not. Carbon feeding control is found to be as important as nanoparticle size control for CVD growth of uniform SWNTs. More importantly, even using polydispersed catalyst naoparticles, the diameters of SWNTs grown can be controlled by controlling the carbon feeding rate. This understanding on carbon feeding effect reveals the importance of growth conditions on the control of diameter distribution for CVD grown SWNTs. Only nanoparticles with sizes close to an optimized size for the specific growth condition would grow SWNTs. Meanwhile, it shows the necessity of tuning the feeding gas composition to achieve the best results on any given set of nanoparticles, explaining the reason for low growth efficiency for many of the earlier results.

(246) **"Super-Growth" Carbon Nanotubes -What Can We Do with This Highly Efficient Synthesis?-**

Don Futaba; National Institute of Advanced Science and Technol

Recently we demonstrated the dramatic effect of adding water vapor in the synthesis of single-walled carbon nanotubes (SWNT). Water-assisted chemical vapor deposition (CVD) (nicknamed "Super-growth") represents a significant advance in material synthesis and has been shown to be a highly efficient carbon nanotube (CNT) synthesis method, which produces a massive growth of vertically-aligned SWNT forests with heights up to 2.5 millimeters and carbon purity over 99.9%. While simultaneously addressing many critical issues, such as scalability, purity, and cost, and opens up innumerable opportunities ranging from fundamental research to commercial applications. This presentation will provide an overview of our recent advances in, (1) the controlled and automated synthesis of CNTs; (2) elucidating fundamental strengths of our SWNTs; and (3) fabricating a new highly densely packed form of CNT material called the "SWNT" solid.

(247) **Reversible Cyclic Peptides and Other Designed Peptide Systems for Use in The Noncovalent Functionalization of Carbon Nanotubes**

Gregg Dieckmann[1,2], Ray Baughman[1,2], Alan Dalton[3], Rockford Draper[1,2], Inga Musselman[1,2], Paul Pantano[1,2]; [1]The University of Texas at Dallas, [2]NanoTech Institute, UTD, [3]University of Surrey

To fully realize the potential utility of carbon nanotubes, strategies for the effective dispersion, separation, organization and

functionalization of these materials must be devised. In this presentation we will focus on the use of reversible cyclic peptides (RCPs) and other designed amphiphilic peptide systems to achieve these goals, with a focus placed on the peptide design and characterization of the resulting peptide/nanotube composites. Results from circular dichroism, Raman, UV/Vis/NIR, SEM, TEM and AFM studies will be discussed which demonstrate that designed amphiphilic peptides are effective at dispersing carbon nanotubes in aqueous solution, debundling the nanotubes yielding long individual nanotubes. Furthermore, the RCPs demonstrate diameter-selective dispersion of HiPco CNTs. The ability to control nanotube organization by utilizing the self-assembly properties of the peptides provides a facile and versatile method for the manipulation of carbon nanotubes for future applications.

(248) **Dispersion and Separation of Single-Walled Carbon Nanotubes**

Takeshi Akasaka[1], Yutaka Maeda[2], Takatsugu Wakahara[2], Yongfu Lian[2], Takahiro Tsuchiya[2], Jing Lu[3], Shigeru Nagase[4]; [1]University of Tsukuba, [2]Tokyo Gakugei University, [3]Peking University, [4]Institute for Molecula Science

Single-walled carbon nanotubes (SWNTs) have excellent mechanical and electrical properties that have led to the proposal of many potential applications. However, SWNTs are typically grown as the bundles of metallic and semiconducting tubes, this hindering the widespread applications. In the applications of SWNTs, it is extremely important to separate semiconducting and metallic SWNTs. We herein show a separation method involving a dispersion-centrifugation process in a tetrahydrofuran solution of amine, which makes metallic SWNTs highly concentrated in a simple way. A typical dispersion procedure1 is as follows: As-prepared SWNTs (AP-SWNTs) were added to a solution of a amine in tetrahydrofuran and then sonicated at room temperature followed by centrifugation of the suspension to remove non-dispersible SWNTs. Luminescence and AFM analyses of a supernatant solution showed that the SWNT are well exfoliated and highly dispersed in the solution. Theoretical calculations indicate that amines interact more preferably with as-prepared metallic SWNTs. The selective decreasing of semiconducting absorption bands and the enhancement of metallic absorption bands were observed after repeating the dispersion-centrifugal process.2 Raman spectra also shows the enrichment of the metallic SWNTs. The resistivity of the bucky paper made from the enriched metallic SWNTs is more conductive than that of AP-SWNTs. These results are also consistent with the NIR and Raman data. This separation method is simple and convenient, suggesting a potential industrial utilization for widespread applications of SWNTs. (1) Y. Maeda et al., J. Phys. Chem. B 2004, 108, 18395. (2) Y. Maeda et al., J. Am. Chem. Soc. 2005, 127, 10287.

(249) **Does Raman Microscopy Play a Significant Role in the Pharmaceutical Chemical Imaging Toolbox?**

Fiona Clarke[1], Jordan Cheyne[1], Linda Jayes[1], Christina Pattoni[1]; [1]Pfizer

The utilisation of chemical images is a critical factor in truly understanding pharmaceutical solid dose production. These images allow for the visualisation of excipients and API distributions within a solid dosage matrix, and hence provide an insight into product performance. The means in which these chemical images can be obtained are varied with a number of different analytical tools available. To date NIR based chemical images have probably been most widely discussed, allowing for a good understanding of the majority of components within a dosage form with spatial resolution of ~25um. Both Raman and x-ray fluorescent based microscopes provide the opportunity to look at 1um resolution or below, but what extra information do these systems provide over NIR? Obviously the matrix is explored a more detailed level, but does this allow for performance prediction? At the opposite end of the extreme terahertz imaging can be used to look at solid dosage forms, with lateral resolutions of ~250um therefore allowing for more of a dosage form to be examined in a single measurement. This however does not make the technique more applicable, but simply opens the scope for what chemical images can be utilised for in the pharmaceutical industry. This presentation will look at the different techniques available to generate chemical images and will discuss the benefits each to pharmaceutical case studies.

(250) **Sampling and Linearity Study for Raman Pharmaceutical Product Analysis Using Raman Mapping Spectroscopy**

Husheng Yang; AstraZeneca Pharmaceuticals

Interest and research in using Raman spectroscopy as a process analytical technology (PAT) tool for pharmaceutical product analysis has increased significantly in recent years. Two major reported applications are content uniformity and coating thickness analysis using multivariate calibration for data processing. One major issue of using Raman spectroscopy for pharmaceutical product analysis is sub-sampling caused by the small spot size of the Raman excitation laser. Even though large spot size Raman spectrometer has been developed recently, the question of whether adequate sampling has been used is still frequently asked when developing a Raman method. Another problem of using Raman spectroscopy for quantitative analysis is the uncertainty in linearity due to the sensitivity of Raman signal to sample positions. Although the linearity problem is not apparent when a multivariate calibration method is used for quantification, its hidden effect on quantification accuracy still should not be neglected. Compared with single-point sampling, Raman mapping spectroscopy allows a much larger sampling area with spatial distribution information being studied. In this work Raman mapping spectroscopy was used to study a set of specially designed powder mixtures and tablets. The ingredients in the powders and tablets were selected in a way that the peaks of interests were completely separated from neighboring bands and quantification uncertainties due to under- or over-fitting of multivariate calibration algorithms were totally eliminated. The purpose of this study was to find out how sampling size, number of samples and the quantity of the compound affect quantification accuracy and linearity so that general rules can be developed for future applications. Another purpose of this study was to solve a problem that we encountered when we used a strong band of titanium dioxide at 143 cm-1 for coating thickness analysis. Our previous work showed that the peak intensity is linearly proportional to the weight gain of the coating, but the line does not pass through the origin when weight gain was extrapolated to zero.

(251) **Raman Spectroscopy In Pharmaceutical Process Development**

Zhihao Lin,; Merck & Co., Inc.

Raman spectroscopy has been increasingly applied in pharmaceutical process development. Its unique characteristics in sampling and spectroscopic selectivity make Raman a complementary tool to FTIR in measuring complex chemical reaction and crystallization processes. In particular, Raman spectrometers can be adjusted to preferentially detect solids in slurry, making it a very powerful tool in monitoring polymorphs and polymorph conversion process in situ. In this presentation, examples will be given to demonstrate how Raman spectroscopy, combined with other PAT techniques, provides detailed process and kinetics information of crystallization and polymorph

conversion. The information plays a critical role in understanding, developing and controlling these processes.

(252) **Raman Spectroscopy: A Technique for the Process Analytical Technology Toolbox**

Jonas Johansson[1], Matti Ahlqvist[1], Henric Brage[1], Anders Sparén[1], Staffan Folestad[1]; [1]AstraZeneca R&D Mölndal

Raman spectroscopy is becoming an important alternative in the toolbox of Process Analytical Technology. In spite of the fact that Raman spectroscopy was introduced for analytical measurements already seventy years ago it is not until the recent development in advanced optronics that Raman can now mature into a fast and reliable tool for real-time at-line/in-line/on-line monitoring and control of pharmaceutical manufacturing processes. Still, although the potential of Raman spectroscopy for process analysis has been demonstrated earlier, e.g. in assessment of chemical content and degree of crystallinity, measurements have so far mainly been conducted off-line or at-line. Therefore Raman spectroscopy need to be further developed for improving its usefulness for in-situ monitoring and control of chemical and physical processes. In particular, a focus on interfacing of Raman instrumentation for in-situ sampling of solid samples is required. In this paper a strategy for Raman analysis in tablet manufacturing will be discussed [1]. In the manufacturing of formulated product, granulation and direct compression with their respective unit operations such as granulation, mixing and compression, are the dominating routes. Although Raman measurements can be utilized in all unit operations, this would not constitute a balanced or cost-efficient monitoring/control scheme. A more adequate strategy for application of Raman in tablet manufacturing is a focus on Raman analysis for some selected operations. Potency and homogeneity that are typical root causes to deviations and failures and also crystallinity/ polymorphism may constitute critical issues where Raman spectroscopy may be used. A few examples on the use of Raman spectroscopy for monitoring quality properties during manufacturing will be given and will be linked to a strategy of Raman measurements in tablet manufacturing. [1]\tS. Folestad and J. Johansson, Raman spectroscopy: Opening the PAT toolbox, Eur. Pharm. Rev. 8 36-42 (2003)

(253) **PAT for Measurement and Control in Continuous Processing of Solid Dosage Forms**

Manoharan Ramasamy[1], John Higgins[1], Gert Thurau[1], Stephen Heidel[1]; [1]Merck & Co, Inc.

Continuous processing has built in lean manufacturing principles including production scalability based on "pull" manufacturing and production efficiency by minimizing non value added manufacturing operations and minimizing variation to reduce waste. Continuous processing of solid dosages in pharmaceutical industry is gaining ground due to many reasons- new 21st century FDA initiative with emphasis on better understanding of processes and controlling process parameters, smooth technology transfer from development to manufacturing and potential for real time release. One of the key enablers of continuous processing is continuous monitoring via analytical methods. In this talk, challenges in development and application of PAT in continuous processing specifically continuous blending of solid dosage forms will be discussed.

(254) **The Use of a Revolutionary Raman System for Quantification of Low Dosage Solid Formulations**

Maryann Ehly[1], Ian Lewis[1], David Strachan[1], Mark Kemper[1]; [1]Kaiser Optical Systems, Inc.

A novel large spot non-contact Raman system has been designed to address historical limitations of Raman for quantitative analyses of solid formulations. This system has revolutionized solids sampling by eliminating sample irreproducibility and focusing sensitivity, by measuring a representative volume of sample, and by offering the benefits of non-destructive sampling. In this study, the use of the large spot Raman analyzer and a non-contact near-infrared analyzer for quantification of low dosage solid formulations have been investigated. Both analyzers were used to measure tablets containing various low-level amounts of magnesium stearate. The large spot analyzer provided significant advantages over the near-infrared system on the basis of reliability, stability, and simplicity.

(255) **Assessing Laboratory Performance for Trace Element Analysis of Clinical Matrices: Experience of The New York State Proficiency Testing Program**

Patrick Parsons[1], Ciaran Geraghty[1], Michael Minnich[1], Christopher Palmer[1], Mary Fran Verostek[1]; [1]New York State Department of Health

The assessment of laboratory performance via interlaboratory studies is an important tool in the overall quality assurance (QA) plans of clinical laboratories. In many countries, such studies are called Proficiency Testing (PT) programs, while in others they are called External Quality Assessment Schemes (EQAS). A number of PT/EQA schemes are available for clinical laboratories that specialize in trace elements analysis. In the US, the New York State Department of Health has offered a PT program for selected trace elements in whole blood, serum and urine since 2001. This paper reports the main findings to date, and on the current performance of methods based on atomic spectrometry in clinical laboratories participating in the NYS program. In addition, this paper compares the approach and experience of the NYS program with that of EQA schemes for trace elements in whole blood, urine and serum operated by (1) L'Institut national de santé publique du Québec (INSPQ), Centre de toxicologie du Québec (CTQ), Canada; (2) the Trace Elements External Quality Assessment Scheme (UK TEQAS), operated by the University of Surrey, UK; and (3) the German External Quality Assessment Scheme (G-EQUAS), operated by the Institute and Outpatient Clinic for Occupational, Social and Environmental Medicine of the Friedrich-Alexander University, Erlangen-Nuremberg, Germany. The results of this comparison will show how different EQA schemes are optimized for clinical laboratories using different analytical methods.

(256) **CDC's Biomonitoring of Trace and Toxic Metal Exposures in the U.S. Population: Analytical Methods and Exposure Results.**

Kathleen L. Caldwell[1], Robert L. Jones[1], Jeffery M. Jarrett[1], Carl Verdon[1] ; [1]Centers for Disease Control and Prevention

The Centers for Disease Control and Prevention (CDC), Division of Laboratory Sciences (DLS) is using state-of-the-art biomonitoring techniques to accumulate exposure data. Lead, mercury and cadmium are being measured in whole blood. Antimony, arsenic, barium, beryllium, cadmium, cesium, cobalt, chromium, iodine, lead, mercury, molybdenum, nickel, platinum, thallium, tungsten and uranium are measured in urine. The urine metals are currently measured with an Inductively Coupled Plasma Dynamic Reaction Cell Mass Spectrometer (ICP-DRC-MS) or high resolution (HR)-ICP-MS. These methods can be utilized to rapidly screen urine specimens from people suspected to be exposed to a number of toxic elements or to evaluate environmental or other non-occupational exposure to these elements. Whole blood is used to determine the exposure to both total and inorganic mercury. The inorganic mercury method uses an automated flow injection system. Due to the interest in possible mercury exposures to people from fossil fuel power plants (elemental, inorganic and methyl), dental amalgams (elemental and inorganic), fish eating (methyl)

and vaccines (ethyl) it is critical that we are able to measure these forms of mercury in people (blood) with specificity, sensitivity and at a high volume of samples per year. We are investigating the use of an HPLC-ICP-DRC-MS method that we anticipate will enable CDC to measure inorganic mercury, methyl mercury and ethyl mercury in whole blood. Cadmium, mercury (total) and lead in whole blood are currently by ICP- MS. Serum metals; copper, zinc and selenium are also being measured with ICP- DRC-MS. Recent research and development work has enabled us to include speciated arsenic in the national population survey. \r\n\r\nThe current (1999-present) National Health and Nutrition Examination Survey (NHANES) is a continuous survey that enrolls about 5000 persons per year to represent the U.S. population. Results of the Third National Report on Human Exposure to Environmental Chemicals (www.cdc.gov/exposurereport) will be presented as well as the application of these state-of-the-art clinical chemistry "biomonitoring" methods on exposed (or suspected exposed) populations will be discussed.

(257) **Arsenic and Other Contaminants in New Hampshire Well Waters.**

Brian Jackson[1], Margaret Karagas[2]; [1]Dartmouth College, [2]Dartmouth-Hitchcock Medical School

In the northeastern US, above average mortality rates for bladder cancer occurred between 1950-1994. Environmental factors such as drinking water quality have been investigated as a possible causative factor. Over 40% of households in New Hampshire receive their drinking water from private bedrock wells and studies have shown that geogenic As levels > 10 µg/L occur frequently and are related to the prevailing bedrock geology. Here we present data for an expanded suite of elements occurring in New Hampshire well waters and present speciation data for aqueous As. Additional preliminary data is presented for total and speciated As in urine samples from New Hampshire residents. HPLC-ICP-MS is used for As speciation and As(III), As(V), DMA(V), MMA(V), MMA(III) and As(V) are considered as analyte species. The use of diethylammonium dithiocarbamate (DDDC) as a preservative for MMA(III) in urine is investigated.

(258) **Contamination Issues During Sample Collection and Analysis of Clinical Samples.**

Anastasia Skipor; Rush University Medical Center

One of the major concerns with clinical samples in regard to trace metal analysis is contamination of the sample(s) during collection, separation or pretreatment and analysis. In this session various routes of contamination and its prevention will be presented.

(259) **Transferability of Serum Aluminum Determinations by Electrothermal Atomic Absorption Spectrometry and Continuum Background Correction**

Pamela Kruger[1], Shida Tang[2], Patrick Parsons[1,2]; [1]University at Albany, [2]New York State Department of Health

Elevated concentrations of aluminum (Al) in human serum can cause serious health problems in people with impaired renal function, especially those on kidney dialysis. Adverse health effects such as dialysis encephalopathy, cognitive damage, adolescent learning disabilities, infant brain function impairment, brain damage of exposed workers, and Alzheimer's disease are associated with Al exposure. Electrothermal atomic absorption spectrometry (ETAAS) is a popular technique for assessing exposure to Al via serum Al measurements. Analytical performance of three different background correction systems was compared for the determination of serum Al in human reference samples by ETAAS. The following ETAAS instruments were compared: a Perkin Elmer (PE) Model 3110 AAS with a longitudinally- (end-) heated graphite atomizer (HGA) and continuum-source (deuterium) background correction; a PE Model 4100ZL AAS with a transversely-heated graphite atomizer (THGA) and longitudinal Zeeman background correction; and a PE Model Z5100 AAS with a HGA and transverse Zeeman background correction. An established method for serum Al determination was successfully transferred from the Z5100 and 4100ZL instruments to the 3110 instrument. Matrix-matched calibration was not required for any of the AAS instruments and, thus, aqueous standards were used throughout the study. When operating the 3110 instrument at the 309.3-nm line, the characteristic mass (m0) was 12.1 ± 0.6 pg. By comparison, operating the Z5100 and 4100ZL instruments at the 396.2-nm line yielded m0 = 16.1 ± 0.7 pg and m0 = 23.3 ± 1.3 pg, respectively. Calculated instrumental detection limits were 3.0, 3.2, and 4.1 µg/L for the Z5100, the 4100ZL, and the 3110, respectively, while the corresponding method detection limits were found to be 9.8, 6.9, and 7.3 µg/L. Archived serum and plasma reference materials were analyzed to assess the accuracy and precision of the three instruments. Serum Al values found for each AAS instrument were within the tolerance limits established for this analysis. No statistically significant differences were noted between any of the instruments for either accuracy or precision. Results obtained suggest that all three instruments are viable options for routine clinical determinations of serum Al.

(260) **Microfluidic Detection of Amphetamines using Laser Induced Fluorescence Detection**

Carla Turner[1], Bruce McCord[1]; [1]Florida International University

Drug Facilitated Assault is a very difficult crime to prosecute because victims are unable to recall events, and concentrations of implicated drugs are low. Current methods are not sensitive enough to detect these drugs. Capillary electrophoresis offers efficiencies far surpassing those of chromatographic techniques, but sensitive detection is still needed. Microfluidic systems are miniaturized forms of CE embedded in a small chip. Samples can be highly concentrated because only a few µL are needed for injection. UV detection is difficult with CE due to short path lengths, but LIF is extremely sensitive because fluorescence is directly proportional to the intensity of the incident light. While most drugs are not naturally fluorescent, basic drugs can be derivatized with amine-reactive dyes. A series of rhodamine-based dyes have been evaluated for reactivity with the drugs and sensitivity of detection. Separation and detection on the microfluidics system can be achieved in under 2 minutes and could allow for very rapid screening of these drugs in clinics and toxicology laboratories.

(261) **Optimization of Non-Contact Human Scent Evidence Collection**

Paola Prada[1], Allison Curran[2], Kenneth Furton[1]; [1]Florida International University, [2]ORISE, FBI Academy

In the US, law enforcement agencies typically utilize sorbent collection methods including direct contact as well as non-contact methods involving dynamic headspace concentration. One non-contact method involves the use of a field portable vacuum device known as the Scent Transfer Unit (STU-100) to collect human scent evidence from objects at a crime scene. Human scent evidence can be evaluated through the use of a canine to associate a suspect with the object or location where a scent pad was created. The STU-100 uses dynamic air flow to capture human scent from the object of interest onto a sterile gauze medium. The Scent Transfer Unit allows for the ability to perform non-contact sampling and collection of human scent from objects without contaminating or altering the object of interest. The materials and the methodology employed for scent collection have not been

previously optimized or standardized within the law enforcement community. This study presents various laboratory experiments designed to optimize sample collection methods with a focus on enhancing the reliability of the Scent Transfer Unit as an instrument for collecting human scent evidence. The STU model used in this project has been modified to include a Teflon coated hood and an air flow controller. Sterile gauze mediums, both natural and synthetic, were compared through headspace solid phase micro-extraction gas chromatography / mass spectrometry (SPME-GC/MS) to determine the material with the lowest chemical background. The nine different airflow rates were evaluated to establish the speed which will produce the greatest trapping efficiency by using a standard mixture of compounds, which vary in functionality and include a range of molecular weights. Further optimization of collection procedures incorporated varying the environmental conditions in order to determine the absorption and desorption capabilities of the tested collection medium as well as the optimization and evaluation of various types of natural and synthetic blends of sorbent material.

(262) **Optimized Analysis of Triacetone Triperoxide by GC-MS**

Doug Clark[1], Michael Sigman[1]; [1]National Center for Forensic Science at UCF

The explosive triacetone triperoxide (TATP) has been analyzed by gas chromatography – mass spectrometry (GC-MS) using both electron ionization and chemical ionization to give sub-nanogram detection limits. Ammonia and Methane were used as chemical ionization reagent gases. Analysis by positive ion chemical ionization (PICI) with Ammonia as the reagent gas gave sub-nanogram levels of detection, while PICI analysis with methane as the reagent gas gave detection limits in the low nanogram range. Analysis by negative ion chemical ionization (NICI) also gave low nanogram detection levels with both methane and ammonia reagent gases. Low detection limits were achieved by optimizing both gas chromatography and mass spectrometry operating parameters Analyses were carried out on linear quadrupole and quadrupole ion trap instruments. Analysis of TATP by PICI GC-MS using ammonia reagent gas is the preferred analytical method, producing lower limits of detection as well as an intense m/z 240 diagnostic adduct ion corresponding to [TATP + NH4]+ (base peak on quadrupole, and 60% of base peak for ion trap). Isolation of the [TATP + NH4]+ ion in the ion trap with subsequent collision induced dissociation (CID) produced weak daughter ions (m/z 168, 132, & 115). Density functional theory calculations at the B88LYP/DVZP level gave a [TATP + NH4]+ binding energy of 25 kcal/mol, which is 11 kcal/mol lower than the peroxide bond energy (36.5 kcal/mol). This result suggests that the [TATP + NH4]+ ion may dissociate under CID, rather than fragmenting the TATP moiety. The calculations also showed an energy difference between [TATP + NH4]+ and [TATP + H]+ + NH3 to be 23 kcal/mol and that the structure of the [TATP + H]+ ion had an excessively long C-O bond (2.605 A). Our CID results are in agreement with our calculations, which suggest dissociation of the complex to form NH4+ and TATP at energies lower than peroxide bond dissociation in the mass spectrometer. The results of our experiment provide a method for pico-gram detection levels of TATP using commercial instrumentation commonly available in forensic laboratories.

(263) **Analysis of Fatty Acids Ethyl Esters by Fast-Gas Chromatography-Mass Spectrometry**

Olivier L. Collin[1], Carolyn M. Zimmermann[1], Glen P. Jackson[1]; [1]Ohio University

Forensic hair analysis has been used for many years as an analysis tool for the detection of drugs of abuse and other substances. Recently, it has been reported that hair analysis can be used to trace alcohol abuse via the detection of fatty acids ethyl esters (FAEE), which are produced by the esterification of free fatty acids by ethanol. FAEE have also been used as biological markers for exposure to alcohol in utero in the hair and meconium of newborns, which is a potential indicator of Fetal Alcohol Syndrome (FAS). This project aims at developing a fast-gas chromatography-mass spectrometry (fast-GC-MS) method for the analysis of FAEE. The advantage of faster chromatography will be the higher sample throughput and lower limits of detection. Separation of the different FAEEs is conducted using a microbore capillary column combined with a fast temperature ramp. The narrower column offers higher separation efficiency and narrower peaks, which in turn requires faster data acquisition. A quadrupole ion-trap mass spectrometer (QIT-MS) is used for the analysis, but the scanning parameters of the instrument require modification in order to accommodate the timescale of fast-GC. The scanning rate is therefore increased by a factor of 6 to insure that sampling frequency provides a sufficient number of mass spectra per chromatographic peak. The effects of the faster scanning rate on the mass resolution and on spectral identification will be discussed, as well as the impact on limits of detection and overall analysis efficiency. Preliminary data for a series of biologically relevant FAEE will demonstrate that the limits of detection are at the least comparable to those currently achieved with standard chromatography. The analysis of standards and real samples will also demonstrate that new fast-GC-MS method offers the same discriminatory capabilities as standard protocols explored so far.

(264) **The Affect of PCR Inhibitors on The Amplification of Low Concentrations of Template DNA Using Reduced-Size STR Primer Sets**

Kerry Opel[1,2]; [1]Florida International University, [2]Center for Neurological Diseases

The presence of source contaminants commingled with DNA template presents a challenge in forensic human identification. The effects of these compounds on the PCR reaction can vary from attenuation to complete inhibition of the amplification reaction. PCR inhibitors can be endogenous or exogenous to the reaction. Endogenous contaminants usually originate from insufficiently purified DNA template, and the inhibitor is co-extracted with the target DNA during the extraction or purification step. Exogenous contaminants arise due to improperly controlled hygienic or laboratory conditions. This project covers the effect of inhibitors on the reduced size STR Miniplex primer sets. The Miniplex primer set produces smaller amplicons, and increases the probability of obtaining a usable profile from degraded DNA. Since the presence of inhibitors can affect the amplification efficiency of any primer set, we initiated studies to determine if the decreased amplicon size would affect the level of inhibition or the concentration at which it occurs. For this study, inhibitors which may be present in the sample itself were examined. These inhibitors can commingle with the DNA sample upon exposure to different environmental conditions. Although a wide range of PCR inhibitors have been reported, six common PCR inhibitors known to affect forensic samples were chosen for these studies: 1) hematin, from blood; 2) indigo, a denim dye; 3) melanin, from pigment in skin and hair; 4) humic acid, from soil and other environmental samples; 5) collagen, from bone; and 6) calcium, a component of bone samples. The inhibitors were tested singularly and in combinations which are likely to be present in forensic samples. Studies were also performed to determine the effect of lower template concentrations on the threshold inhibitor concentration. Three concentrations of inhibitors were tested on different levels of DNA template for each of the Miniplex primer sets. The level of inhibition for each locus and each concentration was calculated and

the results were compared. Finally, combinations of inhibitors which could be found in forensic samples were studied. These were used on different template combinations, and the level of inhibition was calculated and compared between sets and loci.

(265) **The Development of a Hierarchical SNP Typing System to Predict Ethnogeographic Ancestry using Pyrosequencing Technology**

Lynn Sims[1,2], Dennis Garvey[3], Jack Ballantyne[1,2]; [1]National Center for Forensic Science, [2]University of Central Florida, [3]Gonzaga University

The ability to determine ethno-geographic origin of an individual can potentially provide descriptive information of an unknown individual who deposited a biological stain at a crime scene, therefore, serving as a genetic eyewitness. This can potentially be accomplished with the careful selection of population-of-origin specific Y chromosomal single nucleotide polymorphisms (Y-SNPs). Single nucleotide polymorphisms (SNPs) are the smallest and most abundant type of human DNA polymorphisms, occurring ~every 1 kb in DNA. Y-SNPs are increasingly becoming important due to their paternal inheritance, lack of recombination, abundance, and low mutation rate and have been investigated for use in determining population structure and potential for individualization in forensic science. Currently, many of the well characterized Y SNP markers do not distinguish between major populations within the haplogroup. In order to distinguish between some of the major population groups in the United States and increase the discrimination potential of Y-SNPs, the need to find additional genetic markers that can divide the large distribution of individuals belonging to these haplogroups is essential. Here we report 12 new Y-SNP markers, 7 of which create additional paternal lineages. Several methods are available for SNP genotyping, but many do not allow high throughput multiplexing or are not sensitive. Pyrosequencing is our method of choice for detection primarily because the DNA sequence of the region flanking the SNP is detected providing an advantage, with respect to quality control, over other methods. Previously, we have shown that pyrosequencing can be used for hierarchical multiplexing and can detect 5 pg of DNA with a nested PCR amplification strategy. We will describe the technology in detail and the development of a hierarchical Y-SNP typing system using a combination of nested PCR and pyrosequencing, we intend to employ upon selection of the most informative markers.

(266) **Transferring Calibrations and Libraries for Pharmaceutical Analysis in Near-Infrared Spectroscopy**

Tony Moffat; The School of Pharmacy, London

Transferring data from one near-infrared (NIR) spectrometer to another is often required and often unsuccessful. Even libraries generated on one instrument may not transfer when major parts of a spectrometer are changed requiring the library to be re-run from scratch. Understanding what has changed and how these changes may be compensated is not always straightforward. We have developed wavelength correction procedures to transfer libraries between different types of spectrometer for the identification of pharmaceutical excipients and actives which has been successful. We have also developed a procedure and a series of criteria for successful transfer of quantitative calibrations and demonstrated their successful use in practice using a number of real pharmaceutical examples. Calibration transfer was demonstrated between dispersive instruments in reflection mode for paracetamol tablets 500mg (84% m/m active) with a root mean standard error of prediction (RMSEP) of 0.51% m/m. An NIR assay for a product with less active, piroxicam tablets (38% m/m active), was developed using transmittance on two dispersive instruments and gave a RMSEP of 0.73% m/m on the second instrument. Finally the method was used to transfer a transmission calibration made on a laboratory FTIR instrument for atorvastatin tablets containing only 6.6% m/m active to a dispersive instrument and a process FTIR instrument. A RMSEP of about 0.07% m/m was obtained. The procedures used included a wavelength selection procedure as well as a mean spectrum correction method. Only 12-15 samples are necessary to transfer the calibration so long as they are spread across the required concentration range. Work is progressing on the use of chemical reference materials instead of using the pharmaceutical product so that the same reference materials can be used across the world for both refection and transmission measurements. The ideal situation would be for a pure material to be bought anywhere in the world, but otherwise for stable reference materials to be produced by standards agencies.

(267) **Interferometers vs Imaging Spectrometers for NIR Applications**

Franklin Barton[1], James de Haseth[2], David Himmelsbach[3]; [1]USDA,ARS,Russell Research Center, [2]University of Georgia, [3]USDA,ARS, Russell Research Center

For the past few years we have been examining a number of options for small, rugged NIR instruments to be used for field and factory applications. While there are many applications in factories with in line and at line dispersive spectrometers, none require high resolution. Recent studies with “sticky cotton” have demonstrated the usefulness of high (4cm-1) resolution. The instruments we have examined come from several families of instruments, some are process control interferometers, some are small instruments used for field analysis and some are purpose built imaging spectrometers. The process control interferometers have the best chance for success since they parallel the research grade interferometers on which the application was developed. The small field use interferometers have comparable resolution, but lower S/N. The imaging spectrometer has neither advantage, but seems to make up for it in the spatial dimension. Other aspects of instrument design and function such as light throughput and imaging area will be discussed with reference to the Standard Error of Performance of the models.

(268) **Consistent Background Reference for NIR Reflectance Spectroscopy – How and Why it Aids in Model Transfer**

William Muller; FOSS NIRSystems, Inc.

Reflectance NIR spectroscopy has long suffered from lack of a consistent 100% reflectance background reference. Various techniques come close, yet suffer from inconsistency in reflectance value and planar positioning between instruments. This produces sample spectra that show the baseline effects of the background reference material that is unique to the instrument upon which the sample was scanned. Because each background reference has a unique spectral fingerprint, transferability of reflectance spectra between instruments becomes tedious and may require a variety of spectral adjustments. At worst, such a reference may be less reflective than some white powders, producing a condition of “negative absorbance” that is theoretically impossible in spectroscopy. Various techniques are used to handle the problem. The most common method is to ignore the problem and pretend that it does not exist. Other methods include use of 99% Spectralon™ as a background reference material, or various standardization methods using a central master instrument. While better than nothing, these methods have drawbacks. 99% Spectralon is not 100% reflective, and it has a large peak at about 2130nm. Master instrument schemes generally depend upon methods used, and on upkeep and availability of the master instrument, which can be problematic. \r\nAn innovative method is

the use of a traceable reflectance standard which is used to spectroscopically "map" the instrument background reference material on a scale of 0-100% reflectance, or, alternatively, on an absorbance scale. Once the instrument background reference material is spectroscopically mapped, the correction may be mathematically applied by software to produce a spectrum that is correct based upon a 100% reflective background reference material. This method is built upon use of traceable reflective reference standards, careful measurement of the instrument background reference material, and clear, straightforward software methods to apply the correction.\r\nReflectance spectra will be displayed to illustrate several of the problems involved, using common samples. Spectral differences due to background reference material and position will be shown. The same samples will be scanned in the same instruments, after performing a correction called "Reference Standardization". The consistency of the sample spectra will illustrate the reliability and power of the technique.

(269) **Wavelength Selection with Applications to Molecular Spectroscopic Data**

Dongsheng Bu; Camo Software Inc.

This paper discusses factors and considerations in applying several published methods for enhanced regression, the Norris Regression, moving window partial least squares (MWPLS), and searching combination moving window partial least squares (SCMWPLS). These methods enable the construction of better regression models than those based on whole spectra. A review of these methods is given, followed by results from testing on two near-infrared spectroscopic datasets. This paper also proposes new approaches to improve Norris Regression and SCMWPLS. Reducing calculation time and limiting user interaction are issues that are under investigation. For Norris Regression, programming for automatic search and optimization is provided for the determination of the numerator and denominator positions, gap size of Norris Derivative and smoothing segment size. To modify SCMWPLS, several issues are discussed, such as, determining moving window size by bandwidth, screening wavelength region candidates by RMSEC and PC number, and searching wavelength region combination by spectral intrinsic factors. Two well known datasets and applications, NIR data for milk percent fat modeling and Near Infrared spectra of beer were used in the study.

(270) **Expanding The Power of NIR by The Internet Technology**

Ching-Hui Tseng[1], Nan Wang[2]; [1]Cognis/QTA, [2]Cognis/QTA

Near infrared (NIR) technology has been demonstrated to be a powerful analytical tool in many industrial fields. The power of this technology is not just from the instrument itself but the calibration models used to do the analysis. Normally, a user has to purchase a NIR system and develop the application models before it can do any analysis work. Knowledge of spectroscopy and Chemometrics are the key factors of a successful NIR application. It really limits the power and the popularity of this technology. \r\nWith the highly-developed Internet technology, a plug-and-play NIR system with unlimited ready-to-use calibration models becomes a truth. There is no need for expert. A vending machine type of NIR analyzer can be used in a plant, in a farm, in a lab, in a pharmacy store, in a hospital, in a grocery store, or even in a mini Van as a mobile analytical lab. The client NIR units can be everywhere in the world. The calibration models are seated in the central processor. The user can go shopping from the model database via Internet and start the analysis anytime they need. The spectral quality and the instrument performance are monitored by the experts via Internet. The use of NIR becomes very easy. An example of this kind of NIR system with hundreds of ready-to-use calibration models successfully used by many industries will illustrated in this presentation.

(271) **Chip-Based Nanoelectrospray Employed with Conventional Dimension LC/MS Analyses**

Jack Henion[1], Gary Schultz[1], Ellen Pace[1]; [1]Advion BioSciences

Mass spectrometry (MS) is an essential tool in modern research and applied analytical laboratories. Its critical role in the drug discovery/development process cannot be overstated. LC/MS is well-known to provide valuable quantitative and qualitative information on molecules of biological importance. It can provide high throughput analysis capabilities for quantitative analyses, but it can also provide rapid, efficient qualitative characterization of unknown molecules ranging from metabolites to biologics including peptides and proteins. A relatively new area with huge potential is the detection and determination of biomarkers in complex biological samples. Unfortunately no one currently has an optimal strategy for addressing the challenges afforded by detecting and characterizing potentially important biomarkers. It is likely that a combination of strategies, analytical tools, and techniques will be required to address these challenging analytical needs. Our proposed strategy for tackling the challenges of a huge dynamic range in extremely chemically complex samples is to 'divide and conquer' the sample. This means employing minimum or no sample preparation to avoid losses of important unknown compounds, but multi-dimensional separation sciences and multi-dimensional mass spectrometry techniques to drill into the sample. This strategy is provided in part with the TriVersa NanoMate which provides on-line, full-scan LC/MS with simultaneous fraction collection to 'archieve' the chromatogram for subsequent further interrogation via MS and MS/MS. This presentation will highlight the use of conventional HPLC columns and conditions but with nanoelectrospray LC/MS, but with a post-column split for fraction collection and subsequent in depth MS/MS characterization.

(272) **Transforming Nano-LC/MS using Microfluidics Technology**

Tom van de Goor; Agilent Technologies

Nano LC/MS has become one of the methods of choice for high sensitivity, sample limited applications epecially in the area of Proteomics and Biomarker Discovery. It offers the ability to handle small amounts of sample with the least amount of dilution, thus allowing the highest sensitivity. The adaptation of this technology has however been limited to expert users due to the high complexity of the analytical method and the limited robustness of the instrumentation. The use of microfluidics technology has changed this situation. A chip based nano LC/MS system has been developed that significantly reduces the number of connections needed between the enrichment column, analytical separation column and nano electrospray emitter. This reduces band broadening due to dead volume in the system, the risk of leaks, the chance of clogging and the need for manual optimization of the position of the nanospray emitter and therefore makes nano LC/MS accessible to a broader user base. An overview of the microfluidic approach will be given and applications of the technique will be shown in the area of Proteomics. Specific examples for Protein Identification in complex mixtures, Protein Profiling for Biomarker Discovery and Protein Characterization will be used to show the advantages of the microfluidic approach in terms of sensitivity and speed of analysis.

(273) **Antibody- and Mass Spectrometry-Based Peptide Chip Technology for Clinical Diagnostic**

Christoph Borchers[1], Jian Jiang[1], Carol Parker[1], Tom Kawula[1]; [1]University of North Carolina at Chapel Hil

We have developed a peptide chip technology, based on affinity enrichment using immobilized anti-peptide antibodies and MALDI-MS, for detection and quantitation of protein expression level. In our approach, anti-peptide antibodies are immobilized on affinity beads and then incubated with the proteolytic digest of a proteome of interest to immunoprecipitate (IP) the epitope-containing target peptides. After IP, these antibody beads are arranged in a microarray format on a MALDI target plate permitting the direct MS and MS/MS analysis of all affinity-bound peptides after addition of matrix solution. In several proof-of-principle experiments we have demonstrated its high sensitivity (attomole range), capability for absolute specificity (because of the determination of the targeted peptide's MW by MS and its sequence by MS/MS). Furthermore, this technology is safe, is capable of absolute quantitation using isotopically-labeled epitope-containing peptides as internal standards, and has multipex and high-throughput capabilities. This technology is being used to develop diagnostics for bacteria, including the NIAID Category A pathogen Francisella tularensis (F.t.), and for cancer-related proteins in clinical specimens.\r\nFor the F.t. chip, an antibody was raised against a peptide of the F.t. protein p23, which shows great sensitivity in the MALDI-MS and is absolutely specific for F.t. This chip is capable of determining quantitatively colony forming units (CFU) of F.t. in environmental samples (ca. 10 CFU) and serum (a few hundreds CFU) by the addition of isotopically-labeled p23-peptide. This approach is as sensitive as PCR, and we are extending the application of the F.t. peptide chip for detecting F.t. in other clinical specimens, including nasal swabs and urine sample, which are more useful for screening large populations. For the development of a cancer peptide chip we are using both commercially-available (e.g., anti-PSA) and customized antibodies. For example, using a customized EGFR-peptide antibody, our chip is capable of determining EGFR in the low attomole range in buffer and in less than 100 mammalian cells. Currently, we are in the process of developing a peptide chip for detecting the expression and modification levels of proteins involved in signaling pathway, which will be useful for molecular diagnosis and ultimately for predication of clinical therapy.

(274) **Matrix-Free Approach to Laser Desorption Ionization Using Silicon Microcolumn Arrays**

Mazdak Taghioskoui[1], Yong Chen[1], Akos Vertes[1] ; [1]The George Washington University

Matrix-assisted laser desorption ionization (MALDI) is an essential method for the mass spectrometric analysis of biomolecules and synthetic polymers. Due to matrix interferences in the low mass range and the complexities of sample preparation in MALDI, there is a need to develop matrix-free laser desorption ionization methods. Microcolumn arrays with nanoscopic features were formed on a silicon wafer by repeated exposure to 22 ps laser pulses from a frequency tripled mode-locked Nd-YAG laser. The morphology of microcolumn arrays varied with the processing environment, laser pulse length, and the number of pulses. These laser-induced microcolumn arrays (LISMA) demonstrated unique performance as a platform for soft laser desorption ionization of biomolecules and synthetic polymers. Ion yield, internal energy transfer and fragmentation studies indicated that silicon microcolumn arrays offered unique advantages. Using a nitrogen laser for the desorption experiments, the mass range extended up to 6000 Da and the sensitivity down to low femtomoles. For peptides and their mixtures at low laser fluences quasi-molecular ions were observed in the mass spectra. At elevated laser fluences, controlled fragmentation offered structural insight. contrast to MALDI, in which matrix molecules provide the protons for analyte ion generation, laser desorption ionization using silicon microarrays require an external proton source for the ionization process. Two potential sources of hydrogen ions upon laser exposure of LISMA surfaces are the H-Si groups and the solvent residues trapped in the cavities between the microcolumns. To decide if the hydrogen atoms originate from the laser processing of silicon under water or from the deposition of the sample solution, experiments with heavy water were conducted. The production of the LISMA structure in deuterium oxide did not result in deuterated peptide ions, whereas using heavy water as a solvent shifted the ion mass by one Dalton. As the process for producing the microcolumn arrays does not involve special micro-fabrication techniques, the structure shows high potential for use in laser desorption ionization of biomolecules. The feasibility of producing LISMA with simple post process fabrication on silicon makes it suitable for integration in miniaturized analytical devices.

(275) **A Proteomics Chip for MALDI Mass Spectrometry**

Kermit Murray[1], Harrison Musyimi[1], Jeonghoon Lee[1], Hamed Shadpour[1], Steven Soper; [1]Louisiana State University

We are developing a microfluidic chip platform for the analysis of complex protein mixtures using MALDI mass spectrometry for detection. A multidimensional chip separation system is being developed on polymethyl methacrylate (PMMA) microfluidic chips. The capillary gel chips are fabricated from PMMA wafers using a high-speed micromilling machine. The target microfluidic system is a multidimensional separation of peptides formed by the tryptic digestion of proteins. Proteins are separated on the chip in two dimensions: capillary gel electrophoresis (CGE) and micellar electrokinetic chromatography (MEKC). The proteins will be delivered to channels with immobilized trypsin for digestion and the resulting peptides are separated using capillary electrokinetic chromatography (CEC). On-chip conductivity detection is used to monitor the separation progress after the CGE and MEKC separation. Both on-line and off-line interfaces are being developed. This on-line interface is based on a rotating ball inlet, which transfers the output of the microfluidic chip into the vacuum of a time-of-flight (TOF) mass spectrometer. The chip effluent is deposited directly onto the rotating ball that has been coated with a narrow stripe of matrix using a separate capillary and the sample deposited on the ball is rotated past the gasket and into the high vacuum region for ionization. In the second approach, the sample processing is done on the chip, which is later loaded into the mass spectrometer for off-line processing. Results from the above MALDI microanalysis systems will be presented and the outlook for off and on-line microanalysis will be discussed.

(276) **Introducing High-dimensional Hybrid Wavelet Transforms for Optimized Chemometric Analyses of Spectroscopic Imaging Data**

Frank Vogt[1], Robert Luttrell[1], Michael Gilbert[1]; [1]University of Tennessee

In recent studies we have demonstrated that chemometric algorithms can be optimized regarding computation time and model quality by introducing wavelet compression. For high-dimensional data sets -for instance, as acquired in spectroscopic imaging- multi-dimensional wavelet transforms had to be employed. However, such high-dimensional data sets combine different types of measurement data (e.g. spatial and spectroscopic information). Consequently, conventional wavelet transforms utilizing the same wavelet for all dimensions are inherently suboptimal. In order to overcome this limitation, we propose "hybrid wavelet transforms"

which utilize different 1D wavelets for different types of data. As straightforward as this approach appears to be at first glance, the selection of the optimum combination of wavelets is challenging. The most prominent reason is that due to the large number of available wavelet combinations an iterative approach trying out all possible combinations and subsequently picking the best one is highly prohibitive. Computation times for this approach would be without end and would most certainly annihilate the considerable reduction of computation time enabled by wavelet compression. We propose an approach for choosing the optimum hybrid wavelet which is based on randomly selecting a representative subset of the data (hyper)cube; focusing on a subset ensures reasonable computation times. For different applications different figures of merit become important. If time-resolution of an analysis is of uttermost importance, a high data compression must be achieved in order to avoid long computation times. In other applications some acceleration might be required but the quality of the chemometric model is ranked higher. In such cases information preservation during data compression becomes more important. Thus, our approach gives the user the opportunity to select "weights" for different figures of merit including acceleration of the chemometric algorithms, model quality and compression rate; the latter becomes most important when data storage imposes challenges. Our new algorithm determines the optimum (multi-dimensional) hybrid wavelet (= combination of different wavlets) by taking the user's choice into account. We present several examples that display the effectiveness and ruggedness of this algorithm.

(277) **Multivariate Analysis of 3D Hyperspectral Confocal Fluorescent Biological Images**

Howland Jones[1], David Haaland[1], Michael Sinclair[1], Roberto Rebeil[1], Linda Nieman[1], David Melgaard[1]; [1]Sandia National Labs

Multivariate Curve Resolution (MCR) has been a powerful technique for extracting pure component spectra and the relative quantitative concentrations from fluorescent hyperspectral images. Recently we have developed a 3D confocal hyperspectral fluorescent microscope for imaging and studying live biological cells. It has been a desire of many biologists to study live cells with several fluorophores simultaneously to obtain a complete understanding the biological mechanisms occurring within the cell of interest. Combining our 3D hyperspectral imager together with our fast and efficient MCR algorithms allows us to separate many overlapping fluorophores and create interpretable quantitative images, thereby providing a necessary tool for the biologists to study live cells. One challenge that we have with our image datasets is dealing with several noise sources associated with our hyperspectral microscope (shot, structured and read noise) which add errors to our MCR results (both concentrations and pure-component spectra). The structured noise source can distort the pure-component spectra, which ultimately impacts the final image by estimating the concentrations incorrectly. The resulting concentration errors can distort the final image by adding spurious spatial information into the image. For this presentation, I will give examples of several challenging hyperspectral images that were analyzed with MCR and which require innovative MCR analysis techniques to obtain quantitative images. I will also discuss the ramifications of the noise sources on our hyperspectral datasets and how they individually impact our MCR results. New methods to estimate the statistical significance of the concentration estimates for minor spectral components will also be presented. *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.

(278) **An Integrated Graphical User Interface to Facilitate the Visualization and Analysis of Hyperspectral Images**

Christopher Stork[1], David Haaland[1], Howland Jones[1], David Melgaard[1]; [1]Sandia National Laboratories

While hyperspectral imaging is increasingly being used to characterize biological systems and offers distinct advantages relative to multispectral imaging, it has proven difficult in practice to extract all of the useful information from hyperspectral images due to the overwhelming volume of data generated and the complexity of the acquired images. Multivariate curve resolution (MCR) has been proposed as a means to extract the spectral profiles and concentration distributions of chemical and physical components occurring in hyperspectral image sets. Typically, MCR is applied across all pixels or voxels in the hyperspectral image set, and, all too often, the analysis proceeds before the analyst has fully visualized and interrogated the data. In this paper, we highlight an integrated graphical user interface (GUI)-based software package designed to assist data analysts in the visualization of hyperspectral images, the selection of regions-of-interest (ROIs), and subsequent MCR analysis. The spatial and spectral data visualization tools incorporated into the GUI provide the user a means of gaining a better understanding of a given image set, thereby aiding the user in their analysis of the data. The GUI's versatile ROI drawing tools allow the user to select image sub-regions in which to perform MCR. The ROI selection tools incorporated into the GUI are critical in that the quality of MCR results can often be improved by restricting analysis to a subset of pixels. To demonstrate the utility of the GUI, we apply the integrated software package to biological images acquired using a three-dimensional hyperspectral confocal fluorescence microscope. The biological images acquired by this hyperspectral microscope are very complex, containing many spatially and spectrally overlapped components and problematic outlier voxels. We show that superior results can be obtained by restricting MCR to selected ROIs. The improvement in MCR results obtained through the use of ROIs is attributable to a reduction in rotational ambiguity and problem complexity, and improvement in the approximate weighting used to correct for the presence of Poisson-distributed noise in the image data.

(279) **Multivariate Curve Resolution and its Practical Use in Remote Sensing Applications**

Christine Wehlburg ; MITRE Corporation

The nomenclature "hyperspectral image" was one born from the remote-sensing community. In fact, the first tools that the chemometrics community put into use when infrared hyperspectral instruments became commercially available were those developed by the remote sensing community. Given their expertise in developing techniques for full spectrum analysis, it did not take long for the chemometrics community to leverage their own expertise and begin developing alternative algorithms for the analysis of hyperspectral images. Translating the usefulness of algorithms, such as Multivariate Curve Resolution (MCR), to the remote sensing community requires a commitment to understanding the unique challenges of collecting that data and finding practical implementations for use by the typical image analyst or scientist. Presented are a series of analyses performed on data with varying degrees of ground truth, known target signatures and variations in atmospheric correction. The different implementations of MCR and possible combinations with other established techniques provide insight in the potential of all the techniques to provide real solutions in the analysis of hyperspectral images that do not have the luxury of being collected under controlled conditions.

(280) **Genetic Algorithms and Wavelet Packet Transform for Spectral Pattern Recognition – Identification of Waxy Wheat by Near Infrared Reflectance Spectroscopy**

Barry Lavine[1], Nikhil Mirjankar[1], Stephen Delwiche[2]; [1]Oklahoma State University, [2]USDA-ARS, Beltsville Agriculture Research

The feasibility of using diffuse reflectance near infrared spectroscopy to classify durum wheat into its four possible waxy alleles was undertaken. A two-step procedure for analyzing complex near infrared data sets was developed. First, the wavelet packet transform was used to denoise and deconvolute the near infrared spectra by decomposing each spectrum into wavelet coefficients, which represent the sample's constituent frequencies. Second, a genetic algorithm (GA) for pattern recognition was used to identify wavelet coefficients characteristic of the wheat's genotype. The pattern recognition GA employed both supervised and unsupervised learning to identify features that optimize clustering of the samples by class 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 features is about differences between wheat types in the data set. The principal component analysis routine embedded in the fitness function of the pattern recognition GA served as an information filter, significantly reducing the size of the search space since it restricted the search to feature sets whose principal component plots show clustering on the basis of class. In addition, the algorithm focused on those samples and or classes that are difficult to classify as it trains, using a form of boosting. Samples that consistently classify correctly were not as heavily weighted as samples that were difficult to classify. Over time, the algorithm learned its optimal parameters similar to a neural network. Our pattern recognition GA integrates aspects of artificial intelligence and evolutionary computations to yield a "smart" one pass procedure for feature selection, classification, and prediction.

(281) **SPR Measurements of Ion-Ion Repulsion Limited Self Assembly**

Roger Terrill[1], Shaowei Chen[2], Yong Nam Pak[3], Arthur Cheng[1]; [1]San Jose State University, [2]University of California at Santa Cruz, [3]Korean National University of Education

The effects of repulsion between anionic groups on the self-assembly of carboxyl-terminated alkanethiols was studied as a function of pH and ionic strength. Clear differences in both the extent and the kinetics of the assembly process were seen using surface plasmon resonance (SPR) and infrared spectroscopy. Controls were conducted using uncharged thiols as well as simple alkanoic acid anions. The electrostatics of headgroup interactions is a significant determinant of the apparent equilibrium layer thickness, and this influence increased at lower ionic strength. Electrostatic effects on alkanethiol self assembly offer novel insights into the thermodynamics of the layer formation process.

(282) **Characterization of In-Plane Laterally Varying Gradients of Polymer Films and Polymer Brushes by Surface Plasmon Resonance**

Xuejun Wang[1], Paul Bohn[1]; [1]University of Notre Dame

Surface plasmon resonance imaging was used to follow the preparation and characterization of in-plane laterally varying thickness gradients of poly(acrylic acid) (PAA) and poly(acrlamide) (PAAm) films and grafting density gradients of poly(N-isopropylacrylamide) (PNIPAAm) polymer brushes. PAA and PAAm gradients were formed by Zn(II)-catalyzed electropolymerization of acylic acid (AA) or acrylamide (AAm) in the presence of an in-plane electrochemical potential gradient applied to Au working electrodes. Grafting density gradients of PNIPAAm were generated through in-plane electrochemical desorption of uniform PNIPAAm polymer brushes, which were grafted on Au by atom transfer radical polymerization (ATRP). Our results indicate that polymer films thickness gradients or polymer brush grafting density gradients can be easily formed with tunable slope and transition region width in a wide range of physical sizes by combining electropolymerization or ATRP with electrochemical-potential-gradient-based method.

(283) **Microarray analysis of influenza virus with SPR imaging**

Quan Cheng[1], Guangyu Ma[1]; [1]University of California Riverside

Influenza is an acute respiratory disease caused by the influenza virus. The disease occurs annually, causing fatality in the elderly and children and billions of dollars loss in business and productivity. It was estimated that seasonal influenza A kills up to 1.5 millions people around the world. More seriously, a potential human pandemic is emerging as the H5N1 avian flu strain is circulating widely in Asia. A flu pandemic could bring human tragedy and a global economic catastrophe. Although the science and medicine of flu have advanced considerably since last pandemic, our ability to mount an effective public health response has made remarkably little progress over the decades. We will report our recent work in developing microarray sensors for influenza virus with SPR imaging analysis. The research has been focused on fabrication of highly effective antibody arrays for the virus and suppression of non-specific interactions at the interface. A full scale characterization of the microarray and its application in virus detection will be presented.

(284) **Fiber Optic SPR Sensor for Determining Salinity and Dissolved Organic Carbon in Coastal Waters**

Yoon-Chang Kim[1], Jeffrey Cramer[1], Hilairy Hartnett[1], Karl Booksh[1]; [1]ASU

The goal of this research is to develop and implement a real-time sensor that enables collection of data with sufficient spatial and temporal density to better understand the cycling and fate of terrestrial dissolved organic carbon (DOC) in coastal areas. In the coastal cities, the salinity is also an important property in many applications, such as leak detection for landfill liners, saltwater intrusion to drinking water, marine environment monitoring, and seasonal climate prediction. Conductivity sensors are the industry standard for determining salinity in ocean systems. Concurrently refractive index sensors, such as surface plasmon resonance (SPR) spectroscopy based sensors, respond both to salinity and DOC levels. A fiber optic SPR sensor has been employed in conjunction with conductivity meter. Together these platforms can differentiate between salinity and total DOC in coastal areas where both levels may be rapidly and independently changing. To demonstrate the capability of the SPR sensor and a conductivity sensor to collect complimentary data useful in discrimination of salinity and DOC in coastal zone water, conductivity, SPR, and temperature data were collected during passage from the Juan de Fuca ridge area to returning at the University of Washing docks. For conductivity, the research vessel Atlantis's salinometer was employed. The sea water from the intake that is located in the bow was available on the vessel. The sea water is delivered from the intake by pump with 50 gallons / minute. The temperature and conductivity probes are permanently mounted at the pump suction and are tied to ships data system. For the SPR data, the sensor was placed in the sea waters flow through the collection pump. Temperature data were collected at the point of measurement for conductivity and SPR sensors.

(285) **Surface Plasmon Resonance Sensors for Analyses in Biological Fluids**

Karl Booksh[1], Michael Malone[1], Jean-Francois Masson,[1] Tina Battaglia[1], Mergarette Barnhart[1]; [1]ASU

This presentation will focus on the development of a fiber optic Surface Plasmon Resonance (SPR) sensor that is capable of ng/ml detection of protein biomarkers in undiluted serum and selective quantification of small molecules in complex media. SPR spectroscopy has demonstrated great potential as a benchtop analyzer for determining concentration and binding kinetics of large biomolecules in relatively simple media. However, the transition to employing SPR as an in-vitro sensing platform for analyses in complex media such as serum or for smaller analytes such as glucose or ammonia has been difficult. Serum contains 30 mg/ml background proteins compared to ng/ml (or pg/ml) target proteins that serve as biomarkers for disease states such as heart attacks, strokes, or chronic wounds. Thus for in-vitro or in-vivo analyses a sensor must be very resistant to non-specific fouling while having a large affinity for the target analytes. A novel self-assembled monolayer coating has been developed that meets these criteria. Application for detection of proteins such as interleukins, tumor necrosis factor-a, survival of motor neuron protein, cardiac troponin, and myoglobin in relevant biological matrices will be demonstrated.

(286) **Sandwich SERS Substrates for Monitoring Germination of Bacillus Spores**

George Chumanov[1], Jacquitta Daniels[1], David Evanoff[1], Thomas Caldwell[1], Kenneth Christensen[1]; [1]Clemson University

Surface-enhanced Raman scattering (SERS) is a powerful analytical tool that is successfully applied for structure-functional characterization of a large variety of samples including small and large organic and inorganic molecules, (bio)polymers, viruses, and living cells. Nanostructured metal substrates capable of enhancing Raman scattering of adsorbed molecules is a cornerstone of this technique. The ongoing search for the best substrate is largely motivated by the necessity to have good reproducibility for different molecules. This paper describes the development of sandwich SERS substrates (3S) and their application to kinetics studies of the germination of Bacillus subtilis spores which are a benign model of Bacillus anthracis. The development takes advantage of the fact that spores of Bacillus as well as Clostridium species contain dipicolinic acid (DPA) that is released upon their germination and can be readily detected by SERS. 3S utilize the enhancement of the local field in the space between continuous Ag film and adsorbed Ag nanoparticles. The effect of excitation wavelength and nanoparticle size on SERS spectra was studied to optimize the substrates. It was determined that Raman enhancement resulted from the plasmon coupling nanoparticles to the electron density in the film and the lateral plasmon coupling between the nanoparticles themselves. 3S have the advantage of utilizing the optical properties of metal nanoparticles but without the problem of irreproducibility associated with aggregation of the nanoparticles in suspensions. 3S were used to measure the kinetics of the endospore germination at varying concentrations of L-alanine and different temperatures by monitoring the intensity of the Raman peak at 1010 cm-1 that is characteristic of DPA. The kinetics measurement revealed the sample heterogeneity. Different populations of spores begin germinate at different times and their germination is stimulated by different concentrations of the germinant. Initially, several hundred spores was sufficient to generate kinetics curves with low noise. However, further optimization of 3S and experimental conditions allowed the kinetics measurement from a single spore of B. subtilis. It is concluded that SERS on 3S is a method of general utility for detecting and studying the germination of Bacillus and Clostridium spores.

(287) **Near-infrared Fluorimetric Analysis of Single-Walled Carbon Nanotubes: Recent Progress**

R. Bruce Weisman; Rice University

With its high sensitivity, speed, and ability to identify the precise (n,m) structures of semiconducting single-walled carbon nanotubes (SWNTs), near-infrared fluorescence spectroscopy is emerging as the preferred method for incisive sample characterization. Recent refinements to this method will be presented, including a new data analysis process that provides improved speed and robustness, and the use of fluorescence-to-absorbance ratios to characterize sample dispersion and quality. Progress will also be described in a project to calibrate structure-dependent optical factors. When complete, this calibration should allow quantitative (n,m) distributions to be deduced from bulk optical measurements.

(288) **Combining DNA's Molecular Biology Tools with Single Walled Carbon Nanotubes for Purification & Assembly**

Jennifer Cha,; IBM Almaden Research Center

Due to their nanometer sizes and molecular recognition capabilities, biological systems have garnered much attention as vehicles for the directed assembly of nanoscale materials. One of the largest challenges of this research has been to successfully interface biological systems with electronic materials, such as semiconductors and metals. We demonstrate here that long genomic single stranded DNA (>>100 bases) of a completely random sequence of bases can be used to disperse CNTs efficiently through the single stranded DNA\'s (ssDNA) ability to form tight helices around the CNTs with distinct periodic pitches. While this process occurs irrespective of the DNA sequence, we show that this process is highly dependent on the removal of complementary strands. We also demonstrate that although the helix pitch-to-pitch distances remain constant down the length of a single CNT, the distances can be variable from one DNA-CNT and another. I will discuss our current research efforts and discoveries towards using genomic DNA for purification and separation of SWCNTs. I will also discuss our molecular biology techniques to modify long ssDNA for the purpose of directed assembly and placement.

(289) **Towards Chiral Pure Nanotube Samples**

Michael Heben[1], Timothy McDonald[1,2], Chaiwat Engtrakul[1], Jeffrey Blackburn[1], Garry Rumbles[1]; [1]National Renewable Energy Lab, [2]Columbia University

Collections of single-walled carbon nanotubes (SWNTs) with the same physical structure and electronic type are required for many applications. Unfortunately, current synthesis methods result in a distribution of metallic and semiconducting tubes with structure-dependent optoelectronic properties. \r\n\r\nIn order to study the nature of the binding between SWNTs and surfactant species we have developed a fast, versatile, Fourier-transform (FT) photoluminescence excitation spectrometer which is capable of excitation in the visible spectrum and detection of NIR emission. The instrument is well-suited for characterizing solubilized nanotubes, and its sensitivity and speed permits us to measure changes in the PL intensity as suspension equilibrate after having been diluted. By observing the the PL over time as the equilibration process process, at different temperatures, we can extract the surfactant/nanotube interfacial binding energy for a variety of surfactants, as a function of nanotube type. The SWNT PL emission also exhibits a diameter-dependent redshift and emission-width broadening which implies a greater tube-tube interaction as nanotubes come into closer contact with one another and rebundle. Large differences in binding energy are observed:

For example, in one aqueous surfactant the measured binding energy is 86 kJ/mol for one tube species and 7.6 kJ/mol for another. The observations lead to several strategies for chirality-selective purification of SWNT distributions, which will be discussed.

(290) **Silica Functionalization of Carbon Nanotubes**

Stanislaus Wong[1, 2]; [1]SUNY Stony Brook, [2]Brookhaven National Laboratory

Many applications utilizing single-walled carbon nanotubes (SWNTs) require their chemical modification in order to make them more amenable to rational and predictable manipulation. A novel strategy of altering the electronic properties of nanotubes is to chemically functionalize them with a moiety or structure which would allow for SWNTs to be incorporated into practical devices. One such molecular entity is silicon with implications for exciting electronics applications. We have explored a number of different strategies of linking silicon to nanotubes. One of the ideas pursued by our group has been to derivatize SWNTs with relatively bulky inorganic complexes. Another has been via the generation of nanotube-nanocrystal heterostructure assemblies. We will discuss our current, ongoing efforts towards rational silica functionalization of carbon nanotubes as well as relevant properties of these functionalized nanomaterials and their applicability to nanotube separation.

(291) **Understanding the Dispersion of Single-Wall Carbon Nanotubes for Effective Separations**

Kirk Ziegler[1] ; [1]University of Florida

Single-wall carbon nanotubes (SWNTs) have received great attention because of their unique electronic and mechanical properties combined with their chemical stability. However, most synthesis techniques for SWNTs result in polydisperse lengths. Separation processes to date rely on chromatographic or electrophoretic techniques. While these techniques have demonstrated some degree of separation, the nature of these approaches often limits them to analytical-scale separations. To effectively use carbon nanotubes for commercial applications, we need to develop economically feasible and scalable methods for separating SWNTs. Here, I will describe current cutting techniques to achieve short, cut nanotubes and then describe a two-phase liquid-liquid extraction process which is capable of extracting water-soluble SWNTs into an organic phase. The extraction utilizes electrostatic interactions between a common phase transfer agent and the sidewall functional groups on the nanotubes. The colloidal interactions between SWNTs, such as van der Waals interactions and steric repulsion, are important aspects that affect the ability to disperse SWNTs into the organic layer. Therefore, the large length-dependent van der Waals forces for nanotubes allow the ability to control the length of nanotubes extracted into the organic phase. Although several researchers have investigated the interactions of spherical particles, there are few studies that describe the van der Waals and steric interactions for 1-D nanotubes. The ability to describe these interactions will lead to improved dispersion of SWNTs and yield more efficient separations. In addition, improved understanding of the dispersion of SWNTs from these models will also improve the preparation of nanocomposites.

(292) **Biomimetic Polysoaps for SWNT Dispersion and Electric Force Microscopy Characterization of individual SWNTs**

Liwei Chen[1], Zi-Chen Li[2], Dan Wang[1], Ru Zhang[3]; [1]Ohio University, Dept. of Chem and Biochem., [2]Peking University, China, [3]Ohio Univ., Dept. of Phy. and Astronomy

Single-walled carbon nanotubes have exhibited extraordinary properties and showed great potentials in applications ranging from composite materials, nanoelectronic elements, chemical and biological sensors. A current challenge is to disperse SWNTs from naturally formed bundles and separate different species in the mixture.\r\nWe report here the design of polysoap surfactants that mimics the structure and the interaction of ssDNA with SWNT. The polysoaps contain ionic backbone and pyrene functionalized side chains. The aromatic pyrene moieties interact with the side wall of the nanotubes and the charged backbone at the exterior of the micelle stabilize the SWNT-polysoap complexes in aqueous environment. \r\nElectric Force Microscopy (EFM) is used to characterize the individually dispersed SWNT-polysoap complexes. EFM is a variation of atomic force microscopy. It measures the electrostatic field and dielectric responses (static dielectrics) of the sample by applying an AC modulated bias voltage while scanning over the sample at a lifted height. The method probes both the electrostatic charge and the static dielectrics at the same time and thus can be possibly utilized to study the charge screening effects of individual SWNTs. Metal nanoparticles can be assembled onto polysoap wrapped SWNTs and form controlled aggregated nanosystems. We also characterize these metal nanoparticle/ SWNT conjugates with EFM and discuss the interaction between the nanoparticle and the nanotubes.

(293) **Quantitative Biological Raman Spectroscopy**

Michael Feld; MIT

We are developing techniques based on Raman spectroscopy to extract quantitative chemical information in complex biological samples. We focus on blood analytes as a testing ground, with glucose as the target analyte. Data is collected transcutaneously (no needle stick). We have obtained accurate results in human volunteers and dogs. To make the technique truly practical, three technical challenges must be addressed: (1) obtaining large signals, (2) robustness (e.g. the measurement algorithm developed on one patient can be applied to others); and (3) strategies for obtaining accurate measurement algorithms. Our data collection geometry has been optimized to provide adequate s/n. To obtain robust spectral information, we are developing techniques to extract the intrinsic Raman spectrum. To obtain accurate measurement algorithms, we are developing techniques based on regularization in which accurate external spectral information are integrated into the calibration process.

(294) **Modelling, Testing and Improving the Depth Resolution of Confocal Raman Microscopy**

Michael Feld; MIT

Confocal Raman microscopy is a widely used technique for characterising chemical and physical structure with ~micron resolution [1,2]. In principle, transparent samples can be mapped with 1 micron depth resolution by focusing the laser beam below the sample surface and using a confocal aperture to reject out-of-focus light. However, in recent years the adverse effects of spherical aberration have been shown to degrade the resolution that is obtained when using a typically-configured Raman microscope [3]. The commonly-accepted methods for testing the resolution of a Raman microscope turn out to be invalid for testing instrument performance under realistic operating conditions. This presentation will discuss the problem of spherical aberration, will describe ways in which instrument performance can be improved, and most importantly, will suggest a number of simple standards that can be fabricated to calibrate the depth resolution when obtaining confocal spectra deep below a sample surface. The influence of parameters such as the birefringence of test samples will also be discussed [4]. 1 N J Everall, "Raman spectroscopy in Coatings Research and Analysis: Part I", JCT CoatingsTech, 2 (19), 38-44 2 N J Everall, "Raman spectroscopy in Coatings Research and Analysis: Part II",

JCT CoatingsTech, 2, (20) 46-52 (2005) 3 N Everall, "Depth Profiling with Confocal Raman Microscopy", Part I, Spectroscopy 19(10), 22-28 (2004), Part 2 Spectroscopy 19(11), 16-25 (2004) 4 N Everall, F Adar and A Whitley, to be submitted to Appl. Spectrosc.

(295) **Protein and Peptide Structures at Solid/Liquid Interfaces Probed by Sum Frequency Generation Vibrational Spectroscopy**

Zhan Chen; University of Michigan

Protein and peptide structures at interfaces are important in problems such as biocompatibility of biomedical materials, marine anti-biofouling controls, membrane functions, biosensor performance, and antimicrobial potency. Sum frequency generation (SFG) vibrational spectroscopy has been used to investigate orientational and conformational information of proteins and peptides at the solid/liquid interface in situ, supplemented by attenuated total reflection-Fourier transform infrared spectroscopy (ATR-FTIR). Our research is focused on the investigation of secondary structures of interfacial peptides and proteins by collecting and analyzing amide I signals using SFG and ATR-FTIR. A polarization mapping method was adopted to reliably fit the complicated SFG spectra collected from interfacial protein molecules. Polarization analysis has been used to determine orientation of these proteins and peptides.\r\n\r\nThe peptides studied include several antimicrobial peptides such as alpha-helical magainin and melittin, and beta sheet tachyplesin I. Interactions between such peptides and single supported lipid bilayers have been probed in situ in real time to understand molecular mechanisms of such peptides. By using isotope labeled lipids, we can study the structure of each leaflet of the bilayer and the peptide simultaneously during the interaction. Various blood proteins such as FXII, albumin, and fibrinogen have been studied using SFG and ATR-FTIR at the polymer/protein solution interfaces to understand blood compatibility. It was found that the same protein adopts varied structures while contacting different polymers, due to varied molecular interactions. Time-dependent structural changes of interfacial proteins have been examined. To understand enzyme biosensor performance, structures of several enzymes immobilized using different methods have been examined using SFG. Enzyme structural information has been related to biosensing performance. In addition to blood proteins and immobilized enzymes, several membrane active proteins have been studied using SFG to determine their orientation in membrane. Besides standard SFG spectra, SFG chiral spectra have also been detected from beta sheet at interfaces, from which additional structural information of beta sheet can be deduced. Our research demonstrates that SFG is a powerful technique to elucidate structural information of proteins and peptides at interfaces.

(296) **Metallomics - New Analytical Techniques for the Post-Genomic Era**

David W. Koppenaal[1], Charles J. Barinaga[1], Steven J. Ray[2], Duane A. Rogers[2], Gary M. Hieftje[2], Michelle Liberton[3], Jana Stockel[3], HImadri B. Pakrasi[3]; [1]Pacific Northwest National Laboratory, [2]Indiana University, [3]Washington University

The metallome has been defined as the complete complement of metals and metal moieties in a biological cell, tissue, or system. This definition is analogous to that of the genome (genes), proteome (proteins), and metabolome (metabolites). Metallomics accordingly is the study of metals and metal species, and their interactions, transformations, and functions in biological systems. While traditional bioinorganic chemistry has focused on the role and interactions of a single (or few) metals in a protein or enzyme system, metallomics purports to study global, multielement interactions and relationships. The metallomics challenges for analytical chemistry and biochemical characterization are significant. This paper will discuss these challenges and the emergent techniques and tools that are being developed to address them. Mass spectrometry will play an important and pivotal role. Two approaches are currently being developed in our laboratories. At Pacific Northwest National Laboratory, a high-resolution ICPMS approach using linear ion trap/Orbitrap technology is under development. At Indiana University, a rapid, dual-source Time-of-Flight IPC mass spectrometry (TOF-ICPMS) technique is being developed. Both approaches rely on dual inductively coupled plasma (ICP) and electrospray ionization (ESI) sources for elemental and molecular ion generation. \r\n\r\nApplication to the metallomic study of a biologically important micro-organism, the cyanobacterium Cyanothece ATCC 51142, will be described. This organism is of interest to the U.S. DOE because it can harness energy via both photosynthetic and nitrogen fixation processes, using metal-mediated regulatory protein complexes.

(297) **Green Sample Preparation for Metallomics**

Anne Vonderheide; University of Cincinnati

Metals play a vital role in all biological systems. The importance of metals to life is acknowledged in the investigation of their roles in modifying gene expression or as catalysts or signaling agents. Further, essential element patterns can be used to assess the overall health and status of humans, animals, plants or microorganisms. Alternatively, the distribution of toxic elements allows the forensic determination of occupational or environmental exposure and the potential route of entry. This entire area of study, known as metallomics, has escalated exponentially in recent years. Szpunar defined metallomics as the \"comprehensive analysis of the entirety of metal and metalloid species within a cell or tissue type". (The Analyst, 130, 2005, 442-465) Proteins and other metal-bound biological entities originate in an intricate matrix which may yield difficult extraction problems. Care must be taken to preserve the nature of the species and, most importantly, to maintain the metal attachment, bonding or association. Consequently, mild procedures are required. This talk will present an overview of current accomplishments; specific examples from our lab will be given and special focus will be placed on "green" techniques.

(298) **New Separation and Detection Schemes for Metal Speciation of Botanical Products**

R. Kenneth Marcus[1], Timothy M. Brewer[1], Joaudimir Castro[1], M. V. Balarama Krishna[1]; [1]Clemson University

Worldwide, botanical products taken as dietary supplements (i.e., nutraceutics) represent somewhere between $12-15 billion in annual commerce, making up approximately one-third of all dietary supplements. Many questions exist for most of these materials, including the mechanism of operation, cultural differences in risk/benefit ratios, drug interactions, and the role of specific preparations in toxicity/efficacy. The presence of metals in dietary supplements is an important aspect of their potential therapeutic or deleterious effects. The chemical, biological, and toxicological properties of an element in a given system are dependent on its particular chemical form. \r\nIn this laboratory, we are taking a two-pronged approach to the elemental speciation of trace metals in botanical extracts. In the first case, a novel format of liquid chromatography stationary phase, capillary-channeled polymer (C-CP) fibers are being developed to allow high throughput LC separations. These fibers can be employed over a range of chromatographic modes including reversed-phase, hydrophobic interaction, and ion exchange chromatography. Ideally, detection in any speciation experiment would provide unambiguous chemical identification of each eluting compound. To this end, we have

coupled the LC eluent through a particle beam interface to both glow discharge (GD) and electron ionization (EI) sources. In this way, molecular mass spectra are obtained from molecular species, and atomic species simply yield the corresponding isotopic patterns. It is believed that tailoring both the separation and detection schemes is the most pragmatic means of performing "comprehensive speciation" of botanical extracts.

(299) **Elemental Speciation - One Tool in The Fight Against Chemical Terrorism**

Douglas T. Heitkemper[1], Nohora V. Shockey[1], Barbara S. Barnes[1], John R. Urban[1], Catherine Dasenbrock[1], Kevin Kubachka[2], Joseph A. Caruso[2]; [1]Food and Drug Administration, [2]University of Cincinnati

One of the functions of the Forensic Chemistry Center (FCC) is providing laboratory support for incidents involving adulterated or tampered food, drug, and cosmetic products. Application of elemental speciation to some example product tampering investigations will be discussed. More recently, the FCC has been asked to help with the development of methods which can be used in the event of a terrorist act or threat against the US food supply (including the possibility of large sample throughput). Whenever possible, methods developed for counterterrorism should be rapid, simple, robust and easily transferable to other laboratories. They should have broad applicability to a wide variety of matrices and have adequate sensitivity to detect and identify specific toxins, poisons or degradation products of the toxins or poisons. They should be developed using established technology and chemistry and allow for adequate capacity. Recently, the applicability of HPLC-ICP-MS to the analysis of chemical warfare agent degradation products has been demonstrated [1]. The potential application of this methodology to food products will be presented. [1] Richardson, D.D., Sadi, B.B.M., and Caruso, J.A. Reversed phase ion-pairing HPLC-ICP-MS for analysis of organophosphorus chemical warfare agent degradation products. Environ. Sci. Technol. 2005, 39, 5531-5540.

(300) **Selenium Speciation - Implication for Cancer Chemoprevention**

Julian Tyson; UMass Amherst

Results from several preclinical studies indicate that the chemopreventive efficacy of selenium depends not only on the dose, but also on the chemical form in which it is administered. Although a number of potential mechanisms have been proposed for its antitumorigenic effects, the active form, or metabolite, of selenium that is responsible for cancer prevention remains unknown. Consumption in amounts that exceed the recommended dietary allowance (RDA) may protect against prostate and colorectal cancer. The bioavailability of supplemental selenium, acquired through the diet, depends on the source. As yet, the majority of sources are not fully characterized, so the provision of advice concerning improvement of selenium intake is difficult. Gaining a complete understanding of the roles of selenium in nutrition and health will only be possible if reliable information about the chemical composition of relevant materials can be provided. The enormous variety of materials, analytes and concentrations pose considerable challenges, but it is clear that useful information can be obtained by combining high performance separations with element-specific and mass spectrometry detection.

(301) **A Metallomics Approach to Metal Profiling in Clinical Samples**

Joseph Caruso; University of Cincinnati

Koppenaal describes "…the metallome as the complete complement of metals and metal moieties in a biological cell, tissue, or system."1 He further indicates "Metallomics accordingly is the study of metals and metal species, and their interactions, transformations, and functions in biological systems… metallomics purports to study global, multielement interactions and relationships." In this spirit, it may be once again stated that metals and metal-containing compounds are known to play important roles in many biological processes, including metabolic and detoxification pathways as well as the formation and function of proteins. Like all organisms, viruses would be expected to contain a number of different metals. These metals, either by themselves or in the form of metalloproteins, may be involved in the virus' ability to infect as well as replicate within healthy cells. The identification and speciation of these metals using a metallomics approach could be helpful in elucidating these mechanisms, which might in turn, be vital to the development of more effective treatments. However, to date, there have been no extensive investigations into the metal or metalloprotein content of viruses. Further, ongoing studies involve profiling metal and metal species differences in healthy and cancerous prostate cells. This talk will describe the progress in these areas using chromatographically coupled mass spectrometric methods. 1 D. Koppenaal, FACSS 2006 Abstract – this symposium.

(302) **Subsurface Probing in Diffusely Scattering Media Using Spatially Offset Raman Spectroscopy**

Pavel Matousek[1], Ian P. Clark[1], Edward R.C. Draper[2], Michael D. Morris[3], Allen E. Goodship[2], Neil Everall[4], Michael Towrie[1], William F. Finney[3], Anthony W. Parker[1]; [1]Rutherford Appleton Laboratory, [2]Royal Veterinary College, [3]University of Michigan, [4]ICI PLC

One of the most important and at the same time elusive goals of analytical sciences in biomedical research is the provision of a non-invasive method for monitoring the chemical composition of deep layers in turbid media such as living tissue. Such information may be important, for example, in disease diagnosis. Presently, available vibrational spectroscopy techniques that possess the required degree of chemical specificity can access only shallow layers of skin. We will give an overview of a collaborative research project that led to the development of the Spatially Offset Raman Spectroscopy approach (SORS) for subsurface probing of diffusely scattering media [1]. The method is based on collecting a range of Raman spectra from sample surface regions that are laterally displaced by different amounts from the laser incidence point. The spectra obtained in this way exhibit large variations in relative intensities of the surface and sub-surface components. The separation of the two layer components is possible by scaled subtraction of two spectra of different spatial offsets or using multivariate data analysis approaches. The technique performance will be demonstrated on the non-invasive Raman spectroscopy of stratified powder samples, pharmaceutical capsules and human bones in vivo. The presentation will also report on a Raman Kerr gating method developed for the suppression of fluorescence in solutions [2] and its use in Raman spectroscopy of powders [3] and tissue [4]. [1] P. Matousek, I. P. Clark, E. R. C. Draper, M. D. Morris, A. E. Goodship, N. Everall, M. Towrie, W. F. Finney and A. W. Parker, Appl. Spectrosc. 59 (2005) 393. [2] P. Matousek, M. Towrie, A. Stanley, A.W. Parker, Appl. Spectrosc. 53 (1999) 1485. [3] N. Everall, T. Hahn, P. Matousek, A.W. Parker, M. Towrie, Appl. Spectrosc. 55 (2001) 1701. [4] M.D. Morris, P. Matousek, M. Towrie, A.W. Parker, A.E. Goodship, E.R.C. Draper, Journal of Biomedical Optics 10 (2005) Art. No. 014014.

(303) **Probing Plasmas with Photons**

Paul Farnsworth; Brigham Young University

The inductively coupled plasmas that are used for elemental analysis are complex systems. They are heterogeneous, with large

gradients in both temperature and composition. The chemical makeup of the plasma, although dominated by the argon support gas, varies during the course of an analysis. The insertion of a cooled metal sampling cone into the flow of an ICP to exploit it as an ion source for mass spectrometry further complicates its behavior. Full exploitation of the ICP as either an emission or ion source depends on a solid understanding of its behavior and how its properties vary with operating parameters and sample composition. Optical spectroscopy is a powerful tool for probing the harsh environment of an ICP without affecting the properties that one is trying to measure. Over the years we have employed a variety of spectroscopic techniques to probe the inner workings of analytical ICP's and to address a range of questions about the plasmas' performance. In this talk I will address a few of those questions, focused primarily on the ICP's behavior as an ion source for mass spectrometry. The questions include: How does the addition matrix species affect the fundamental chemistry of the plasma? How do the mass and charge of ions entering the vacuum interface of an ICP-MS affect those ion's transport to the mass spectrometer? How does the flow of ions into an ICP-MS differ from that predicted by fluid models, and why? The pursuit of answers to these questions has been a fascinating exercise that is yielding valuable insights into the ICP's behavior.

(304) **Application of Isotope Dilution for the Accurate Determination of Cr(III), Cr(VI) and Total Cr in Yeast**

Lu Yang; National Research Council Canada

Chromium has been extensively studied in the fields of environmental science and toxicology as well as nutritional and analytical sciences due to their significantly different toxicities of Cr(III) and Cr(VI). Cr(VI) is toxic and carcinogenic to humans and other animals. On the other hand, Cr(III) is an essential nutrient at trace level to humans for normal carbohydrate and fat metabolism with intake derived mainly from foods. Studies have shown that chromium supplements can help in many conditions, including reducing blood sugar levels as well as the amount of insulin needed by diabetics, lowing cholesterol levels in the blood; and improving lean body mass and reducing body fat for weight loss. As a result, consumption of Cr supplements has become popular. Because the nutritional bioavailability and toxicity of Cr are highly dependent on its chemical forms and concentrations, speciation of Cr in such supplements is of paramount of importance for safeguarding consumer's health. Speciation of Cr(VI) and Cr(III) is a most challenging analytical task for analytical chemists due to their complicated chemistry. The relative amounts of Cr(VI) and Cr(III) in a sample depends highly on the electrochemical potential of oxidation and reduction reactions and pH. This is further influenced by the presence of oxidizing and reducing agents in the sample matrix. Cr(III) is stable at low pH, while high pH favors Cr (VI). Conversions between Cr(III) and Cr(VI) during the measurement processes can lead to inaccurate data for these species when using methods which are incapable of correcting for species interchanges. Despite the dramatically different toxicities of Cr(III) and Cr(VI) and the increasing use of Cr supplements, accurate determination of these species in such supplements is lacking. In this presentation, a method is presented for the simultaneous determination of Cr(III) and Cr(VI) in yeast using species specific double spike isotope dilution (SSDSID) with anion exchange liquid chromatography (LC) separation and sector field inductively coupled plasma mass spectrometric (SF-ICP-MS) detection. Total Cr is quantitated using ID SF-ICP-MS. The presentation will cover several aspects of the procedure that were developed to achieve accurate results.

(305) **Characterization of Nuclear Materials Using Time-of-Flight ICP-MS**

Stefan Bürger[1], Lee R. Riciputi[1], Debra A. Bostick[1], Douglas C. Duckworth[1]; [1]Oak Ridge National Laboratory

The investigation of illicit trafficking of nuclear materials, nuclear safeguards analysis, and non-proliferation control requires sensitive and isotope-selective detection methods to gain crucial nuclear forensic information like isotope 'fingerprints' and multi-element signatures. The advantage of time-of-flight (TOF) mass spectrometry – quasi-simultaneous multi-mass analysis – combined with an inductively coupled plasma (ICP) ion source provides an analytical instrument with multi-element and multi-isotope capability and good detection limits. A TOF-ICP-MS system thus appears to be an advantageous choice for the investigation and characterization of nuclear materials. We present here results using a GBC OptiMass 8000 time-of-flight ICP-MS for the isotope screening of solid samples by laser ablation and the multi-element determination of impurities in uranium ore concentrates using matrix matched standards. A laser ablation system (New Wave Research, UP 213) coupled to the TOF-ICP-MS instrument has been used to optimize the system for analysis of non-radioactive metal samples of natural isotopic composition for a variety of elements including Cu, Sr, Zr, Mo, Cd, In, Ba, Ta, W, Re, Pt, and Pb in pure metals, alloys, and glasses to explore precision, accuracy, and detection limits. Similar methods were then applied to measure uranium. When the laser system is optimized, no mass bias correction is required. Precision and accuracy for the determination of the isotopic composition is typically 1 – 3% for elemental concentrations of as little as 50 ppm in the matrix, with no requirement for sample preparation. The laser ablation precision and accuracy are within ~10x of the instrumental limits for liquid analysis (0.1%).We have investigated the capabilities of the TOF-ICP-MS for the analysis of impurities in uranium matrices. Matrix matching has been used to develop calibration curves for a range of impurities (alkaline, earth-alkaline, transition metals, and rare earth elements). These calibration curves have been used to measure impurities in a number of uranium samples. The results from the TOF-ICP-MS will be compared with other mass spectrometric methods. Research sponsored by the Office of Nonproliferation and International Security (NA-24), National Nuclear Security Administration (NNSA), U.S. Department of Energy, under contract DE-AC05-00OR22725 with Oak Ridge National Laboratory, managed and operated by UT-Battelle, LLC.

(306) **Low Level Boron Analysis in Plutonium Oxide**

Jeffrey Miller[1], David Gallimore[1], Frances Martin[1], Alexander Martinez[1], Joseph Rodriguez[1], Lawrence Drake[1]; [1]Los Alamos National Laboratory,

The Actinide Analytical Chemistry group (C-AAC) within Chemistry Division at Los Alamos National Laboratory works with Nuclear Materials Technology (NMT) Division on several non-proliferation projects. One of these projects involves processing plutonium from retired weapons into a mixed plutonium-uranium oxide (MOX) reactor fuel. The MOX program is required to meet program specific requirements of 1 ppm of boron in the final product. In order to accomplish this using our current methods for PuO2 analyses an instrumental detection limit of 250 parts per trillion (ppt) of boron is required. This detection limit is not obtainable with our current instrumentation. In order to obtain acceptable detection limits, new methods were developed.\r\nThe Actinide Analytical Chemistry group routinely uses Inductively Coupled Plasma – Mass Spectrometry (ICP-MS) to measure a wide variety of analytes in plutonium samples. The detection limits and quantification of certain elements that includes boron by this technique suffers due to a mass dependent signal suppression

resulting from the Pu matrix. Typically, matrix dilution and signal normalization using internal standards are employed to mitigate the signal suppression. Unfortunately, matrix dilution is detrimental to the detection limits and is not a viable technique for the analysis of boron as required by the MOX program. This report describes the new method of sample preparation, chromatographic separation of boron and analysis by ICP-MS that was developed to meet the required detection limit for boron.

(307) **Speciation of Plutonium under Environmental Conditions**

Buda Razvan Aurel[3]; [1]Institut für Kernchemie, Universität Mainz, [2]Oak Ridge National Laboratory, USA, [3]TU Graz, Austria

In order to investigate the migration of plutonium in the eco system, very sensitive and selective detection methods are required. For the redox speciation of plutonium, the online coupling of Capillary Electrophoresis (CE) to Inductively Coupled Plasma-Mass Spectrometry (ICP-MS) was developed. The different oxidation states of plutonium are separated by CE, due to the different migration times through the capillary as a consequence of the radius/electrical charge ratio,. Afterwards the separated species are detected by means of ICP-MS. In this way, the oxidation states III, IV, V and VI of plutonium could be separated. The detection limit of this method with a quadrupole ICP-MS is 20 ppb or □109 atoms for one oxidation state of plutonium with a reproducibility of the retention times ≥ 99%. Furthermore, the coupling of CE to resonance ionisation mass spectrometry (RIMS) is under development. RIMS is an extremely sensitive and selective technique for isotopically resolved analysis of long-lived radionuclides. Using a multiple resonant laser excitation and ionisation of the element of interest with subsequent mass analysis, it provides an excellent element and isotope selectivity as well as a good detection limit (as low as 106 -107 atoms). For the routine analysis of plutonium samples, a pulsed Nd: YAG pumped titanium-sapphire laser system combined with a time-of-flight mass spectrometer is applied. The coupling of CE to RIMS is only possible in the off-line mode. The combination of CE-ICP-MS with a Diode Array Detector (DAD) is being developed. This technique will be used for the complexation studies of plutonium with humic substances. With DAD the humic substances in the capillary can be detected, whereas the ICP-MS enables the detection of plutonium as described before. In this way it is possible to quantify the amount of free and complexed plutonium as well as humic substances. The method should have similar detection limits for plutonium (≈ 20 ppb),, and 25 mg/L for humic acid. The results obtained so far will be presented.

(308) **A New Interference Management Solution for ICP-MS - The Unique Collision Reaction Interface (CRI)**

Doug Shrader[1], Shane Elliott[1], Xue Dong Wang[1], Iouri Kalinitchenko[1]; [1]Varian, Inc.

A novel new interference management system for ICP-MS, the Collision Reaction Interface (CRI), will be discussed. This unique (patents pending) technology employs simple collision and reaction gases injected directly into the plasma through the tips of the interface cones. This approach quickly and effectively reduces / removes common polyatomic interferences on elements such as As, Se, Cr, V and Fe, achieving lower detection limits in hot plasma, even for samples with complex matrices. Coupled with revolutionary 90-degree reflecting ion optics and a low noise, double off axis quadrupole mass analyzer, the CRI-ICP-MS offers an efficient yet simple solution to interference management in ICP-MS. The design features of this unique CRI-ICP-MS will be discussed, along with basic principles of operation and performance attributes. Application results for environmental and biological sample types, including speciation examples, will be presented.

(309) **Elemental Speciation by Non-Aqueous Capillary Electrophoresis - Inductively Coupled Plasma Mass Spectrometry and Its Applictions in Pharmaceutical Process Reaseach**

Xiaodong Bu[1], Tiebang Wang[1], Xiujuan Jia[1], Qiang Tu[1], Gene Hall[2], Christopher Welch[1],; [1]Merck Research Lab, [2]Rutgers university

Removal of trace metal impurities has become a critically important task in pharmaceutical process research, paralleling the growing use of organometallic reagents and catalysts in pharmaceutical synthesis. Studies of catalyst metal speciation during the reaction are necessary for a basic understanding of this important metal removal processes since simply knowing the total concentration of the metal is not sufficient. Capillary electrophoresis (CE) coupled with inductively coupled plasma mass spectrometry (ICP-MS) has shown great potential for metal speciation study. The majority of works found in the filed of applying CE for speciation study has focused on the use of aqueous buffers as background electrolytes. The problems in applying aqueous CE method on pharmaceutical compound analysis are including poor water solubility of certain pharmaceutical drugs and drug precursors, inability of directly analysis organic reaction steam and potential hydration/hydrolysis processes. In this study, a non-aqueous CE-ICP-MS system was developed and optimized. The advantages of using non-aqueous electrolytes in CE including greater ability to manipulate separation selectivity due to a wide range of physicochemical properties of different organic solvents, lower separation current and joule heating, and none disturbing to original species will be demonstrated. The feasibility of its application for the synthesis of pharmaceutical products, particularly, for understanding of reaction mechanism and kinetics of catalyst formation by identification and quantitation of various catalyst metal species during the course of the reaction will be discussed. The potentials of using elemental speciation as a tool to develop time and cost effective routes for removing catalyst metal impurity will also be discussed.

(310) **Observation of Plasma Jet in Interface Region for Microplasma Mass Spectrometer**

Hidekazu Miyahara[1], Taichi Kageyasu[2], Kazuyasu Takimoto[2], Wataru Kumagai[2], Eiki Hotta[2], Ryuichi Shimada[1], Akitoshi Okino[2]; [1]Laboratory for Nuclear Reactors, Tokyo Institute o, [2]Department of Energy Sciences, Tokyo Ins

Inductively coupled plasma (ICP) is generally used as an ionization or excitation source for trace elemental analysis because analytical equipments based on ICP have very high detection performance. In recent years, the focus of element analysis has been shifted to smaller samples such as nano-particles, cells, etc□c But the plasma genereted in ICP source has large volume so it spends more than RF power of 1 kW and needs argon gas flow of around 15 L/min. In the result, large amount of sample solutions, more than 1 mL/min, are required for analysis. Therefore, ICP is not suitable for these purposes. Moreover, high sensitive detection of halogen elements was difficult because halogens has higher ionization potential than argon. To analyze small amount samples and halogen elements, we designed and developed hollow cathode type microplasma source. By atomic emission spectrometry, halogens are not detected using argon plasma but with helium plasma those are detected with high sensitivity. The detection limits are 5.7 pg, 10 pg and 5.0 pg for fluorine, chlorine and bromine, respectively using halon1211 (CBrClF2) as a sample. To improve these detection limits, we have a plan to apply this microplasma as an ionization source to Agilent HP4500 ICP mass spectrometer. To introduce all analyte ions generated in the microplasma into the mass spectrometer, the microplasma source□@is set directly to the

sampler. In this case, small electrode hole of the microplasma source play the orifice of the sampler. The microplasma source consumes low plasma gas flow rate of 60 mL/min. This value is about 1/300 compare with typical flow rate of ICP source in HP4500. Therefore, Mach disk position in the ion extract interface region will be changed and so the distance between the microplasma and the skimmer have to optimize or the microplasma source have to modify. In this study, to observe behavior of the plasma-jet and Mach disk position in the interface region, an acrylic vacuum chamber is designed and developed. Observed results will be presented. This study was partly supported by in Industrial Technology Research Grant Program in □f05 from New Energy and Industrial Technology Development Organization (NEDO) of Japan and fellowship of Japan Society for the Promotion of Science Research.

(311) **Long Term Exposure to Lead – Measuring Lead in Bones by ICP-MS**

Ela Bakowska[1], Anna Foror[1], Michael Kraky[1], Tatyana Kandova[1]; [1]National Medical Services

The toxic nature of lead is well documented. Lead affects all organs and functions of the body to varying degrees. The frequency and severity of symptoms among exposed individuals depends upon the amount of exposure. Lead exposure can cause: neurological effects, peripheral neuropathy, encephalopathy, gastrointestinal effects, reproductive effects, renal effects, impaired concentration, fatigue, hearing loss and seizures. Lead in bones measures long-term exposure to the metal, whereas blood lead usually indicates recent exposure. Lead entering the respiratory and digestive systems is released to the blood and distributed throughout the body. More than 90% of the total body burden of lead is accumulated in the bones, where it is stored. Lead in bones may be released into the blood, re-exposing organ systems long after the original exposure. The half-life of lead in the human body is about 22 years, with 95 percent of "old" lead residing in the skeletal structure. In this study we are comparing different analytical approaches for the determination of lead in five pulverized bone samples. One of the samples was a certified reference material (SRM 1486 – Bone Meal). The samples were first digested in a commercial microwave digestion oven and then were analyzed by Inductively Coupled Plasma Mass Spectrometry. Different aspects of samples' preparation and analyses were compared. Day-to-day variations were determined. The effect of drying samples prior to the digestion was evaluated. The analysis with an external calibration was compared with the method of standard additions. The precision, accuracy and % recovery will be presented. Additionally, the isotopic ratios information will be shown. The stability of the digestates was evaluated. The tests were performed on different ICP-MS instruments: Elan 6000, Elan 6100DRC and Agilent 7500ce and the results were assessed.\r\nFinally, the comparison of the results from analyzing the digested samples and direct analysis of pulverized bones by laser ablation (LA-ICP-MS) will be offered.

(312) **Examination of Coal Utilization Byproducts by Pulsed Glow Discharge Plasma Spectrometries**

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Examination of Coal Utilization Byproducts by Pulsed Glow Discharge Plasma Spectrometries. A pulsed glow discharge plasma (GDP) was used as the atomization/excitation/ionization source for the determination and speciation of trace elements in the most ubiquitous coal utilization byproduct (CUB), coal fly ash. Increasingly there is growing interest in the utilization of CUB to minimize the waste generated by the combustion of coal. In the course of such use, the concentration of toxic elements becomes a concern. The GDP source was coupled with atomic emission spectroscopy (AES) and time-of-flight mass spectrometry (ToF-MS), for the determination of potentially hazardous trace elements in CUB and their secondary materials, such as wallboard, in which CUB is utilized. Time-gated signal acquisition techniques were employed to take full advantage of the distinct temporal regimes created within the pulsed GDP. Sampling of this kind allows for the acquisition of signals from both structural fragments and intact molecules through the use of a single ionization source. This, in turn, enables speciation as well as elemental determination.

(313) **Monitoring Metals Hypersensitivity by Measuring Chromium, Cobalt and Molybdenum in Whole Blood**

Ela Bakowska[1], Judy Vinosky[1], Michael Welsh[1]; [1]National Medical Services

Metal hypersensitivity is commonly reported in the literature and can include hypersensitivity related to pacemakers, dental implants and orthopedic hardware. Up to 13% of people are reported to be sensitive to nickel, cobalt, or chromium.. Some patients who have undergone an orthopedic joint replacement, are monitored for Chromium, Cobalt and Molybdenum levels in blood. There are many challenges associated with those measurements: individual patients variability, contamination issues and analytical instruments' complexities. Cobalt and chromium blood levels can change depending on physical condition of the patient, working environment, individual feeding and metabolism. The normal range for Chromium in blood is listed as 0.5 - 5 mcg/L, for Cobalt in blood is 0.5-3.9 mcg/L, and for Molybdenum in blood is below 3 mcg/L. Dealing with such low levels in biological materials presents additional challenges. Use of non-certified for trace element analysis collection tubes may cause contamination. The contamination control during the specimens' preparation and analysis required additional attention. The samples preparation and analyses were performed in a clean-room environment. Agilent 7500ce ICP-MS was used for the determination of Cobalt and Molybdenum. In order to further minimize the contamination, the standard nebulizer system was replaced with 100% PFA cross-flow nebulizer from Savillex. Determination of Molybdenum at very low levels is additionally complicated by the potential of carry-over from measuring of a specimen with elevated levels. It was established that a rinse time of up to 10 minutes was required to minimize the carry-over issue. This would negatively affect the productivity, if the sample-to-sample analysis time will be approximately 12 minutes, this would allow only 5 samples to be analyzed within 1 hour. The Agilent's 7500ce ICP-MS software provided the "intelligent rinse" option. This option involved monitoring of the Molybdenum's signal during the rinse cycle and comparing it with a pre-set threshold value. As a result, the rinse time was reduced down to 3 minutes for most of the samples. Perkin Elmer Aanalyst 600 Graphite Furnace AA system was employed for the determination of Chromium. Some preliminary work on including chromium in blood measurements by ICP-MS will be discussed.

(314) **Arsenic Speciation of Selected US Rice Samples**

Melanie N. Allen[1,2], Nohora V. Shockey[1], Douglas T. Heitkemper[1]; [1]Food and Drug Administration, [2]Oak Ridge Associated Universities

In a recent study, Williams, et al. (1) reported that US long grain rice had the highest mean arsenic level (0.26 ± 0.02 µg/g) when compared with samples of European (0.18 ± 0.01 µg/g), Bangladeshi (0.13 ± 0.02 µg/g) and Indian rice (0.05 ± 0.00 µg/g). In addition, arsenic speciation results showed US rice to have a lower percentage of inorganic arsenic (42%) than European (64%), Bangladeshi (80%) and Indian rice (81%); however, a limited

number (n = 7) of US rice samples was analyzed in this study. The results reported by Williams, et al. [1] for US rice were in relatively good agreement with our previous results for arsenic in rice which also included only a limited number of samples [2]. In this study, thirty-one rice samples grown in Arkansas, California, Louisiana and Texas, between 1980 and 1982 were analyzed for total arsenic and individual arsenic species. TFA was used to extract the arsenic species from these samples prior to analysis by HPLC-ICP-MS [2]. Arsenic levels in the samples ranged from 0.042 µg/g to 1.0 µg/g; and the results show significant variation by growing location. The primary arsenic species found include inorganic arsenic species and dimethylarsinate. In the speciation analyses, several chromatograms exhibited an unidentified arsenic-containing peak and studies are currently underway to identify this peak. The results obtained are also compared with several samples collected more recently from local markets. Certified reference material NIST SRM 1568a, Rice Flour was used to validate the method used. [1] Williams, P.N., Price, A. H., Raab, A., Hossain, S.A., Feldmann, J., and Meharg, A. A., Variation in arsenic speciation and concentration in paddy rice related to dietary exposure. Environ. Sci. Technol. 2005, 39, 5531-5540. [2] Heitkemper, D.T., Vela, N.P., Stewart, K.R., and Westphal, C.S., Determination of total and speciated arsenic in rice by ion chromatography and inductively coupled plasma mass spectrometry. J. Anal. At. Spectrom., 2001, 16, 299-306.

(315) **A New Approach for Calibration in Trace Analysis of Ultrahigh Purity Materials by Glow Discharge Mass Spectrometry**

Ulrich Panne[1], Tamara Gusarova[1], Heinrich Kipphardt[1], Ralf Matschat[1], Joachim Hinrichs[2]; [1]Federal Institute for Materials Research BAM, [2]Thermo Electron Corporation

A new type of glow discharge mass spectrometer (GD-MS) was employed in this study to investigate pressed copper and iron powder calibration samples for analysis of ultrahigh purity materials. The GD-MS featured a Grimm type discharge cell of for flat samples. Two series of powder samples were prepared for each of the copper and iron matrices. The powders were quantitatively doped with solutions of graduated and defined concentrations of 40 or 20 analytes, respectively. The mass fractions of the analytes in the dried and homogenized metal powder samples ranged from levels of µg/kg up to levels of 10 mg/kg. A special technique was developed to press the samples and to form mechanically stable pellets with small risks of contamination. The ion beam ratios of analyte ions to matrix ions were used as measurands. The calibration curves were determined and the linear correlation coefficients were calculated for different intervals of the curves. Good linear correlation was observed for most of the calibration curves which include the higher segments of mass fractions, while less agreement was determined fo the lower segments of the calibration curves. However, in many cases promising results were achieved even for these lower segments representing mass fractions of analytes at ultra-trace level. The comparison of the certified values of different reference materials with the measured values based on calibrations with the pressed powder samples led to deviations less than 30% for most of the considered examples. Hence, this study yielded a concept for quantitative calibration in GD-MS which allowed reliable and metrologically traceable results. It can be safely assumed that the technique can be further improved and applied to the analysis of other pure metals.

(316) **Speciation of Vanadium in Some Environmental Samples by ICP-OES and HR-ICP-MS Combined with Liquid Chromatography**

Jerzy Mierzwa; University of Central Florida

A number of studies concerning chemical speciaton of vanadium in environmental samples is very limited. The author of this present speciation study has used liquid chromatography (LC) combined with inductively coupled plasma optical spectrometry (ICP-OES) and high-resolution inductively coupled plasma mass spectrometry (HR-ICP-MS), respectively. Some results (including analytical figures-of-merit) will be presented and both two methods of vandium detection will be compared.

(317) **Determination of Burn-up Monitors for Use in Nuclear Forensics**

Jeffrey Giglio[1], Daniel Cummings[1], James Sommers[1], Kevin Carney[1]; [1]Idaho National Laboratory

The use of a burn-up monitor or fission product, typically 148Nd, has been routinely used to characterize the performance of a nuclear fuel, i.e. the number of fissions. The inductively coupled plasma mass spectrometer is able to monitor a variety of other burn-up monitors accurately and precisely, without additional work. These additional elements include 99Tc, 139La, 141Pr, 142Ce, 143Nd, 145Nd and 148Nd. This presentation will detail the determination of the burn-up monitors given above in a variety of nuclear fuels. A comparison of the fission products will then be used to interpolate vital nuclear forensic information such as original enrichment based on the estimated number of fissions the fuel that has produced. This is particularly important for mixed (U, Pu) oxide (MOX) fuel and advanced fuels containing Am-241, Np-237 and Pu-239 as major constituents.

(318) **Summing Multiple Internal Standards to Track Serum Calcium During Reference Analysis by Inductively Coupled Plasma-Mass Spectrometry**

Jonathan Good[1], John Butz[1]; [1]Mayo Clinic

An Inductively Coupled Plasma–Mass Spectrometry (ICP–MS) serum calcium reference method was developed in lab. Serum calcium determination by ICP–MS faces a significant challenge in that its primary isotope, 39.9626, overlaps with argon's primary isotope, 39.9624. Historically this was overcome by using cool plasma analysis. Today this obstacle can be circumvented by employing Dynamic Reaction Cell™ (DRC™) technology to remove the plasma-based interferences, while maintaining a robust plasma. Unfortunately, calcium's major isotope was still deemed unsuitable for our purposes due to the relatively high concentration of calcium in human sera– approximately 9.0 to 10.5 mg/dL. The detector was routinely pushed into the analog mode and the requisite level of precision was difficult to attain. Because of ICP-MS's low detection limits, we were able to develop a method for calcium analysis by ICP-DRC-MS which sums the four minor isotopes of calcium: 42Ca, 43Ca, 44Ca, and 48Ca. Unfortunately, calcium's second-most abundant isotope suffers spectroscopic interferences form 12C16O2 and 14N216O+ , which were again dealt with by using a DRC charged with ammonia gas. A novel approach to deal with internal standards that would not track steadily with calcium has been employed. Four internal standards (Yttrium, Cobalt, Gallium, and Scandium) were summed to provide an extremely precise and accurate analysis. Analysis of twenty replicate samples of NIST 909a-2 (target value of 13.4 mg/dL +/- 0.2 S.D.) yielded a mean value of 13.5 mg/dL with a standard deviation of 0.1 mg/dL, and a coefficient of variation of 0.6%. When replicates of NIST 909a-2 were analyzed once a day, for twenty days, the resulting mean value was 13.4 mg/dL, with a standard deviation of 0.1 mg/dL and a coefficient of variation of

1.0%. This novel approach to calcium analysis on ICP-DRC-MS has yielded a reference method that can be held within very tight specifications, and provide extremely reliable results.

(319) **Induction Heating ETV for ICP MS**

Eric Salin[1], Rebecca Lam[1]; [1]McGill University

The induction heating-electrothermal vaporizer (IH-ETV), first developed in our laboratory, eliminates the need for laborious sample digestion or extraction. The solid sample is placed directly into a graphite sample cup, which is then inductively heated via an RF field generated by a coil. The vaporized sample is then transported by a carrier gas to an inductively coupled plasma (ICP) instrument. Unlike most commercial ETV systems, there is no electrical contact between the cup and any part of the instrument, which eliminates the need for precision parts. The inexpensive graphite cup can also be easily interchanged and customized in shape or size to suit a particular sample. Applications of the IH-ETV in our lab have extended to biological and environmental samples. In particular, we have demonstrated that Hg can be quantified for single human hair strands at a relatively low vaporization temperature of 800 C and detection by ICP-MS. We have also explored multi-element determination in hair strands at higher vaporization temperatures, achieving pg detection limits – low enough to detect natural levels within a single hair strand. We are also interested in the direct analysis of metal-laden chromatographic material, such as what may be found in micro-columns left on remote environmental sites for long term monitoring or those used in solid-phase extractions. Along with the IH-ETV-ICP-MS results for direct hair analysis, we will discuss results of detecting metal chelates adsorbed on C18-bonded silica gel with IH-ETV-ICP-AES.

(320) **Time-Resolved ICP-MS Measurement of Part-Per-Trillion Level of Analyte Ions Adsorbed onto Carbon Nanotubes**

Wing-Tat Chan[1], Michael H.P. Yau[1], Thomas K.O. Lui[1]; [1]The University of Hong Kong,

Metal ions adsorbed onto individual nanoparticles are measured using time-resolved inductively coupled plasma - mass spectrometry (ICP-MS). The mixture of the test element-nanoparticles in the original sample solution is introduced into the ICP by conventional solution nebulization. The adsorbed analyte ions on each particle produce a plume of gaseous analyte ions in the ICP. The plume was detected as a current spike in the mass spectrometer. The signal-to-background ratios (SBR) are significantly improved. The sample modulation method improves the ICP-MS detection limits by at least one order of magnitude [1]. In our previous study, part-per-trillion levels of Ba2+, Cd2+ and La3+ ions were adsorbed onto 100-nm Fe(OH)3 particles of concentration of part-per-billion. In this study, carbon nanotubes (CNTs) were used as the adsorbent. CNTs are chemically more stable than the Fe(OH)3 particles. The carbon matrix is also lighter than the Fe matrix of the Fe(OH)3 particles. The CNTs were treated in concentrated nitric acid at elevated temperature to oxidize the CNTs partially by insertion of oxygen-containing functional groups (e.g., hydroxyl and carboxyl groups) onto the particles [2]. The treated CNTs can be dispersed in water readily. ICP-MS spikes were readily observed for trace metal ions of concentration of parts-per-trillion (ppt). The spike intensity varied linearly with analyte concentration up to 50 ppt. Experimental conditions of analyte preconcentration (equilibration time, temperature, and solution pH) and ICP-MS operating parameters (sampling depth and carrier gas flow rate) will be discussed. Time-resolved inductively coupled plasma-atomic emission spectrometry (ICP-AES) was also used to investigate the vaporization process of the analyte-adsorbent particles in the ICP. The details of the experimental set-up and signal characteristics will be discussed.\r\n\r\n[1] M.H.P. Yau, W.T. Chan, A novel detection scheme of trace elements using ICP-MS, J. Anal. At. Spectrom., 20, 1197-1202 (2005).\r\n[2] A.G. Rinzler, J. Liu, H. Dai, P. Nikolaev, C.B. Huffman, F.J. Rodriguez-Macias, P.J. Boul, A.H. Lu, D. Heymann, D.T. Colbert, R.S. Lee, J.E. Fischer, A.M. Rao, P.C. Eklund and R.E. Smalley, Large-scale purification of single-walled carbon nanotubes: process, product, and characterization, Appl. Phys. A., 67, 29-37 (1998).

(321) **Exploring the Analytical Utility of LA-ICP-TOFMS for the Provenancing of Archaeological Materials**

John Dudgeon[1,4], William Balsanek[2], Hector Neff[3,4], Andrew Saint[2]; [1]Department of Anthropology, University of Hawaii,, [2]GBC Scientific Equipment, Hampshire, IL, [3]Department of Anthropology, California, [4]Institute for Integrated Research in Ma

Until recently, isotopic compositional analysis of archaeological materials has relied heavily on high precision measurements usually determined by thermal ionization mass spectrometry (TIMS) or, in some limited cases, by multi-collector ICP-MS. While both TIMS and MC-ICP-MS have traditionally been considered 'standard technologies' for isotopic material analysis, they are either costly, or time consuming, or both. LA-ICP-TOFMS offers an alternative in terms of speed, cost, and volume of data collected. Additionally, sample volume requirements are minimal, and the non-destructive nature of analysis makes this technology particularly desirable for unique or valuable specimens. Preliminary LA-ICP-TOFMS results for Sr isotopic ratios from a dataset of archaeological materials previously analyzed by TIMS demonstrate the promise of the technique.

(322) **Exploring the Benefits of ICP- oTOF (orthogonal time of flight) MS for a Variety of Multi-Element Applications**

William Balsanek[1], Andrew Saint[2]; [1]GBC Scientific Equipment, Hampshire, IL 14060, [2]GBC Scientific Equipment, Dandenong, Vi

While ICP-MS has rapidly attained acceptance as the choice in trace metal analysis, most commercially available instruments are equipped with quadrupole based mass analyzers. Quadrupole mass spectrometers do provide rapid analysis compared to alternative single and multi-elemental techniques (e.g., graphite furnace atomic absorption and ICP-OES); however, they do suffer limitations in terms of speed of spectral acquisition, precision at high speed, precision of isotopic ratios and multi-element transient signal capability. This poster will illustrate the benefits of the GBC Scientific Equipment Optimass 9500 ICP- oTOFMS. Examples of design, routine data from commercial laboratories, isotopic ratio results and transient signal application will be presented.

(323) **Determination of Ultra-Trace Levels of Uranium, Thorium and Potassium in High Purity Materials by ICP-MS**

Patricia Grinberg[1,2], Ralph Sturgeon[1], Andreas Piepke[3], David Sinclair[2]; [1]National Research Council Canada, [2]Carleton University, Dep. of Physics, [3]University of Alabama, Dep. of Physics

The Enriched Xenon observatory (EXO) is a project in particle physics aiming to detect "neutrino-less double-beta decay" using large amounts of xenon isotopically enriched in the isotope 136. One of their goals is to make the first measurement of the absolute mass of the electron neutrino by detecting "neutrino-less double-beta decay", a rare nuclear process that occurs when a disintegrating nucleus emits 2 electrons. Construction of a detector is now underway and although all materials selected for use in the detector must be of high-purity, one particular concern is the concentration of U, Th and K, as these elements increase the

background because their decay chain generates emission of a gamma ray simulating the neutrino-less double beta decay. The preconceived upper limit on the concentrations of these elements that can be tolerated is the sub pg g-1 range. Although these elements have been traditionally measured by radiometric techniques, such as alpha spectroscopy, gamma spectroscopy and neutron activation analysis, these are not ideally suited to rapid and/or accurate determinations. Inductively Coupled Plasma Mass Spectrometry (ICP-MS) is considered one of the most powerful analytical methods for trace and ultra-trace analysis, offering sub pg/ml detection limits with minimal analysis time. However, one of the main limitations of this technique is the need for sample preparation prior to analysis, as higher levels of matrix components can give rise to deposition of matrix constituents on the sampler and skimmer cones of the spectrometer. Thus, a dissolved sample may need to be diluted, which clearly degrades achievable detection limits and, in this case, prevents determination at ultratrace levels. Attempts to use ICP-MS, in combination with matrix separation, for the analysis of these elements in a variety of materials will be demonstrated.

(324) **High Repetition Rate Femtosecond Laser Ablation-ICP-MS**

Jhanis Gonzalez[1], Alberto Fernandez[2], Dayana Oropeza[1], Xianglei Mao[1], Richard Russo[1]; [1]Lawrence Berkeley National Laboratory, [2]Universidad Central de Venezuela

Laser-material interaction is known to depend on several laser parameters among these are: wavelength, energy, pulse duration, spatial energy profile, and repetition rate. In addition to these parameters the irradiance (energy per unit time and area) plays a dominant role in defining the quantity and chemistry (fractionation) of the ablated aerosol. The influence of these parameters have been well documented for nanosecond laser ablation1;2. Research studying femtosecond laser ablation is based on the need to better understand the fundamentals controlling the amount of ablated material, particle size distribution, matrix dependence and fractionation. Femtosecond laser ablation sampling into the ICP-MS have been shown to improved chemical analysis precision and accuracy compared to nanosecond laser pulses, by reducing systematic errors related to the particle size distribution and resultant spikes on the signal intensity3;4. Matrix dependence reduction have been also shown in the analysis of glass and alloys samples when used femtosecond laser pulses 3-5. In this study the influence of the femtosecond laser pulses repetition rate on the ablation rate and particle size distribution, which are two of the most important parameter that affects LA-ICP-MS performance (accuracy and precision), as well as craters profiles and ICP-MS performance were investigate for a glass sample (NIST 612). Results show that when increasing the repetition rate (Hz) from 1 to 1000 at a fixed scan speed (m/sec 10) the particle size distribution function does not change. However the total concentration of particles increases when increase the frequency. In the other hand, a heat affected zone started to growth around the crater after 50Hz. And when the repetition rate was fixed (1000Hz) and the scan speed was varied from 1 to 200m/sec the heat affected zone disappear at 200m/sec. This data seems to indicate that there is a heat accumulation effect with each pulse similar to the observed for nanosecond laser pulses6. The ablated material generated with a fixed frequency of 1000Hz and different scan speeds was analyze with an ICP-MS. Results show that ICP-MS signal increase when increase scan speed, this effect could attributed to the accumulation of particles in front if the surface decreasing the ablation or transportation efficiency due to the absorption/diffusion of the laser beam.

(325) **Depth Profile Analysis of Thin Film by Using Dc Voltage Modulation Glow Discharge Optical Emission Spectrometry (GD-OES)**

Hyunkook Park[1], Kazuaki Wagatsuma[1]; [1]Institute for materials research, Tohoku Univ.

Commonly, a normal dc GD-OES has ability for analytical depth ranging from some §- up to 50 §- and more. There still have various problems when GD-OES is applied for thin films which have less than 100 nm in thickness. The most crucial problem is the high sputtering rate and the bad crater shape of GD-OES. It had not been applied for depth profiling of thin films since the sputtering rate of GD-OES (generally 1§-/min) is so fast rather than other surface analytical methods such as X-ray photoelectron spectroscopy (XPS), Auger electron spectroscopy (AES), and secondary ion mass spectroscopy (SIMS). Furthermore, the crater produced by the sputtering process has not flat bottom because of some specific GD-OES effect such as crater edge effect, re-deposition of the sample atom, and roughening of the crater bottom. These effects are contributed to a poor depth resolution. The dc voltage modulation applied GD-OES technique has been used for the analysis of trace elements in steel samples with a good precision and sensitivity. It can reduce the sputtering rate order of 1/5 with no loss of crater shape because of applying pulsed voltage. Furthermore, only the modulated component can be detected by using phase-sensitive detection with a lock-in amplifier; therefore, the resulting increase in the signal-to-noise ratio can contribute to get more precise analytical values and then make the detection limit lower. In this study, the sputtering rate and crater shape were compared with various modulation parameters, and depth profiles measured for some thin film samples at an optimized condition. 20, 40, 60, and 80 nm of pure Cu, Au, and Cr metals which were deposited on Si wafer by using an ion-beam physical vapor deposition (PVD) were prepared, respectively. Finally, we compared the results with that of Auger electron spectroscopy (AES), and discussed the usefulness for thin film analysis.

(326) **Single Event Spectroscopy with VSMS™ Spectrograph – Applications in Physical Chemistry**

Radek Sobczynski[1,2], H. Lange[3], Dr. Huczko[3], Markus Berger[4], Stephan Dietrich[4]; [1]Princeton Instruments; [2]Acton Research; [3]University of Warsaw; [4]Dipl. Phys. Group of Frau Priv. Doz. Dr. Ing. Ursel Fantz, Uni. Augsburg, Experimentelle Plasmaphsik

Conventional spectrometer design typically limits the user to choose either high resolution or wide spectral coverage. For example, a typical 500mm spectrograph can produce approximately 0.08nm resolution with a 1200 l/mm grating. The tradeoff is the limited spectral coverage across the CCD, which is usually less than 100 nm. We will present a new design for optical spectroscopy; the Vertically Segmented Multi Spectra, (VSMS™) – Czerny Turner Spectrograph. This instrument provides extended spectral range in single spectroscopic acquisition. A traditional grating is split vertically into 5 segments, thereby increasing the spectral coverage by a factor of 5. As an example we will present molecular and atomic spectra acquired with 1200 l/mm VSMS 5 segment grating and 300 l/mm VSMS 5 segment grating in different experiments. Instrument performance is compared to classic Czerny Turner Spectrograph and Echelle Spectrograph.

(327) **Four-Point Standardization Reduces Bias in Spectrometric Determinations**

James W. Anderson

Conventional two-point standardization used to control spectrophotometric determinations introduces a bias that can be minimized by using a statistically viable four-point standardization consisting of the slope of a normal linear regression and a modified

intercept or constant that anchors the correction to the average of the low concentration reference materials. This, in conjunction with using a verifier that is close in concentration to where high and low standardant biases counter each other when they are opposite in sign, reduces the frequency in which a false indication of drift is indicated. The reference materials used for control and verification may be represented by sets of random numbers, normally distributed, adhering to average values (mu), and true standard deviations (sigma). When calculations are made from samples of these sets to determine standardization corrections and applied to expected true values, the resulting deviations clearly are standardization bias, a decision that could not be made readily with actual measurements. Using an example of an optical emission spectrophotometer determination involving a broad concentration range of silver in tin base and tin/lead material that entails gross differences in standard deviations of readings, it is possible to calculate how much bias occurs each time a standardization is performed either by 2-point or 4-point standardization. The bias from the 4-point standardization was about 2/3 of the 2-point bias. This was corroborated in a study of a case of weak signals of arsenic in the same base. These reductions in bias were greater than could be attributed to a doubling of measurements. The study supports that control charts can best be done by using a verifier with a relatively low concentration in which there is a small standard deviation and close to where high and low concentration biases may cancel each other. As expected, the data clearly shows this reduction in bias of the lower concentration materials. What was not anticipated was that the 4-point standardization shows this reduction more clearly. Using a relatively low concentration verifier, the silver determination showed only 3 cases out of 100 in which the calculated bias was at or above 2-sigma, whereas the 2-point showed 9 cases out of the same 100. Extending the study to assume a one percent drift in the verifiers after a standardization had been made, there were very few cases where the negative 2-sigma were exceeded. For the excesses of the positive 2-sigma, the silver biases showed about the same for the extreme concentrations in either type of standardization. But there was a marked reduction in the number of excesses when the more ideal, lower concentraions verifiers were used with the 4-point standardization.

(328) **A Dedicated, Interactive Tool for Multi-Line Selection in ICP-AES**

Albert Brennsteiner[1], Philippe Hunault[1], Agnès Cosnier[2], Yves Danthez[2], Cendrine Dubuisson[2], Emmanuel Fretel[2], Jean-Michel Mermet[3], Olivier Rogerieux[2]; [1]Horiba Jobin Yvon, Inc, [2]Horiba Jobin Yvon SAS, [3]Spectroscopy Forever

Multi-line analysis, i.e. the use of several lines per element, is beneficial in ICP-AES not only because of an efficient use of the information emitted by the ICP, but also for the verification of unexpected spectral and non-spectral interferences. As a whole, reliability of the measurement will be improved. However, line selection is a crucial, complex and time-consuming task in ICP-AES, and the selection of several lines per element is even more complex. To facilitate multi-line analysis and selection, Horiba Jobin Yvon has developped a dedicated tool. This tool is based on the availability of a comprehensive spectra data base that includes wavelengths, line widths, limits of detection, background intensities, sensitivity and dynamic range. Acquisition of the single-element spectra was performed using the CCD-based ACTIVA ICP system under standard operating conditions. The tool consists of a filtering and display procedure. In the filtering procedure, line selection is conducted first as a function of the element concentration ranges, and then by taking into account possible spectral interferences. The filtering procedure will then suggest a potential list of lines. To validate this list, the tool contains a display procedure, which consists of a visual inspection of the suggested lines by combining single-element spectra of concern from the data base. An interactive display of the analytical lines with their vicinity will permit the analyst to verify the absence of spectral interferences. As a blank spectrum is available for each element, the background in the vicinity and below the analyte line profile can also be visualized for an optimized background correction. This tool is a major advance in ICP-AES because it is really based on ICP experiments and avoids tedious experiments.

(329) **Determination of Total Cesium in Irradiated Samples by Inductively Coupled Plasma Atomic Emission Spectroscopy (ICP-AES)**

Jana Northam[1], Daniel Cummings[1], James Sommers[1], Jeffrey Giglio[1]; [1]Idaho National Laboratory

The determination of Cs is problamatic by inductively coupled plasma atomic emission spectroscopy (ICP-AES). Typically, detection limits are in the tens of part per million (ppm) using the 455 nm line (with normal sample introduction). In addition, the analysis of irradiated samples is a further complication. This presentation will detail the installation of an ICP-AES instrument into a lead lined glovebox. In addition, the method development for determining Cs using the 894.347 nm line will be presented. The 894 nm line shows an improvement in detection limits by approximatley a factor of 100. The method will be applied to irradiated samples for the determination of total Cs. Results will be compared with inductively coupled plasma mass spectrometry (ICP-MS) and figures of merit for the determination of Cs by ICP-AES will be presented.

(330) **Determination of Lead And Arsenic by ICP-OES In Cosmetic Products**

Hee Yun Kim[1], Young Me Song[1], Myung Hee Kang, Sun Kun Hong[1], Soo Yeul Cho[1], Chul Joo Lim[1]; [1]Gyungin Regional Korea Food & Drug Administration

With the aim of obtaining a set of common decomposition conditions allowing the determination of lead and arsenic in cosmetics, a factorial experiment was carried out using as factors of the sample weight and acid addition. The optimal sample weight were about 0.5g of shampoo, rinse, and hairspray and about 0.25g of the other kinds of cosmetic products. The appropriate conditons of microwave digestion were the combination of nitric acid, hydrochloric acid and hydrofluoric acid (3ml, 3ml, 4ml) for powder and of nitric acid, hydrochloric acid and hydrofluoric acid (3ml, 3ml, 2ml) for other cosmetic products. Using sample digested by this microwave procedure, the method for the determination of lead and arsenic in cosmetics by ICP-OES was validated. The recoveries of lead were 83.47~88.79%, 96.11~103.33%, 94.81~97.08%, 97.31~100.41% for lipstick, shampoo, mascara and powder, respectively. The recoveries of arsenic were 83.06~86.39%, 80.83~84.44%, 79.72~90.85%, 83.89~89.33% for lipstick, shampoo, mascara and powder, respectively. The RSD of lead was within 9.99% and the RSD of arsenic was within 6.42%. The developed methods are applicable for determination of lead and arsenic in cosmetic products.

(331) **Exposure Assessment Considerations in Utilizing Conventional Chemical and Physiological Based Extraction Techniques Prior to Arsenic Speciation Analysis in Seafood Samples**

John T. Creed[1], Patricia A. Creed[1], Christina M. Gallawa[2], Andrea R. Young[2], Carol A. Schwegel[1]; [1]US EPA, NERL, MCEARD, Cincinnati, OH 45268, [2]Student Services Contract

People are exposed to arsenic principally through water and food. The arsenic associated with drinking water is predominately

inorganic arsenic while the chemical form of the arsenic associated with dietary exposures is comprised of 15-20 different arsenicals. Seafood represents a large percentage of the dietary exposure and is a food group which contains the most diverse set of arsenicals. Assigning relative risks to these exposures is problematic because the chemical form of the arsenic influences the toxicity. Although speciation based data improves the dietary risk assessment, it is important to differentiate between quantitative and non-quantitative speciation based data. Non-quantitative speciation based data generates sources of uncertainty in assigning relative risks to arsenic exposures because some arsenicals remain in the dietary matrix unavailable for speciation analysis. However, quantitative speciation based data are particularly useful in assigning risk because it is designed to maximize the percentage of the total arsenic that is speciated. The first part of this presentation will report on the use of tetra methyl ammonium hydroxide (TMAOH) as an extraction fluid which is capable of solubilizing 85-100% of the arsenicals from seafood. The chromatographic limitations imposed by samples containing both thio-arsenosugars and oxide based arsenosugars will be discussed. Although arsenic speciation studies dramatically improve risk assessment by providing chemical form specific information, they fall short in estimating biotransformation which may occur within the digestive tract. They also provide little guidance with respect to bio-accessibility of dietary arsenicals. Most dietary speciation based studies include a chemically based extraction of the arsenicals in order to liberate the arsenicals from the proteins, fats and starches associated with dietary matrix. Because the chemical extraction step is not physiologically based, it does not provide a good estimate of the bio-accessibility of the arsenic within a dietary sample. The second part of this presentation will report on utilizing an in-vitro technique to estimate the bio-accessibility of the arsenic in seafood samples. Finally, the speciation results from both the in-vitro and the TMAOH extraction will be compared. Although this work was reviewed by EPA and approved for publication, it may not necessarily reflect official Agency policy.

(332) **Analysis of Environmental Samples Following US EPA Guidelines Utilizing a New Simultaneous CCD Detector ICP-OES System**

Doug Shrader[1], Vincent Calderon[1], Andrew Ryan[1] ; [1]Varian, Inc.

The United States Environmental Protection Agency (US EPA) Contract Laboratory Program (CLP) defines the analytical methods accepted for the isolation, detection and quantitative measurement of target analytes in both water and soil / sediment environmental samples. Data from the Statement of Work (SOW) for Multi Media, Multi Concentration Inorganic Analysis (ILM05.3) is used to define the nature and extent of contamination, and determine appropriate cleanup actions, emergency response actions and enforcement / litigation activities.1 This presentation will describe the use of a new simultaneous CCD detector ICP-OES system to carry out the US EPA / CLP compliant analysis of water samples. ILM05.3 requirements, the ICP-OES system utilized and method parameters developed will be briefly discussed. Results for water samples including the numerous CLP required performance, interference, recovery and quality control tests will be presented. 1 ILM05.3, EPA Publication 540-F-04-001, 2004.

(333) **Droplet Direct Injection System for Inductively Coupled Plasma Source**

Kazuyasu Takimoto[1], Hidekazu Miyahara[2], Taichi Kageyasu[1], Masato Watanabe[1], Eiki Hotta[1], Akitoshi Okino[1],; [1]Department of Energy Sciences,Tokyo Instutute of T, [2]Laboratory for Nuclear Reactors, Tokyo

Argon inductively coupled plasma mass spectrometry (Ar-ICP-MS) and Ar-ICP atomic emission spectrometry (Ar-ICP-AES) have attracted widespread interest because of their analytical figures of merit, such as the excellent performance of detection and the ability to measure isotope ratios. Recent years, target of elemental analysis has been shifted to smaller amount samples such as nano-particles, cells, etc. However, the conventional ICP system consumes relatively large volume (over 1 ml/min) of sample solutions, so it is not suitable for these samples. In order to decrease consumption of sample solutions, direct injection systems have been studied. For example, direct injection high efficiency nebulizer (DIHEN) made by Montaser group consume small samples (<85 mL/min) and realize excellent analytical performance. Our group also developed direct injection ICP torch for both argon and helium plasma in 2003. The torch is shorter than usual argon ICP torch and so it is able to use a conventional concentric nebulizer as a direct injection nebulizer. With these direct sample injection system, aqueous solutions directly introduced into the plasma and so it is achieved almost 100% introduction efficiency. Not only in direct injection ICP but even in usual nebulizer system ICP, sample aerosols diffuse in cone shape into the plasma. In this study, to realize more efficient sample introduction, droplet type direct injection system is designed. In this system, aqueous solutions injected in droplet shape on a straight line through a small ejection hole by high pressure. So, aqueous droplets can be introduced accurately just onto the axis of the plasma. The volume of the droplets can be accurately defined by hole diameter and the applied pressure. Therefore, very small and accurate sample introduction can be achieved with this new droplet direct injection system. Results of spectroscopic characteristics will be presented. This study was partly supported by in Industrial Technology Research Grant Program in '05 from New Energy and Industrial Technology Development Organization (NEDO) of Japan.

(334) **Molecular Species in Glow Discharge Emission - A Connection with Matrix Effects?**

Arne Bengtson[1], Thomas Björk[1]; [1]KIMAB

The introduction of RF (radio frequency) glow discharge sources has extended compositional depth profiling (CDP) to non-conductive surface layers, primarily polymer coatings. When quantifying polymers according to the standard method based on emission yields (EY), it has been observed that the EY for carbon is normally considerably lower than for inorganic materials. It has also been established that when sputtering polymers, substantial emission is observed from several diatomic molecules formed by light elements (CO, CH, OH, NH, C2). In this work, the possible correlation between these phenomena is investigated. A Leco GDS 750 spectrometer equipped with an RF source was used. The instrument has been fitted with fixed channels to monitor emission from CO, CH, OH and NH. Several Inorganic RM's were used to determine the EY for carbon; low alloy steels, cast irons, tungsten carbides and a silicon carbide. A 4 mm anode was used, and the conditions were 14W plasma power at 700 V RMS. As expected, data points from the inorganic RM's fall on a smooth calibration curve. A few well-characterised polymer coatings, analysed by wet chemical methods, were also measured. The data points from all of these coatings show considerably lower EY's for carbon compared with the inorganic materials. The emission intensities of the

molecular channels from the polymer coatings were measured and evaluated. It was found that there is a certain correlation between molecular emission and loss of EY, but the scatter in the data does not allow far reaching conclusions. A few polymer coatings were also run at different excitation conditions, the variations in EY for carbon and molecular emission intensity was evaluated. The results indicate that the relative loss of EY for carbon is almost independent of the discharge conditions, while the molecular emission intensity increases with voltage. The implications of these investigations for quantitative CDP of polymer coatings will be discussed.

(335) **Efficient Determination of Phosphorus Levels – How to Handle Hundreds of Stool Samples**

Ela Bakowska[1], Joan Schemmer[1], Matthew McMullin[1], Cecelia White-Powell[1], Kirsten Trbovich[1]; [1]National Medical Services

Phosphorus and calcium are vital in maintaining strong, healthy bones and teeth. They are also important for the cells for energy storage and in nerve function. The amount of phosphorus (in the form of phosphate) in blood is tightly regulated by the parathyroid hormone (PTH) and by controlling the amount of phosphate absorbed from the food and excreted in urine and stool. Phosphate stores are depleted (hypophosphatemia) in people with severe malnutrition, with impaired kidney function or who use diuretics or aluminum-containing antacids for a long time, diabetic ketoacidosis, severe alcohol intoxication, or severe burns. As a result of kidney failure, excess phosphate starts to build up in blood (hyperphosphatemia). Phosphorus levels in blood can be controlled through diet, dialysis and phosphate binders. Phosphate binders help to pass excess phosphate into stool by combining with phosphate to form a compound that is not absorbed by blood. Measurements of Phosphorus in stool, urine and other specimens were conducted by Inductively Coupled Plasma – Atomic Emission Spectroscopy (ICP-AES). ICP-AES can only handle liquid samples. The stool samples require additional preparation prior to the analysis by ICP-AES. For some studies, the 24-hour collection of stool is conducted and a sub-sample is analyzed. The nature of stool samples is their lack of homogeneity, hence some additional steps are taken to assure that a sub-sample which is representative of the whole specimen will be analyzed. The homogenized stool specimens are then acid digested. With a standard microwave digestion (MWD) system, only 30 specimens can be prepared during a day. We employed a specialized MWD system (ETHOS 1200 with Teflon micro inserts) to facilitate higher throughput of samples: 60 per day. The results obtained by method of standard addition were compared with those obtained from external calibration. Analytical figures of merit: accuracy, precision and % recovery data will be shown. Additionally the comparison between results obtained from measurements by ICP-AES and ICP-MS will be presented.

(336) **The Determination of Mercury in Solids and Liquids: Bringing Together USEPA Methods 1631, 245.1, 245.7 and 7473**

David Pfeil[1], Peter Brown[1]; [1]Teledyne Leeman Labs

Mercury determinations are required in a variety of sample matrices and across a very wide range of concentrations. Sensitive techniques, such as purge and trap cold vapor atomic fluorescence spectroscopy, are available that can achieve detection limits at sub part-per-trillion levels but which cannot handle higher concentrations without massive dilutions. On the other hand, there are less sensitive techniques, such as direct combustion mercury generation that can handle diverse matrices with little to no sample pretreatment. Instrumentation designed for the differing techniques share much in terms of their detection systems but little in terms of sample introduction. In all cases free gaseous mercury is the species that is ultimately quantified. The processes to produce the mercury gas, however, diverge significantly. Methods 1631, 245.1, & 245.7 employ chemical reactions with acids, oxidants, and reductants. Method 7473 employs sample heating followed by vapor catalysis. We will introduce a combustion-based instrument to determine mercury in matrices such as solids, tissues, coal, and soils without sample pretreatment that can be equipped with a high sensitivity liquid introduction system.

(337) **On The Use of Collisional Transfer in A Cesium Cell to Enhance Its Application as A Resonance Fluorescence Detector**

Benoit Lauly[1], Benjamin W. Smith[1], Nicolo Omenetto[1], James D. Winefordner[1]; [1]University of Florida

In many fields of science, there is an increasing demand for detectors with both high spectral resolution and high sensitivity. Although conventional systems frequently excel in one these aspects, it is often at the expense of the other. Atomic vapor detectors have a spectral resolution that is governed by the properties of the atomic vapor used as the sensing element, while maintaining the same high value of the luminosity. Cesium vapor cells have been extensively investigated because of its high number density at low temperature and its strong resonance transition in the infrared at 852nm (62S1/2 → 62P3/2). A resonance fluorescence detection scheme has been demonstrated in our laboratory: two successive excitations at 852nm and 917nm (62P3/2 → 62D5/2), followed by the detection of the green fluorescence at 455nm (72P3/2→ 62S1/2). A promising fluorescence scheme for cesium is proposed here that includes a single transition at 852nm and detection at 894nm (62P1/2 → 62S1/2). For efficient detection, a rapid fine-structure mixing (62P3/2 ↔ 62P1/2) is required and is provided by the presence of ethane in the cell. The absorption properties of the cell are investigated in this work with tunable narrow-bandwidth diode lasers as well its potential application to selected analytical problems such as Raman spectroscopy.

(338) **The Determination of Halogens by Inductively Coupled Plasma Optical Emission Spectroscopy in The Ultralow Uv Wavelength Range**

David Pfeil; Teledyne Leeman Labs

Interest in determining halogens, along with other elements more commonly measured by ICP-OES, has grown significantly in the last ten years. The most sensitive emission wavelengths for the halogen elements are below 160nM, a region which presents different challenges in optical design from most commercial plasma spectrometers to achieve good light transmission and signal detection. Results for halogens and other elements for several matrices will be shown. Elements determined will demonstrate performance across a wavelength range of 134-900nM. Instrumental figures of merit including optical configuration, wavelength coverage and resolution will be presented. Optimal plasma operating conditions, wavelength selection and background correction will be discussed..

(339) **Spectroscopic Diagnostics of a Thallium Glow Discharge Lamp by Absorption, Emission, and Laser-Induced Saturated Fluorescence Spectroscopy**

Nicholas Taylor, Nicolò Omenetto, Benjamin W. Smith, James D. Winefordner; [1]University of Florida

Absorption, emission, and fluorescence diagnostic measurements are made in a thallium glow discharge to characterize it as a photon detector. The electronic transitions investigated are the 7 2S1/2- 6 2P1/2 (377.57 nm) transition as well as the 72S1/2 - 6 2P3/2 (535.046 nm) transition. The shapes of emission and absorption profiles obtained are examined for varied currents applied to the

discharge. Emission measurements are made by means of a piezo-electric scanning Fabry-Perot spectrometer. Absorption measurements are made by means of focusing wavelength modulated light from a Xenon arc continuum through the glow discharge. The resulting emission and absorption profiles are evaluated in order to determine the thallium number density and Doppler temperature for each discharge source over a range of currents. Spectroscopic evaluation of the thallium number density and Doppler temperature of the thallium glow discharge is also preformed using laser-induced saturated fluorescence and the steady state rate equation model. The resulting saturation curves are evaluated for number density and Doppler temperature over a range of currents used. Results obtained from the three methods and results previously reported in the literature are discussed.

(340) **Approaching a Universal Pneumatic Nebulizer – The Next Step**

Ronald Stux[1], Gerald Dulude[1], Vesna Dolic[1], Paul Neal[2]; [1]Glass Expansion, Inc, [2]Thermo Electron, Inc

In earlier work (2006 Winter Conference) we described a concentric nebulizer designed to operate at high pressure, and showed initial evidence that detection limits and precision improve when running at pressures higher than most ICP instruments typically supply. The recently introduced Thermo iCAP6000 series instruments can supply nebulizer pressures up to 80 psi, offering us the opportunity to test our design in "real-world" situations. This presentation describes the performance of the high-pressure nebulizer when used with a variety of real-world samples.

(341) **Molecular Gas Interference in Diode Array Glow Discharge Optical Emission Analysis**

Kim Marshall[1], Kevin Brushwyler[1] ; [1]Leco Corporation

Glow Discharge Optical Emission Spectrometry (GD-OES) is a well-established technique for compositional depth profiling. It is an outstanding tool for compositional depth profiling (CDP) of both conductive and non-conductive samples. Quantification in this technique relies on an assumption that the emission yield of the analyte atoms is matrix independent. Fortunately, this assumption is true for most applications. But there are exceptions and, with the advent of the radio frequency source, which widened the applicability of GD-OES to organic layers and other non-conducting surfaces, this assumption of constant emission yield has been found to be less valid. Some of these apparent changes in emission yield are related to the concentration of plasma species such as hydrogen. More recently other plasma constituents such as CO, CH, OH and NH have been shown to cause similar deviations. Building on similar work by Arne Bengtson, we will further explore these apparent emission yield deviations using a diode array spectrometer in order to collect a broad range of spectral information in the presence of gas mixtures while analyzing several different sample materials. The implications of this gas contamination on various spectral features and the subsequent calibrations will be investigated. Suggested approaches to minimizing these interferences will be discussed.

(342) **Indicator and Novel Correction Methodology for Plasma-related Matrix Effects in Inductively Coupled Plasma-Atomic Emission Spectrometry;**

George Chan[1], Gary Hieftje[1], [1]Department of Chemistry, Indiana University

Matrix effects in inductively coupled plasma–atomic emission spectrometry (ICP-AES) have been widely reported in the literature. The presence of matrix effects, without the awareness and subsequent correction by an analyst, would lead to an analytical error. Therefore, there is a need to develop indicators for plasma-related matrix effects as warning signals for routine ICP analysis. To date, the ionic-to-atomic line-intensity ratio (and especially the Mg II/Mg I ratio) has been used universally for this purpose. Alternatively, since it is well known that the direction and magnitude of plasma-related matrix effects are functions of the observation height, it might be a convenient means for flagging plasma-related matrix effects by using vertically resolved emission intensities of the whole plasma for analysis. In addition, for typical plasma operating conditions, the matrix effects generally change from an enhancement effect at very low positions in the plasma to a depression effect at higher positions. The transition where the enhancement effects are balanced by the depressions results in a spatial region with no apparent matrix effects (the so-called cross-over point). In this presentation, the analytical characteristics and effectiveness of using the whole vertical emission profile of the plasma as an indicator for the presence of plasma-related matrix effects will be examined, and the feasibility of using a novel approach for *in-situ* determination of the cross-over point location for the compensation of matrix effects will be evaluated.

(343) **Induction Heating-Electrothermal Vaporization for Direct Mercury Analysis of a Single Human Hair by Atomic Fluorescence and Atomic Absorption Spectrometry**

Eric D. Salin[1], David Duford[1], Josiane P. Lafleur[1], Rebecca Lam[1], Cameron D. Skinner[2], [1]McGill University, [2]Concordia University

The heavy metal mercury (Hg) is a neurotoxin known to have a serious health impact even at relatively low concentrations. Analytical methods play an important role in monitoring Hg exposure from environmental and dietary sources. The amount of Hg in an individual's body has been correlated to the amount of Hg in an individual's hair. Typically, human hair contains approximately 1 ug/g of Hg. Indirect conventional methods for the determination of Hg in hair require up to approximately 100 strands of hair and include a lengthy digestion step that introduces a potential for contamination and analyte loss. Up to now, direct methods require expensive instrumentation. We present here a rapid, cost efficient and potentially field portable system for the total analysis of Hg in human hair. The system combines the simple direct sample introduction of induction heating-electrothermal vaporization (IH-ETV) with a gold amalgamation (GA) trap in tandem with detection at 253.7 nm by either atomic fluorescence spectrometry (AFS) or atomic absorption spectrometry with background correction (AAS-BC). Using these techniques, detection limits of 0.1 ng or 0.2 ug/g and 0.08 ng or 0.1 ug/g (based on a 0.6 mg sample) of Hg were achieved respectively. With the AFS system, only Hg fluoresces at 253.7 nm. In the second system, automatic background correction using the broad band absorption near 253.7 nm compensates for the absorption of trace organic vapours. The IH-ETV technique also offers several advantages. First, it required no sample preparation. Second, the time of analysis was reduced to a few minutes. Third, the use of interchangeable cups and non-contact heating reduced contamination as well as alignment and handling problems that occur with conventional electrothermal vaporizer systems.

(344) **Tandem Calibration Methodology using a Dual Nebulizer Sample Introduction System for The Analysis of Micro Sample by ICP-OES.**

Zully Benzo[1], Domingo Maldonado[2], José Chirinos[3], Eunice Marcano[1], Clara Gomez[1]; [1]Centro de Química. IVIC, [2]CICBa, Departamento de Química. UNEFM, [3]Centro de Química Analítica. UCV

The work is focused on the optimization and evaluation of the main analytical figure of merits of a dual micro-nebulizer sample introduction system. The system is essentially a modified cyclonic spray chamber that allows the simultaneous operation of two high efficiency nebulizers (HEN). Optimization of the instrumental plasma parameters using this system was carried out taking the

plasma robustness as the instrumental response. Evaluation of the main analytical figure of merits: sensibility, short and long-term precision were carried out. The full versatility of this system has been exploited by checking its capability in carrying out standard additions on line (tandem calibration methodology, TCM) in ICP-OES. Results show that sensitivity (Signal to Background Ratio, SBR) and detection limits are improved compare with conventional cyclonic spray chambers. However, precision was slightly poorer than the conventional system. Long term stability obtained indicates that the system is stable for at least two and a half hours of continuous operation. The analytical applicability of the dual system was checked by analyzing a standard reference material NIST 1577b, Bovine Liver. Analytical results for the reference material, obtained from three different calibration modes showed that for the elements determined Ca, Cu, Fe, Mg, Mn and Zn, the precision expressed as the relative standard deviations (RSD) was found to be better for TCM (3%), followed by standard addition method (4%) and external calibration (matrix-matching) (7%) modes. The results show that the accuracy achieved when using the different calibration techniques are comparables.

(345) **A New Upstream Electrothermal Vaporization (Etv) Device - Properties and Understanding of Analyte Condensation and Transport**

Gerd Hermann, Alexander Trenin

A newly constructed ETV device with Axially Focusing Convection (AFC) upstream shows high uniformity for analytes of different volatility. The main feature of the unit is the upstream inside a vertically oriented tube. The hot gas flow released from the outlet hole in the center of the tube containing the analyte vapor and condensed particles strives for the center of the AFC graphite tube. Thereby an axially focused convection zone is formed, where vapor condensation occurs predominantly apart from the walls. The upstream is shielded against emission of incan-descent ETV walls and surrounded with several cooling argon flows in order to increase tem-perature gradients right above the tube outlet and facilitate vapor condensation. The temperature course above the outlet has been measured with a fast thermocouple. Particles were collected beginning at 2.5 mm above the tube outlet hole and inside the furnace for analyzing the sizes of condensed particles with SEM and TEM. Analyte transport efficiencies were directly measured with electrostatic precipitation of the transported aerosol onto secondary platforms and analysis via atomic spectrometry. The effect of K and Pd as matrix/carrier modifier has been investigated as well as of gaseous modifier cyclohexane. Directly determined analyte transport efficiencies are 70-80% for medium volatile ele-ments (Fe, Ni). Increase in the number of native carbon-containing compounds during the va-porization step makes the analyte transport more efficient. In order to stabilize the carbon pres-ence varying with the tube aging a hydrocarbon vapor is introduced into the ETV tube with the inner argon gas flow. Measurements with modifiers show a positive effect of potassium and palladium modifiers as well as of gaseous carbon hydrates, especially on the transport efficiency of volatile ele-ments. Thus, sample analytes are transported to an analytical instrument with more equal ratios (60-70% for Ag, Cu, Mn, Pb; 70-80% for Fe, Ni). It is shown with micrographs of particles deposited on substrates via thermophoresis that carbon particles are already present inside the furnace and in the released gas flow. These par-ticles are crucial for the analyte condensation process at the carriers. They are analyzed via scanning and transmission electron microscopy (SEM and TEM) The results are compared with calculations on the bases of a simple model that is pre-sented in another paper (poster) on this conference. It allows the calculation of analyte losses in different parts of the ETV and tubing system, and of analyte transport efficiencies for medium and high volatile analytes, with and without matrix/carrier modifiers, such potassium and palla-dium, as well as of hydrocarbons added as gaseous modifiers.

(346) **Interferometric Droplet Imaging for In-situ Aerosol Characterization in an Inductively Coupled Plasma**

Ryan Brennan[1], Kaveh Jorabchi[1], Jonathan Levine[1], Maryam Farmand[1], Mazdak Taghioskouei[1], Akbar Montaser[1]; [1]The George Washington University

Size, velocity and evaporation rate of droplets in an Ar inductively coupled plasma (ICP) are simultaneously measured for the first time using a novel laser based imaging technique. In interferometric droplet imaging (IDI), an interference pattern created by the reflected and refracted rays from a droplet are collected in an out-of-focus image. The droplet diameter is determined by counting the number of fringes in the collected interference pattern. Combination of IDI and particle tracking velocimetry (PTV) provides the capability of monitoring droplet properties during the journey inside ICP. Using a demountable-direct injection high efficiency nebulizer, droplets in the range of 3-30 μm in diameter traveling at 15-70 m/s are observed in the analytical zone of the ICP. The upper velocity threshold for surviving droplets is determined by the nebulizer gas flow rate whereas the lower threshold is mainly influenced by thermal expansion of the plasma gas. Droplet evaporation rates (0.26-0.36 mm2/s) are in good agreement with other reports and theoretical simulations for droplets in a 3000 K Ar environment.

(347) **Micro Plasma Chips for Chemical Analysis**

Mazdak Taghioskoui[1], Kaveh Jorabchi[1], Mona Zaghloul[1], Akbar Montaser[1]; [1]The George Washington University

Inductively coupled plasma (ICP) spectrometries are the methods of choice for analytical atomic spectrometry. However, large size, heavy instrumentation, and high gas and electrical power consumption limit the use of plasma spectrometries exclusively to laboratories. A miniaturized device for plasma generation resolves problems related to portability (required for field analysis) and operation cost, providing an attractive approach for several micro analytical applications such as lab-on-chip. In this research, general concepts of plasma generation on small scales are considered and various geometries for micro plasmas are investigated. Experimental setups required for generating micro plasmas are examined and simulated using the finite element approach. These simulations predict optimum conditions for generating the most intense micro plasmas. The effects of operating parameters such as gas pressure, frequency, and device geometry and dimensions on micro plasma properties are investigated.

(348) **Statistical Determination of the Uncertainty Associated**

Ralph Obenauf[1], NImi Kocherlakota[1]; [1]SPEX CertiPrep, Inc.

Certified values of Reference Materials (CRM) are not useful unless accompanied by a stated and precisely defined uncertainty. If certificates of analysis are examined, one often finds inconsistencies, misstatements and errors related to uncertainty (dispersion of the value that could reasonably be attributed to the measurand) and stability (change in value over time). A precise understanding of measurement uncertainty on the part of the user is required as well as confidence that the reported uncertainty is calculated and defined correctly. Your measured values are only as good the uncertainty of those results. The paper will cover the evaluation of the total expanded uncertainty arising from all sources and covering all processes involved in determining the certified value of an ICP CRM. This determination will be for a chromium (VI) reference material whose certified value was determined by titration against a standardized sodium thiosulfate solution which was in turn standardized against a potassium dichromate standard reference material, SRM. Chromium (VI) is

one of the six substances listed in the EU RoHS (Restriction of Hazardous Substances) directive 2002/95/EC requiring electronic equipment producers to limit these substances in their products. The above method was selected for discussion as it contains examples of many of the common procedures used in analytical determinations, wet or instrumental. Therefore the uncertainty calculations here can be directly applied to other analytical methods to determine the statistical uncertainty of other common laboratory measurements such as those by ICP and ICPMS.

(349) **A Simplified Approach for Absolute Qunatitation of Nucleic Acids using ICP-OES**

Myungsub Hahn[1], Euijin Hwang[1], Yong-Hyeon Yim[1], In-Chul Yang[1], Sang-Ryoul Park[1]; [1]Korea Research Institute of Standards and Science

Traceability is being recognized as an important element in the biological analysis with the recent advance of biological science and technology. Many national measurement institutes (NMIs) are making enormous efforts to establish the measurement standards in the biological analysis. We're developing an absolute nucleic acid quantitation method which is potentially traceable to SI. The method takes advantage of the stoichiometric existance of phosphorous atoms in nuclei acid molecules. By measuring the amount of phosphorous in acid-digested nucleic acid solution using high-accuracy ICP-OES method, amount of nucleic acid in the solution can be determined within standard uncertainty of 1 %. The technology is one of the most important breakthroughs for the development of nucleic acid related certified reference material (CRM). To overcome the present limitation of the method, which requires relatively large amount of materials and extensive digestion, simple digestion or dilution method has been developed and evaluated.

(350) **Detection of Contaminated Metal Ion on Solid Surface Using Nano-Electrospray**

Deok-im Jean; Dankook University

Chemiluminescence scanning has been used to react with metal ion contaminants. This study aims to make a novel contribution to silicon wafer surface analysis using luminol-H2O2 and metal chemiluminescence reaction. As a first step, the research focuses on detection of contaminated metal ion on solid surface using the nano-electrospray (nano-ES) method. Depending on the achieved level of optimization, nano-ES can be applied to detect metal ion on silicon wafer surface analysis. Nano-ES for reagent or sample injection is likely to be a substantial improvement over current tedious and cost-ineffective conventional methods. This method allows for detection of luminescent emission of 10000ppm down to about 1ppm Co deposited on the surface. The research targets to achieve the detection of a similar level of contaminant using nano-ES compared with conventional chemiluminescence . And it provides fast analysis and reduced possibility of contamination with spatial resolution of metal contaminants on the solid surface, given that sample pretreatment is not required.

(351) **FTIR Spectroscopy as a Function of Molecular Weight Distribution of Wood Coatings**

Richard Papez; Armstrong World Ind.

As outsourcing becomes more prevalent in US industry, coatings are used and applied on products without a complete knowledge of the chemical composition by the user. Basic requirements are safety to the employees/consumer and processing/performance of the coating. Analysis by the application company is often not done unless there is a problem in one of these areas. Wood coatings are no exception. This poster shows some examples of the use of combinations of analytical techniques to better understand the chemistry of such coatings. In particular molecular weight distribution by Gel Permeation Chromatography (GPC) with Fourier Transform Infrared (FTIR) Spectroscopy is an extremely useful technique for wood coating analyses. Some of the examples also include the use of FTIR-microscopy on cured coatings and contributions from GC-MS, NMR and SEM. In order to solve a coating problem, it is often helpful to know its composition. Many of today's wood coatings contain very complex chemistry. In addition there are often multiple coating layers on a wood product. Our microscopy laboratory has detected as many as ten layers on a single product. If one can obtain the liquid coating before it is applied and cured, the likelihood of identifying all the components is better than working only from the cured product. GPC/FTIR chromatograms/spectra with interpretations are shown for several wood coatings and sub-layers. As noted above, supporting information from GC-MS and NMR is included.\r\n\r\nIf the liquid coatings cannot be obtained, one is forced to work with the cured coatings on the wood. The poster shows two examples in which the coated wood is defective. In these cases, FTIR-microscopy was used to obtain a better understanding of the problems. In the first example the problem was cracking of the veneer/coating. In the second example the defect was inconsistency in the absorption of stain. GPC/FTIR results are shown in combination with SEM observations of the wood structure.

(352) **Imaging Studies of Phase Separation and Diffusion in Polymers by FTIR Transmission and ATR Spectroscopy**

Heinz W. Siesler[1], Christian Vogel[1], Elke Wessel[2] ; [1]Dept. of Phys. Chem., University of Duisburg-Essen, [2]Beiersdorf AG, Hamburg, Germany

FTIR imaging with focal plane array detectors provides a unique possibility of rapid chemical visualization of samples by a combination of vibrational spectroscopic and spatial information. Thus, selected sample areas can be analyzed with reference to the distribution of chemical species by FTIR transmission or ATR spectroscopy with high lateral resolution (up to 3-4 µm). In the present contribution we focus on the domain formation of the amorphous and crystalline regions in biodegradable poly(hydroxy-alkanoates)(PHA´s) and the phase separation of PHA blends with other polymers. These phase separation phenomena have a significant impact on the thermal and mechanical properties of the investigated polymers. Furthermore, for the first time real-time imaging data of the diffusion process of deuterated water into an aliphatic polyamide will be discussed in some detail.

(353) **Detection of Explosives by Hyperspectral Imaging**

Diane Williams[1], Hina Ayub[2] ; [1]Federal Bureau of Investigation, [2]Oak Ridge Institute of Science Education

The detection and identification of microgram quantities of explosives has been accomplished by the use of a Visible/Near Infrared Imaging System (V/NIR HSI). Since the data set represents three dimensions, two spatial and one spectral, the system allows for the collection of a spectral profile of an explosive while providing visualization of the explosive on fabrics. We will present data obtained from the analysis of pentaerythiotoltetranitrate (PETN) and cyclotrimethylenetrinitramine (RDX).

(354) **Water Sorption Process into a Biocompatible Polymer Film: Time-Resolved In-Situ ATR-IR Observation**

Shigeaki Morita[1], Masaru Tanaka[2], Yukihiro Ozaki[1]; [1]Kwansei-Gakuin University, [2]Hokkaido University

Water sorption process into a biocompatible polymer, poly(2-methoxyethyl acrylate) (PMEA), was investigated by time-resolved in-situ ATR-IR spectroscopy. A polymer film was prepared onto a ZnSe prism, and an ATR-IR absorption by evanescent wave of near-filed light generated at the prism/polymer interface was

monitored. A series of time-resolved in-situ ATR-IR spectra was collected during water vapor or liquid water sorption process into a PMEA film from 0 to 600 s every 1.86 s. Since a thickness of the film sample was adjusted to be thicker than the penetration depth of the near-field light, only sorbed water into the polymer matrix excluding bulk water contacting the film surface is detected. A spectral shape variation in the broad and overlapping O-H stretching band from higher wavenumber to lower wavenumber regions was observed, demonstrating a hydration structure change of PMEA with time. Three typical bands around 3600, 3400 and 3200 cm-1 were distinguished in the O-H stretching region at different time. Subtraction spectrum analyses revealed that respective bands arise from non-freezing water, freezing bound water and freezing water, respectively, which have been reported to be in PMEA matrix by differential scanning calorimetry and gravimetric method. Evidences for hydrogen bonding interaction between the carbonyl group in the PMEA side chain and water molecule was also found in the spectra. Hydration structure changes of PMEA will be discussed in detail from the time-resolved in-situ ATR-IR spectra.

(355) **Water Sorption Process into a Biocompatible Polymer Film: Effects of Small Molecules on Water, Studied by ATR-IR**

Akiko Tanabe[1], Shigeaki Morita[1], Masaru Tanaka[2], Yukihiro Ozaki[1] ; [1]Kwansei-Gakuin University, [2]Hokkaido University

It has been reported that highly biocompatible materials have unique hydration structures. In addition to the well-known hydrated water (namely, "freezing water" and "non-freezing water"), there exists another kind of sorbed water, which is unique to the biocompatible materials, called "freezing bound water". A new polymer material, poly(2-methoxyethyl acrylate)(PMEA) exhibits high blood compatibility and was used to study its hydration structures. It has been known that some water-soluble compounds break the structure of bulk water since these molecules attract water and become hydrated as they dissolve. By using these concentrated solutions instead of water, sorption process into the polymer film became very distinct form the usual one. When a concentrated NaCl solution was injected in the specially designed ATR-IR flow cell, only sorption of non-freezing water (ca. 3600 cm-1, OH st.) occurred, by means of HO---O=C interactions between water and polymer (ca. 1700cm-1, C=O st.). Since most water molecules were taken up by sodium and chloride ions in the solutions, only the small amount of non-interacting water penetrated into the polymer film. This is consistent with the result of the sorption process of water vapor (Morita, et al., submitted). After the sorption of NaCl solution, bulk water was injected, replacing the NaCl solution; as a result, the polymer film swelled further as freezing bound water and freezing water were sorbed. Interestingly, the driving force of this sorption process was not by the hydrogen bonding of carbonyl group since no shift in the carbonyl C=O band was observed. Also, all the processes were entirely reversible when injecting the desired liquid into the flow cell. The contribution was made for the study of hydration structures of PMEA, especially the support for the band assignment in the OH stretching region and the cause of water-polymer interaction. Other interesting studies were done using the same system, by changing the solute compounds (NaCl, urea, glucose, and glycine) and their concentrations. They all have different solubilities and different hydration structures, so the unique sorption processes were observed by time-dependent or concentration-dependent IR series spectra for each solution.

(356) **Infrared Study of Degradation and Degradation Products of Poly(amides) and Poly(phthalamides)**

Katherine Robertson[1], Xiaodong Liu[1], Richard A. Nyquist[2]; [1]Impact Analytical, [2]Nyquist Associates,

Nylon and Nylon-type polymers are widely used in manufacturing industries, especially the automotive industry, for their physical properties, as well as heat and chemical resistance. Failure of manufactured nylon parts is often attributed to environmental conditions or physical stress, although processing issues such as exposure to moisture, and melt and mold temperature can also play a role in the cause of failure of molded parts. Mid-Infrared Spectroscopy, used in conjunction with thermal analysis techniques such as DSC and TGA-MS, was employed to study the effects of thermal degradation and oxidative degradation on several polyamides and poly(phthalamide) resins. Attention was paid to changes in the infrared spectra and thermal physical/chemical properties of virgin material to that of material following exposure to moisture and high temperature. This information will be useful as an aid in the determination of the cause of failure in manufactured nylon and nylon-type molded parts.

(357) **Promoting Method Globalization Through Internal Infrared Reference Libraries**

Jessica Jarman; GE Industrial - Plastics

The Industrial world continues to expand upon both geographical and intellectual boundaries, but the standardization of methods and results across several laboratories is a daunting task. Some aspects such as instrumentation capabilities must remain unique, while other procedures and features of sample analyses can be more standardized. Our Analytical Technology group, a true global organization, has attempted to reconcile these differences by creating a globally-accessible reference library that contains data from each site and incorporates both raw materials and final products. Although quantitative method standardization is not addressed by these measures, qualitative identification of unknown materials is significantly enhanced, which allows faster turnaround time for customer interface teams. As an added bonus, start-up time for new laboratories is decreased because they now have access to the same historical data as other established sites, instead of waiting for years to develop similar reference capabilities. Measurements such as site-to-site usage, search speed from several global locations, and database holding statistics will be presented.

(358) **UV Radiation Effects on Reflectance FTIR Microscopy of Clean B. Subtilis Spores**

Heather Brooke[1], Barbara Setlow[2], Peter Setlow[2], Burt Bronk[3], Michael Myrick[1]; [1]University of South Carolina, [2]University of Connecticut Health Center, [3]Air Force Research Laboratory

A study was conducted to determine how exposure to 254 nm light affects the mid-infrared (MIR) absorption spectra of bacterial spores. Bacillus subtilis endospores filtered across a reflective surface were analyzed by Fourier transform infrared (FTIR) reflectance microscopy. Spectra were measured before and after four hour intervals of exposure to a handheld lamp up to a total of 24 hours of exposure. It was that photochemically induced changes cause the absorbance in the Amide bands to decrease, broaden, and blue shift. A new peak also emerges at 2180 cm-1. These effects appear after only 4 hours of exposure and become more pronounced after longer exposures. Calcium dipicolinic acid (CaDPA), a major constituent of bacterial endospores, was also studied using this method to help determine the cause of the observed effects on the bacterial spores.

(359) **Dipole Moment Derivatives of Benzene in the Liquid and Gas Phases: Evidence for Pseudo-Hydrogen Bonding**

Dale Keef ; Cape Breton University

Interest in the vibrational properties of benzene dates back over 70 years to the pioneering work of Wilson. This paper presents an analysis of the infrared intensities found for C6H6, C6D6 and C6H5D in the liquid and gas phases, motivated in part by the quite

marked intensity differences between the fundamentals of C6H6 and C6D6 in the liquid, and between corresponding vibrations in the liquid and gas phases. The experimental intensities are different for the three isotopomers in the liquid and gas phases, and these differences are due mainly to a difference in the CH stretch dipole moment derivatives in the two phases. This difference was related qualitatively to the intermolecular interaction of the H with the pi-cloud of the nearest neighbour creating a pseudo-hydrogen bond. Since the experimental integrated intensities depend only on the magnitudes of the dipole moment derivatives, their directions cannot be determined from experiment. To help determine the directions of the dipole moment derivatives, the dipole moment derivatives of benzene were calculated at the HF, MP2, MP3, CCD and CCSD levels of theory with several basis sets.

(360) **Diffuse-Reflectance Mid-IR and NIR Spectroscopic Properties of Mycorrhizal and Non-mycorrhizal roots.**

Francisco Calderon[1], Veronica Acosta-Martinez[2]; [1]USDA-ARS, Akron, CO, [2]USDA-ARS, Lubbock, TX

In this experiment, we measured the diffuse-reflectance Fourier-Transformed Mid-IR and NIR spectral properties of crop roots infected with symbiotic mycorrhizal fungi, as well as and non-mycorrhizal control roots. Corn, sorghum, sunflower, and wheat plants were grown in the greenhouse on heat treated soil with and without mycorrhizal inoculum. The plants were harvested after six weeks, then the roots were rinsed, lyophilized and ground for scanning with the diffuse reflectance FT-IR. Root samples were also analyzed for fatty acid content in order to quantify mycorrhizal markers. The data shows that mycorrhizal corn roots had more 16:1 w5c, 18:2w6, and/or 18:1 w9c fungal markers than non-mycorrhizal roots, confirming mycorrhizal infection. Principal Components Analysis of the Mid-IR spectra show grouping according to mycorrhizal or non-mycorrhizal roots in Sorghum, while the NIR region was useful to separate mycorrhizal and non-mycorrhizal corn roots. Preliminary PCA results with sunflower spectra did not show a grouping pattern.

(361) **FT-Infrared Spectroscopic Studies of Lymphoid and Myeloid Leukaemia Cell Lines**

Jaspreet Babrah[1], Nicholas Stone[1], Richard Lush[2], Adam Rye[2], Keith McCarthy[3], Conrad Bessant[4], [1]Biophotonics Research Group, Gloucestershire Royal, [2]Department of Haematology, Gloucestershire, [3]Department of Histopathology, Gloucester, [4]Cranfield University, UK.

ABSTRACTIntroduction FT-Infrared spectroscopy was applied to the analysis of lymphoid and myeloid leukaemia cell lines in order to detect spectral parameters. The resulting FT-IR spectra can define several spectral peaks and biochemical differences between the cell lines, which might be useful biomarkers for the rapid and reliable detection of leukaemia and its subtypes. Methods Lymphoid and myeloid cell lines were obtained from the Institute of Cancer in London and examined by FT-IR spectroscopy. Transmission spectra were acquired by first washing and diluting cell lines with saline, transferring small aliquots of cell lines onto CaF2 slides by cytospin, air-drying as thin circular disk films and acquiring twenty point spectra at different locations across each cell line sample. The data obtained was a combination of hyperspectral IR intensity image maps and several point spectral absorbance maps from each cell line. Principal component analysis (PCA) and cluster analysis was used for evaluation of the spectral maps. Results Point spectra collected at different sites were averaged for each examined cell line as representative spectra for further spectral analysis. Results have shown spectral differences in the absorption intensities of the peaks, particularly in the 4000 to 720 cm-1 spectral region. Bands in averaged spectra for the cell line were assigned to Amide I, II and III proteins (1650, 1544 and 1235 cm-1 respectively) fatty acids (1450 cm-1), carbohydrates (1085 cm-1) and DNA (965 cm-1). Principal component analyses (PCA) were used to identify the major differences in the spectra across each map. Cluster analysis of the obtained spectra at these specific regions provided classification of the cell lines. Conclusion The analysis of spectra by PCA and cluster analysis gave a reasonably good delineation between the cell lines. The finding of comparably subtle IR spectroscopic differences within the cell lines indicates diminutive intra-sample variability with significant variation between the different cell lines. Spectral differences between the cell lines differ according to the cellular biochemistry, which can serve as potential biomarkers of acute leukaemia. These results indicate that FT-IR spectroscopy could be used as a basis for developing a spectral method for the detection and identification of leukaemia.

(362) **Topographic Dependence of ATR-FTIR Signal and its Applications**

Dongmao Zhang[1], Olivier Guise[1]; [1]General Electric

With its shallow sampling depth Attenuated Total Reflectance Fourier Transformed Infrared spectroscopy (ATR-FTIR) has been a method-of-choice for surface composition analysis [1,2]. In polymer/biopolymer studies ATR has been used to examine chemical changes introduced by various chemical/physical treatments [3-6].In those applications the ATR spectra are acquired before and after the treatment of the sample; the chemical changes are then deduced from the difference in their ATR spectral features. However, for many polymer/biopolymer samples, chemical changes on the sample surface are commonly associated with surface topographic changes [7-9]. Since ATR signal has a critical dependence on the quality of the contact between the sample surface and the internal reflectance element (IRE), such topographic change will also introduce ATR spectral variations. It is thus important to differentiate ATR spectral variations originating from a chemical change from those originating from a topographic change.\r\nIn this work, the topographic dependence of the ATR signal has been demonstrated using a series of poly (Methyl Methacrylate) (PMMA) samples and a diamond ATR accessory. Three-dimensional scanning electronic microscopy (3D-SEM) has been used to characterize the surface topographic features. It was found that large ATR spectral distortions can be observed once the surface features changed at the micrometer scale. Various digital methods, including internal reference peak normalization, 1/lamda and 1/(lamda-k) penetration depth compensation methods, were also evaluated for ATR signal correction and it was found that none of those methods is effective for many practical applications. Based on the findings in this work, practical guidelines are proposed for ATR applications in polymer/biopolymer studies. [1] Gron, H.; Borissonva, A.; Robert, J. K.; Ind. Eng. Chem. Res. 2003, 42, 198-206 [2] Yang, P.; Meng, X.; Zhang, Z.; Jing, B.; Yuan J.; Yang, W. Anal. Chem. 2005, 1068-1074. [3] Taddei, P., Arai, T.; Boschi, A.; Monti, P.; Tsukada, M.; Freddi, G. Biomacromolecules ASAP. [4] Kazarian, S. G.; Chan, K. L. Macromolecules 2004, 37, 579-584. [5]\t Motyakin M. V.; Schlick, S.; Macromolecules 2002, 35, 3984-3992. [6] Makamba, H.; Hsieh, Y.; Sung, W.; Chen, S. Anal. Chem. 2005, 77, 3971-3978. [7] Yang, J.; Tian, W.; Li, Q.; Cao, A.; Biomacromolecules. 2004, 6, 2258-2268. [8] Wu, Y.; Sellitti, C.; Anderson. J. M.; Hiltner, A.; Lodoen, G. A.; Payet, C. R. J. Appl. Polym. Sci. 1991, 46, 201-211. [9] He, Y.; Shuai, X.; Cao, A.; Kasuya, K.; Doi, Y.; Inoue, Y.; Polym. Degrad. Stab. 2001, 73, 193-199.

(363) **An ATR/FT-IR Spectral Database To Identify Foreign Matter In Cotton**

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The presence of foreign matter in cotton seriously affects the cotton grade and thus the price per bale paid by the spinner, the efficiency of the spinning and ginning operations and the quality of the final woven product. Rapid identification of the nature of the extraneous matter in cotton at each stage of cleaning and processing is necessary permit actions to eliminate or reduce its presence and improve efficiency and the quality. Although several instruments are being successfully employed for the measurement of contamination in cotton fibers based on particle size/weight, no commercial instrument is capable of accurate qualitative identification of contaminants. To this end, ATR/FT-IR spectra of retrieved foreign matter were collected and subsequently rapidly matched to an authentic spectrum in a spectral database. The database includes contaminants typically classified as "trash": cotton plant parts (hull, shale, seed-coat fragments, bract, cacyx, leaf, bark, sticks and stems) and grass plant parts (leaf and stem), "foreign objects and materials": synthetic materials (plastic bags, film, rubber, bale wrapping and strapping), organic materials (other fibers, yarns, paper, and leather) plus entomological and physiological sugars and inorganic materials (sand and rust). The spectral matching resulted in consistently high-score identification of the foreign matter based on chemical composition, irrespective of its particle size. The method is envisioned to be employed with stand-alone rugged infrared instrumentation to provide specific identification of extraneous materials in cotton as opposed to only general classification of the type by particle size or shape.

(364) **Thermal Behavior o Poly(Beta-Propiolactone) Studied b Infrared Spectroscopy ad Wide Angle X-Ray Diffraction**

Yohei Ando[1], Harumi Sato[1], Tadahisa Iwata[2], Hiroshi Yamaguchi[1], Yukihiro Ozaki[1]; [1]Kwansei Gakuin University, [2]Riken

Recently, one of the biodegradable polymers, PHB (poly hydroxyl butyrate) gathers more attentions with increasing awareness to the environment. It has been reported poly (beta-propiolactone) (PPL), which has a similar chemical structure to PHB, can be chemically synthesized and has three different crystal modifications (alpha, beta and gamma form). This gamma form modification of PPL film was prepared by solvent casting. On the other hand , the other modification is defined as beta form which was generated by hot-drawing of gamma form to 700% at room temperature and then annealed at 74 oC for 2h. It was investigated the thermal behaviors of different crystal modifications by using infrared (IR) spectroscopy and X-ray diffraction. Of note in the comparison of the IR spectra of beta and gamma form in the C=O stretching region is that the unique bands at 1726 cm-1 due to the gamma form and at 1750 cm-1 arise from beta form were observed. In the CH stretching band region, it was observed the band at 2990 cm-1 arise from gamma form. On the other hand, in beta form, this band appears near 2990 cm-1, which is higher by about 5 cm-1 compared with the frequency of the stretching band of gamma form. From the temperature-dependent X-ray diffraction spectra, it was found that only the lattice constant a was gradually increasing with temperature due to the expansion of the crystal. It is very likely that the quite different thermal behavior between beta and gamma form caused from the different molecular interactions arise from these crystal modifications.

(365) **Dipole Directions o Low Frequency Vibrations i Biological Single Crystals Observed b Terahertz Time-Domain Spectroscopy**

Katsuhiro Ajito[1], Yuko Ueno[1], Isao Tomita[1], Rakchanok Rungsawang[1]; [1]NTT Basic Research Laboratories

Orientation dependent absorption spectra of amino acid and sugar single crystals were observed in the 0.5-3.0 THz range. The responses of molecular motions with low frequencies were detected on a femtosecond timescale using a terahertz time-domain spectroscopy (THz-TDS) technique. Low frequency vibrations in this frequency region may contribute to a long-length hydrogen bond, torsional or out-of-plane vibrational modes, and van der Waals interactions. THz-TDS has been a promising tool for observing spectral features in the far infrared region because it achieves a high signal to noise ratio in the low photon energy region. Typical biological samples observed by THz-TDS are in a poly-microcrystalline form, hence the obtained spectrum shows macroscopic features of the sample. Well-arranged molecules and a hydrogen bonding network in a large single crystal were assumed to reveal information hidden in the polycrystalline spectrum. The angular dependence of the far-infrared spectra of monocrystalline amino acids and sugars were observed with a fixed THz electric field direction. A comparison of poly- and monocrystalline spectra measured at room temperature shows significant differences in the number of absorption peaks and some absorption features. As a result, the origins of some peaks can be determined as well as the dipole direction of the vibration. An ab initio frequency calculation of a single amino acid molecule was used to predict the vibrational modes. The validity of the calculation models was confirmed by comparing the results with experimentally obtained data in the Raman spectral region. References [1] Y. Ueno, R. Rungsawang, I. Tomita, and K. Ajito, Anal. Chem., 78, 5424-5428, 2006 [2] R. Rungsawang, Y. Ueno, I. Tomita, and K. Ajito, Opt. Express, 14, 5765-5772, 2006.

(366) **Organogelation Kinetics of a C22 Tailed Bis-urea Organogelator Examined by FTIR**

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The kinetics of organogel assembly were investigated by infrared spectroscopy using a bis-urea organogelator with C22 tail groups. These organogelator molecules self-assemble in a variety of organic solvents by hydrogen bonding between the urea groups to form molecularly thin threads, which then aggregate into thicker fibers. These fibers then entangle to produce the gel and the junction zones formed by their overlap provide structural rigidity. Gels were prepared in benzene at different concentrations of gelator and infrared spectra were acquired over a period of 1 to 2 hours while the gels solidified at room temperature. The degree of assembly was followed in two different regions of the spectra. First, the shift in the amide I and II bands of the urea were monitored to assess the degree of hydrogen bonding and determine the progress of the molecular assembly process. Secondly, the conformational order of the alkyl chains in the gelator was determined by examining bands in the C-H bending region corresponding to three conformational deformations. Reaction rates were determined and it was found that less concentrated gels assembled more slowly and into more perfectly ordered structures. Higher concentration gels assembled more quickly and into more disordered structures. Over the course of gelation, the long alkyl tails of the organogelator were found to display increasing amounts of conformational deformation, suggesting significant entanglement in the final gel structure. These results are fit to Avrami theory, which describes the kinetics of a physical sol-gel transition.

(367) **Infrared Chemical Imaging with MCT, InGaAs, or InSb Detection and Synchrotron or Thermal Sources**

David Wetzel; Kansas State University

Synchrotron infrared microspectroscopy of thin frozen sections of tissue, fiber, or film produces high spatial resolution, particularly with confocal image plane masking. Rectangular or linear focal-plane arrays offer rapid data acquisition and image display in the liquid nitrogen cooled MCT region but, without confocal operations. With an unmodified stock mid-IR microspectrometer part of the near-IR is accessible from 4000 cm-1 to the 5800 cm-1 cutoff of the germanium coating of the KBr beamsplitter. In this region combination bands of either amide-I or amide-II with the fundamental NH stretch vibration provide useful data. Dedicated commercial near-IR systems, specifically designed for imaging, use a Liquid Crystal Tunable Filter (LCTF) and either an indium gallium arsenide (InGaAs) or indium antimonide (InSb) focal-planearray. The InGaAs range from visible to 1700 nm has good penetration to perform nondestructive analysis and imaging below the surface of whole intact specimens. Extension of the wavelengths range beyond 1700 nm to 2400 nm and has a tradeoff of strong combination band and first overtones but, with slightly reduced specimen penetration. Functional groups imaging, principal component factor imaging, and spectra are exploited to achieve spatially resolved chemical characterization of morphological structures within biological materials of plant and mammalian origin.

(368) **Nondestructive Testing For Sprout Resistance In Wheat Via Chemical Imaging With Ingaas Focal Plane Array Spectroscopy**

David Wetzel[1], Hicran Koc[1], Virgil Smail[1]; [1]Kansas State University

Nondestructive early generation identification of sprout resistance in breeding lines is a distinct asset. The sensitivity of subsurface polychromatic contrast enabled by focal plane array simultaneous imaging of multiple kernels in a single field of view provides an \r\nadvantage over visual examination. The germination process must be so advanced before visual detection is possible that severe damage to starch in the kernel has already occurred from release of alpha amylase enzyme. After exposure of kernels to moist condition \r\nfor 3, 6, 12, 24, 36 and 48 hour periods, the imaging method clearly distinguishes between those cultivars that show no evidence of germination prior to 36 hour treatment and those in which there was evidence of germination with shorter exposure times. The traditional destructive bulk test by direct alpha amylase determination applied to kernels from the same lot was unable to detect germination of the more susceptible cultivars at the shorter exposure times. Viscosity testing, dependent on alpha amylase, has the same limitation. More than three thousand kernels were analyzed in this study. Multiple images resulted from each kernel. A GO / NO GO classification of each kernel was done from the contrast provided by select optical factors. For each pixel a full spectrum is captured by the liquid crystal tunable filter in series with the focal plane array. From these data the log 1/R at a chosen wavelength or a principal component analysis factor produces image contrast.

(369) **Determining Drug Distribution in Hair Samples Utilizing ATR and IR Microscopy Techniques**

Ali Kocak[1], Ronald Birke[2], Sue Barrets[3]; [1]John Jay Coleege of Criminal Justice, [2]The City College of CUNY, [3]Harrick Scientific Products

Spectroscopic methods for examining neat human hair have the potential to provide important forensic evidence quickly and efficiently. Hair samples are generally easy to acquire and the medulla component of hair has been shown to change with drug exposure. This investigation focuses on the feasibility of using diamond ATR infrared spectroscopy to detect changes in the medulla of neat human-scalp hair samples resulting due to both external and internal drug exposure. Hair samples were spiked externally with different concentration of Clozapine and the effect on the medulla over time was observed. Hair samples were also obtained from patients being on antidepressant medications, Alprazolam and Paxil, and were analyzed to determine their effect on the lipid of the medulla was observed.

(370) **Wheat Aleurone Fraction Purity Via Diamond Internal Reflection Infrared Spectroscopy**

David Wetzel[1], Emily Bonwell[1], Scott Frazer[2], Steve Ellis[2]; [1]Kansas State University, [2]Horizon Milling

Commercially isolated wheat aleurone fractions provide a useful supplement to enhance the fiber and antioxidant content of cereal foods. Purity of the aleurone concentrate is dependent on physical separation of the aleurone layer from the adjacent pericarp layer and the endosperm. For commercial production an on-site rapid purity assessment is desirable. This study is concerned with the use of diamond internal reflection infrared spectroscopy as a means of naleurone purity assessment. The spectroscopic signatures of individual botanical parts of wheat were previously obtained from frozen sections in situ by infrared microspectroscopy in a transmission mode. In the past, milling fractions from conventional dry flour milling operations were probed by the same technique. The spatial resolution of the microspectrometer allowed particles of a heterogeneous mixture to be traced to their individual botanical parts of origin. With the commercial, finely ground aleurone product a small amount is used to obtain its infrared spectrum as a granular solid placed in optical contact with the internal reflection optical system. The idealized pure product has its own specific spectrum when it is free with respect to neighboring botanical parts within the wheat kernel. Spectral features of the adjacent botanical layers (toward the inside of the kernel) and (beyond the aleurone toward the outside) are sufficiently different from the spectrum of the pure commercial aleurone product to allow detection when their presence is at a significant level. Not only is this spectroscopic technique useful in final product inspection, but the nature of the contributing spectral features identifies which tissue is accompanying the aleurone.

(371) **Integration of an IR Analyzer as an Intelligent Internet Appliance**

Bertrand Lanher[1], Alexander Seyfarth[1]; [1]Aspectrics, Inc.

Developing IR methods for laboratory analysis is a well known process. Transferring chemometrics methods to the field for in-line process and environmental applications is a more arduous task. Pre-calibrating, integrating and remotely maintaining dedicated IR analyzers can be construed as the next step in deploying and cost-effectively operating chemical sensing solutions. This paper proposes an illustration of such an integrated field analytical solution, inclusive of on-board spectral information processing, remote maintenance and real-time data transmission, enabling the capability of real time automated decision making as pertaining to process control and environmental monitoring.

(372) **Plasma-assisted Deposition of Fluorocarbon Films for Molecular Recognition Layers in Mid-Infrared Attenuated Total Reflection Chemical Sensors**

Gary T. Dobbs[1], Balamurali Balu[1], Christina Young[1], Ashwini Sinha[1], Dennis W. Hess[1], Boris Mizaikoff[1]; [1]Georgia Institute of Technology

Fourier-transform infrared-attenuated total reflection (IR-ATR) spectroscopy is an established optical sensing approach for in situ

quantitative assessment of dissolved organic compounds in aqueous solutions by implementing membrane-coated internal reflection waveguides. This sensing strategy enhances signal generation by extracting organic species into a thin membrane probed via the evanescent field along the waveguide surface resulting in LODs ranging from mid-ppb to low-ppm concentration levels. Both polymer and sol-gel membranes are commonly utilized as chemical sensing layers with reversible, concentration dependent extraction of targeted organic species. For sensing applications in harsh environments, materials with high chemical resistivity and mechanical stability are required. Sol-gel membranes have been considered advantageous to typical spin-cast or drip-coated hydrophobic aliphatic polymer layers for operation in harsh environments, due to their favorable mechanical stability, while providing tunability of their chemical properties during preparation. In this study, fluorocarbon films generated by plasma-assisted deposition from pentafluoroethane monomers (CF3CHF2) are investigated as solid-phase enrichment layers for mid-infrared evanescent field sensors. Plasma polymerized fluorocarbon films are of particular interest, as they share advantageous characteristics of sol-gel layers including thermal stability and chemical resistance, while providing the opportunity of tuning their enrichment properties by varying the plasma conditions and monomers. Furthermore, plasma-assisted film deposition enables tunable batch processing of membrane-coated waveguides. Characterization studies on these films as sensing membranes on ZnSe waveguides for IR-ATR spectroscopy will be presented for the model analyte tetrachloroethylene. Additionally, interfacial bonding properties of the fluorocarbon films at the polycrystalline waveguide substrate are evaluated by X-ray photoelectron spectroscopy.

(373) **Advantages and Limitations of Searching FTIR Difference Spectra**

Kenneth Laughlin; Rohm and Haas Company

Searching FTIR difference spectra against libraries of difference spectra can be a valuable method to quickly identify contaminants in a material. FTIR-ATR spectra of liquids or very soft solids show highly reproducible optical path length. The difference spectrum, calculated using a subtraction factor of one, results in positive and negative peaks. The contaminant is identified by comparing the difference spectrum with libraries of difference spectra, such as difference spectra of potential contaminants minus the reference material. This approach identifies not only the contaminant, but also the material which has been depleted. Because expert judgment in choosing a subtraction factor is eliminated, the analysis can be semi-automated. As with all FTIR library searching, assessing the quality of the match still requires careful inspection of the spectra. The method relies on 3 basic assumptions: 1. A single component or matrix increases in concentration at the expense of another; 2. The spectral changes due to interactions in the matrix are similar to those in the pure reference materials. 3. ATR shifts related to refractive index are similar in the mixture compared to the pure reference materials. Examples will be shown, illustrating the advantages and limitations of the method.

(374) **Mid-IR ATR Imaging Using a Linear Detector Array System**

Jerry Sellors[1], Tony Canas[1], Ralph Carter[1], Robert Hoult[1], Sharon Williams[1]; [1]PerkinElmer, Beaconsfield, UK

ATR microspectroscopy at single sample points has proved to be an invaluable technique for a range of sample types, particularly where standard transmission techniques prove to be difficult. Recent developments have extended the technique to imaging using focal plane array detectors coupled with FT-IR microscopes. We have developed a system for ATR imaging using a linear MCT detector array combined with a motorized stage to deliver high quality infrared images using the so-called 'pushbroom' method of data collection. The system overcomes certain limitations of alternative designs and provides greater sampling flexibility for imaging selected regions of interest. Compared with transmission infrared imaging, improved spatial resolution is obtained with this system. We have applied the technique to a number of samples types in IR imaging and compared the strengths and weaknesses with those of other reflectance techniques. This paper outlines the principle of the system, and illustrates our findings with various application examples.

(375) **Resolution in Mid-IR ATR Microscopic Imaging: Measurement and Meaning**

Tony Canas[1], Ralph Carter[1], Robert Hoult[1], Jerry Sellors[1], Sharon Williams[1]; [1]Perkinelmer, Beaconsfield, UK

Infra-red ATR microscopic imaging is a powerful method for analysing the surfaces of "hard-to-see" samples which cannot be measured conveniently using conventional transmission or reflection microscopy. ATR imaging also offers the potential for improved spatial resolution because it is an "immersion" technique in which the sample is viewed through a high-refractive index material such as diamond or germanium. We have developed an ATR imaging accessory for an FTIR imaging system using a linear detector array which demonstrates improved spatial resolution compared with other IR imaging techniques. Suitable mid-IR test targets for measuring resolution are hard to come by, especially for ATR imaging. A novel method is presented for measuring the optical resolving power of any infra-red ATR microscopic imaging system, using the Perkin Elmer Spotlight microscope and the new imaging ATR accessory as an example. Results from the Spotlight system are presented and compared to theoretical expectations. Comparisons are also drawn with conventional infrared imaging systems. The practical features and consequences of finite optical resolution are discussed using real-world examples in a bid to clarify the confusion over what precisely is meant by the term "resolution" and what a given microscope can "see".

(376) **Viscosity and NIR Studies of Lithium Halides in Binary Solvent Systems.**

Bobbie Hood[1], Alex Williamson[1]; [1]N. C. A&T State University

Electrical conductivities, viscosities and NIR spectra have been recorded for a series of fluorides, chlorides, bromides and iodides of lithium in binary mixtues of oxygen donor solvents. The solvent systems consisted of propylene carbonate mixtures with lower other solvents of lower dielectric constants. The solvents include tetrahydrofuran, dimethoxyethane, dimethylcarbonate and diethylcarbonate. Solution concentrations ranged from 0 -2M in lithium halides and the temperature ranged from 5 - 75 degrees celcius. All NIR spectra were recorded at room temperature.

(376a) **Mid-Infrared Gas Sensors Using Hollow Waveguides For Sensing Volatile Organic Pollutants**

Christina Young[1], Boris Mizaikoff[1]; [1]Georgia Institute of Technology, [2]School of Chemistry and Biochemistry

Benzene, toluene, butadiene, and the xylenes are volatile organic compounds (VOCs) that in part present carcinogenic hazards in workplace environments. There is an increasing demand to monitor these compounds continuously at trace levels with molecular selectivity. Current on-site analytical methods are predominantly based on gas chromatographic techniques and colormetric detector tubes following appropriate sampling procedures for monitoring individual exposure levels in hazardous areas. However, these techniques have either limited sensitivity or uncertainty in the ppm-ppb concentration range, or are of limited

applicability for continuous real-time analysis in field environments. The primary goal of the studies presented here is to demonstrate a concept for continuous real-time monitoring of volatile organic contaminants with sufficient molecular selectivity and sensitivity for exposure limit monitoring. Mid-infrared gas sensing utilizing hollow waveguides as miniaturized gas cells has been demonstrated as an effective approach for monitoring trace gases in real-time. In the study reported here, a compact FT-IR sensing system operating in close to real-time has been developed and applied to spectroscopic measurements of benzene, toluene, butadiene, and xylenes in air simultaneously utilizing a 2 mm inner diameter straight silica hollow waveguide as a gas cell and waveguide for propagating infrared radiation. The selected VOCs have unique molecular signatures in the fingerprint range of the mid-infrared spectrum (3-20 μm) allowing for both qualitative and quantitative simultaneous multianalyte monitoring. FT-IR is currently selected as a proof-of-concept for in situ continuous multianalyte optical sensing of benzene, toluene, butadiene, and xylenes in ambient environments based on hollow waveguide gas cells. Analytical figures of merit of this gas sensing concept will be presented, along with limits of detection at high ppb concentration levels.

(377) **Comparison of Deep UV Lasers and LEDs for Fluorescence Detection of Organic Compounds in Water**

Anna Sharikova[1], Dennis Killinger[1]; [1]University of South Florida,

Conventional methods of water analysis can achieve a high degree of sensitivity necessary for water quality monitoring, but they often require special sample preparation, additional reagents or chemicals, and often are not conducted in real time or on-line. Recently, we have investigated the use of deep UV laser induced fluorescence (LIF) for the detection of trace levels of Dissolved Organic Compounds (DOCs) in water at the ppb to ppt detection level. We have performed the study using our custom-made pulsed laser-induced fluorescence system. The LIF system light sources were two interchangeable high pulse-repetition frequency (8.6 kHz) UV lasers, 266 nm and 355 nm, illuminating a quartz cell with a flowing water sample. The optics included focusing lenses and filter wheels with cut-off and optical interference filters selecting different wavelength ranges. The fluorescence signal detected by a PMT was sent to the gated integrator and boxcar averager. The system was integrated with a notebook computer and provided data in real time. The LIF system was used to record fluorescent spectra of different water samples, such as distilled, tap, and river water. We have observed considerable differences in spectra between different brands of distilled bottled water. The river samples displayed large fluorescence peaks near 450-500 nm corresponding to the fluorescence of DOCs. We have also recorded the spectra of water processed by a reverse osmosis (RO) water purification unit. Lately, we have begun investigating the performance of UV LEDs (268 nm and 320 nm) as light sources for our system. The LEDs are compact, low power devices that can make the system cheaper and easily transportable. However, their light output is several orders of magnitude lower than that of lasers, and they have much greater beam divergence. The spectra of the same samples acquired using both laser and LED light sources will be presented.

(378) **Spectrophotometric and Spectrofluorophotometric Determinations of Iron with 4'-(2,2'-Bithienyl-5-yl)-2,2':6',2''-terpyridine**

Riichiro Nakajima[1], Kazuaki Mima[1], Kou Kyou[1], Keiich Noda[1], Yasuro Kawauchi[1], Takashi Tamura[1], Takeko Matsumura-Inoue[2], Kazuhiko Tsukagoshi[1]; [1]Doshisha University, [2]Minerva Light Laboratory, L.L.C.

Various derivatives of 1,10-phenanthroline and 2,2':6',2''-terpyridine, which were originally prepared for colorimetric determination of Fe(II), Cu(I), or both, have been recently prepared as interesting compounds for conducting polymers, light-emitting devices, photosensitizers for solar energy conversion, sensors, and so on. One of the derivatives, the title compound (bttpy), which contained a 4-(2,2'-bithienyl-5-yl)pyridine skeleton corresponding to a photostable, intense fluorophore, has been prepared for synthesis of osmium and ruthenium complexes, but no details have been described on the optical properties of this ligand in the absence or presence of the other metal ions. On the other hand, we have synthesized a series of 2,6-diarylsubstituted-4-(2-thienyl)pyridine derivatives and evaluated their fluorescence properties. As a result, bttpy was found to be a novel fluorescent compound for the determination of iron(II) to ca. 0.1-ppb levels, which levels were less than 10-2 of those of the reported compounds. The relationship between the fluorescence intensity and the concentration of iron(II) was linear, where decrement of the intensity was fiftyfold larger than that of intensity predicted from an amount of the free fluorescent uncomplexed ligand, and distinct from that based on static fluorescence quenching described by the Stern-Volmer equation. The linear dynamic ranges for Fe(II) on absorption and indirect fluorescence methods were 7 x 10-7 M - 3.6 x 10-5 M and 7 x 10-10 M - 8.6 x 10-9 M, respectively, and their detection limits at 3 sigma were 3.4 x 10-7 M and 3.4 x 10-10 M. Some optical properties of 4'-(2,2'-bithienyl-5-yl)-2,2':6',2''-terpyridine and its metal complexes will be also discussed.

(379) **Analytical Data: So Much to See - So Little Time**

Gene Hall[1], Michael Boruta[2] ; [1]Rutgers University, [2]Advanced Chemistry Development, Inc.

Many problems in analytical spectroscopy require insight from several different techniques to adequately resolve the problem. A common difficulty with using several techniques is often the ability to manage the various data types and making the data available for review, analysis and reporting. This can involve several pieces of software for viewing and analysis along with a cut and paste approach for reporting. Additional problems arise when it is desired to include structures or to keep all of the relevant data together for use when addressing similar problems in the future. This paper will look at one approach to this problem that simplifies the tasks of data handling, data management and reporting when dealing with IR, Raman, and X-Ray Fluorescence spectra.

(380) **Anomalous Fluorescence of an Amino-Substituted 4-Nitropyridine N-Oxide Prone to Intra- or Intermolecular Excited-State Proton Transfer**

Joost de Klerk[1], Anna Szemik-Hojniak[2], Freek Ariese[1], Cees Gooijer[1]; [1]Laser Centre Vrije Universiteit Amsterdam, [2]University of Wroclaw, Poland

Pyridine N-oxides derivatives form a class of compounds which are widely studied in various chemical disciplines, especially in photochemistry and biochemistry, where the 4-nitro derivatives show exceptionally high bioactivity. As far as photochemistry is concerned the compound considered here, i.e., 2-butylamino-6-methyl-4-nitropyridine-N-oxide (2B6M) may undergo excited-state intra- or intermolecular proton transfer (ESIPT) reactions. It is known from the literature that in non-polar aprotic solvents 2B6M exhibits anomalous fluorescence behavior: there is a substantial difference between the excitation and absorption spectra. It is the objective of this research to interpret these results. For this purpose steady-state fluorescence excitation and emission spectra in the liquid state were recorded. In addition, high resolution fluorescence spectra as well as absorption spectra under cryogenic conditions – in n-octane Shpol'skii matrices in a home made setup – have been studied. Finally, fluorescence lifetimes were measured using the time-correlated single photon counting technique. The results suggest that in the liquid state only one (monomeric) ground state

species dominates, that can emit via two different pathways (from the normal and the tautomeric excited state). The anomalous excitation spectra point at internal proton transfer processes starting both at the S1-state as well as at the S2- and S3-state, thus violating the Kasha rule. In the n-octane crystalline samples at 5 K two monomeric isomers (rotamers) can be distinguished – detailed vibrational frequencies are presented – and additionally the emission of an aggregate (dimer species) is observed.

(381) **Choosing the Right Solvent for the Analysis of Polycyclic Aromatic Hydrocarbons Metabolites Via Laser-Excited Time-Resolved Shpol'skii Spectroscopy**

Shenjiang Yu[1], Huiyong Wang[1], Keerthika Vatsavai[1], Andres Campiglia[1]; [1]University of Central Florida

Guest-host compatibility issues have hampered the analysis of metabolites of polycyclic aromatic hydrocarbons (PAH) via Shpol'skii spectroscopy. The presence of hetero-atoms in their molecular structure limits their solubility in the frozen matrix (usually an n-alkane) and broadens their fluorescence spectra. Direct "fingerprint identification" is not longer possible as closely related isomers show very similar spectra. Here, we present a simple solution to this problem by suing an alcohol of appropriate molecular length as the host in the frozen matrix. This approach is well suited to a wide variety of PAH metabolites and particularly useful to the direct analysis of optical isomers without previous separation.

(382) **Getting It Right with Fluorescence: Where Do We Stand and What Do We Need?**

Ulrich Panne[1], Ute Resch-Genger[1], Dietmar Pfeifer[1], Katrin Hoffmann[1], Angelika Hoffmann[1] ; [1]BAM

The use of fluorescence techniques is been ever increasing in the life and material sciences with new instrumentation and promising techniques quickly evolving. The comparability of luminescence data across instruments is, however, hampered by instrument-specific contributions to measured signals that are time-dependent due to aging of instrument components. Moreover, for unexperienced users, often complex instrumentation favors erroneous results as multiple instrumental parameters influence the quality and reproducibility of the acquired data. To rule out instrumentation as major source of variability and to improve the comparability of fluorescence data, reliable, yet simple chemical and physical standards in combination with tested protocols for instrument characterization and performance validation are required, thereby also meeting the increasing desire for quantification from measurements of fluorescence intensities. This eventually provides the basis for the application of fluorescence techniques in strongly regulated areas like e.g. medical diagnostics. Here, easy-to-operate liquid and solid fluorescence standards are presented that enable the determination of the spectral characteristics and long-term performance of different types of fluorescence instruments like e.g. spectrofluorometers and confocal laser scanning fluorescence microscopes thereby linking fluorescence measurements to radiometric units.

(383) **The Legacy Continues, Seventeen Years in the Wake of the Exxon Valdez Oil Spill**

James Jordan[1], Karl Booksh[1], Kristin Kirk[2], David Gort[2]; [1]Arizona State University, [2]Grand Canyon University

Many have published on the subject of anthropogenic causes of Polynuclear Aromatic Hydrocarbon (PAH) pollution. Much controversy still surrounds the degree of impact upon the ecological health and diversity of the Prince William Sound (PWS) after the disaster of the Exxon Valdez Oil Spill. Persistence of carcinogenic PAH levels continue to disrupt one of North America's richest food stocks and some say that the cleanup effort may have made a short-term (decade) economic and ecologic interruption into a long-term disaster. Some believe that the current contamination levels can be attributed to many sources including the continued exposure of tar beds from the uplifting of the PWS during the Great Earth Quake of 1964 and that no Valdez bunker crude is present. Current research into the use of fiber optics as in-situ optical sensors has been moving forward despite the challenges that face performing spectroscopic analysis in hostile and turbid environments such as the open ocean. To date, detection of PAHs in aqueous media is possible down to the low part-per-billion (ppb) and has been demonstrated in our laboratory work and real world applications via the Co-axial Fiber Optic Excitation-Emission Matrix Fluorometer (Ca-FOCS-EEM). This poster presents the data collection and handling methodologies that should enable future scientific exploration and identification of PAH's sources in-situ.

(384) **Designing Analytical Instrumentation for use with Fluorescing Samples using Traceprotm Optical System Design Software**

Richard Hassler; Lambda Research Corporation

This paper/poster describes the unique challenges faced in designing analytical instrumentation for use with fluorescing samples. While fluorescence tag and Raman technologies enable very sensitive detection, the nature of fluorescence severely complicates system design. Furthermore, the inherently interdisciplinary nature of developing life science instrumentation requires a high level of collaboration between scientists and engineers across the areas of analytical and clinical chemistry, optics, mechanics, material science and biology. The paper/poster demonstrates how TracePro™ optical design software's fluorescence modeling capability enables a methodical design process and facilitates the application development process by communicating design elements and system performance across technical disciplines. Two design studies are used for illustration: (1) a multi-channel fluorometer and (2) a Raman spectrometer. Common to both systems are critical design parameters that include cost, limit of detection and the ability of the platform to accommodate a breadth of samples. The fluorometer design is optimized for maximum emission fluorescence reaching the detector, while the Raman spectrometer design is optimized for minimum emission fluorescence reaching the detector. In both systems, TracePro (1) tests system design alternatives, (2) evaluates off-the-shelf and custom components and fluorophores, and (3) tolerances for robustness with the goal of minimizing cost and time associated with iterative hardware prototyping and validating data in the laboratory. Optical and mechanical design elements are designed and documented in commercially available Computer Aided Drafting (CAD) and lens design software, and then shared with TracePro for system level modeling and analysis of light distributions, stray light, throughput, flux absorbed by surfaces and bulk media and fluorescence effects.

(385) **Sensitive Quantification by Nested-RT-PCR to Detect Viable Spores of a. Acidoterrestris after Inhibition Treatments by CE With LIF using Microchips**

Emanuel Carrilho[1], Maribel Funes Huacca[1], Juliana Alberice[1], Sheila B. Guterres[1]; [1]Instituto de Química de São Carlos – USP

Nested reverse transcriptase PCR (nested RT-PCR) using microchips technology assays have been used to detect and quantify viable spores from Alicyclobacillus acidoterrestris in orange juice. Nested primers were designed based on the 16S rRNA gene sequence, to improve the sensitivity. Nested RT-PCR products amplified a 191-bp fragment. We studied rRNA viability from A. acidoterrestris in orange juices, which were inactivated by extreme heat, moderated heat and natural inhibitor (Sapindus saponaria). Separation, detection, and quantification of the RT-PCR

and nested RT-PCR products were accomplished in microchip technology using an Agilent 2100 bioanalyzer in conjunction with the DNA 500 LabChip® kit. The thermal inhibition effect on the growth of A. acidoterrestris spores C for□ 104 CFU mL-1) was 96.3%, when heated to 99□inoculated in orange juice (4 1h, however, upon addition of a purified fraction from S. saponaria extract (200 mg mL-1) in different incubation temperatures, we could further improve the C for 1h,□C for 2 days or 99□reduction of viable spores. Incubation at 45 reduced to 93.6% and 98.7% in the same saponin concentration, respectively. In order to detect the remaining low levels of bacteria, the sensitivity for viable spore detection was increased by Nested RT-PCR using microchips technology for amplicon quantification. Sensitivity quantification by nested RT-PCR assay was able to detect 0.1 CFU mL-1 of spores in pure culture and on artificially inoculated orange juices. The microchip technology is a potentially useful approach for rapid in vitro determination of A. acidoterrestris and monitoring of inhibitor susceptibility for prevention of spoilage caused in all acidic drinks.

(386) **Generation of Hydrophilic Poly(Dimethylsiloxane) Microfluidic Devices**

Charles Henry[1], Jonathon J. Vickers[1], Brian M. Murphy[1], Xinya He[1], David W. Grainger[1], David S. Dandy[1]; [1]Colorado State University

Point-of-Care (POC) technologies have the potential to revolution modern medicine by making it more accessible through primary care physicians and emergency response personnel while at the same time, making it more affordable through low cost engineering methods. Our laboratory is interested in engineering modular multi-functional tools for analysis of disease biomarkers from serum, plasma, and urine. To accomplish this task, we are developing POC systems that integrate optical and/or electrochemical detection with chemical separations (electrophoresis and/or heterogeneous immunoassays) to provide selective detection of biomarkers. One major challenge in the development of POC devices is selection of substrate material. Poly(dimethylsiloxane) (PDMS) is particularly attractive for POC devices because the fabrication is very simple and the material is inexpensive and flexible. PDMS is not a good material for separations because the surface is hydrophobic and unstable. In this presentation, a new approach to the generation of stable hydrophilic PDMS. In our method, the PDMS is first extracted to remove unreacted oligomers that cause the surface instability. Further oxidation in a simple air plasma generates a hydrophilic surface with channels that self-wet through capillary action. Theoretical plates increase from 17,00 to 50,000 plates in a 5 cm channel using a 450 *f*Ým double-T injector and 10 *f*ÝM catechol.

(387) **Progress Towards LC-based Microfluidic Devices for Medical Diagnostics**

Vincent Remcho[1], Carlos Gonzalez[1], Daniela Hutanu[1], Jack Rundel[1]; [1]Oregon State University

Microfluidic technology has the capacity to transform current bench-scale bioanalytical practices into quasi-continuous, low sample volume processes with rapid, uniform mixing and precise temperature control. Additional advantages of microsystems technology include eliminating air contact thereby minimizing contamination and degradation of analytes; minimizing the environmental impact of bioanalysis through low-volume mixing, integrated multistep separation techniques and reagent recycling; and the possibility of performing analyses at the point of care with reduced required reagent volumes and in user-friendly platforms. Key components in these devices include high-specificity extractors, miniaturized and ruggedized liquid chromatography systems, and low-poer-requirement/high specificity detectors. In this presentation, progress is reported towards the development of high-throughput nanoextraction technology for implementation in microsystems. In particular, novel methods for fabrication of microfluidic devices, in situ production of porous chromatographic supports, design and assembly of chip-based optical detectors, and in situ sorbent surface modification with high specificity agents are described. Implementation of the microfluidic device is within a stiff polymer sheet architecture with the capability to integrate valves for injection and extraction. The fabrication architecture bears the added advantage of providing an economical pathway to "numbering up" for high-throughput production.

(388) **Synthesis, Characterization, and Testing Of Novel Block Copolymers as Substrate Materials for the Fabrication of Microfluidic Devices**

Christopher Culbertson[1], Scott Klasner[1], Gregory Roman[1]; [1]Kansas State University

In order to successfully perform separations of biomolecules on microfluidic devices the channel walls generally must be coated either covalently or with some type of dynamic coating which both reduces adsorption and electroosmotic flow. This not only increases the fabrication expense, but it also introduces a potential source of migration time reproducibility error due to variations in coating efficiency and the degradation of the coating over time. It would be much better if the bulk properties of the polymer used to mold the microfluidic devices could intrinsically produce a surface that was resistant to the adsorption of biomolecules. Many previous studies have shown that the ideal surface should be hydrophilic but not ionic in nature. Although several polymers can provide such surfaces, they have other physical properties which make them unsuitable for use as a substrate material. We have recently developed a set of block copolymers from which we can mold microfluidic devices and that provide an intrinsic surface which is capable of preventing the adsorption of biological molecules and cells. The synthesis, fabrication, and characterization of this polymer will be presented, and the results of protein separations and cell transport on these devices will be discussed.

(389) **Multiple Tissues Occupying a Single Channel in a Microfluidic Device: Determination of Possible New Mechanisms of Drug Efficacy**

Nicole Villiere[1], Jamie Carroll[1], Teresa Oblak[1], Paul Root[1], Dana Spence[1]; [1]Wayne State University

Our research group has previously shown that microfluidic devices fabricated in poly-(dimethylsiloxane) (PDMS) can be used to successfully mimic the sheer forces applied to erythrocytes within the microcirculation in vivo. This study examines the production of endothelium-derived nitric oxide (NO) stimulated by adenosine triphosphate (ATP) using fluorescence microscopy in a microfluidic channel. Work has been done to demonstrate that erythrocytes or red blood cells (RBCs), will release low micromolar amounts of ATP when the cells are subjected to mechanical deformation in microbore tubing or channels whose diameters are similar to resistance vessels in vivo. Iloprost (6,9á-methylene-11á,15S-dihydroxy-16-methyl-prosta-5E-dien-18-yn-1-oic acid), a stable analog of prostacyclin (PGI), was developed to inhibit platelet aggregation and as a treatment for hypertension by inducing vasodilation. It has been shown by other groups that iloprost stimulates ATP release from RBCs via activation of adenylyl cyclase and interestingly, ATP has been shown to stimulate endothelium-derived NO. Our group has shown that when pumping RBCs through 50 micrometer tubing at a flow rate of 6.7 microliter/min, the ATP release from RBCs stimulated with 10 nM iloprost was approximately 0.207 micromolar compared to 0.334 micromolar without the presence of iloprost, resulting in a

161% increase. Collectively, these results suggest that iloprost-induced vasodilation may be RBC-mediated via the erythrocyte's ability to release ATP. Here, a multicellular system incorporating an endothelium-lined microfluidic channel is employed to determine if the efficacy of iloprost in vivo is indeed RBC-mediated. Bovine pulmonary arterial endothelial cells (bPAECs) immobilized in a microfluidic channel coated with 100 microgram/milliliter Fibronectin, were incubated with 50 micromolar diaminodifluorofluorescein diacetate (DAF-FM DA), a known fluorescence probe for NO and 5 mM L-Arginine, a substrate for the production of NO. Separately, RBCs incubated with iloprost (1-100 micromolar) and RBCs alone, were passed over the bPAEC-lined microfluidic channel. An increase in fluorescence intensity of intracellular NO production due to the iloprost stimulated, erythrocyte-derived ATP was measured. Results from this study suggest that iloprost directly affects the amount of ATP that is released from RBCs, which in turn affects the intracellular concentration of NO that is able to diffuse and ultimately result in vasodilation.

(390) **Analysis of Phenolic Contaminants using Microchip-Capillary Electrophoresis and Electrochemical Detection**

Carlos D. Garcia[1], Maria Fernanda Mora[1], Yongsheng Ding[1], Eric Mejia[1], [1]The University of Texas at San Antonio

In tandem with rapid industrial and economic development, human activities have produced widespread pollution of the natural global environment. Among other organic pollutants, phenols and phenolic acids are considered the most important components of industrial waste. These compounds also originate from the degradation of organic matter and for this reason they are widely spread, owing to both natural and anthropogenic sources. Regardless of the toxicological and biological effects, determining the concentration of phenols is a key parameter to adopt corrective actions and to enforce regulations. Various methods have been proposed for the determination of environmentally important phenolic compounds such as chromatographic, bioanalytical, optical, and electrochemical. Recently, capillary electrophoresis (CE) has been also used for the analysis of organic acids. CE offers high performance, reagent economy, speed, and automation capabilities. Another advantage of CE is that it can be easily miniaturized, allowing the precise control of fluids without the need of mechanical pumps. CE-microchips can also provide custom design, versatility, reduced consumption of reagents and sample, low waste generation and increased analysis speed and portability. In this report, a PDMS microchip with an integrated gold electrode was used to perform the simultaneous analysis of several phenolic compounds considered contaminants. The effect of the separation potential, buffer pH and composition, injection time and pulsed amperometric detection parameters were studied in an effort to optimize both the separation and detection of these phenolic compounds. In order to demonstrate the aptitude of these devices to deal with potential applications, the microchip was used to measure these compounds in different water samples.

(391) **Stable isotopes of explosives provide additional forensic information**

James Ehleringer; IsoForensics Inc.

There are differences in the natural abundances of carbon, nitrogen, and oxygen isotopes in high explosives (HMX, RDX, PETN, and TNT) that make it possible to establish the relatedness of two or more explosive samples of identical chemical composition. In some cases there are sufficient differences in the isotope ratio composition of explosive compounds produced by different manufacturers that allow identification of the manufacturer or manufacturing process. The stable isotope ratio composition of explosive residues are closely related to that of the undetonated materials. The forensic application of stable isotope ratios in explosives is discussed through its application to a specific criminal case.

(392) **The Application of CE and Ion Chromatography to Explosives Residue Analysis**

Bruce McCord[1], Megan Bottegal[1]; [1]Florida International University

Black powder substitutes are alternative propellants that generate less smoke, and are less corrosive to gun barrels These powders come in a variety of formulations and grain sizes, but generally contain inorganic oxidizers and organic fuels. These propellants are commonly used in antique firearms and other weapons but can be potentially misused as fillers in improvised explosive devices. In our laboratory we are investigating the development of improved procedures for the detection of these and other inorganic explosives residue. We are particularly interested in the use of techniques such as ion chromatography and capillary electrophoresis to detect the wide range of organic and inorganic ions produced as a result of the explosive deflagration of these materials. These two techniques provide complementary results and aid in the identification of the individual components in the residue. In our work with ion chromatography we are developing isocratic methods that utilize low capacity ion exchange resins and ion pairing agents to permit the elution of a wide range of anioinc components. Capillary electrophoresis procedures are used to confirm the IC results. Dual opposite injection techniques can be used to achive simultaneous detection of anions and cations or single injection CZE systems can selectively target specific components in the mixture by appropriate choice of buffer components. These methods have been applied to the analysis of a number of black powder substitutes to provide investigative leads for law enforcement personnel. The goal of the work is to determine specific target ions that can be used to aid in the identity of the specific explosive material.

(393) **Advances in Identification of Dyed Textile Fibers using Capillary Electrophoresis/Mass Spectrometry**

Stephen L Morgan[1], Amy R Stefan[1], Anthony R Trimboli[1], Edward G Bartick[2]; [1]University of South Carolina, [2]FBI Laboratory

Advances in identification of dyed textile fibers using capillary electrophoresis/mass spectrometry Stephen L. Morgan1, Amy R. Stefan1, Anthony R. Trimboli1, and Edward G. Bartick2 1Department of Chemistry and Biochemistry, University of South Carolina, 631 Sumter Street, Columbia, South Carolina 29208 2FBI Laboratory, Counterterrorism and Forensic Science Research Unit, FBI Academy, Quantico, Virginia 22135 Fiber evidence is frequently used in forensic science to associate a suspect to a victim or crime scene. The fibers are found as trace evidence in crimes of personal contact such as homicide, assault, sexual offenses, and hit-and-run accidents. In forensic fiber comparison, fibers are screened by visual inspection using optical microscopic techniques such as polarized light microscopy (PLM) and by spectroscopic methods such as UV/visible and fluorescence microspectrophotometry. If spectra of the known and questioned fibers are consistent, the hypothesis that the fibers originate from a common source should not be rejected. The premise of our current research is that additional discrimination may be achieved by extraction of the dye from the fiber, followed by trace analysis by a high resolution separation technique. A sensitive and selective technique such as capillary electrophoresis/mass spectrometry (CE/MS) is needed to analyze the small amount of dye (2-200 ng) present on forensically relevant fiber samples. CE/MS can separate extracted dye components and provide semi-quantitative estimates of dye amounts as well as qualitative information to identify the dye present (via the molecular weight and mass spectra). A decision tree for extraction of unknown dyes from textile fibers is has been developed that employs three capillary electrophoresis methods

with diode array detection for the separation and identification of dyes from the six major textile dye classes. Although this approach is destructive to the sample, only an extremely small sample is required (~1-2 mm of a single 15 micron diameter fiber). Automated micro-extractions and CE offer the forensic analyst reproducible analyses (% RSDs ranging from 5-25%) with limits of detection in the picogram range. The combined extraction/CE-MS system is capable of achieving both highly discriminating and highly sensitive identification of dyes for improved discrimination of trace fiber evidence.

(394) **UV-visible, Fluorescence, and Raman Microspectrophotometry for Identification of Dyed Textile Fibers**

Edward G Bartick[1], Stephen L Morgan[2], Suzanna H Hall[2], Anthony R Trimboli[2]; [1]FBI Laboratory, [2]University of South Carolina

UV-visible, Fluorescence, and Raman Microspectrophotometry for Identification of Dyed Textile Fibers Edward G. Bartick1, Stephen L. Morgan2, Suzanna H. Hall2, Anthony R. Trimboli2 1FBI Laboratory, Counterterrorism and Forensic Science Research Unit, FBI Academy, Quantico, Virginia 22135 2Department of Chemistry and Biochemistry, University of South Carolina, 631 Sumter Street, Columbia, South Carolina 29208 Trace evidence found at the crime scene, or found on a victim or suspect, has a vital role in forensic investigations. Fiber evidence is class evidence (i.e., not unique) because many fibers from different sources could be indistinguishable. The discovery of a fiber and its identification as a particular fiber type (e.g., acrylic, cotton, nylon, polyester) may not, of itself, provide much support for a forensic investigation. The probative value of particular fibers found at a crime scene depends on their uniqueness relative to the background of fibers normally encountered at that location in the absence of the crime. What is often required is information that makes the trace evidence more specific and discriminating. Our current database of dyed textile fibers consists of more than 1,500 fibers collected from commercial sources and over 35,000 UV-visible, fluorescence, and Raman spectra. This talk will demonstrate the use of this database to validate the discrimination between different polymer classes and dyed textile fibers using multivariate statistical methods. In particular, principal component analysis and linear discriminant analysis allow visualization of differences between groups of spectra, enable the confirmation of statistical validity of discrimination, and tracking of spectral changes with environmental changes. The fibers and associated spectra in the database, in combination with validated computer programs, represent an extensible tool for fiber comparisons in forensic casework.

(395) **Application of Laser Ablation Inductively Coupled Plasma Mass Spectrometry (LA-ICP-MS) to solid matrices of forensic interest.**

Tatiana Trejos[1,2], Jose Almirall[1,2]; [1]Florida International University, [2]International Forensic Research Institut

Laser ablation is a leading technology for direct solid sampling in analytical chemistry and is becoming a valuable tool for elemental analysis in forensic science. During laser ablation, a laser beam removes tiny amounts of solid in the form of a dry aerosol that can be later transported into an ICP-MS for ionization and detection. Some of the advantages of LA-ICP-MS include direct characterization of solids, elimination for the need for chemical procedures for dissolution, minimum consumption of the sample (~nanograms) and reduced risk of contamination during sample storage, sample preparation and measurement. These advantages make LA-ICP-MS a very attractive technique for forensic samples, especially for trace examinations where the amount of sample always represents a challenge. Nevertheless, the capabilities and limitations of this novel technique may vary from matrix to matrix and therefore a comprehensive evaluation of its applicability to different type of samples was conducted. The use of this novel technique in trace evidence such as glass, architectural and automotive paint, soil, bones and hair is presented. A critical evaluation of parameters of forensic interest is discussed in detail, including the analytical performance of the technique, discrimination potential, homogeneity of the samples at micro-scale, reproducibility, quality control, sampling strategies, sampling size requirements, availability of matrix match standards, data analysis and interpretation of results. Practical considerations such as laser wavelength, carrier gas, quantification strategies, quality control and use of internal standardization are also presented. The aim of this presentation is to provide the forensic community with a critical evaluation of the value of using LA-ICP-MS for the elemental profiling of some forensic samples.

(396) **Trace Chemical Detection using Laser Ablation Ion-Storage Time-of-Flight Mass Spectrometry**

Greg Klunder[1], Jason Holt[1]; [1]LLNL

Detection of trace amounts chemicals plays an important role in forensic analysis. Also the ability to provide spatial chemical information can be very valuable to understanding the sample and an investigation. Laser ablation can analyze solid materials without any sample preparation, thus eliminating any sample loss or dilution due to wet chemistry dissolution. Laser ablation is commonly used as a sampling technique to introduce particles into an ICP for vaporization and ionization. In our laboratory, laser ablation and ionization of solid materials is performed inside an ion-storage time-of-flight mass spectrometer (ISTOFMS) for analysis. Atomic and molecular ions generated during the ablation process are stored in the trap and then ejected into the TOF for analysis. Using a nanosecond Nd:YAG laser, sensitivities in the picogram to femtogram range have been demonstrated with a single laser pulse for ablation and ionization. Analyte concentrations have been measured in the low ppm to ppb range, however, the sample matrix plays an important role in the ionization efficiency of the analyte. We have investigated a number of different materials including NIST standard glasses, solutions extracted on resin beads, and metallic thin-films on silicon. In some cases fractionation has been observed with a TOF-SIMS chemical imaging system. Thus, matrix effects presents a major concern when applying laser ablation to unknown samples that normally require matrix matched standards. During the analysis of glasses using LA-ISTOFMS, ion signals have been observed to increase with increasing storage times up to 500 microseconds. Advantages and drawbacks to laser ionization mass spectrometry for forensic analysis will be discussed.

(397) **Simultaneous Microraman Spectroscopy and X-Ray Microdiffraction**

Richard Davies[1], Manfred Burghammer[1], Christian Riekel[1]; [1]ESRF

Raman spectroscopy and X-ray diffraction (XRD) results are often reported together within individual studies because of the complimentary information they provide. Whilst Raman can access information relating to individual molecular bonds, XRD provides access to information over longer 'crystallographic' length scales and beyond. In addition, their different phase and volume selectivity provides a means of separating different contributions within complex heterogeneous materials. As a result, the techniques are frequently employed together within a range of scientific areas, from geology and materials science to archaeology and biology. Over recent years, both techniques have independently evolved microbeam capabilities. For Raman spectroscopy,

laboratory based microRaman systems (μRaman) are now relatively inexpensive whilst microfocussed X-ray diffraction (μXRD) can be carried out at synchrotron radiation facilities as a matter of routine. These developments have allowed smaller sample volumes to be studied and have provided an increased spatial resolution for scanning experiments. However, these advances seriously complicate sequential combinatorial studies. In particular, reproducing sampling regions between different experimental methods is problematic at microscopic length. The ID13 beamline of the European Synchrotron Radiation Facility offers the unique capability of combined μRaman and μXRD.1 Raman spectra and XRD data can be collected from the same point on the sample simultaneously, using a novel on-axis geometry. With both the laser beam and X-ray beam having a spot size of approximately 1 μm (at the common focal position),1 their combination is particularly meaningful. This development opens up many new possibilities for combined μRaman and μXRD experiments. Not only does this overcome reproducibility issues for scanning studies, but it also benefits in situ studies (such as hydration, deformation etc..) and reduces experimental time. 1 R. J. Davies, M. Burghammer and C. Riekel, Applied Physics Letters, 87(26), 264105 2005

(398) **A New Class of Substrates for Surface Enhanced Raman Micro-Spectroscopy**

Alexandre Brolo[1], Jason Anema[1], Reuven Gordon[2], Karen Kavanagh[3]; [1]University of Victoria, Dept. of Chemistry, [2]University of Victoria, Dept Elect. Eng, [3]Simon Fraser University, Dept Physics

The transmission of normally incident light through arrays of sub wavelength holes (nano-holes) in gold thin films is enhanced at the wavelengths that satisfy the surface plasmon (SP) resonance condition. The enhanced transmission is accompanied by strong field localization and has potential for applications in several fields, ranging from quantum information processing to nanolithography. We will present several examples of applications of the arrays of nano-holes in enhanced micro-spectroscopy. Surface-enhanced Raman scattering (SERS) and surface-enhanced fluorescence were observed from dyes adsorbed on these arrays. The enhanced spectroscopic signal was dependent on the fabrication parameters of the array. The largest enhancement was observed when the periodicity of the nanoholes matches the energy of the laser excitation. All the results mentioned above suggest that arrays of nanoholes are excellent substrates for enhanced micro-spectroscopy and could potentially be used as chemical sensing elements in analytical devices. Among the main advantages of this substrate for chemical sensing is the tight light focusing provided by the nanostructure and the collinear optical geometry of the experimental setup.

(399) **The Critical Challenges Facing Surface-Enhanced Raman Spectroscopy for Trace Chemical Detection**

Nicholas Pieczonka[1], Ricardo Aroca[1]; [1]University of Windsor

Surface-Enhanced Raman Spectroscopy (SERS) has been demonstrated to be an extremely powerful analytical technique for trace chemical detection. Under certain conditions, enhancement factors of 10^10 over that of the normal Raman process are achieved. Unfortunately, this augmentation of the spectroscopic signal is not without complications. Difficulties, which can arise both from the nature of the phenomenon and the conditions under which the experiments are conducted, can make chemical identification by SERS very challenging. Here we will present an overview of the perturbations that are of concern when performing SERS experiments, particularly those that involve Raman microscopy. Examples from our group's many SERS projects involving trace detection and single molecule SERS, will be shown to illustrate these key issues.

(400) **Low Frequency Raman Measurements and Lattice Dynamic Calculations for Pharmaceutical Polymorph Characterisation**

Mike Claybourn[2], Graeme Day[1], Storey Richard[2]; [1]Cambridge University, [2]AstraZeneca

Conventional Raman and IR spectroscopies have been successfully used for polymorph identification and quantification of pharmaceutical drug substances. The success of the analysis is based on the strength of perturbation of internal vibrational modes by structural changes in the crystal lattice. Published data shows peak shifting or intensity changes are the general observations. The effects are difficult to predict and invariably an empirical approach is used for interpretation. A more direct approach, and one that allows prediction and assignment of the spectral bands is to probe the lattice vibrational modes (phonons). These modes are very sensitive to intermolecular interactions in the crystal lattice resulting from, for example, molecule orientation, packing and hydrogen bonding. The energies for these modes are in the far infrared <200cm-1) and can therefore, be probed using far-IR absorption or near-laser line Raman measurements. The prediction of phonon modes characteristic of a polymorph is often based on rigid body type calculations, either using observed or lattice energy minimised unit cell dimensions. This approach assumes separation between the inter- and intra- molecular modes. Previous work on the comparison of measured (THz) and predicted modes in carbamazepine has shown that lattice vibrations can be identified and fully characterised for polymorphs I – IV. For this work we have predicted phonon modes observed by Raman for polymorphs I, II and III, and the acetone solvate. The calculations were based on unit cell parameters obtained from X-ray powder diffraction data taken at room temperature, -50C, -100C and –150C. At room temperature, Form III (monoclinic P21/c) has 13 observed phonon modes and Form 1 (triclinic P-1) has 9 between 20 and 200 cm-1. Symmetry analysis of the calculations show that there are 12 and 24 Raman active lattice modes for forms III and I, respectively, although the intensities of some may be too low to be observed. The additional modes observed are mixed inter- and intra-molecular modes. Cooling to liquid nitrogen temperature gives band sharpening. In the case of Form III, additional bands were resolved, but not for Form I. The bands also shift to higher frequencies as a result of the contraction of the unit cell volume; in the case of Form III this reduces from 1169 $Å^3$ at 25 C to 1157 $Å^3$ at –150 C. The shift in frequency differs for different modes depending upon the impact of the unit cell contraction on the various intermolecular interactions. Calculations also show that the rigid body approximation holds well for pure phonon modes and that these occur for bands <130cm-1.

(401) **Hyphenated-Raman Microscopy for Materials Analysis**

Ken Williams; Renishaw PLC

Hyphenated Raman microscopy for materials analysis K P J Williams Renishaw plc Spectroscopy Product Division, Old Town, Wotton-under-Edge, Glos, GL12 7DW, UK Raman microscopes have dominated the market for the last ten years. Their ease of use has led to an expansion in applications over many diverse fields. New demands are now being made to move away from using optical microscopy to visualise samples. This paper illustrates the recent advances in combining other microscopes to identify the sample area of interest. We have combined Raman and FT-IR microscopes, Raman microscopy with atomic force and near field microscopy and a Raman system for analysis from inside an SEM. The combination of Raman and infrared microscopes provides

complementary vibrational information, a clear benefit of having integrated systems being that the same sample area is analysed. The benefits of combining the worlds of AFM and Raman spectroscopy will be illustrated with samples such as nanoindentation in silicon. The AFM image shows that the indentation has caused plastic deformation of the silicon, but does not give any indication whether the deformed regions have undergone any phase changes. The Raman spectra clearly show the presence of different phases of silicon, along with residual stresses. Data obtained from apertureless NSOM experiments, also called tip enhanced Raman, will be shown. Differential Raman spectra recorded using a standard 1μm laser spot focus are obtained with the tip in the near and far field, respectively. The difference spectrum obtained represents the spectral enhancement observed around the tip (50 – 100 nm diam) in the near field. The SEM structural and chemical analyser (SEM-SCA) combines both SEM and Raman techniques that utilises the high spatial resolution afforded by the SEM, and the chemical information revealed by Raman. Raman spectroscopy meets unfulfilled SEM/EDS requirements. EDS yields elemental information only and is poor in analysing light elements whilst Raman provides full structural and chemical information. The instrument can also perform photoluminescence and cathodoluminescence studies as the SEM-SCA collection optics are fully compatible with both spectroscopies. Examples are given from various application areas of materials science.

(402) **25 Years of On-Site Analysis with Mobile Mass Spectrometers**

Thomas Ludwig[1], Thomas Arthen-Engeland[1], Jochen Franzen[1], Joachim Stach[1]; [1]Bruker Daltonik GmbH[4]

Mobile Mass Spectrometers have been available around the beginning of the 1 980s and they have been used in various applications, e.g. for the detection of chemical warfare agents for military purposes or for the on-site analysis for environmental purposes. The series of application reaches from on-site analysis by fire brigades during chemical accidents to on-site analysis on former waste sites to on-site trace analysis of deep-sea waters on research icebreakers in the antarctic sea. Also mobile GC/MS systems have been used as key tools for checking the compliance to the international Chemical Weapons Convention (CWC) during inspections of the Organisation for the Prohibition of Chemical Weapons. Mobile mass spectrometers apply different technologies but altogether they are based on a rugged quadrupole technology, e.g. the mobile mass spectrometers MM1, Viking 573, modified Agilent MSDs, EM 640 or MM2. The systems mainly differ in technology regarding design, vacuum generation or system complexity; but common is their very rugged design that makes them applicable for the application in the field. With regard to their main application there are some criteria for the on-site use of such systems: robustness analytical capabilities, e.g. fast analysis or transfer of laboratory SOPs into the fieldgeneration of information on-site (analytical results) that are used for the progress of an operation ("information adapted operation strategy")In this presentation some key applications of mobile mass spectrometers and mobile GC/MS systems will be presented and their acceptance will be discussed. Finally we also present our recent developments in the miniaturisation of mass spectrometers.

(403) **HAPSITE Portable GC/MS Chemical Identification System**

Bob Felty[1], Ben Shultes[1], Teresa Kristoff[1], [1]INFICON Inc.

HAPSITE Portable GC/MS Chemical Identification System; Ben Shultes, Teresa Kristoff, Ann Marie Heizmann; INFICON, Two Technology Place, East Syracuse, NY 13057; www.inficon.com INFICON produces the only truly portable Gas Chromatograph/ Mass Spectrometer available in the market called the HAPSITE. HAPSITE is an acronym for Hazardous Air Pollutants on Site. It is designed for on-scene detection, identification and quantification of Volatile Organic Compounds (VOCs) such as Toxic Industrial Chemicals (TICs) and Chemical Warfare Agents (CWAs). GC/MS technology, the benchmark for the analysis of these and other organic compounds, is currently considered the most accurate analytical instrumentation in use for this purpose. The Non-Evaporative Getter Pump (NEG) technology has allowed for the portability of the Mass Spectrometer. The vacuum is maintained chemically within the NEG pump, a rechargeable nickel metal hydride battery provides a source of remote power for field operations and the carrier gas canister fits within the system. Portability allows for "information now", the ability to detect, identify and quantify toxic substances onsite within minutes. A built-in Global Positioning System (GPS) provides an automatic record of the exact field location, along with the date, time, and method information. The weatherproof unit is designed for "hot zone" or affected area usage, and can be fully decontaminated. The HAPSITE can also be configured for stationary usage if desired by using external sources of power, vacuum and carrier gas. Despite the compact size, the HAPSITE is as accurate as a laboratory system. It is also capable of analyzing liquids and solids by using the Headspace Sampling System accessory. The newest accessory for the HAPSITE, the SituProbe, is designed for continuous in-line water monitoring. The HAPSITE is currently in use both domestically and abroad. The United States military, HAZMAT emergency responders, police and fire departments have adopted the HAPSITE as part of their cache of detection equipment. The low-level detection capability of the HAPSITE provides confidence as to when it is environmentally safe. Detection data, pictures of the unit and its components and application examples will be presented at this presentation.

(404) **Development of Field Applications for Mass Spectrometers**

Garth Patterson[1], John Grossenbacher[1], J. Mitchell Wells[1]; [1]Griffin Analytical Technologies

Mass spectrometers are very powerful laboratory analysis instruments but have found limited use outside the lab due to a variety of issues including complexity and sample preparation. Described here are methods utilized for field applications that significantly decrease these issues. An integrated sampling system that can accept liquid and gas samples and perform analyses applicable to a broad range of chemical species will be described. An additional sampling system will be described that can pre-concentrate analytes and directly transfer those analytes to the mass analyzer for MS/MS analysis (requiring no chromatographic separation). To separate mass spectrometers will be described that can operate in the field and that reduce the requirements for consumables.

(405) **Quantitative Gas Analysis via Field Portable Mass Spectrometer System**

C Richard Arkin[1], J. Andres Diaz[2], Timothy Griffin[3], Elian Conejo[2], Kristel Heinrich[2], Carlomagno Soto[2], Guy Naylor[1], Charles Curley[1], David Floyd[1], Oliver Gomex[2]; [1]ASRC Aerospace, [2]Universidad de Costa Rica, [3]National Aeronautics and Space Administr.

A small mass spectrometer system, called AVEMS, was developed for field analysis under various conditions including ground and aircraft operations. Originally designed for aircraft deployment, AVEMS is also suitable for car or hand-transport. The 85 pound system employs a 200 Da quadrupole mass analyzer, requires 250

W of power at steady state, and can operate up to an altitude of 41,000 feet above sea level (–65 C; 50 torr). The system uses on-board gas bottles for NIST-traceable on-site calibration and is capable of monitoring and quantifying up to 16 gases simultaneously. Common components monitored include hydrogen, helium, carbon dioxide, sulfur dioxide, hydrogen sulfide, nitrogen, oxygen, argon and acetone. An integrated GPS allows the chemical data to be plotted in three-dimensional space, while also providing UTC time stamping. Presented here are a number of applications this system has been used over the few years. These applications include air monitoring of refinery emissions via aircraft, volcano plume analysis using several aircraft, volcanic emission analysis from the ground and municipal air quality analysis mapping by automobile. Also presented will be the current effort to combine the two- and three-dimensional data with ground imagery, topography and remote sensing data collected by other instruments.

(406) **GC-MS System Based on a Miniature Toroidal Ion Trap Mass Spectrometer for Field Detection of Chemical Threats**

Milton L. Lee[1], Stephen A. Lammert[1], Samuel E. Tolley[2], Jesse A. Contreras[1], Jacolin A. Murray[1], James R. Oliphant[2], H. Dennis Tolley[1], Edgar D. Lee[2], [1]Brigham Young University, [2]Palmar Technologies

There is an increasing demand for hand-portable gas chromatography-mass spectrometry (GC-MS) instrumentation for detection of target chemicals in environmental, forensic, defense and homeland security operations. The requirements of such instrumentation include operational considerations of robustness, and small size and weight, in addition to performance requirements of sensitivity, selectivity, and speed. The MS developed in this work is a miniature toroidal RF ion trap that can be operated at RF voltages significantly lower than required for conventional traps. The large trapping volume characteristic of the toroidal geometry allows miniaturization while still preserving high sensitivity. A low thermal mass GC with 5 m x 0.10 mm i.d. capillary column provides rapid analysis with low power consumption. Helium mobile phase is supplied by a small pressurized gas cartridge. Sample introduction is based on solid phase microextraction (SPME), which can be applied to a variety of sample matrices. A new SPME syringe with identification chip was developed for one-hand operation. The complete system weighs approximately 8.2 kg and has a volume of 0.014 m3, including batteries. A peak capacity of 110 was obtained for a 3 minute analysis. Unit mass resolution was obtained using the miniaturized ion trap with peak widths of 0.4 da (full width, half maximum).

(407) **In-Situ Mass Spectrometry for Field Chemical Analysis**

Ryan Bell[1], Tim Short[1], Strawn Toler[1], Pete Wenner[1], Friso van Ameron[1], Bob Byrne[1]; [1]Center for Ocean Technology /USF

An underwater mass spectrometer (UMS) has been developed by the Center for Ocean Technology at the University of South Florida to acquire real-time, in-situ measurements of natural and anthropogenic chemicals in aqueous ecosystems. Design and deployments to date have been directed toward observations of dissolved gases and volatile organic carbon species (VOCs). The UMS is based on a 200-amu linear quadrupole mass analyzer with a closed ion source (Transpector CPM-200 Residual Gas Analyzer, Inficon, Inc., Syracuse, NY). Introduction of analytes into the mass spectrometer occurs through a polydimethlyl siloxane (PDMS) membrane introduction system that has been pressure tested to a depth equivalent to 2000 meters. The membrane interface provides parts-per-billion (ppb) level detection of many VOCs and sub parts-per-million (ppm) detection limits for many dissolved simple gases. The underwater MIMS system has been deployed on moorings, tethered depth-profiling rosettes, remotely-operated and autonomous aquatic vehicles. Recent field deployments include diurnal monitoring of primary productivity in the Hillsborough River (Tampa, FL) by continuous measurements of dissolved gases (e.g., oxygen and carbon dioxide), and measurements of dissolved-gas depth profiles to 200 m in Saanich Inlet, BC and 500 m in the Gulf of Mexico. Construction of a new underwater mass spectrometer system extends deployments to depths in excess of 1000 m. Collection of precise and accurate data in the field necessitates instrumental calibration. Therefore, current work has focused on calibration of UMS response to dissolved analytes at variable water temperature, pressure and salinity, as well as assessment of the influence of variations of sampling parameters (e.g., pumping speed). Details about deployments and calibration of the UMS along with new system configuration will be presented.

(408) **What Is The Extent of The PAT Toolbox?**

Martin Warman[1], [1]Ke Hong; [1]Pfizer

With the recent changes in Pharmaceutical manufacturing becoming a 'way of life', this paper will provide a review of the analytical technologies available to provide information into a Science Based Approach. The intention is to give case studies and examples of all types measurement technology, whether being used within a Development (sometimes called Pre-PAT) implementation (where the toolbox maybe be used to establish process variance and process understanding), through to those being used at a Monitor and Control level (where the variance is removed or controlled in order to establish process robustness). In this way, examples of novel technology can be covered along with those now becoming more mainstream, and so more widely found across the Pharmaceutical Industry. The paper will also show the need to establish the linkage between the metric and the attribute in question, an important aspect in order to allow a control strategy for the process parameters (which will impact the attribute and therefore effect the quality of the product), to be defined. With an overall object to highlight the full range of the PAT toolbox and the role it could play within a current manufacturing paradigm.

(409) **Development of Mid-infrared Methods for Real World Process Analysis**

John Ryan[1], Brian Wittkamp[1]; [1]Mettler Toledo

There is more then one way to obtain valuable information from process chemistry. Many practitioners only use a calibration method to determine concentration values. The development of a method for process monitoring or control involves more then just the collection of a ‘training’ set of spectra with a ‘quality’ set of concentration values. Examples will be discussed showing how a mid-infrared method is developed and validated. In addition, trend analysis of the data can yield the same or similar results to concentration values and still provide the process engineer with valuable information on the process. Further to this, additional information from a fundamental vibration spectroscopic technique is possible through use of the entire spectrum. Several examples from chemical and pharmaceutical industries will be presented showing the advantage of mid infrared monitoring in manufacturing environments.

(410) **Near-Infrared Chemical Imaging for In-Situ Monitoring of Pharmaceutical Blends**

Neil Lewis[1], Kenneth Haber[1], Fiona Clarke[2]; [1]Malvern Instruments, [2]Pfizer, Inc.

It is generally recognized that understanding and optimizing the blending of the chemical components comprising a pharmaceutical product is a critically important step for the preparation of tablets that have both the desired physical and chemical attributes.

Measuring these attributes, which in summation describe the overall performance of the final product, can also provide insight into the stability and ultimately the efficiency of the manufacturing process. While a number of experimental approaches (optical and non-optical) are currently being employed and evaluated for measuring pharmaceutical blending both off-line and on-line, near infrared chemical imaging offers the capability for direct, on-line, non-contact assessment of the relative API and excipient distributions within the blend at the micro-scale while simultaneously measuring the evolving bulk composition of the mixture at the unit dose level. The additional value of the distribution data from the microanalysis of the mixture will be discussed, as well as practical aspects of the design and implementation of instrumentation to perform these measurements in a pharmaceutical manufacturing facility.

(411) **Isotope Selective Laser ionization Spectrometry as a Process Analytical Technology**

Summer Randall[1], Bruce A. Bushaw[1]; [1]Pacific Northwest National Laboratory[4]

Isotope selective laser ionization spectrometry (ISLIS) is being developed for the analysis of long-lived and rare radionuclides. Current emphasis is on reducing 'physics-scale' experiments to reliable benchtop analytical instrumentation applicable for at-line process analysis, while expanding the range of applications in fields from low-dose medical tracer isotopes to analysis of ultrapure materials. Newly discovered high-angular-momentum autoionization states are accessed by triple-resonance excitation with diode laser systems to yield extremely sensitive and selective detection of targeted isotopes. The high degree of optical isotopic selectivity and near zero background from low-power continuous lasers has been demonstrated capable of directly quantifying rare isotopes at relative abundances down to 10-7 without the need for subsequent mass analysis of the laser produced ions.

(412) **Using AOTF-NIR Analyzers for "Real-Time" Monitor and Control Blending and Drying Operations.**

Igor Nazarov[1]; David Chong[1]; [1]Brimrose Corportaion

We will discuss the use of rugged and miniaturized AOTF-NIR Analyzers as cost-effective solutions for various Real-time On-line applications in Pharmaceutical. We concentrate on using the Miniature AOTF-NIR Analyzer for non-destructive and non-contact process application such as Drying, Blending. Examples and data of using NIR on different types and configurations of Blenders and Fluid Bed Dryers will be shown. Those examples will show advantages of using Real-time analysis. The 21CFR Part 11 compliant data management System is used for on-line results monitoring, backing up data and controlling the processes based on NIR analysis.

(413) **Carbon Nanotube Networks as Detection Platform**

Christian Valcke[1], Jean-Christophe Gabriel[1], Ying-Lan Chang[1], Eugene Tu[1]; [1]Nanomix

Carbon nanotube (CNT) networks provide a unique platform for gas and liquid analyte detection. The unique electrical properties of the CNT material combined with scaleable manufacturing processes provide a novel platform for commercial deployment of a new generation of detection applications. Although a lot of research publications have demonstrated the use of single carbon nanotubes or nanowire devices as highly sensitive transducers, the difficulties in transferring this technology to a high-yielding manufacturing process have stalled the progress towards commercial devices. We will present on overview of our platform using both CVD grown tubes and solution based CNT material. Characterization of the devices using both traditional semiconductor metrics and advanced microscopy allows optimization of manufacturing processes for a range of performance specifications. We will also present the power of the platform through examples where detection is accomplished based on the semiconducting properties of the network and in addition other applications of capacitive and electrochemical measurements on the same platform. An area of significant interest for the application of this nanoelectronic platform is the detection of DNA in liquid samples. Although current laboratory techniques are very powerful, they are also highly complex requiring significant personnel expertise and infrastructure for reagent, instrumentation and sample handling. We will review some of the research in this area and the trade-offs that can be made towards a point-of-care realization of these assays on a CNT platform.

(414) **One-Dimensional Nanostructures as Spectroscopic Sensing Platforms**

Andrea Tao[1], Donald Sirbuly[1,2], Peidong Yang[1,2]; [1]UC Berkeley, [2]Lawrence-Berkeley National Laboratory

Inorganic nanowires, nanoribbons, and nanotubes comprise a new class of sensing elements that will have a significant impact on a broad range of applications relating to national security, health care, the environment, energy, food safety, and manufacturing. Due to their intrinsic physical properties, one-dimensional structures allow for novel detection mechanisms with a wide range of functionality and specificity in addition to improvements on current detection strategies. The most widely explored sensing scheme thus far utilizes a field effect which, at the nanoscale, is extremely sensitive to local changes in electrostatic environment. For example, we have demonstrated nanotubes as ideal platforms for probing individual biomolecules such as DNA by monitoring ionic conductivity. Here, we focus on one-dimensional structures as sub-wavelength optical elements with environmental and chemical sensing capabilities. We present two different nanostructure architectures: 1) silver nanowire arrays for surface-enhanced Raman spectroscopy (SERS), and 2) tin oxide waveguides for individual photonic-based sensors. In the first scheme, silver nanowires are assembled into a macroscopic film using the Langmuir-Blodgett technique. Due to electromagnetic coupling, these wire films experience huge near-field enhancements when excited with light. As a result, molecules adsorbed at the metal surface experience orders-of-magnitude increases in their Raman scattering cross-sections. We employ these nanostructure films as substrates for the chemical-specific sensing of non-resonant organic molecules, such as dinitrotoluene. The second sensing scheme integrates our functional nanomaterial with a microfluidic device, demonstrating an all-optical sensing platform that utilizes the evanescent field of a single-crystalline tin dioxide nanoribbon. Utilizing the ribbon as an optical waveguide, we perform a wide array of spectroscopic analyses on sub-picoliter probe volumes, including absorption and fluorescence. These methods provide a quantitative method for sensing analyte concentrations. The nanoribbons can also be physically coupled to metallic nanoparticles which strongly scatter the waveguided light. This pairing provides a means for not only detecting local changes in refractive index of the surrounding environment, but also allows for collection of a SERS response. This architecture represents a major step in the development and design of an on-chip photonic sensor.

(415) **Multiwalled Carbon Nanotubes: Interconnecting Solid State Electronics With Biosystems**

Alan Cassell[1], Jun Li[1], T.D. Barbara Nguyen-Vu[1], Hua Chen[1], Jessica Koehne[1], Russell Andrews[1], M. Meyyappan[1]; [1]NASA Ames Research Center

Multiwalled carbon nanotubes (MWNTs) are essentially highly conductive metallic wires with extremely high aspect ratios. Vertically aligned MWNTs can be grown directly on prefabricated electronic circuits with the nanoscale precision. Such materials are ideal metallic wires to interconnect solid-state electronics and biosystems. We demonstrate the advantage of this system in two studies. First, inlaid MWNT nanoelectrode arrays directly link underlying circuits with an extremely small amount of DNA molecules are demonstrated as an ultrasensitive electronic DNA sensor. Second, multiplex MWNT nanoelectrode arrays are employed for developing a closed-loop implanted device for electrical stimulating and recording.

(416) **Integration of Metal Oxide Nanobelts with Microsystems for Nerve Agent Detection**

Li Shi; University of Texas at Austin

We have assembled tin dioxide nanobelts with low-power microheaters for detecting dimethyl methylphosphonate (DMMP), a nerve agent simulant. The electrical conductance of a heated nanobelt increased for five percent upon exposure to 78 parts per billion DMMP in air. The nanobelt conductance recovered fully quickly after the DMMP was shut off, suggesting that the single-crystal nanobelt was not subjected to poisoning often observed in polycrystalline metal oxide sensors. While the sensitivity can be improved via doping nanobelts with catalytic additives, directed assembly or growth of nanobelts on microsystems will potentially allow for the large-scale fabrication of nanosensor arrays.

(417) **Dynamic Infrared Microspectroscopy Using a Prism Based Infrapid Spectrograph**

Andre Sommer[1], Zachary Keltner[1], Katherine Kayima[1], Luis Lavalle[1], Adam Lanzorotta[1], Marina Canepa[1], Curtis Marcott[2], Gloria Story[2], Anthony Dowrey[2]; [1]Molecular Microspectroscopy Laboratory, [2]The Procter & Gamble Company

Infrared microspectroscopy has been employed over the last two decades in a wide variety of disciplines to elucidate chemical information from small spatial domains. The technique is relatively mature however one drawback is the methods temporal resolution. Measurements in the mid-infrared spectral region continue to be dominated by interferometers whose temporal resolution is directly related to the modulation efficiency of the detector. Recently, infrared spectrographs using modern day mid infrared focal-plane array (FPA) detectors have been investigated.[1-6] The sensitivity and speed of infrared measurements made using such a planar array infrared spectrograph (PAIRS) could someday substantially surpass that of conventional FT-IR spectrometry. We have recently reported on the design of an infrared microscope which employs a prism based spectrograph (7). This system allowed transmission, trans-reflectance and attenuated total internal reflection (ATR) spectra to be collected on a variety of systems where the sample dimension was as small as 15 micrometers. This presentation will focus on the fundamental design and optimization involved in coupling an infrared microscope to an infrared spectrograph. Specific examples will be presented which demonstrate the optimized system. [1] H. H. Richardson, V. W. Pabst and J. A. Butcher, Appl. Spectrosc., 44, 822 (1990). [2] H. H. Richardson, V. W. Pabst and J. A. Butcher, Appl. Spectrosc., 47, 1626 (1993). [3] P. Hamm, S. Wiemann, M. Zurek and W. Zinth, Opt. Lett., 19, 1642 (1994). [4] D. L. Elmore, M. W. Tsao, S, Frisk, D. B. Chase and J. F. Rabolt, Appl. Spectrosc., 56, 145 (2002). [5] C. Pellerin, C. Snively, Y. Liu, D. B. Chase and J. F. Rabolt, Appl. Spectrosc., 58, 639 (2004). \r\n[6] C. Pellerin, S. Frisk, J. F. Rabolt, D.B. Chase, Appl. Spectros., 58, 799 (2004). [7] A. J. Sommer et al. 2006 Pittsburgh Conference and Exposition, Paper 370-1.

(418) **Application of Planar Array IR (PA-IR) to Early Detection of Disease**

John Rabolt[1], Chris Snively[1], Bruce Chase[2], Andrea Persapane[1]; [1]University of Delaware, [2]DuPont CR&D

Much of the medical instrumentation developed over the last several decades has been aimed at the detection of a specific disease (e.g., cancer) or condition once it is present. Hence the focus has been on technologies that portray the presence or absence of a specific signal, image, etc. that is indicative of a particular disease. While this is critically important, recent advances in technology may be able to detect the precursors of disease and, hence, provide an "early warning" signal to the medical community so that a prescribed therapy can be administered so as to either stabilize the development of disease or, perhaps, even diminish or remove the precursors. The advanced detection of disease is the goal of numerous global research initiatives into noninvasive in vivo methods of characterization. Many of these focus on the non-specific detection of the early manifestations of disease (e.g., pressure in the eye - glaucoma, etc.) while others are designed for disease prevention and check for the presence or absence of a specific chemical component (e.g., enhanced glucose levels in blood – diabetes). For the medical industry, infrared spectroscopy has seen very few clinical applications in the past three decades. The main obstacle in bringing infrared spectroscopy into the healthcare environment, especially for in vivo applications, is the lack of an easy-to-use instrument and the lack of flexibility in sample positioning. The moving parts in a conventional Fourier transform infrared (FT-IR) instrument intrinsically limit the portability of such an instrument, confining it to a benchtop location in the laboratory. In addition, the stringent optical alignment needed for FT-IR instruments further limits the sample position flexibility. tRecently a planar array infrared (PA-IR) instrument has been described in the literature. It is portable, fast and chemically specific, i.e., it provides a chemical signature or "fingerprint" of the molecule present in the sample (Pellerin et al., 2004). If multiple components are present, then the "fingerprint" of each will be present in the spectrum obtained with the PA-IR spectrograph. This allows a multicomponent analysis to be carried out simultaneously and when applied to the field of disease diagnostics, it can provide an "early warning" diagnosis since, as has been shown previously, with a PA-IR instrument sensitivities to parts per billion (molecular concentrations) are achievable. One can envision a number of different ways to sample gases (e.g., breath), liquids (e.g., blood, saliva) and solids (e.g., tissue) that could be coupled to an ultrafast PA-IR instrument for quick, routine analysis. A description of an application to the early detection of eye disease will illustrate the potential of the PA-IR approach.

(419) **High Spatial Resolution Infrared Imaging with a Solid Immersion Lens and a Broadband Laser Source**

Chris Michaels; NIST, Surface and Microanalysis Science Division

Infrared microscopy is a powerful technique for the chemical characterization of a wide variety of materials, with applications in fields ranging from forensics to cancer diagnostics. The power of this technique lies in the combination of the chemical specificity of infrared absorbance spectroscopy and nominal spatial resolution in the 20 micrometer range, allowing for the spatial mapping of microscale variations in the chemical composition of heterogeneous materials. Improvement in the attainable spatial resolution is an important goal for the ongoing development of this technique,

potentially extending its utility to a class of analysis problems for which it is not currently suitable. Several factors limit the typical spatial resolution, including the brightness of thermal radiation sources and the relatively low numerical aperture (NA) of the commonly employed, reflective imaging optics. One approach to increasing the spatial resolution involves the application of hemispherical solid immersion lens (SIL) technology. Hemispherical, solid immersion lenses are fabricated from transparent, high refractive index materials. The hemispherical lens produces image formation free of geometric aberration at the center of the flat surface of the lens, wherein the effective NA and magnification are increased by a factor of n, the material index of refraction. Research in the SIL imaging area has been largely directed towards optical data storage applications in the visible spectral region. Little effort has been focused on SIL-based IR microscopy, despite a number of readily available, relevant optical materials (e.g., ZnSe, Si, and Ge). A microscope platform designed for exploration of IR SIL imaging based on a ZnSe SIL, an InSb focal plane array detector and an IR laser source will be described. The imaging characteristics of this system, including the spatial resolution attainable in the imaging of organic test samples, will be reported. Finally, the acquisition of spectral images based on several prospective approaches to source dispersion will be discussed.

(420) **Novel Search Algorithms for a Mid-IR Spectra Database of Cotton Contaminants**

J. Brian Loudermilk[1], David S. Himmelsbach[2], Franklin E. Barton, II[2], James A. de Haseth[1]; [1]The University of Georgia, [2]United States Department of Agriculture

Cotton lint contamination from the cotton plant itself and transportation debris is a serious problem for the cotton industry. Buildup of foreign substances on processing machinery can lead to decreased production rates and decreased yarn quality. The USDA has been developing a mid-IR spectra database of cotton contaminants to be used for contaminant identification. Identification of these contaminants is used to increase the efficiency of cotton processing and the quality of cotton yarn. Search algorithms that can distinguish extremely similar spectra are necessary to identify the contaminants. Novel search algorithms have been developed and tested.

(421) **Vibrational Spectroscopic Characterization of Poly(ethylene terephthalate) Nanotube Composites**

Vasilis Gregoriou[1], Spiros Tzavalas[1], Dieter Fischer[2], Dionysis Mouzakis[3], Vasilis Drakonakis[3]; [1]FORTHICE-HT, [2]IPF, [3]University of Patras

Polymer-Nanotube composites were prepared both with chemically modified and neat tubes. Multiwall nanotubes that have undergone acidic treatment for 0.5, 2 and 4 hours were melt-compounded with Poly(ethylene terephthalate) (PET) in a batch-mixer. The samples were pressed into films and annealed at 180 oC for 3 minutes. Fourier Transform Infrared (FT-IR) as well as Raman Spectroscopies were utilized to monitor the gauche to trans transformations due to the annealing process with respect to the duration of the treatment of nanotubes. Differential scanning calorimetry (DSC) measurements were incorporated for the study of the crystallinity changes due to the presence of the tubes. Acidic treated nanotubes were found not only to increase PET's crystallinity but also to lead to a more perfect crystal formation. Raman and IR spectroscopic measurements in correlation with the DSC findings showed that neat PET has more trans conformers in the non-crystalline phase than the PET-NT samples. In other words the presence of the nanotubes transformed the trans conformers of the non-crystalline phase into crystalline domains. In addition, an other series of samples with various NT contents (0, 0.1, 0.2, 0.5, 1, 1.5, 2, 2.5, 3, 5 and 15%) were prepared by the melt mixing of PET with a PET-MWNT (Hyperion) master-batch. The FT-IR results are in agreement with the Raman measurements and showed an increase in trans over gauche conformers as the NT content increased at low concentrations.

(422) **Attenuated Total Reflectance Infrared Imaging Using a Large Radius Internal Reflectance Element**

Brian Patterson[1], George Havrilla[1], Curt Marcott[2], Gloria Story[2]; [1]Los Alamos National Laboratory, [2]Procter and Gamble

The number of techniques and instruments available for infrared (IR) imaging has increased significantly over the past few years. Through the use of either a focal plane array (FPA) or a linear array detector, coupled with a chemometric analysis package, infrared imaging has become a powerful analytical tool. Attenuated total internal reflectance (ATR) infrared microspectroscopy reduces sample preparation time and has simplified the analysis of many difficult samples. Studies with ATR-IR-FPA imaging have focused on the use of small stationary, approximately 1.5 mm radius, germanium, silicon, or diamond internal reflection elements, and a field of view (FOV) of 50 micrometers in the micro regime. Through the use of an automated stage and a large radius hemisphere, micro-IR imaging has now been demonstrated of areas up to 2.5 x 2.5 mm. Through the use of a either a single point, a linear array or a FPA detector, the FOV of ATR-IR microspectroscopic imaging area can be increased by several orders of magnitude. Method characteristics to be evaluated include the change in penetration depth by both wavelength and beam displacement, measurements of the active area, magnification factor, and change in spatial resolution over the imaging area. Drawbacks such as large file size will also be discussed. Through the use of a Cu grid as a mask on a Parafilm polyethylene polymer film, spatial resolution, imaging area and sensitivity can be easily measured. Image banding characteristics on both a linear array and a FPA detector will be compared. This technique has been successfully applied to a variety of interest areas including materials characterizations, forensics, and inorganic powder mixtures.

(423) **Non-Invasive Raman Spectroscopy of Human and Animal Tissue**

Michael D. Morris,; University of Michigan

We discuss time-resolved and fiber-optic Raman spectroscopy for non-invasive measurement of Raman spectra of human and animal bone tissue. Light scattering by the tissue is a major experimental problem and requires deep red or NIR lasers for tissue penetration. While scattering and fluorescence (especially melanin fluorescence) problems require long excitation wavelengths, water absorption becomes limiting if the laser wavelength is much greater than 1 micron. The need for high laser power without thermal damage to tissue means that a defocused or loosely focused laser beam is needed. While time-resolved spectroscopy has been successful in recovering bone spectra of mice transcutaneously, the specialized equipment needed is bulky and expensive. Consequently, we have turned to fiber optic Raman spectroscopy with conventional NIR Raman spectroscopy systems. With attention to the tissue optics problems and laser exposure limits we have been able to measure important bone quality parameters including carbonate/phosphate ratio with good accuracy (2%-5%) using with the fiber optic approach. In this talk we will present our most recent results for non-invasive measurements in human and animal tissue,. We will also methods to prevent tissue damage and new ways to improve the signal/noise ratio of the recovered spectra.

(424) **Time Resolved Raman Photon Migration for Depth Profiling Opaque Samples**

Neil Everall[1], Pavel Matousek[2], Mike Towrie[2], Tony Parker[2], Michael Morris[3]; [1]ICI PLC, [2]Rutherford Appleton Laboratory, [3]University of Michigan

Photon migration is the process whereby photons propagate in turbid media along tortuous flight paths induced by multiple scattering events at phase boundaries. Photon migration following the incidence of a short laser pulse leads to a measurable delay, up to hundreds of picoseconds, before a Raman photon is emitted from an opaque material. This effect has been demonstrated using a picosecond kerr-gated Raman spectrometer, and the decay kinetics of the Raman signals have been modelled using Monte Carlo calculations [1,2]. More recently, we have shown that layered opaque systems can be depth profiled using time-resolved Raman spectroscopy [3]. This application depends on the fact that "late" Raman photons tend to have been generated more deeply within an opaque sample than their "early" counterparts. This presentation will review the basics of Raman photon migration, and will present data that shows its potential and limitations for depth profiling, using layered powder samples as model systems. Experimental results are compared with Monte Carlo modelling studies. 1N Everall, T Hahn, P Matousek, A Parker and M Towrie, Appl. Spectrosc. 55(12), 1701-1708 (2001) 2 N Everall, T Hahn, P Matousek, A Parker and M Towrie, Appl. Spectrosc. 58(5), 591-597 (2004) 3 P Matousek, N Everall, M Towrie and A Parker, Appl. Spectrosc. 59, 200 (2005)

(425) **Future Possibilities in Diagnosis of Breast Cancer by Subsurface Probing of Calcifications with Kerr-Gated & Surface Offset Raman Spectroscopy (SORS).**

Nicholas Stone[1], Pavel Matousek[2], Kate Ronayne[2], Rebecca Baker[1], Tony Parker[2], Keith Rogers[3]; [1]Gloucestershire Royal Hospital, UK, [2]CCLRC Rutherford Appleton Laboratory, UK, [3]Cranfield Health, Cranfield University

Breast calcifications can be found in both benign and malignant lesions. However the composition of these calcifications can indicate the possible disease state. Calcium oxalate may be found in and around both benign and malignant lesions, however calcium hydroxyapatite is found only in malignant tissue. As current practices such as mammography and histopathology examine the morphology of the specimen, they cannot reliably distinguish between the two types of calcification, which frequently are the only features that indicate the presence of a cancerous lesion. Therefore this information can be used to make a simplistic diagnostic decision, if the biochemistry of the calcifications can be probed. Furthermore, it is postulated that the calcifications not only accompany the malignant process, but could actually stimulate mitogenesis and may be necessary for the action of matrix metalloproteinases on the basement membrane to enable invasion into surrounding tissues. A programme of work has been undertaken to establish the possibility of using Kerr-gated and surface offset Raman spectroscopy (SORS) to probe the local tissue biochemistry around breast calcifications. To date this has been performed on either excised human breast tissue or a chicken breast phantom. Breast calcifications have been modelled by using calcium hydoxyapatite and calcium oxalate (monohydrate and dihydrate) crystals. These have been placed at depths ranging from 1 to 10 mm in tissue and measured utilising one of the two mentioned techniques. Results demonstrate that the Kerr-gated technique, utilising a 1 ps pulsed laser at 490nm and a 4ps Kerr-gate is able to probe calcified material through up to 2mm of tissue; whereas the SORS technique, utilising a cw 827nm laser and a collection offset of 3mm enabled a probing of calcified material through up to 10mm of tissue.

(426) **Subsurface Raman Spectroscopy of Pharmaceutical Tablets and Capsules**

Pavel Matousek[1], Anthony W. Parker[1]; [1]Rutherford Appleton Laboratory

In a number of analytical applications, the primary target of analysis may be the bulk content of analyte rather than its microstructure. An example can be chemically specific screening of pharmaceutical tablets for the presence of different polymorphs, solvates or undesired salt forms or starting materials of chemical reactions. Ideally, this information should be obtainable quickly and non-destructively as is required on production lines. Raman spectroscopy is a powerful analytical tool for the examination of pharmaceutical materials with a great potential for wider use in PAT applications. Its major limitation in its conventional form for probing the bulk content of tablets is its strong bias to the surface layers of probed turbid medium. We discuss two simple approaches that enable the reduction and even elimination of this bias. The methods are also well suited to probing coated pharmaceutical tablets or coloured capsules non-invasively by suppressing fluorescence emanating from capsule shell or tablet coating.

(427) **Raman Kerr Gating in the Study of Street Drugs**

W.Ewen Smith[1], Rachael Littleford[1], Karen Faulds[1], Pavel Matousek[2], Mike Towrie[2], Antony Parker[2], Geoffrey Dent[3], Richard Lacey[4]; [1]Strathclyde University; [2]CLRC Rutherford Appleton Laboratory; [3]Avecia Ltd; [4]HOSDB

Raman spectroscopy is attractive as a simple stand-off method for the detection of street drugs. It provides molecularly distinct signals enabling identification of an analyte without a separation step or any direct contact other than with the laser beam. However, this "white powder" type of detection has two limitations. Firstly, it is not particularly sensitive and secondly many of the materials used to cut the drugs before sale on the street can cause fluorescent interference. Sensitivity can be improved by a simple technique of adding drug solutions to a colloidal gold suspension and measuring SERS. For cocaine, detection limits down to about 10-5 or 10-6M are easily achieved. The SERS technique has an advantage in that fluorescence is diluted out on addition of the sample to the colloidal suspension and any fluorescence material which adsorbs on the surface is fluorescence quenched. This technique and simple Raman spectroscopy are now much more practical since small hand held spectrometers have become more readily available. Solid street samples are more difficult to analyse because of the amount of fluorescing material. Using visible excitation, the fluorescence background prevented the detection of Raman scattering. On applying the Kerr gate, good spectra were obtained for cocaine and other peaks attributed to the cutting agents were detected. These initial results indicate that Kerr gating is useful to identify in situ some drugs of abuse in street samples. However, we were less successful in detecting heroin in heavily cut samples and Kerr gating is still expensive.

(428) **Kerr Gated Resonance Raman Spectroscopic Studies on The Photochemistry of Papers and Prints**

Anna-Stiina Jaaskelainen[1], Katri Vikman[1], Anna-Maija Saariaho[1], Jouko Vyorykka[1], Tapani Vuorinen[1], Pavel Matousek[2], Anthony Parker[2]; [1]Helsinki University of Technology, [2]Rutherford Appleton Laboratory

Resonance Raman spectroscopy has been found to be a powerful tool in wood-based material research. Unfortunately, many of these types of samples are highly fluorescing and therefore mainly NIR or deep UV excitation have been used in most applications. However, to detect selectively the chemistry of chromophores at very low concentrations it would be of great benefit to utilise resonance Raman spectroscopy. This requires visible light

excitation and the detection of Raman spectra in the presence of very intense fluorescence. In this paper, we show how resonance Raman spectroscopy equipped with Kerr gate fluorescence rejection system can provide detailed chemical information on photochemistry of paper samples. The resonance Raman spectra of mechanical pulps (newsprint paper) showed that the slightly yellowish color originates mainly from lignin and coniferyl aldehyde structures present in the samples. Alkaline hydrogen peroxide treatment oxidises these structures and results in increased brightness. On the other hand, ageing the paper under UV light causes drastic yellowing, which correlates with the formation of quinone-type of structures. Yellowing was observed to be more pronounced for the bleached pulp than for the unbleached reference. The application of yellow ink on coated paper samples resulted in shifts in its resonance Raman lines. This could be attributed to chemical interactions between the colorant and the coating components. Exposing the printed sample to the UV light resulted in remarkable intensity drop of the Raman band at 1393 cm-1, illustrating degradation of azo groups in the ink.

(429) **Some Remaining Issues in Plasma Source Mass Spectrometry**

John Olesik; The Ohio State University,

ICP-MS is certainly one of the most successful and widely used techniques for elemental and isotopic analysis. However, several issues related to both fundamental understanding of the processes that convert sample to signals and practical use remain. For example, the commonly accepted models of ion sampling and transport do not fit experimental observations by Farnsworth's group. While multicollector ICP-MS have provided exciting new capabilities that have unveiled small but significant isotope fractionation in nature mass bias correction remains complex, poorly understood and concentration dependent. While many spectral overlaps can be overcome using either high mass spectral resolution or collision/reaction cells, some remain a problem. Previously unexpected molecular ions have been reported. Chemical matrix effects also remain a potential source of error. The Ar ICP is limited as a sample vaporization source. Even some submicron particles are incompletely vaporized in a dry Ar ICP. These issues will be discussed in this presentation. Several of these issues will also be addressed in detail by others in the two Wednesday symposia

(430) **Experimental and Theoretical Studies of Energy and Mass in Laser Ablation Plumes**

Richard E Russo[1], Sy-Bor Wen[1], Xianglei Mao[1]; [1]Lawrence Berkeley National Laboratory

The objectives of our research are to elucidate fundamental mechanisms underlying laser ablation processes as they relate to direct solid sample chemical analysis. Ablation processes include laser-material-interactions, mass ejection, laser-plasma interactions, plume/plasma dynamics, and particle formation. The research emphasis has been on shockwave behavior and particle formation. For chemical analysis, the ablated mass must be either excited vapor for LIBS (laser induced breakdown spectroscopy) or particles for ICP-MS (inductively coupled plasma mass spectrometry). Dynamics of the shockwaves and the plume/plasma govern the character of the ablated mass. From the beginning of the laser pulse to ~1 after the laser pulse, the propagation of the vapor plume and shockwave were studied by using shadowgraph and spectral emission imaging. We found that the strong expansion of the vapor plume starts at ~2ns after the beginning of the laser pulse. A laser supported detonation wave (LSD) is observed at the top of the shockwave between ~4 to ~9ns after the beginning of the laser pulse, which blocks the coupling of the laser energy to the sample. In addition to the shockwave in the background gas region, an internal shockwave in the vapor plume is observed to coincide with the interaction of the internal shockwave with the sample surface. A theoretical analysis was developed to describe the shockwave during this time interval, and simulated trajectories of the vapor plume and shockwaves show good agreement with the experimental results. By using this analysis, we are able to determine the laser energy conversion ratio and the sample mass vaporized during the laser ablation. A significant effort involved the measurement and understanding of particles. The cooling rate of the laser plume plays a strong role in the size and size distribution of the ablated particles. In addition, particles are formed by melt ejection and spallation. SEM images, DMA (differential mobility analyzer) and chemistry are used to study nanoparticle formation mechanisms.

(431) **Diagnostic Measurements in Laser Induced Plasmas: a Critical Look**

Nicolo Omenetto[1], Galan Moore[1], Igor Gornushkin[1], Benjamin Smith[1], James Winefordner[1]; [1]University of Florida, Gainesville, FL 32611, USA[4]

Laser induced plasmas as analytical emission sources are currently the subject of a continuously increasing number of investigations discussing the plasma radiative properties and the temporal and spatial evaluation of its physical parameters. As a consequence, rather old and well established methods of plasma diagnostics and radiative energy transfer are continually revisited, reformulated and applied to different kinds of plasmas obtained under a variety of experimental conditions. This talk attempts to summarize the limitations and practical applicability of several popular diagnostic approaches applied to the evaluation of plasma parameters such as temperature and number densities (neutrals, ions, electrons) as well as to the characterization of line profiles, line broadening mechanisms and plasma optical thickness. Other well established, but less popular, approaches will also be discussed. Examples taken from the literature and from our own work will be critically scrutinized in terms of their conceptual novelty and practical applicability to laser plasmas created on analytical targets.

(432) **Matrix Effects in Laser Ablation Inductively Coupled Plasma Mass Spectrometry**

Detlef Günther[1], Zhongke Wang[2], Bodo Hattendorf[1], Kroslakova Ivana[1], Joachim Koch[1], Markus Wälle[1], Jorge Pisonero[1]; [1]ETH Zürich, [2]Laser Technology Lab., Japan

The vaporization of laser generated aerosols in the ICP has been evaluated to importantly influence elemental sensitivities and therefore elemental fractionation in LA-ICPMS. Several studies provide evidence for incomplete vaporization of particles within the ICP, which influences the ion sampling through the interface and subsequently precision and accuracy of the analytical results. The vaporization process depends on the matrix and on the particle size distribution produced by the laser. Therefore, the radial and axial ion distributions in the ICP of an ICPMS for aerosols generated from silicate samples by various laser ablation systems using different ablation conditions (wavelength, pulse duration, carrier gas) were studied. The radial and axial ion distributions were measured at different positions of the plasma using various gas compositions (argon and helium). It will be shown that helium is most suitable for the particle size distribution formed during ablation. However, the helium leads to higher temperatures within the plasma and to significantly higher ion losses due to increased diffusion processes within the ICP. It will be furthermore demonstrated that the ion generation and sampling depends on the mass introduced into the ICP. A single matrix was introduced into the ICP using different crater diameters in combination with a

dilution system. The lower the mass introduced into the ICP, the more stable become element ratios. These studies were carried out using ns and fs lasers. To demonstrate that the fundamental studies on a single matrix are not representative for "all" matrices, results from a glass and a zircon matrix will be discussed.

(433) **Ion Trap ICPMS - New Instrumentation and Methods**

Charles J. Barinaga[1], David W. Koppenaal[1]; [1]Pacific Northwest National Laboratory

Our research group first investigated and demonstrated the coupling of 3-D, Paul-type ion trap MS systems with ICP ion sources in the mid-1990's. The results of these experiments demonstrated efficient and sensitive detection of atomic ions, although with a reduced dynamic range compared to conventional quadrupole ICPMS systems. The primary benefit derived from this work was the demonstration that ion-molecule reaction chemistry could provide significant, real advantage in reducing plasma gas and polyatomic ion interferences. One of these benefits was the realization of 'chemical resolution', ie the ability to resolve polyatomic ion interference using simple gas-phase reaction chemistry. We achieved chemical resolution of ~600, 000 R in separating Xe and I interferent/analyte isobars at m/z 129 using this approach. We have recently revamped our ion trap ICPMS approach using newly available linear ion trap MS systems. Linear ion trap systems afford several advantages, including better sensitivity and higher dynamic range. In addition, linear ion traps provide the opportunity to eject and detect ions radially in the x-or y-direction (single or dual radial detectors can be used). A further advantage then exists to alternatively pass ions axially to another, end-positioned MS or detector system. Examples of high-resolution spectrometers that can be used in this mode include FTMS or Orbitrap MS systems, as have recently been demonstrated by Thermo Instruments for proteomic and metabolomic applications. We will describe work that interfaces an ICP ion source to a linear ion trap MS system, and which will ultimately be developed into a custom ICP-LIT-Orbitrap MS system. The system will also include a collision/reaction cell to be used in conjunction with the physical high-resolution capability. The versatile high resolution capabilities afforded by such a system will enable the ultimate in atomic and polyatomic isobar resolution, as needed for certain demanding elemental and isotopic applications (e.g. radioanalytical, metallomics problems)

(434) **A High-Performance Multichannel Mass Spectrometer for Elemental Analysis**

Gary M. Hieftje[1], Gregory D. Schilling[1], Francisco J. Andrade[1], M. Bonner Denton[2], Roger P. Sperline[2], David W. Koppenaal[3], Charles J. Barinaga[3]; [1]Department of Chemistry, Indiana University, [2]Dept. of Chem., University of Arizona, [3]Pacific Northwest National Laboratory

In retrospect it is somewhat surprising that the multichannel revolution that has changed atomic emission spectrometry has barely begun in atomic mass spectrometry. At present, almost all commercial instruments for inductively coupled plasma mass spectrometry are single-channel, and operate in a sequential, peak-hopping mode. This situation is all the more puzzling because of the relative simplicity of atomic mass spectra compared to atomic emission spectra. Whereas emission spectra must be obtained over a broad wavelength range (typically 200 nm to 800 nm) and at high resolution (on the order of 0.005 nm), atomic mass spectra are usually collected only over a mass-to-charge range from 7 (Li) to 250 (actinides) and at unit-mass resolution. As a result, a multichannel detector for atomic mass spectrometry would require no more than 1500 individual detector elements, even if each peak is to be sampled with 6 points; in contrast, a suitable detector for emission measurements would need on the order of 300,000 pixels. Clearly the reason for this disparity is the absence of an appropriate multichannel detector for mass spectrometry. In this presentation, just such a detector will be described. The current generation has only 128 channels, although larger devices are being developed. The detector arrays feature direct, continuous integration, truly simultaneous multi-mass detection, random-access interrogation on a pixel-by-pixel basis, the option for destructive or non-destructive readout, rapid measurement, high sensitivity, and broad dynamic range. The performance of the new detectors with a range of atomic sources and sample-introduction systems will be evaluated.

(435) **Perchlorate, Wherefrom, Wherein and Where Do We go From Here?**

Purnendu Dasgupta,; Texas Tech University

Perchlorate has been much in the American news media since the discovery of the significant contamination of the lower Colorado river with perchlorate seeping from the Las Vegas Wash, the source apparently being a single plant that manufactured ammonium perchlorate for use as Rocket fuel. Perchlorate, which was once regarded as a harmless, essentially nontoxic anion, may now be regulated at a maximum permissible level of a few parts per billion in drinking water. Perchlorate competes with iodide, which is essential for proper thyroid function in adults and for neural development in infants. There are two sodium iodide symporters in mammals, one is in the thyroid glands and the other is present in female mammary glands, the only means by which iodide is delivered to a breastfed infant. Much like most synthetic anion exchangers, perchlorate has much greater affinity for the symporter sites than iodide, effectively reducing iodide transport even at low perchlorate levels. There is naturally great concern about the presence of perchlorate in drinking water. While the production of perchlorate as a fuel oxidizer may indeed be to blame for the contamination of the lower Colorado, easily measurable levels of perchlorate in groundwater in many places in the Texas panhandle, hundreds of miles away from any known perchlorate production facility, suggests that all perchlorate did not originate as rocket fuel. George Ericksen of the USGS continued a noble tradition of trying to solve a century old puzzle and spent a lifetime figuring out how the Chilean Saltpeter deposits (which is mostly sodium nitrate but contains 0.1-0.2% perchlorate) originated. Based on isotopic evidence, his 1997 paper, published posthumously, concluded that the nitrate has atmospheric origin. With sufficient sensitivity brought about by collaboration with scientists at Iowa State, we can now see perchlorate everywhere, in rain, snow, even ice core samples from Greenland. Does perchlorate too naturally originate in the atmosphere?

(436) **The Analysis of Club Drugs by CE and CE/MS**

Bruce McCord; Florida International University

An increasing problem in the US and abroad is the ready availability of club drugs such as GHB, MDMA, benzodiazepines and ketamine. The compounds can be found at rave parties and also are implicated in drug facilitated sexual assault. We have been developing approaches for the detection of these drugs using capillary electrophoresis and capillary electrophoresis/mass spectrometry. For screening a wide variety of drugs we utilize a technique involving in-line preconcentration followed by separation at high pH with additives such as beta cyclodextrin and organic modifiers to increase selectivity. The inline extraction process enhances sensitivity through stacking, and proper selection of the organic modifier permits separation of a wide variety of suspect drugs. For trace detection of these compounds we have developed a process to demethylate, derivatize with fluorescein and detect using laser induced fluorescence. More recently we have

used CE/MS with time of flight detection as for the analysis of these drugs. The MS/TOF system permits rapid detection since the enhanced resolution (3ppm) of the detector combined with efficient CE separations results in highly specific data. Proper selection of inlet voltages permits in-source CID, further enhancing the specificity of the analysis. The presentation will conclude with a discussion of the potential applications of high mass resolution CE/MS as a confirmation tool in forensic analysis.

(437) **Determination of Biomarkers in Biological Fluids, Tissues, and Cells by Immunoaffinity Capillary Electrophoresis**

Norberto Guzman; Johnson & Johnson Pharm. R&D

Advances in instrumentation and methodologies are urgently needed to achieve, rapid, simultaneous, and sensitive determination of multiple substances found at a wide range of concentrations in biological fluids, tissues, and cells. The application of immunoaffinity capillary electrophoresis in life sciences is already having an impact on the quantification of many biomarkers for diagnosis and monitoring the prognosis of diseases. This presentation explains how immunoaffinity capillary electrophoresis, the combination of highly selective antibody capture agents with the high resolving power of capillary electrophoresis, can provide highly specific assays leading to the selective isolation, concentration, separation, and quantification of analytes of interest in complex biological matrices. In addition to a discussion of the technology, some applications of clinical and pharmaceutical relevance will be presented.

(438) **Protein Aggregate Separations by Capillary Electrophoresis**

Doug Gilman[1], Julia Moses[1], David Schrum[1], Ryan Picou[1]; [1]Louisiana State University

We are developing analytical methods based on capillary electrophoretic separations to study protein aggregation. Protein misfolding and protein aggregation are closely linked to more than 25 diseases including Alzheimer's Disease, Parkinson's Disease and prion diseases. Protein aggregates are difficult to study quantitatively. In our studies of amyloid-beta peptide (linked to Alzheimer's Disease), a single solution can contain monomeric peptide, fragile oligomeric aggregates, intermediate aggregates of nanometer dimensions, and large, insoluble aggregates more than a micrometer in length. We are using capillary electrophoresis to resolve these structures and a range of detection methods to quantify them. These detection methods range from simple absorbance detection to detection of individual aggregates by fluorescence and light scattering. The ultimate aim of our work is to develop improved approaches to quantitatively study protein aggregation and to apply these methods to better understand the role and nature of protein aggregates in related diseases.

(439) **Predicting Physical Protein Stability by Self-Interaction Chromatography**

Charles Henry[1], Joseph Valente[1], Robert Payne[1], Beth Fryksdale[2], Douglas Dale[2], Alfred Gaertner[2], Mark Manning[3], William Wilson[4]; [1]Colorado State University, [2]Genencor International, [3]Legacy Biodesign, [4]Mississippi State University

Proteins are playing an ever more important role in industrial and pharmaceutical applications. For example, there are currently over 300 products in phase III clinical trials that are based on biological macromolecules. Unlike traditional therapeutics, physical stability (solubility, aggregation, etc) plays an important role in defining long term product viability by controlling solubility and aggregation. From a fundamental perspective, physical stability also plays a critical role in protein crystallization as well as common protein misfolding patterns that occur in diseases such as Alzheimer's. Protein physical stability can be quantified by many indirect methods but is best measured quantitatively through the osmotic second virial coefficient, B. Unfortunately B measurements are not widely employed because the traditional measurement techniques are slow and protein intensive. In this presentation a new form of chromatography, self-interaction chromatography (SIC) that can be used to measure B will be presented. Application of the method to screening protein physical stability for both soluble and membrane proteins will be shown as well as correlations to protein solubility and activity.

(440) **Isotopic and Elemental Analysis for Forensics and Attribution of Biological Agents**

Douglas C. Duckworth[1], Juske Horita Horita[1], Mark Lavelle[3], Stefan Bürger[1], Lee R. Riciputi[1], Brad Knippel[1], Debra A. Bostick[1], Craig C. Brandt[1], Helen Kreuzer[2]; [1]Oak Ridge National Laboratory, Chemical & Isotope, [2]Pacific Northwest National Laboratory, C, [3]New Scotland Yard, Broadway, London, UK

In the event of a biological weapon intercept or attack, the agent and strain are initially identified, but yield limited attribution information. There is a need for more diagnostic forensic analyses for attribution of the agent to a source and its production method. Chemical composition such as that provided by elemental and isotopic analysis may provide insight into production processes and growth media used. Ideally, one may be able to compare known and questioned biological weapon agents to determine the degree of association based on isotopic and elemental content. In support of the U.S. Department of Homeland Security, a series of investigations have been performed to develop and validate methods for high precision isotope ratio analysis. The focal point of this research is to identify isotopic signatures for BW agents that may allow an association (or lack thereof) between a known and question sample to be established. Relationships between growth media and spores will also be investigated. Isotopic and elemental analysis of several bacterial agents, grown under controlled growth conditions, will be presented. Results will focus heavily on method development and analytical characterization of "light" (C, N, O, and H) and "heavy" (e.g. Sr, Pb) isotope ratio measurements for forensics and attribution of bioagents. Light isotope ratio signatures of bacteria as well as growth media and additives are performed by elemental analyzer/isotope ratio mass spectrometry. Isotopes of Pb and Sr are measured by both multiple collector inductively coupled plasma mass spectrometry and multiple collector thermal ionization mass spectrometry, respectively. Effects of growth media on elemental and isotopic profiles will be highlighted. Research sponsored by the Office of Research and Development, U.S. Department of Homeland Security, under contract DE-AC05-00OR22725 with Oak Ridge National Laboratory, managed and operated by UT-Battelle, LLC. HKM gratefully acknowledges support from the US Central Intelligence Agency, and , and ML support from the Fulbright Foundation.

(441) **Classification of Two-way Data for Forensic Fingerprinting of Fuels by Gas Chromatography-Mass Spectrometry and Gas Chromatography-Differential Mobility Spectrometry**

Peter Harrington[1], Ping Chen[1], Yao Lu[1], Christopher Bunker[2], John Karnes[2]; [1]Ohio University, [2]Air Force Research Laboratory

Forensic fingerprinting typically matches chromatographic profiles to identify or characterize complex samples that include fibers, inks, paint chips, accelerants, and explosives. Typically, only the chromatographic profile is used for comparison, even when the detector is a multichannel detector such as a mass spectrometer. Each sample will furnish a two-data object with one-way corresponding to retention time and the other way to the detector

channels. Each way may comprise hundreds or thousands of dimensions. With a GC-MS a typical measurement may have several thousand retention time measurements and several hundred mass-to-charge measurements. Chemometric tools are useful for evaluating and classifying multi-way data, which is more difficult to compare visually. The advantage of multi-way classification is that greater informing power is obtained than by using an integrated response from the detector channels. Analysis of variance-principal component analysis (ANOVA-PCA) provides a valuable tool for assessing the experimental factors and optimizing measurements. Fuzzy rule-building expert systems (FuRES) and temperature constrained cascade correlation networks (TCCCN) are two robust self-configuring classifiers that can be used for matching two-way samples of unknown origin. These classifiers will be demonstrated for the characterization of fuels by GC-MS and GC-DMS.

(442) **Laser Ablation in LIBS and ICP-MS: Plasma and Aerosol Formation Processes**

Rick Russo[1], Sy-Bor Wen[1], Jhanis Gonzalez[1], Xianglei Mao[1]; [1]Lawrence Berkeley National Laboratory

LIBS and laser ablation ICP-MS are becoming ubiquitous technologies for rapid screening and identification in forensics applications. These analytical technologies allow real-time chemical analysis without sample preparation, without consumables, and with minimal chemical exposure to forensic personnel. The basis of these technologies is removal of mass from a solid (or liquid) sample using a pulsed laser beam. The ablated mass undergoes several transitions from vaporization, excitation to emission, and condensation to an aerosol. The efficiency of these processes is critical in defining the performance metrics for the application; excited neutrals and ions are required for LIBS whereas nanoparticles with a narrow particle size distribution is required for ICP-MS. The laser ablation process can be tailored to optimize each measurement modality if the fundamental processes are understood. The basis of this talk will be to describe experimental and simulation research that addresses the efficiency of laser energy coupling into the sample target, mass removal processes, shockwave propagation, and particle formation processes. An overview of these fundamental processes and some general forensic application will be presented.

(443) **Forensic Provenancing by NITE.**

Jurian Hoogewerff[1], Simon Kelly[1], Members NITECRIME Network[2], Members TRACE Consortium[3], [1]Institute of Food Research, [2]NITECRIME Network, [3]TRACE Consortium

Due to the globalisation of trade in legal and illegal goods and the limits of paper/electronic mandatory or voluntary traceability systems there is an increasing demand for techniques which can verify and/or validate the claimed source of such goods. The definition of “source” can range from production method, to specific production plant, to the geographical location of the raw material. Provenancing of raw products like geological materials, gold nuggets, diamond and other raw ore and building materials, raw food commodities like mineral water, vegetables and fruits and natural drugs has the highest feasibility for geographic profiling as these items have a strong geochemical relation with the host rock and/or soil. As certain rock and soil types have a limited spatial distribution on earth, the chemical signature the products inherit from their geochemical and/or bio-climatic environment, may enable geographical sourcing. The bio-geo-chemical Natural Isotope and Trace Element (NITE) signatures consist of elemental and isotopic profiles related to regional climate (H and O isotopes), bio-environment (C and N isotopes) and geology (elements and S, Sr, Nd, Pb and other isotope systems). \r\n A very important aspect of sourcing is the validation method. The most commonly suggested, but often prohibitively expensive, method is the construction of an analytical database based on authentic samples from specific areas which needs to be maintained indefinitely. However inspection of any item from an un-authenticated area might lead to false positives. The second method, expensive only in its implementation phase, is to develop an understanding of the relation between the NITE profile in a certain product and its geo-bio-climatic environment. The latter method has the advantage that often knowledge about the geo-bio-climatic environment of un-authenticated area is available, e.g. D/H and 18O isotope precipitation maps, geological and geochemical maps. The presentation will present the latest developments in the establishment of a worldwide geographical analytical profiling platform, funded by the EU TRACE project (€19M) and other sources which will initially enable the geographical profiling of food commodities but will lay the foundations for a general forensic profiling tool.

(444) **Improved Location of Forensic Traces Through Optimized Biological and Instrumental Detection of Vapor Signatures**

Kenneth Furton[1], JoNell Aarons[1], Laura Conner[1], Robert Griffith[1], Michael Macias[1], Samantha Tolliver[1]; [1]Florida Int'l University

This paper describes ongoing studies involving the identification and quantification of dominant odor signature chemicals that can be used by certified law enforcement detector dogs and instruments to reliably locate forensic specimens including accelerants, biotoxins, currency, drugs, explosives and humans (living and deceased). In this work, headspace analysis is performed primarily by Solid Phase Microextraction / Gas Chromatography ¡V Mass Spectrometry, and used to identify dominant odor chemicals seen at room temperature. The results demonstrate that canines are generally not using the relatively low volatility parent substances but instead us characteristic volatile headspace components to accurately locate specimens. The implications of these results on the optimal selection of canine training aids and the tuning of instruments for these compounds are also discussed. Hand held electronic instruments for arson investigations were found to be not as accurate as canines and susceptible to background interferences. In the biotoxins/mold detector dog studies the microbial volatile organic compounds from samples grown in vitro and purified in the laboratory and compared to those seen for species-specific mold drywall training aids. Laboratory and field studies of drug dogs demonstrate that they do not alert to directly to the drugs cocaine and MDMA but rather methyl benzoate (1-10*f*Ýg spiked) and 3,4-methylenedioxybenzaldehyde (10-100 mg spiked) and these chemicals have been found exclusively to be a dominant odor chemical in illicit cocaine and MDMA tablets. The volatility of the signature drug odor chemicals identified has demonstrated that alerts by properly trained drug dogs to odor residues emanating from currency can provide reliable information linking money to illicit drug activity. For the explosives project, the results presented indicate that TNT and cast explosives share common odor signatures such as DNT and 2-ethyl-1-hexanol is a dominant odor signature chemical for many plasticized explosives such as Composition C-4 and Deta-Sheet. In the cadaver dog studies, approximately fifteen compounds have been the focused on including biological amines, alcohols/cresols, indoles, methyl sulfides and organic fatty acids with a method developed allowing for the rapid detection of odor signature chemicals emanating from decomposing human remains.

(445) **A Novel LIBS system for Forensic Analysis of Materials**

Jose Almirall[1], Benjamin Naes[1], Hanh Lai[1], Scott Ryland[2]; [1]Florida International University, [2]Florida Department of Law Enforcement

Materials analysis and characterization can provide important information as evidence in legal proceedings. Although the utility of trace elemental analyses for comparisons for glass, paint fragments, bullet lead and metal fragments has been shown to offer a high degree of discrimination between different sources of these materials, the instrumentation required for the generation of good analytical data in forensic comparisons can be beyond the reach of many forensic laboratories. Scanning Electron Microscopy with an Energy Dispersive Spectrometer (SEM-EDX), X-Ray Fluorescence (XRF), Laser Ablation Inductively Coupled Plasma Atomic Emission Spectroscopy (LA-ICP-AES) and, more recently, LA-Inductively Coupled Plasma Mass Spectrometry (LA-ICP-MS) have been used in forensic laboratories for elemental analysis determinations. Two different and newly developed Laser Induced Breakdown Spectroscopy (LIBS) instruments have been evaluated as tools for the forensic elemental analysis of glass and compared in performance to other elemental methods in order to determine the utility of comparing casework sized glass samples. Developments in the instrumental design of these LIBS systems, specifically designed to address the analytical requirements of the forensic laboratory, are presented. The power of LIBS-based elemental analysis to discriminate between different glass samples is also compared to the discrimination power of XRF and LA-ICP-MS. The relatively low cost, ease and speed of operation and non-destructive nature of the LIBS analysis makes the technique a potentially viable forensic elemental analysis tool.

(446) **Raman Spectroscopy in the Female Reproductive System**

Elizabeth Kanter[1], Alanna Patsiokas[1], Amy Robichaux-iehoever[1], Anita Mahadevan-Jansen[1]; [1]Vanderbilt University

Cancer in the female reproductive system will cause many cancer related deaths in the United States this year. In both cervical cancer and ovarian cancer an accurate early diagnosis is essential in the effective management of the disease. In recent years Raman spectroscopy has received considerable attention for non-invasive, in-situ, near-real time diagnosis of cancer. It exploits for diagnosis subtle changes in the spectra of tissue as tissue transforms from normal to malignant. We present in this presentation the typical Raman signatures observed from different tissue sites of cervix and ovary, and also a comparison of the changes in the spectral patterns associated with precancerous, cancerous and normal state of tissues of these two different organs. A multi-class diagnostic algorithm based on state-of-the-art statistical pattern recognition techniques has been developed and used to quantify the spectral changes between the tissue types and also to classify them into their respective histopathological categories. The details of these results will be presented.

(447) **In Situ fs-Coherent anti-Stokes Raman Microscopy of Stem Cells**

Stanislav Konorov[1, 2], Michael Blades[1], Georg Schulze[2], Robin Turner[2]; [1]Chemistry Dept., UBC, Canada, [2]Michael Smith Laboratory, UBC, Canada

Femtosecond-CARS microscopy was used to image differentiated and undifferentiated mouse embryonic stem cells (mES) in vitro. The use of a femtosecond laser system allows high intensities while minimizing the risk of thermal damage to the sample. Excitation pulses are generated using a Ti:Sapphire laser/amplifier system with a pulse duration about 150 fs, a pulse energy of 2 mJ at 1 kHz repetetion rate. We show that with CARS microscopy is can be used to make nondestructive images of differentiation of embryonic stem cells without using special chemical markers.

(448) **Raman Spectroscopy of Murine-derived Osteogenic Stem/Progenitor Cells**

Gurjit S. Mandair[1], Michael D. Morris[1], Pieter Steenhuis[2], Michael A. Ignelzi Jr[2]; [1]University of Michigan, Department of Chemistry, [2]University of Michigan, Dental School

The goal of this study is to monitor the synthesis and conversion of mineralization intermediates in calvarial stem/progenitor cells using Raman spectroscopy. Osteogenic Sca-1 negative cells isolated from fetal mouse calvaria were plated onto UV fused silica slides and allowed to differentiate over a period of 42 days. At specific time points, the cells were fixed in ethanol and dried. For each slide, 14-19 Raman spectra of the cells were collected using a Raman microprobe. Between 5 and 14 spectra with good signal-to-noise ratio were averaged. Bands that are known markers for phenylalanine (Phe), octacalcium phosphate (OCP), amorphous calcium phosphate (ACP), hydroxyapatite (HAP), and mixed proline-hydroxyproline (Pro-Hyp) were selected for analysis. The areas of these bands and band area ratios were used to follow mineralization and matrix formation from initial formation of ACP to the stable HAP. The sum of Pro-Hyp band areas was used as a measure of matrix content. ACP and OCP, precursors of the final bone mineral, an impure poorly crystalline HAP appear around day 17 and their content peaks around day 28. After day 28, the rate of ACP and OCP synthesis declined, whereas the rate of HAP synthesis reached a plateau. Furthermore, we show that early mineralization proceeds at different rates and is dependent on the maturity of the differentiating cells. After Raman analysis, the fused silica slides were Von Kossa stained to provide spatial correlative Raman/histologic data on mineralization. Using Von Kossa staining mineralized bone nodules were visible around day 21. The number of nodules and the degree of mineralization gradually increased until day 35. These results are consistent with our Raman data as they show an increase in mineralization around day 21. Our results show that Raman spectroscopy can provide invaluable quantitative measurements on mineralization processes. A clear understanding of mineralization processes is highly desirable as it would enable the development of tissue-engineered osteogenic therapies for treatment of craniofacial bone defects caused by trauma, tumor removal, or degenerative skeletal diseases (e.g., osteoporosis, osteogenesis imperfecta).

(449) **Analysis of Plant Surfaces Using Raman Spectroscopy**

Marcia M.L. Yu[1], Stanislav Konorov[1], Georg Schulze[1], Reinhard Jetter[1], Michael W. Blades[1], Robin F.B. Turner[1]; [1]The University of British Columbia

The above-ground organs of plants are covered by a cuticle, an extracellular membrane consisting of the fatty acid-derived polymer cutin and waxes. The two most common techniques currently used to study the morphology and chemical composition of the cuticular wax are scanning electron microscopy (SEM) and gas chromatography – mass spectrometry (GC-MS), respectively. Although GC-MS proves to be a useful technique by providing the concentration of the different components in the wax, it is a destructive method and the sampling techniques have very limited spatial resolution. To achieve high spatial resolution, confocal Raman microspectroscopy is used here to determine the spatial chemical composition of leaf cuticles. We have performed preliminary studies with artificial wax mixtures consisting of the 2 triterpenoids most abundantly found on the cuticles of Prunus laurocerasus. In this presentation, we will also present our findings on the spatial distribution of the chemical components of isolated P. laurocerasus cuticular membranes. Results reported here complement the quantitative results of the bulk composition of plant cuticles analyzed by GC-MS and SEM.

(450) **MCR-ALS Analysis of Two-Way UVRR Spectra of Biologically Relevant Compounds**

John Simpson[1], Gurusamy Balakrishan[2], Ying Hu[2], Janina Kneipp[2], Thomas Spiro[2], Renee Jiji[1] ; [1]University of Missouri-Columbia, [2]Princeton University

The UVRR spectra of proteins contain a wealth of information including their secondary structural composition. However, it is extremely difficult to unambiguously resolve discrete amide bands as the amide regions contain numerous overlapping spectral components. This limitation is only accentuated by the presence of aromatic side chains which introduce many addition vibrational modes that often overlap and further complicate the UVRR spectra of proteins. Through the use of MCR-ALS, along with the application of rigid or flexible preprocessing methods and the inclusion of chemically relevant constraints, we can begin to deconvolute the spectra and resolve the information contained in multi-way UVRR data of proteins.

(451) **Virus Assembly and Architecture Investigated by Raman Spectroscopy**

George J. Thomas[1], Edward H. Egelman[2], Stacy A. Overman[1] ; [1]University of Missouri-Kansas City, [2]University of Virginia

The class-I filamentous bacteriophage fd (~6 x 880 nm) consists of a covalently closed, single-stranded DNA genome (6408 nucleotides) sheathed by 2750 copies of a predominantly helical capsid subunit (pVIII) plus a few copies of minor proteins at the filament ends. The 50-residue pVIII subunit is characterized by an acidic N-terminal domain, a hydrophobic central domain and a basic C-terminal domain. Although investigated extensively by fiber X-ray diffraction and solid state NMR methods, the structure of the fd particle has remained elusive. Previously proposed molecular models for the capsid are in substantial conflict with one another. Details of subunit structure and residue orientations in the native virion, which have been revealed by methods of solution Raman spectroscopy and polarized Raman microspectroscopy, provide initial constraints for evaluating the architecture of the fd assembly. Recently acquired image reconstructions of native fd by electron cryomicroscopy provide a firm experimental basis for understanding further details of virion morphology and supramolecular assembly, including subunit structure and orientation. This approach appears to be well suited also for class-II filamentous particles.

(452) **A Review of The Changing Needs for Measuring Trace Elements in Clinical Matrices: from Occupational Medicine to Environmental Biomonitoring.**

Patrick Parsons[1,2]; [1]New York State Department of Health, [2]University at Albany

Clinical matrices have always presented unique challenges to the analytical chemist. The nature of the sample, or specimens as clinical chemists call them, can be highly variable from one subject to another (e.g., urine). Some specimens, (e.g., capillary blood, and tissue biopsies) are obtained in very small quantities that necessitate sensitive methods that will consume only a small amount of sample. This paper examines the changing needs in clinical laboratory medicine for trace element analysis. The needs depend on whether the purpose of the measurement is to assess exposure to toxic, non-essential elements, such as Pb, Cd and Hg, or to assess nutritional status for essential elements such as Cu, Zn and Se. With respect to the former, there is a clear demarcation between measurements that are conducted as part of routine monitoring for occupational exposures, where concentrations are likely to be relative high, compared to measurements conducted for biomonitoring purposes, where the need is to assess relatively low background exposures in various populations. These differing needs require different analytical approaches. Lead is a toxic element that has long been measured in clinical matrices for occupational monitoring and for environmental biomonitoring purposes. The most widely used matrix for assessing short-term Pb exposure has been the determination of Pb in blood (BPb). Clinical needs (and analytical capabilities) for BPb measurements have changed markedly over the last four decades; however, measurements have been dominated by methods based on atomic spectrometry. Early flame AAS methods were characterized by poor precision and accuracy, at least by modern standards, and the need for 5 to 7mL of blood. In 1970, techniques based on microsampling flame AAS (Delves-cup) were developed that enabled mass lead screening of children to be accomplished using small capillary blood specimens. The Delves-cup technique gave way to methods based on electrothermal AAS. In many respects, ETAAS remains the workhorse for most routine BPb measurements, and it is ideal for occupational monitoring and/or childhood lead screening purposes. Biomonitoring studies are better conducted with ICP-MS instrumentation, in part because its greater sensitivity coupled with increased blood dilution yields superior detection limits compared to ETAAS.\r\n

(453) **High-Throughput Screening of Environmental Samples with Collision-Cell ICP-MS.**

Neal Julien; Midwest Research Institute, FL Division

Preliminary screening of samples is often a starting point in the analytical process when presented with totally unknown samples. Approximation of concentration for specific analytes is the usual goal, but in some cases information on matrix composition and other components in the sample may be useful for the analyst. In other cases, the screening information alone may be sufficient. The ability to rapidly and fully characterize the elemental composition of a sample makes ICP-MS ideally suited to this task. Developments in detector technology, sample introduction systems, collision/reaction cells, and the availability of novel after-market accessories have all contributed to an increase in productivity and reliability of modern ICP-MS systems. Dual-mode detectors make measurement of matrix and trace components in a single analysis routine, while online manipulation of the ion-beam in cell based systems reduces interference. A wide selection of spray chambers, nebulizers with a range of sample uptake rates, and injectors of various materials and diameters are currently available from multiple vendors. These advances give an operator the ability to modify the instrument configuration and operating parameters for maximum performance according to the sample matrix and analytical requirements for any given project. Midwest Research Institute recently completed a study in which approximately five thousand environmental samples were screened in a semi-quantitative mode for seventy elements in 10 days on a single instrument. This presentation will discuss the logistical requirements, problems encountered and solutions employed to meet the throughput demands of this project. Analytical and quality control results, as well as details on the specific instrument configuration and operating parameters for a novel sample introduction approach will be presented.

(454) **Removing Some Analytical Limits Using ETV-ICP(TOF)MS**

James Holcombe[1], Adam Rowland[1]; [1]Univ of Texas at Austin

Traditional introduction techniques using nebulizers often require extensive sample preparation to insure compatibility with nebulizers. Sample size, high levels of dissolved salts and organic solvent are just some examples where conventional nebulizers used in conjunction with ICPMS frequently encounter problems. Electrothermal vaporization (ETV) can circumvent many of these concerns. The improvement in isotope ratio determinations by a TOF compared with a quadrupole can be combined with the

flexibility of the thermal ramp of an ETV permit venturing into the arena of geochronology (i.e., isotopic dating) where the samples frequently represent "rocks" dissolved in HF-HNO3 solution, which can be injected into the ETV. An example of Sr-Rb dating of a mica sample will be used to illustrate the analytical possibilities.

(455) **Chemical Analysis for Forensic Attribution: Atomic Spectroscopy in Action**

Vahid Majidi[1], Lav Tandon[1], Elizabeth Hastings[1], James Barnes[1], David Gallimore[1], Cris Lewis[1], Robert Steiner[1]; [1]Los Alamos National Laboratory

Comprehensive analysis for traditional forensic samples is based on many different analytical techniques. Different instrumentation is used to establish the connectivity of a sample to a specific source, process, person or location. This is also true for nuclear forensics where chemical, physical and radiological characteristics for a given sample can yield potential clues to the origin and intent of a material. In this talk, we will present an analysis flow path for determination of key signatures necessary for attributing an unknown material to a source. Analytical results will be presented for a test "unknown" sample characterized by this process.

(456) **ICPMS – Emerging Player in Organic Trace Analysis**

Joseph Caruso ; University of Cincinnati

When ICPMS entered the marketplace in the mid-1980s, it was clearly thought to be a technique with applications to total trace element analyses. However, with important developments over time, such as collision/reaction cells, important advances in organic analyses have been achieved. S and P functional groups provide elemental tags for the organic backbone. Work over the past several years has shown sensitivities and detectabilities superior to commonly used methods for trace analysis of substances containing these groups. Our studies have focused on P containing pesticides, herbicides, fire retardants and warfare agent hydrolyzates. Both gas and liquid chromatography coupled to ICPMS and to other mass spectrometries have been utilized. Often, it is difficult to find suitable standards to help identify the species of interest by retention time, std. spike or both. In those cases the synergy of using elemental mass spectrometry in tandem with molecular mass spectrometry, is exceptional. ICPMS does the elemental screening with molecular MS for identification. Our most current studies on fire retardants and warfare agent hydrolyzates by GC-ICPMS and GC-TOFMS will be presented.

(457) **Three-Dimensional Nonstationary Model of an ETV-ICP System**

Albert Gilmutdinov[1], Shamil Araslanov[2], Rinat Ibragimov[1], Mjakzjum Salakhov[1], Andrey Staroverov[1]; [1]Kazan State University, [2]Research Institute of Mechanics and Math

In spectrochemical analysis with an ICP, electrothermal vaporization provides a number of advantages over conventional sample nebulization into the plasma: possibility to handle complex matrices, direct analysis of solids and slurries, in situ sample pre-treatment, thermal separation of various species, much higher transport efficiency, possibility for microanalysis. Despite numerous practical applications, there is a lack in understanding of operation of the ETV-ICP system at a fundamental level. In this work, a comprehensive description of the ETV-ICP system is provided based on truly three dimensional consideration of the problem and direct accounting for transient nature of the processes involved. The model developed is free of a priory assumptions and allows quantitative description of any kinds of electrothermal vaporizer and a plasma torch. All the known physical processes occurring in the system are taken into account (variety of heat transfer mechanisms, gas viscosity, temperature dependence of all the key parameters, etc.). The problem is solved in three steps. First, based on the solution of the full set of Navier-Stokes equations transient heating of a tubular electrothermal vaporizer is considered in all three dimensions. Temporal development of spatial distributions of temperature and gas flow velocities are obtained for typical conditions of ETV operation. It is shown that gas phase temperature of the vaporizer is highly nonuniform. Secondly, the ICP torch by itself is modeled without being connected to the ETV. 3-dimesional distributions of temperature, gas flow velocities, electromagnetic field intensities are obtained based on joint solution of the Navier-Stokes equations together with Maxwell equations. Finally, an attempt is made to combine into one model the whole ETV-ICP system. Comparison of the computed results with available experimental data is provided. Predictions of the model are analyzed.

(458) **Spectroscopic Interfacing Then and Now: Part 1: Interfacing to the Process; Part 2: Interfacing to the World**

Mike Doyle, Axiom Analytical, Inc.

Over the past two or three decades, molecular spectroscopy has expanded from being a general purpose technique for laboratory analysis to finding application in a wide variety of dedicated process analytical applications. This progression has involved numerous developments both in hardware for interfacing to various processes and in software to allow standardized instrument control and interfacing to enterprise wide data systems. The present paper reviews some of the more significant of these developments. Part 1 reviews some of the challenges that had to be faced in developing process sample interfaces capable of providing both the needed optical performance and the robustness required by harsh process conditions. The discussion will then proceed to the current state of the art related to applications involving mid-IR, near-IR, UV-Visible, and Raman spectroscopy. Part 2 traces the evolution of process analytical software from adaptations of instrument-specific laboratory software to the development of standardized software for instrument control, data analysis, and interfacing to data historians and other data systems.

(459) **Spectroscopic Sampling Interfaces used in Pharmaceutical Process Analysis**

Mary Jo Wojtusik; Axsun Technologies

In today's highly regulated pharmaceutical industry Quality Control (QC) laboratories and manufacturing facilities are more heavily examined then ever before. "Process Analytical Technology" (PAT) is an FDA initiative to improve pharmaceutical quality by measuring raw and in-process materials and observing manufacturing process. This replaces today's typical quality management system that relies primarily on measuring quality of products at the end of the manufacturing process. In order to improve the process of analysis in support of PAT, sampling interfaces are one of the most important tools in process analysis to be considered; thus enabling manufacturers to measure various aspects of product production directly by acquiring data, without requiring samples to be taken to conventional laboratory equipment for the analysis. As an example there are many ways to monitor various points in the blending process. One most valuable is to measure the position of a point as the sample moves. In this experiment, qualitative approach has been taken further with a moving block being applied as a way to measure the points as the sample moves. The absorption values are added into a data block and the average for the block is plotted. By selecting a block that relates to the blend, final absorption trend is smoothed effectively without loosing any information. The plot is then updated at every acquisition. Spectroscopic sampling optics are extremely vital to

this process because of the way how they deliver light to a sample and how the diffusely scattered radiation is collected and focused onto a detector. Illumination beam and collection optics also allow the measurements of different dosages of tablets as well as measurement of crystal formulations during a reaction monitoring process. Variety of sampling interfaces used in multiple applications throughout pharmaceutical manufacturing process will be presented along with the results.

(460) **Interfacing Spectrometers: Beyond the Sample**

Zafar Kamal; Thermo Electron

Increasing requirements for online process characterization and analytical measurements in process manufacturing – and, particularly in pharmaceutical manufacturing requires the use of complex analytical instruments such as spectrometers. Interfacing these instruments to the process is pushing the traditional notion of instrumentation and control integration with respect to operations, technology, ergonomic and usability. In this presentation, the basis for achieving successful human and operational goals, and to effectively collect and interpret data critical to the successful implementation of complex process analyzers is presented. Examples from pharmaceutical processing and other process industries are used for reference.

(461) **Barrier properties of SAMs on Gold Nanoparticle Surfaces**

Bernadette Quinn[1], Serge Lemay[2], [1]Helsinki University of Technology, [2]Delft University of Technology

During the past decade, controlled modification of the interfacial properties of electrodes using self-assembled monolayers (SAMs) has generated enormous interest. In particular, SAMs formed due to the adsorption of alkanethiols on planar metal surfaces have been widely used in fundamental studies of electron transfer (ET) reactions. However, much less in known about the properties of comparable SAMs formed on nanoparticle surfaces. I will discuss how electrochemical measurements can be used to shed light on the ion and electron "permeability" alkanethiol SAMs on gold nanoparticle surfaces. I will discuss how the discrete charging of the sub 2 nm gold nanoparticles can radically affect the barrier properties of the SAM on nanoparticle surface; the permeability to ions can be gated through the size of the counter-ion in solution and the dielectric properties of the solvent. Experimentally, this effect is comparable to ion association with conventional redox molecules, indicating that MPCs despite their large size and the fundamentally differing nature of the electron transfer process can be treated analogously to redox molecules. The second part of my talk concerns the kinetics of electron transfer across the SAM on nanoparticle surfaces. I will show that the rate of electron transfer, compared to a similar SAM on a macroscopic electrode, is enhanced due to the "looser" structure of the SAM on the highly curved surface of the nanoparticle. Secondly, in small systems, energy associated with single-electron charging (Coulomb blockade) has a profound influence on the electrochemical kinetics at the nanoparticle "nanoelectrode".

(462) **Irreversibly Adsorbed Adatoms as In Situ Surface Probe of Two-Dimensional Domains at Platinum Surfaces**

Enrique Herrero[1], Paramaconi Rodríguez[1], José Solla-Gulón[1], Antonio Aldaz[1], Juan M. Feliu[1]; [1]Universidad de Alicante

Practical electrocatalyst are normally based on nanoparticles supported on an inert electrode material. Since most of the electrochemical reactions are surface sensitive, the surface structure of the nanoparticle has to be also characterized in order to optimize the electrocatalyst performance. In this work, irreversible adsorption of Te and Tl will be used to simultaneous determine the fraction of (111) and (100) sites. The results can be compared with those obtained with Bi and Ge. The surface redox process of adsorbed tellurium on the Pt(111) electrode takes place at 0.82 V in a well defined peak. The behavior of this redox process on the Pt(111) vicinal surfaces indicates that the tellurium atoms involved in the redox process are only those deposited on the (111) terrace sites. Hence, this charge density can be used to measure the number of (111) terrace sites on any given sample. Structural information about tellurium adsorption is obtained from atomic resolution STM images for the Pt(111) and Pt(10,10,9) electrodes. On Pt(100) electrodes, the surface redox process of adsorbed tellurium takes place at 1.03 V in a well defined peak. STM images indicate that the adsorbed surface structure of the tellurium adlayer is ($\sqrt{2}$x$\sqrt{2}$) R45º, corroborating the coverage value measured from the voltammetry. However, the oxidation of the adsorbed tellurium on the (110) sites also takes place in the same potential range. For that reason this contribution at 1.03 V cannot be used to determine (100) sites. Nevertheless, it is possible obtain the fraction of step and edge sites on a platinum surface, by using the fraction of (100) sites determined from Ge probes. A similar situation is found for irreversibly adsorbed Tl on (100) and (111) sites in perchloric acid solutions. In this case, the contribution of the redox process for adsorbed Tl on (100) and (111) ordered sites appear at different potentials without overlapping from other contributions. These contributions are only observed for terraces having more than 4 atoms. Adsorbed Tl can be used to determine simultaneously the fraction of sites on wide (100) and (111) ordered domains.

(463) **Room Temperature Ionic Liquid Based Hybrid Materials: Applications in Direct Electrochemistry and Biosensors**

Xianbo Lu[1], Jinghong Li[1]; [1]Department of Chemistry, Tsinghua University

Room temperature ionic liquids (RTILs), which are relative viscous liquids comprised entirely of ions at ambient temperature and are promised to be environmental benign solvents, have received much interest recently for their unique physicochemical properties, such as high thermal stability, negligible vapor pressure, high ionic conductivity and wide potential windows. The combination of RTIL with conventional materials can create unique hybrid materials that might open up new opportunities for studies in many fields. In our recent research work, several kinds of RTIL based hybrid materials, like RTIL based sol-gel, RTIL based biopolymer and RTIL functionalized single-walled carbon nanotubes, are explored as novel immobilization matrixes to entrap redox-active proteins and enzymes. Hemoglobin (Hb), Horseradish peroxidase (HRP) and glucose oxidase were chosen as model proteins to investigate these RTIL based hybrid system. Dramatically enhanced bioactivity and excellent thermal stability of HRP (or Hb) were obtained in both the RTIL based sol-gel silica and the RTIL based biopolymer chitosan. Meanwhile, these RTIL based hybrid materials were for the first time used as immobilization matrixes for biosensing. A pair of well-defined and quasi-reversible redox peaks of Hb (or HRP) were obtained at the RTIL based chitosan film modified glassy carbon electrode by direct electron transfer between the protein and the underlying electrode. The prepared biosensors based on these hybrid materials demonstrated good performance, like good sensitivity and reproducibility, wide linear range, low detection limit and excellent long-term stability. The combination of RTIL with these conventional materials enables these hybrid materials to become excellent biosensing platforms for realizing direct electrochemistry of redox proteins and for constructing biosensors with good performance, and can find wide potential applications in biocatalysis, bioelectronics and biosensing.

(464) **Electronic Communication between Redox Centers in Hydrogen-Bonded Systems**

Angel Kaifer[1], Hao Sun[1]; [1]Unievrsity of Miami

Hydrogen bonding is one of the most commonly used intermolecular forces in supramolecular chemistry. While one hydrogen bond between two interacting molecular partners does not stabilize the complex or adduct to a significant extent, hydrogen bonding motifs capable of establishing more than one bond are much more effective to build supramolecular assemblies. In this regard, self-complementary hydrogen bonding motifs containing neighboring donor-donor-acceptor-acceptor (DDAA) groups are becoming very popular for structure building. The well-known Meijer's DDAA ureidopyridimine motif has been recently modified by Sanjayan and coworkers to avoid the complications arising from keto-enol tautomerism. In this presentation I will describe very recent results obtained with Sanjayan's DDAA system bearing covalently attached electroactive or fluorescent groups. For instance, a ferrocenyl derivative self-recognizes to form very stable dimers in chloroform or dichloromethane solutions. Very strikingly, the voltammetric oxidation of these dimers in dichloromethane solution reveals two different oxidation waves whose half-wave potentials are separated by 390 mV. This value suggests a suprisingly strong level of electronic communication between the two equivalent ferrocene centers in the hydrogen-bonded dimer, which was further confirmed by the observation of an intervalence charge transfer (IVCT) band in the near IR spectrum of the dimer. Analysis of this absorption band using the Hush formalism confirms the strong electronic coupling between the ferrocene centers, in spite of the fact that they are separated by at least 1.0 nm in the dimer. Intrigued by these unexpected results we have prepared similar compounds with pyrene and porphyrin units directly attached to the DDAA hydrogen bonding motif. Our results with these systems also support the excellent level of electronic communication which the seam of four hydrogen bonds elicit in all these compounds. Some of the biological implications of these results will also be explored.

(465) **DNA and Carbon Nanotube Self-Assembled Monolayers on Metallic Surfaces: An Electrochemistry and Surface Analysis Study**

Carlos Cabrera; [1]University of Puerto Rico, Rio Piedras

Self-assembled monolayer formation on metallic surfaces has been of interest because of its application in sensors, lithography, electronics, and others. Recently, DNA and carbon nanotube self-assembled monolayer formation has been of interest due to its application in DNA arrays and in Li batteries, respectively. Our group has been studying DNA-self-assembled monolayers by a combination of electrochemical techniques and in-situ fluorescence. The effect of the electrode potential on the conformational structure of thiolated-DNA and alkanethiol-fluorescein has been studied. The modulation in fluorescence as the monolayer desorbs and moves away and returns to the surface has been related to the electrochemical cyclic voltammetry potential cycle. Electrochemical impedance spectroscopy was used as a technique to determine the single strand DNA absorption on Au as well as its hybridization process. Results indicating the possibility of using EIS methods, as detection method, will be presented. Carbon nanotube self-assembled monolayers on Pt and Au were done by chemical derivatization of a SAM surface as well as by forming hybrids with single stranded DNA thiolated biomolecules. Electrochemical and surface characterization results will be presented.

(466) **Single-Molecule Electron Transport: From Photochemistry to Electrochemistry**

Ling Zang[1], Xiaomei Yang[1], Tammene Naddo[1], Aniket Datar[1], Kaushik Balakrishnan[1]; [1]Southern Illinois University, Dept of Chem

This talk will be primarily focused on the single-molecule level control and modulation of electron transport through molecules, with the goal to better understand the factors that influence the electron transport. Such understanding is crucial for guiding the future application-development of optoelectronic devices (such as chemical sensors and optical switches), as well as assist in the electronic miniaturization (single-molecule devices represent the ultimate scale of molecular electronics). The measurement of electron transport is based on both the single-molecule spectroscopy and STM break-junction techniques. These two techniques provide reliable measurement of electron transfer at the single-molecule level, which is a critical step towards the modulation of electrical current through molecules, and thus the design of FET based sensors. Moreover, measurement of electron transfer with both electrochemistry (in liquid electrolytes) and photoexcitation (on dry surface) enables comparative exploration of the kinetics of electron transport (and the dependence on local electrical field), thus making a link between solution chemistry and molecular electronics.

(467) **Discrete Charge Transfer in Nanoparticle Solids**

Shaowei Chen[1], Sulolit Pradhan[1]; [1]University of California, Santa Cruz

Organically capped nanosized particle molecules exhibit (sub)attofarad molecular capacitance which can be manifested by the quantized charge transfer in voltammetric and scanning tunneling microscopic measurements. Such electrochemical quantized charging phenomena have been well exemplified by monodisperse alkanethiolate-protected gold nanoparticles dispersed in solutions. More recently, for the first time, we demonstrated that in gold nanoparticle solids, with deliberate control of the nanoparticle structures and interparticle interactions, single electron transfer across the particle arrays could also be achieved. The kinetic and energetic characteristics involved in these unprecedented charge transfer processes were then evaluated. In this presentation, we will employ two approaches, namely, the Langmuir and Langmuir-Blodgett techniques, to prepare particle organized assemblies and compare their charge transfer properties. Whereas in both cases, the particle solids exhibit clearly-defined and consistent discrete charge transfer behaviors, in the former, the electronic conductivity of the particle monolayers can be examined in situ at controlled interparticle separations (interactions); and in the latter, the conductance of the particle solid films can be studied at varied temperatures and film layer thicknesses. The effects of chemical environments on the film conductance will also be discussed within the context of chemical sensor applications.

(468) **SERS Nanotags: Multiplexed Biodetection with a Raman-Based Readout**

Michael Natan; Oxonica, Inc.

A central conundrum in clinical diagnostics is the development of detection tools that are capable of high-level multiplexing, high sensitivity, excellent quantitation, AND can be used both in the point-of-care and central laboratory (high-throughput) settings. Oxonica has developed a series of nanoscale optical detection tags based on surface enhanced Raman scattering (SERS). These glass-coated, molecule-loaded gold nanoparticles are excited in the near-infrared, allowing detection in whole blood, and as many as a dozen different types can be simultaneously quantified using a handheld reader. The tags can also be detected in live animals

using portable instrumentation. This presentation will highlight the basic properties of these novel nanomaterials, and will then describe our recently-developed multiplexed, quantitative lateral flow immunoassay (LFI) for Flu A, Flu B, and RSV. In all practical respects (time, sample volume, cartridge appearance, etc.), the assay is identical to typical rapid-test LFIs. However, in this case, the single test line contains all three capture Abs, and the readout involves a single beam interrogating a single spot. Preliminary, unoptimized results show LoDs by eye in the 30-50 ng/ml range for single antigens, a result better than can be obtained with commercially available kits. Using a portable reader and our proprietary analysis software, improved LoDs can be obtained for all three analytes simultaneously. Finally, we will highlight several additional applications under development.

(469) **Rapid Characterisation of Bacteria Using SERS and Chemometrics**

Roy Goodacre[1], Roger Jarvis[1]; [1]University of Manchester

Raman spectroscopy has recently been shown to be a potentially powerful whole-organism fingerprinting technique and is attracting interest within microbiology for the rapid identification of bacteria and fungi. However the drawback of the technique lies in the low probability of a Raman scattering event occurring, with typically only 1 in 10^6 to 1 in 10^8 photons Raman scattered. We have been developing alternative strategies to the normal Raman technique based on surface-enhanced Raman scattering (SERS) which can enhance the Raman effect by some 10^3-10^6-fold if the molecules are attached to, or microscopically close to, a suitably roughened surface. Like Raman spectra, the SERS spectra generated from bacteria are information rich and simple visual interpretation is not possible, therefore we have been employing chemometric methods for their analysis. This presentation will detail our work on SERS for making measurements from bacteria in a few seconds. We shall also describe our data analysis approach based on the multivariate statistical techniques of principal components-discriminant function analysis (PC-DFA) that can be used to group bacteria based on their SERS fingerprints.

(470) **Novel Methods for Molecular Diagnostics by SERRS**

Duncan Graham[1], Karen Faulds[1], W. Ewen Smith[1], Karen McCarney[1], Alastair Ricketts[1], Jennifer Dougan[1], David Thompson[1], Camilla Karlsson[1]; [1]University of Strathclyde

Surface enhanced resonance Raman scattering, SERRS could be an analytical technique with everal advantages over competitive techniques in terms of improved sensitivity and multiplexing, however, the lack of quantitation and data relating to real examples has prevented more widespread adoption of the technique. Here we show the multiplexed detection of two infectious diseases by a SERRS based DNA assay. SERRS active probes were used in conjugation with PCR to allow detection of sequences corresponding to the presence of Chlamydia and Gonorrhoea simultaneously. Silver nanoparticles were used to provide the enhancement and permit the creation of a solution phase assay compatible with existing instrumentation. Two assays have been studied and the data can be obtained in a single tube format and offers the flexibility to add further targets as desired. The technique is more sensitive than corresponding fluorescence detection and has provided quantitative data for the first time. This study demonstrates how SERRS can be a useful tool for meaningful analysis in molecular diagnostics.

(471) **Vibrational Spectroscopic Elucidation of The Gross Biochemistry Associated with Carcinogenesis**

Nicholas Stone[1], Catherine Kendall[1], Mike Sowa[2], Jon Aning[1], Consuelo Hart Prieto[1], Martin Isabelle[1], Geeta Shetty[1], Hugh Barr[1]; [1]Gloucestershire Royal Hospital, UK, [2]Institute for Biodiagnostics, Canada

Advances in technologies have brought us closer to routine spectroscopic diagnosis of early malignant disease. However, there is still a poor understanding of the carcinogenesis process. For example it is not known whether many cancers follow a logical sequence from dysplasia, to carcinoma in situ, to invasion. Biochemical tissue changes precede morphological and structural changes. These can be probed using Raman or FTIR microspectroscopy and the spectra analysed for biochemical constituents. Local microscopic distribution of various constituents can then be visualised. Raman mapping and mid-FTIR imaging has been performed on a number of tissues including oesophagus, breast, bladder and prostate. The biochemical constituents have been calculated for each pixel point using basis spectra and ordinary least squares analysis. The residual of the least squares fit indicates any unfit spectral components. Errors of fit estimates are made based upon the noise in the signal and the use of more advanced algorithms, such as non-negative least squares and semi-parametric models are discussed. The biochemical distribution is compared with the defined histopathological boundaries. The distribution of nucleic acids, glycogen, actin, collagen I, III, IV, lipids and others appear to follow expected patterns with regard to carcinogenesis.

(472) **New Opportunities in Plasma Source Mass Spectrometry**

John Olesik; The Ohio State University

The strengths of ICP-MS include high selectivity, wide linear dynamic range, low detection limits and species independent sensitivity. While ICP-MS is most commonly considered a technique for inorganic analysis, its unique capabilities are complementary to molecular mass spectrometry for many biological applications. In part, this is due improvements in ICP-MS measurement of P and S using high mass spectral resolution or ion-molecule reactions. Use of elemental tags for biological analysis has also opened exciting new opportunities. In some cases an entirely new instrument using ICP-MS provides otherwise unattainable results. Examples of these new opportunities from our lab and others will be discussed.

(473) **New Plasma Based Ionization Sources for Organic Mass Spectrometry**

Francisco Andrade[1], Steven Ray[1], Gerardo Gamez[1], Michael Webb[1], William Wetzel[1], Gary Hieftje[1]; [1]Department of Chemistry, Indiana University

The information provided by mass spectrometry (MS) is increasingly becoming essential for the generation of knowledge in both the scientific and industrial sectors. In order to cope with this growing requirement, considerable improvements in detection capabilities have been achieved during recent decades. Nowadays, mass spectrometers provide extremely high sensitivity, excellent mass resolution and fast response time. Less attention has been paid to the ionization source, which has become a bottleneck in many MS strategies. Low ionization efficiencies, bias, interferences and non-linear response, difficult sample introduction, etc. are typical drawbacks in which the ionization source plays a major role. In order to fully exploit the analytical capabilities of modern spectrometers, the development of alternative ionization sources is imperative. In the present study, a novel plasma-based ionization strategy for organic compounds was developed. A direct-current glow discharge sustained in helium at atmospheric

pressure is used for the generation of reactive species, which are then used to ionize the target compounds. Polar and non-polar compounds can be easily ionized with very high sensitivity and linear response. In both cases, limits of detection in the single femtomole range have been achieved. Additionally, solid substances can be directly volatilized and ionized simply by exposing them to the cold beam of the helium glow discharge. In this case, limits of detection in the single picomole range can be readily obtained for a wide variety of compounds. This strategy allows the analysis of real samples, such as pills, foods, natural products, etc. without sample pretreatment and with an extremely simple sample-introduction scheme. Excellent stability, low maintenance and simple operation should be added to the list of advantages of this new device. The operating principles of this source will be presented along with some figures of merit illustrating its outstanding analytical performance, together the new and exciting fields of applications that it opens.

(474) **Novel RF Ion Containment Strategies for Electron Ionization Mass Spectrometry**

Milton Lee[1], Bingfang Yue[1], Jesse Contreras[1], Alan Rockwood[1,2], Stephen Lammert[1,2], Samuel Tolley[1,2], Dennis Tolley[1], Edgar Lee[1,2]; [1]Brigham Young University, [2]Palmar Technologies

Superimposition of a cylindrically symmetric axial magnetic field around an rf-only quadrupole ion guide compresses electrons from an electron gun into a long narrow volume along the ion guide while, at the same time, ions are compressed radially along the same axis by collisional focusing. Electron ionization occurs inside the ion guide with improved efficiency resulting from more effective use of electrons, prolonged interaction time, and nontraditionally large ionization volume. Limits of detection in the subfemtogram range (octafluoronaphthalene) were obtained in gas chromatography-mass spectrometry operation using this new ionization source. In an unrelated ion trap mass spectrometer design in which ions are produced by electron ionization, a toriodal rf ion trap is used to store the ions in a larger-than-typical volume by distributing them within a circular storage ring. The device can be viewed as a linear quadupole curved to form a ring and connected end to end. Because of the increased storage capacity of the ion trap, it could be miniaturized to a radius of 0.2 cm and still retain approximately the same ion storage volume as a full size, conventional ion trap. However, instead of requiring rf voltages of ca. 15 kVp-p, as for commercial ion traps, this device operates at less than 1 kVp-p. This miniature ion trap has been incorporated in a hand-portable gas chromatograph-mass spectrometer system for field applications.

(475) **Atom and Ion Densities Immediately Upstream from The Sampling Cone of an ICP-MS.**

Jeff Macedone[1], Haibin Ma[1], Paul Farnsworth[1]; [1]Brigham Young University

Inductively coupled plasma mass spectrometers (ICP-MS) detect elements at exceptionally low levels (fg/L). The ability to achieve low detection limits derives from the fact that the plasma source is an efficient ion source and the mass spectrometer is a sensitive detector. These two high performance elements of the instrument are separated by a vacuum interface. The flow of ions into the vacuum interface is an important step in the ion sampling process of delivering ions to the mass spectrometer. However, the flow of ions into the sampling cone, and the effect it might have on ion populations entering the vacuum interface, is not well understood. The flow of ions at the tip of the sampling cone is of particular interest. Several authors have published papers regarding the effects of the sampling cone on the plasma source. To investigate the flow of ions and atoms, we have used A gated-intensified CCD to collect laser-induced fluorescence images at the upstream tip of the sampling cone in an ICP-MS. This approach provides fine detail in an area where experimentation is very difficult. We will present images of the flow of ions and atoms into the vacuum interface as a function of ICP power, nebulizer flow, and concentration of different matrix elements.

(476) **A Comparison of Neutral Atom and Ion Behavior in the First Vacuum Stage of an ICP-MS**

Jordan Olsen[1], Paul Farnsworth[1]; [1]Brigham Young University

The first vacuum stage of the inductively coupled plasma mass spectrometer (ICP-MS) has typically been modeled based on the characteristics of a neutral fluid. The overriding assumption is that positively and negatively charged particles are present in equal numbers, and that the flow characteristics of the plasma are dominated by neutral argon atoms. Some researchers have called this assumption into question, but experimental support for a revised model of the interface has been tenuous. In this presentation we will report a direct comparison between the velocities of argon metastable atoms and calcium metastable ions measured in the first vacuum stage of an ICP-MS. The velocities are determined from Doppler shifts in the excitation spectra of the probe species, which were measured by high-resolution diode laser fluorescence spectroscopy. Argon and calcium are ideal species for comparison because each has a transition that is accessible by a commercial diode laser, both are present in measurable quantities in the supersonic expansion, and they have very similar masses. The Doppler shift experiments have revealed small but significant differences between the velocities of the two probe species, with the kinetic energy of the Ca ions exceeding the energy of the Ar atoms by approximately 0.3 eV under typical operating conditions.

(477) **Gas Flow Simulations via Direct-Simulation Monte Carlo in the ICP-MS**

Ross Spencer[1], Paul Farnsworth[1], Jaron Krogel[1], Jamie Palmer[1], Adam Payne[1], Andrew Sampson[1], William Somers[1], [1]Brigham Young University

A simulation of gas flow through the first stage of an ICP-MS has been developed using the Direct-Simulation Monte Carlo technique. This makes possible the detailed study of flow lines, density, and temperature as the gas makes its way through the orifice. This simulation method allows the transition to supersonic flow and the zone of silence to smoothly be made including the effects of viscosity, thermal conduction, and cone temperature. Reasonable agreement is found between the simulation and the hemispherical sink model of Douglas and French when flow from the ICP torch is neglected. When ICP flow is included the details of separation between orifice flow and exhaust flow can be studied. Comparisons between the simulation and experiments at Brigham Young and elsewhere will be presented.

(478) **Ultrahigh-Resolution Mass Spectrometry for Separation and Identification of Complex Analytical, Biological, and Environmental Organic Mixtures**

Alan Marshall; Florida State University

Fourier transform ion cyclotron resonance mass spectrometry (FT-ICR MS) offers 10-100 times higher mass resolving power (m/delta(m)50% > 300,000 over a wide mass range) than any other mass analyzer, and is thus the mass analyzer of choice for complex mixture analysis. First, viewed only as a separation device, FT-ICR MS has 200x higher peak capacity than the best single-stage wet chemical separation (GC, LC, CE, gel, etc.). Thus, it becomes possible to separate complex mixtures without prior chromatographic or gel separation, for much faster analysis. Second, elemental composition may be determined from accurate

(sub-ppm) mass measurement alone for unknown molecules up to ~1,000 Da. The chemical formula in turn reveals the numbers of N, O, and S (hetero) atoms (i.e., the compound "class"), the number of rings plus double bonds (compound "type"), and the carbon number distribution (degree of alkylation). Up to 20,000 different elemental compositions can be resolved in a single petroleum electrospray ionization (ESI) mass spectrum, and even more become accessible by field desorption (FD) and/or atmospheric pressure photoionization (APPI). Biological applications include posttranslational modifications, bio-markers, and mapping contact surfaces in protein assemblies for drug targets. The state of the art in FT-ICR MS instrumentation will be reviewed Work supported by NSF (DMR-00-84173), the National High Magnetic Field Laboratory, and Florida State University. Marshall, A. G.; Hendrickson, C. L.; Jackson, G. S. "Fourier Transform Ion Cyclotron Resonance Mass Spectrometry: A Primer," Mass Spectrom. Rev. 1998, 17, 1-35

(479) **A Validated SPME-GC-MS Method for the Quantification of Four 'Club Drugs' in Human Urine**

Stacy Brown[1], Daniel Rhodes[1], Boyd Pritchard[1]; [1]The Citadel Chemistry Department

A solid-phase microextraction-gas chromatographic-mass spectrometric (SPME-GC-MS) method has been developed and validated for measuring four club drugs in human urine. These drugs include gamma-hydroxybutyrate (GHB), ketamine (KET), methamphetamine (MAMP), and methylenedioxymethamphetamine (MDMA). These drugs are referred to as 'club drugs' because of their prevalence at parties and raves. Deuterium labeled internal standards for each of the four drugs was included in the assay to aid in quantitation. The drugs were spiked into human urine and derivatized using pyridine and hexylchloroformate to make them suitable for GC-MS analysis. The SPME conditions of extraction time/temperature and desorption time/temperature were optimized to yield the highest peak area for each of the four drugs. The final SPME parameters included a 90oC extraction for 20 minutes with a 1 minute desorption in the GC injector at 225oC using a splitless injection. All SPME work was done using a 100 micron PDMS fiber by Supelco. The ratio of pyridine to hexylchloroformate for derivatization was also optimized. The GC separation was carried out on a VF-5ht column by Varian (30m, 0.25mm i.d., 0.10 micron film thickness) using a temperature program of 150oC-270oC at 10oC/minute. The instrument used was a ThermoFinnigan Trace GC-Polaris Q interfaced with a LEAP CombiPal autosampler. The data was collected by using extracted ion chromatograms of marker m/z values for each drug from the total ion chromatograms (full scan mode). Calibration curves with R2>0.99 were generated each day using the peak area ratios (peak area drug/peak area internal standard) versus concentration. The validated method resulted in inter-day (n=15) and intra-day (n=5) %Relative Standard Deviation (%RSD) and %Error of less than 15% for a concentration range of 20-0.05 ppm (MAMP) and 20-0.10 ppm (GHB, KET, and MDMA). This method has the advantage of an easy sample preparation with acceptable accuracy and precision for the simultaneous quantitation of these four drugs of abuse.

(480) **Simultaneous Analysis Method of 21 Pesticides using LC/ESI-MS**

Jae Chun Choi[1], Weun Sook Jung[1], Sang Bae Han[1], Chan Soon Kang[1], Hee Ju Choi; [1]Seoul Regional Food & Drug Administration, [2]Korea Health Supplement Association Sub.,

Rapid and sensitive simultaneous analytical method based on LC/ESI-MS has been developed for determination of pirimicarb-a, pamocarb-b, oxamyl-c, methomyl-d, aldicarb-e, metolcarb-f, oxadixyl-g, bendiocarb-h, propoxur-i, carbofuran-j, carbaryl-k, thiodicarb-l, ethiofencarb-m, isoprocarb-n, fenobucarb-o, methiocarb-p, diethofencarb-q, fenoxycarb-r, thiobencarb-s, benfuracarb-t, pyributicarb-u in raw agricultural commodities. In the optimized CV, m/z and ionization mode of LC/ESI-MS using 0.1% formic acid and acetonitrile as mobile phase in 225 nm, the method provided L.O.D(L.O.Q) of 0.034(0.114)mg/L for a, 0.019(0.062)mg/L for b, 0.150(0.500)mg/L for c, 0.167(0.556)mg/L for d, 0.136(0.455)mg/L for e, 0.150(0.500)mg/L for f, 0.375(1.250)mg/L for g, 0.017(0.057)mg/L for h, 0.115(0.385)mg/L for i, 0.088(0.294)mg/L for j, 0.250(0.833)mg/L for k, 0.750(2.500)mg/L for l, 0.150(0.500)mg/L for m, 0.500(1.667)mg/L for n, 1.000(3.333)mg/L for o, 0.273(0.909)mg/L for p, 0.136(0.456)mg/L for q, 5.000(16.667)mg/L for r, 0.600(2.000)mg/L for s, 0.031(0.102)mg/L for t, 0.034(0.113)mg/L for u. The result of this paper showed that the LC/ESI-MS can be used as routine method for analysis of carbamate, thiocarbamate, and urea based pesticides such as pirimicarb, propamocarb, oxamyl, methomyl, aldicarb, metolcarb, oxadixyl, bendiocarb, etc., in raw agricultural commodities, if nessessary, using SIM mode to obtain maximum selectivity and sensitivity for quantitative analysis.

(481) **Analysis of Volatiles in Flavored Coffees by Head Space GC-Ion Trap MS and Liquid Chemical Ionization**

Evaldo DeArmas[1], Marisa Bonilla[1]; [1]Thermo Electron Corporation

Chemical Ionization is normally done using a gas reagent such as methane or ammonia at a relatively high source pressure. This technique has been well characterized and is well-behaved. However, chemical Ionization can also be done using liquid reagents at low pressure. Is there a potential advantage in using a liquid as Chemical Ionization reagent? By selecting a liquid reagent for chemical ionization it is possible to select different proton affinities (PA) resulting in better control of the ionization process. In this work we present results we have obtained in the use of methanol, acetonitrile and acetone as liquid reagents for chemical ionization. This technique was used to analyze a number of flavored coffees by head-space gas chromatography and an ion trap mass spectrometer as the detector. Data obtained from different types of flavored and non-flavored coffees will be presented.

(482) **Analysis of Volatiles in Flavored Coffees by Static Headspace GC/MS: Are They Really Different?**

Marisa Bonilla[1], Evaldo DeArmas[1]; [1]Thermo Electron Corporation

Coffees are now available with different flavors, but are they really different? Volatile and non-volatile compounds have an effect on coffee's flavor, taste, color, aroma and smell. The purpose of this study is to compare different types of flavored coffees. Analysis of volatiles compounds in ground coffee was done by static headspace and GC/MS. Headspace was performed using the Thermo TriPlus autosampler, which can be easily interchanged between liquid and headspace injection modes. This allows the user to use the same chromatographic system for both liquid and headspace injections. The Thermo headspace system consists of a gas-tight syringe and an incubator. Each has its own temperature control. After sample vial is incubated and shaken the syringe takes the headspace and injects it directly into the GC/MS injection port. No transfer lines or valves are used; minimizing the potential of having sample loses due to adsorption, condensations and leaks. A Thermo Trace DSQ GC/MS with CI and PPNICI capabilities was used, which allows acquiring data in positive and negative chemical ionization modes simultaneously in a single run. Data obtained from different types of flavored and non-flavored coffees will be presented.

(483) **Electron Monochromator Mass Spectrometry Analysis of Nitro-Aromatic Compounds in Tobacco Smoke**

Kent J. Voorhees[1], A. John Dane[1], Crystal D. Havey[1], Christy Abbas-Hawks[1]; [1]Colorado School of Mines

Electron monochromator-mass spectrometry (EM-MS) applied to the analysis of electrophilic compounds offers a versatility that was previously not available. Of particular interest is the fact that the EM-MS produces an electron beam with an ionization energy to ±0.4 eV which results in a controlled fragmentation of the analyte. This adds a degree of selectivity and specificity that has not been realized by traditional electron capture detection systems. The work presented here will discuss the application of EM-MS to the analysis of nitro-aromatic compounds in mainstream and sidestream tobacco smoke. The tobacco smoke samples were produced from three pure tobacco type cigarettes, an experimental reference cigarette, and 11 commercial cigarettes. Cambridge filter pads were used to collect all smoke particulate material. The collected samples were first extracted into methanol and then subjected to a phenyl solid phase extraction (SPE), an acid wash, an amino SPE, and normal phase LC fractionation. Following cleanup, the samples were specifically analyzed for nitro compounds using a GC/EM-MS. All nitro-containing compounds previously studied produced an m/z 46 peak (NO2-) with a dissociative electron capture resonance energy of 3-4eV. Mass 46 is a unique negative ion that clearly distinguishes nitro compounds from non-nitro containing species. Additionally, molecular radical anions for nitro compounds can be produced using a near zero eV ionization energy EM setting. The GC retention time correspondence between the m/z 46 anion peaks produced at electron energies between 3-4eV and the near zero eV molecular anion peaks was used to identify the nitro compounds found within a sample. Nitrated single ring aromatic and double ring aromatic compounds were identified in the mainstream smoke at a concentration range of 0.020-3.7 ng/cigarette and in the sidestream smoke at a concentration range of 0.60-1.2 ng/cigarette. During the investigation of these nitro compounds, dinitroaniline pesticides were also identified in both the mainstream and sidestream smoke of all the cigarettes tested. These pesticides ranged in concentration from trace levels to 48 ng/cigarette. The identity of the nitro aromatic compounds and the dinitroaniline pesticides will be discussed as they relate to each cigarette tested.

(484) **Complete Electrostatic, Diffusion, and Air Flow Modeling for Ion Mobility: Case Study of Drift Tube Designs**

Jill Scott[1], David Dahl[1,2], Timothy McJunkin[1], Paul Tremblay[1]; [1]Idaho National Laboratory, [2]Retired

Our goal has been to establish a modeling foundation for ion mobility spectrometry (IMS) similar to that which is available for mass spectrometry. The advent of SIMION established the capability to fully model any mass spectrometry instrument; however, the commercial version of this SIMION has not been amenable to modeling ion mobility because it does not model ion trajectories in the viscous pressure regime. With the development of the statistical diffusion simulator user program, SIMION can model the effects of diffusion as well as model the electrostatic potentials in an IMS. SIMION by itself can also model rudimentary air flow effects assuming the equivalent of "slug" flow. However, SIMION will allow flow vectors from fluid dynamics programs (e.g., COSMOSFloWorks™) to be imported to model "real" effects of air flow within an IMS. To demonstrate these features, we have modeled two drift tube designs because the drift tube is the heart of traditional IMS systems. One drift tube used the traditional stacked or alternating electrode/insulator design that has been used for decades. The other model is for a perfectly linear drift tube. To determine if the real electrostatic fields within the drift tubes matched those predicted by the model, drift tubes were constructed and the electrostatic fields within the tubes were determined experimentally. Insights gained into the effect that the electrostatic fields, diffusion, and air flow have on ion trajectories will also be presented.

(485) **Biosignature Identification Using Laser Desorption Fourier Transform Mass Spectrometry and Infrared Spectroscopy**

Jill Scott[1], Beizhan Yan[2], Daphne Stoner[2], Michelle Kotler[3], Nancy Hinman[3], William Bauer[1]; [1]Idaho National Laboratory, [2]University of Idaho, [3]University of Montana

Laser desorption/ionization Fourier transform mass spectrometry (LD-FTMS) and attenuated total reflectance infrared spectroscopy (ATR-IR) have been used to detect biosignatures associated with geomatrices and examine biomolecule-mineral interactions that lead to development of biosignatures. Effects of Martian mineral analogues on mass spectra obtained for microbial biomass, microbial exudates, microbial precipitates, amino acids and peptides were examined. There was an indirect correlation between presence of iron and detection of amino acids and peptides as well as microbial biosignatures. To investigate this observation, biomolecules on Na-bearing and Fe-bearing mineral analogues were examined. Na-bearing mineral analogues resulted in the ionization and detection of intact amino acids and peptides. However, Fe-bearing minerals resulted in formation of highly-fragmented spectral patterns that did not contain the parent ion, presumably due to the excited status of Fe+ in the gas phase that resulted in the breakage of the C-C bonds. In contrast, other organic compounds, such as PAHs, associated with geomatrices appear to be independent of mineral type when analyzed by LD-FTMS. Mixtures of organic and biomolecule compounds were also examined. Noteworthy, in the presence of chrysene, threonine was detected in negative mode on the surface of Fe-bearing minerals, suggesting that PAHs have the potential to assist desorption/ionization of biomolecules in natural geomatrices. Natural iron-bearing minerals that also contain other cations (e.g., jarosite) and iron precipitates derived from acidophilic microbial cultures were also analyzed. Using ATR-IR, signals indicative of microbes or microbial exudates were weak and ambiguous. In contrast, LD-FTMS clearly detected bioorganic constituents in some desorption spots. However, the signals were sporadic and required the laser scanning/imaging capability of our laboratory built system to locate the microbial signatures in the heterogeneous samples. Although issues associated with mineral types that are heavily dominated by Fe still need to be resolved, LD-FTMS with laser scanning capability is suitable for detecting and interpreting biosignatures in many terrestrial and extraterrestrial geomatrices.

(486) **Photosensitized Dimerization of m-dinitrobenzene**

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Photo-sensitized dimerization of m-dinitrobenzene has been studied in aqueous alkaline medium. Benzophenoneis used as a photosensitizer.m-dinitrobenzene is used in plastic industies,manufacturing for the papers,explosives and also in dye-drug indusries as an inetrmediate.It's allowed concentration in the atm.is only 1-ppm. So, it's trace amount is hazardous for the living beings The 100W tungsten lamp was used for the irradiation. Different parameters like effect of pH, concentration of the substrate, concentration of the sensitizer, effect of the light intensity and the rate of the dimerization have been studied. The quantum efficiency of the product has been evaluated with the use of potassium ferrioxalate actinometer.The indentification of the product is conform with the use of U.V.spectrophometer,GC-

MSand LC-MS.The possible reaction mechanism has been suggested.

(487) **Why Is Automating The Determination of Molecular Ions so Hard and How Might It Be Used?**

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Molecular ion identification is the cornerstone of all MS1 data analyses for scientists across all sectors of mass spectrometry disciplines. Because molecular ion identification is a complex and time-consuming task, several chemometric approaches have been proposed to help accelerate the process. A number of highly accomplished algorithms have been created that make the problem more tractable by using reduction or removal of low frequency noise approaches, such as CODA from Windig et al. or MEND from Karger et al. However, while these extremely sensitive peak extraction algorithms simplify the analysis task, the output still requires a considerable amount of review by the scientist, which can be time-consuming. All of the extracted peaks, at a particular retention time, still need to be manually sorted and related to a particular eluting chemical component, and then the molecular ion needs to be picked out from amongst all the fragments, isotopes, and adducts. In fact, identification of the associated ions for an eluting component is an integral and necessary part of identifying and verifying the molecular ion identity. A novel approach geared toward automatically grouping and identifying ions related to eluting components is presented. This approach builds on the CODA peak extraction algorithm in a way that overcomes the limitations imposed by the inherent noisy nature of MS1 data and that helps identify component ions. To limit the amount of algorithm parameter optimization carried on a per data set basis, a self-modeling approach was used to filter and automatically select optimal values. To determine the molecular ion for each eluting component, it was necessary to determine all ions within a particular retention time region using accurate retention times. The determination of molecular weight was made possible using as much information from the contributing ion clusters as possible, solving for classical adducts, multimers, and ion losses from the 12C molecular ion.

(488) **A Coaxially-Heated Hollow Fibre Membrane Introduction Mass Spectrometry Interface for Trace Volatile and Semi-volatile Molecules in Air and Water**

Chris Gill[1,2], Alexander Thompson[1,2], Skye Creba[1,2], Robyn Ferguson[1,2], Erik Krogh[1,]; [1]Malaspina University College, [2]Applied Environ. Research Labs

A pneumatically assisted (flow-over geometry) membrane introduction mass spectrometry (MIMS) interface with an internal co-axial heater is presented (patent filed). This device can be operated in both continuous and pulsed heating modes, enabling both real-time and trap and release measurement of bot volatile and semivolatile organic compounds (VOCs and SVOCs). Because a thermal gradient is established counter to the analyte concentration gradient, this system demonstrates superior detection limits over other \'conventional\' flow over MIMS interfaces for SVOCs (typically pptr) in water. In addition, the response times for SVOC measurements are greatly improved. Recent developments for this interface and its applications for measurements in air and water sample matrices will be presented.

(489) **Membrane Introduction Flame Ionization and Electron Capture Detection (MIFID/MIECD) as a Real Time Monitor for Drinking Water Dis-Infection By-Products**

Chris Gill[1,2], Jason Devlin[1,2], John Amaral[1]; [1]Malaspina University College, [2]Applied Environ. Research Labs

Membrane introduction mass spectrometry (MIMS) is recognized as a rapid, selective, and real-time analytical technique. However, mass spectrometry requires relatively expensive instrumentation with high power as well as high vacuum requirements. This work presents an alternative analytical device in which a pneumatically assisted (flow over geometry) membrane interface is coupled to several alternate detectors: a flame ionization detector (FID) and an electron capture detector (ECD). This hybrid system (MIFID/MIECD) was used to measure a variety of compounds in artificial samples as well as monitoring dis-infection by-product formation kinetics in natural waters. Detection limits were in the parts-per-trillion range for some compounds and strong correlation coefficients were obtained in most cases. Direct comparisons between MIMS and MIFID/MIECD show similar results in model systems. Selectivity for halogenated compounds is achieved using the ECD, making this system a potential candidate for the on-line measurement of drinking water dis-infection by-products. In summary, MIFID/MIECD shows promise as a rapid, sensitive, selective on-line screening method.

(490) **Mass Spectrometry and Biology Combined Tools for Biochemical Markers for Source Identification of Fecal Pollution in Surface Water**

Vesna Furtula[1], Heather Osachoff[1], May Chiu[2], Randy Englar[1], Al Colodey[1]; [1]Pacific Environmental Science Centre, Science and, [2]Commercial Chemicals Division, Environme

The Fraser Valley in the province of British Columbia (BC), Canada is under heavy pressures from agricultural activities and industries (poultry, dairy, swine, berry, etc.) as well as rapid urban development. These activities tremendously affect quality and supplies of water courses. In order to identify new pollutants at low concentrations modern chemical detection and biological methods are combined for an assessment of run-off from agricultural lands into surface water. The possible effects of manure application to surface water quality have been analyzed by gas chromatography mass spectrometry (GC-MS) in scan mode, sterol analysis (GC-MS) single ion monitoring (SIM) mode and by Bacterial Source Tracking analysis. GC-MS-SIM method was developed in house for 17 sterols: mestranol, norethindrone, equol, estrone, equilin, norgestrel, 17 á-ethinylestradiol, 17 á-estradiol, 17 â-estradiol, estriol, coprostanol, epicoprostanol, cholesterol, desmosterol, campesterol, stigmasterol and â-sitosterol. Some sterols were present at high concentrations that were detected by qualitative GCMS scan method. Bacterial Source Tracking (BST) is a novel method that can identify the organism or organisms responsible for fecal pollution in aquatic environments. The technique is based on detecting a prevalent intestinal bacterium called Bacteroides by amplifying a portion of the 16S rRNA gene using PCR (Polymerase Chain Reaction). Since the Bacteroides species and strains differ from host to host, the type of Bacteroides species present in a sample will identify the source of the fecal contamination (e.g. cow manure vs. human waste). Samples were collected from 4 sites in the Nathan Creek, Fraser Valley and analyzed for sterols and BST. An effort has been made to correlate sterol composition with BST results.

(491) **Fractal Lotus Leaf Surfaces to Improve Sensitivity of MALDI**

Melissa McLauchlin[1], Mark Hayes[1], Antonio Garcia[1], Tom Picraux[1,2,3], Devens Gust[1]; [1]Arizona State University, [2]Sandia National Laboratories, [3]Center for Integrated Nanotechnology

A new method to constrain droplets during evaporation to fabricate MALDI (Matrix Assisted Laser Desorption Ionization) targets is described. Superhydrophobic silicon nanowire (NW) surfaces with laser ablated hydrophilic (LAH) spots are used to improve the sensitivity of MALDI time-of-flight mass spectrometry (MALDI-TOF MS). MALDI is currently one of the most widely used tools for identification of biomolecules. The advantages of MALDI include low detection limits, soft ionization and analyses of both complex mixtures and large biomolecules, such as whole proteins. However, the UV laser spot size used to ionize and desorb the protein/matrix samples is typically only ~100micrometers in diameter, while the standard MALDI target spot is 2.5 mm in diameter. Thus, only a small fraction (less than 1/25, not accounting for depth of ablation) of the sample is desorbed/ionized with each shot of the laser. This work utilizes fractal NW surfaces with LAH spots to concentrate the protein/matrix samples down to a ~250 micrometer diameter spot size, improving both efficiency of laser desorption/ionization and sensitivity of the instrument. Myoglobin samples at various concentrations were analyzed by MALDI on a standard MALDI plate and on NW supports with LAH spots. Accumulations of signals were recorded and averaged to represent both the efficiency of obtaining a signal and the sensitivity of the instrument. Preliminary results indicate an average improvement in MALDI sensitivity for whole proteins by a factor of 5. Previous studies utilize Teflon-coated plates with 200micrometer diameter gold "anchor" spots to confine and concentrate small biomolecule samples for improved MALDI sensitivity. However, their results show while the sample droplets prefer to remain within the confines of the anchor spots, some droplets, during the evaporation process, actually migrate away from the anchor spots and dry on the hydrophobic Teflon coating. Our NW MALDI supports are unique in the sense they are superhydrophobic and the protein/matrix droplets remain permanently confined to the LAH spots throughout the entire evaporation/crystallization process. This phenomenon offers an advantage over previous methods because the NW supports may be used for feasible automation of MALDI and coupling with separations techniques, such as capillary electrophoresis.

(492) **Clinical Proteomics: Validation of Global Chromatin Modifications as Biomarkers in Chronic Lymphocytic Leukemia (CLL)**

Michael A. Freitas[1], Xiaodan Su[1], David M. Lucas[1], Amy R. Sklenar[1], Mark R. Parthun[1], Michael R. Grever[1], John C. Byrd[1]; [1]The Ohio State University

This abstract describes the development of an LC-MS method to reproducibly profile histone isoforms present in chronic lymphocytic leukemia. CLL is characterized by an accumulation of B-cells in blood, bone marrow, lymph nodes and other organs. A comparative proteomics study of global histones from normal individuals and patients with CLL revealed that the histone H2A variants, H2AFL/G and H2AFM*, were altered in expression suggesting a correlation between global chromatin modifications and the CLL phenotype. The histone profiles were obtained from acid extracted nuclear chromatin, separated by RP-HPLC and mass analyzed by use of an ESI LC-Q-TOF MS. From a sample cohort of 40 CLL patients and 5 normal B-cell populations, we observed a statistically significant decrease in the abundance of variants H2AFL/G and H2AFM* relative to the normal B-cells. In addition, large changes in the abundance of two H3 variants (LC fractions 8 and 11, increased in CLL) and two unidentified proteins (LC fractions 3 and 7A) were observed for 90% of the patient samples. The data supports the assertion that a correlation exists between global chromatin modifications and the CLL phenotype. Protein identification was verified by nano-LC-MS/MS following LC fractionation, AU-PAGE separation and in-gel tryptic digestion. Rigorous method validations were undertaken to isolate methodological variability from biological variability. For example, variations in protein relative abundances due to changes in instrument parameters, sample preparation and variations within individuals over time were assessed. Furthermore, a variety of cell sorting strategies were assessed to determine the influence of cell selection and the homogeneous nature of the B/CLL population on LC-MS profiles. The variations were statistically insignificant between histones extracted from high B-cell count patients without cell selection as compared to rosette selection and CD34+ MACs purification (the profiles differed by less than 3% in terms of relative abundance of H2A variants). The experiments are being extended to examine a larger cohort of CLL patients (>40) and normal B-cell (>30 obtained from tonsils).

(493) **Differential Analysis of High Resolution Mass Spectrometric Data**

Jennifer Busby[1], Valerie Cavett[1], Jeremiah Tipton[1], Moyez Dharsee[2], Ian Stewart[2], Robert Ewing[2], Bruce Pascal[1]; [1]Scripps Florida, [2]Infochromics

Accurate and robust identification of differences in protein abundance or post-translational modification states between cells or tissues with genotypic, disease or drug-related perturbations is rapidly becoming a fundamental requirement in biomedical research. We have developed a software suite (Proteomarker) for identification of quantitative differences in protein profiles between samples from high-resolution mass-spectrometric data. Proteomarker (Infochromics, Toronto, Ontario) detects relative signal changes of peptide features between samples. Peak detection, feature selection, chromatographic alignment, and peak matching algorithms are applied the LC/MS data set to produce a peptide abundance matrix. Peptide and protein grouping and statistical analysis are then applied to generate quantitative protein profiles. We have used this approach with unlabeled and isotopically labeled peptides and applied it to the differential identification of proteins and peptides in cancer cellular based systems and in stages of cellular differentiation. In all samples, the protein sample was digested with trypsin and the peptides were loaded onto a C18 capillary HPLC column for gradient elution. Gradients of 1 hr to 4hrs were used based on the complexity of the samples. Peptides were eluted into a Thermo Electron LTQ Orbitrap mass spectrometer at a flow rate of 50 nL/min. The mass spectrometer was set to collect high resolution data at 75,000 resolution in the Orbitrap for each MS spectra. From the MS spectra, top 3 data dependent MS/MS scans were performed in the linear trap portion of the instrument. All MS/MS spectra were submitted to database searching using an in-house automated workflow. The MS spectra were submitted for peak picking and differential analysis. Peptide ID information from database searching was correlated with chromatographic peaks from the MS scans and differential peptides and proteins are presented.

(494) **Identifying Protein Nucleotide Binding Sites with Photoaffinity Nucleotide Analogues and High-Resolution Mass Spectrometry**

Jeremiah Tipton[1], Bruce Pascal[1], Jennifer Busby[1]; [1]Scripps Florida

The identification of protein nucleotide binding sites with photoaffinity nucleotide crosslinking agents and mass spectrometry

(MS) has traditionally been laborious. Here, we present a high-throughput MS-based proteomics approach to identify peptides which have been covalently crosslinked. The method relies on the availability of high-resolution MS data acquired on a ThermoElectron LTQ Orbi Trap (San Antonio, TX) and custom bioinformatics. Furthermore, this method does not rely on pre-existing knowledge on the active-site of a protein and does not require radiolabeled nucleotide analogues. The probability of identifying a labeled peptide with MS-based proteomics has improved due to previous advancements in all technologies applied during this study. First, many photoaffinity nucleotide analogues are commercially available. Second, many proteases with different specificities are commercially available. Third, improvements in MS instrumentation allows for high-throughput, high-resolution analysis. Fourth, high-resolution MS data improves the quality of bioinformatics. Lastly, proteins which have crystal structures available and are similar to targeted proteins which do not have crystal structures may be threaded. Presented are all the tools available for identifying derivatized proteolytic peptides with MS-based proteomics and newly identified protein active-site peptides. Following crosslinking, proteins are digested in-solution or in-gel with a variety of different proteases for increased sequence coverage. Preliminary data using multiple proteases has resulted in greater than 80% protein sequence coverage on a 110-kDa protein. For labeling experiments, nucleotide binding proteins were irradiated with photoaffinity nucleotide analogs, digested with different combinations of common proteases, analyzed with a ThermoElectron's (San Antonio, TX) LTQ OrbiTrap in top 5 data-dependent mode, and analyzed with custom peptide mass fingerprinting software (PepSense) and LC/MS differential comparison software (ProteoMarker, InfoChromatics). Exact mass measurements of the precursor ion with OrbiTrap allows for identification of possibly derivatized peptides with PepSense. LTQ MS/MS of the precursor ion allows for sequencing possible peptide hits.

(495) **Automated Identification of Multiply Digested Peptides by Comparison of Theoretical to Observed Peptide Masses**

Bruce Pascal[1], Jennifer Caldwell Busby[1], Jerimiah Tipton[1]; [1]The Scripps Research Institute - Florida

Efficient identification of non-standard or non-biologically modified peptides in a complex mixture using a peptide mass fingerprinting approach has proven to be challenging. Biological modification lists are continuously being updated but they do not often correspond to the covalent modifications that can occur when small molecules interact with a protein. To determine these types of modification sites data is produced from instruments with differing resolution and mass accuracy using multiple enzymatic and chemical digestion techniques. Existing software tools address some of these issues, but there is currently no freely available solution that combines the functionality of multiple enzymatic cleavages and allows for user defined modifications sets and mass error range. also factoring in instrument resolution. We have created a software program "PepSense", which takes input of up to two proteases, the maximum number of missed cleavages sites, the protein sequence, the modification set masses, and a the precursor mass data file. The output is a consensus list of matches based on the comparison of the theoretical and observed precursor masses. The algorithm uses the protein sequence and the first protease to produce a comprehensive list of theoretical digests based on the specified number of allowable missed cleavages. The process is repeated with the second protease , producing list of all possible digested peptides. The algorithm then calculates the monoisotopic mass for each peptide and for each of these masses, an additional list is created considering each possible modification present from the set selected. This theoretical list of masses is compared to the observed precursor masses and all consensus masses are reported within the defined error range. The software has been used for Thermo Electron LT-Orbitrap data with resolution of at least 7500 which allowed for fewer possible matches in comparison of the potentially modified peptides to the real mass list. Using this scheme, a single protein resulted in less than 20 possible mass peak matches for a potential modification, down from approximately 150 with non-high-resolution mass spectral mass data. Those 20 spectra were manually denovo sequenced and the site of non-biological covalent modification was identified.

(496) **Small Volume Analytical Technique of Affinity Capture Igg Subclass Proteins Separated by CIEF and Offline Couple to MALDI-TOF Ms**

Nicole Zwick-Kozup[1], Mark Hayes[1]; [1]Arizona State University

Proteomics encompass the analysis on the diversity of expressed proteins, potentially providing better understanding of health and disease of the human body. Analytical proteomic technology capabilities are inadequate to meet the demands to identify, characterize, and quantify complex protein samples and therefore many opportunities exist to improve the technology. Offline coupling of capillary isoelectric focusing (CEIF) and matrix assisted laser desorption ionization time of flight mass spectrometry (MALDI-TOF ms) is one strategy for improvement. This technique can generate 2D-gel like data for comparative analysis in an automable format with cycle times on order of hours. To simplify complex biological samples a micropreparation is performed prior to CIEF. An efficient micropreparation is affinity capture of groups of proteins that have a common noncovalent molecular attraction to a molecule, such as antibodies to specific antigens. An immunoassay-like strategy is used to capture all the immunoglobulin (IgG) subclasses in human serum (HS) prior to CIEF. IgG has four subclasses, IgG1-4, which have distinct immune functions and different levels of IgGs in HS and cerebrospinal fluid (CSF) can provide information on a patient's health. Increases in intrathecal synthesis IgG in CSF is accepted as a clinical diagnostic for multiple sclerosis, and is part of the McDonald diagnostic criteria of MS. The etiologic agents of MS are unknown; however an analysis of the different IgG subclasses in CSF may provide clues to the type of antigen involved. The small volume process of affinity capture proteins separated by CIEF, and off-line coupled to MALDI-TOF ms will provide a rapid multi-dimensional separation of complex biological fluids, which will provide significant information to understand and diagnosis diseases.

(497) **GC/MS Analysis of Pahs in Well Water Samples from the Niger Delta Region of Nigeria**

Chimezie Anyakora[1], Herbert Coker[1]; [1]University of Lagos

Water samples from several hand dug wells in the Niger Delta region of Nigeria were analyzed for the presence of sixteen United States Environmental Protection Agency priority polynuclear aromatic hydrocarbons using a gas chromatograph coupled to ion trap mass spectrometer. The specific target compounds are acenaphthene, acenaphthylene, anthracene, benz(a)anthracene, benzo(a)pyrene, benzo(b)flouranthene, benzo(ghi)perylene, benzo(k)flouranthene, chrysene, dibenz(a,h)anthracene, flouranthene, flourene, indeno(1,2,3-cd)pyrene, naphthalene, phenanthrene and pyrene. The sum of the sixteen PAHs in the samples vary depending on the proximity of the sample source to crude oil production facility. The concentration ranged from 1.92 ìg/L to 40.47 ìg/L. High molecular mass PAHs such as benzo(ghi)perylene, dibenz(a,h)anthracene and indeno(1,2,3-

cd)pyrene were mostly absent confirming low water solubility of these compounds

(498) **Ion Distribution Profile in Atmospheric Pressure Photoionization (APPI) Source for LC-MS**

Mahmoud Tabrizchi[1, 2], Michael Blades[1], Damon Robb[1]; [1]The University of British Columbia, [2]Isfaha University of Technology

Ion Distribution Profile in Atmospheric Pressure Photoionization (APPI) Source for LC-MS\r\nM. Tabrizchi, M. Blades, D. Robb. In this work the radial distribution of ions in an atmospheric pressure photoionization (APPI) source under applied electric field was studied. This information was particularly required in design and optimization of an improved APPI source for LC-MS. The photo ionization source was a UV lamp and Toluene was used as the dopant. The ion distribution was measured by a special collector plate constructed from seven co-centric copper rings, separated from each other by ~0.3 mm insulation bands. This collector was vertically mounted at a fixed distance from the lamp. The ion current on each separate ring was measured at various lamp-collector voltages. The measurement was repeated at various lamp-collector distances. The results show that the electric field has a positive effect on both the ion density and the profile of the ions. However, the ion distribution becomes considerably broader as the ions distance from the lamp. It was found that the ion density at the centre is directly proportional to the applied electric but reduces with the distance from the lamp so that ion current is proportional to V/d2 where V and d are the lamp-collector voltage and distance, respectively. The ultimate sensitivity of LC-MS depends on the number of analyt ions transmitted to the mass spectrometer which itself depends on the dopant ion density in front of the orifice plate as well as the reaction time. Decreasing the distance or increasing the electric field between the ionization source and the orifice results in more ion current but on the other hand, it reduces the reaction time. So there will be an optimum spacing and field to observe the maximum sensitivity for analyt. The second part of the experiment deals with understanding the effect of field and distance on the analyt signal intensity.

(499) **A Monolithic Phase Based On-line Extraction Approach for Determination of Pharmaceutical Components in Human Plasma by HPLC-MS/MS**

Raymond Xu[1], Leimin Fan[1], Grace Kim[1], Tawakol El-shourbagy[1]; [1]Abbott Laboratories

An automated procedure using monolithic phase based on-line extraction is described for pharmaceutical component analysis in plasma by LC-MS/MS. In this approach, a short monolithic C18 4.6×10 mm cartridge is used for high flow extraction at 4 mL/min. Plasma samples were subjected to protein precipitation first with acetonitrile, and the supernatant was diluted and loaded onto the monolithic cartridge. Sample elution was accomplished with narrow-bore LC-MS/MS system. A method for determination of Amprenavir (APV) and Atazanavir (AZV) in human plasma was developed with this approach. After 0.1 mL of plasma was transferred into each well of a 96-well plate by a liquid handler, the rest of sample preparation time typically only takes about 20 min. A phenomenex Luna C18 (2) 2.0×150 mm analytical column was used for the separation at a flow rate of 0.3 mL/min. The run time for each sample was 4 min. The standard curve range was 2.770 – 1517.520 ng/mL for Atazanavir, and 4.501 – 2562.880 ng/mL for Amprenavir. The inter-day %bias and %CV of the quality control samples of Atazanavir were

(500) **Novel Nanospray Emitter Design with a Custom Interface for Peptide/Protein Nanolc/MS Analysis**

Ananya Dubey[1], James Murphy[1], Jeffrey Finch[1], John Gebler[1], [1]Waters Corporation

A widely used method for protein/peptide identification incorporates nanobore liquid chromatography (nLC-MS) with nanoelectrospray ionization mass spectrometry. This combination has proven to provide superior detection limits compared to conventional LC due to low elution volumes. Coupling a nanobore column with an efficient nanospray emitter fashioned from fused silica tubing is critical to peptide/protein analysis as insufficient column emitter coupling can lead to loss in sensitivity and band broadening. However, loss of conductive coating, frequent clogging and fragility of the emitter tip has limited the lifetime of such a format. Here we present an alternative emitter design which is physically robust, can frequently be regenerated and provides stable spray for protein/peptide analysis. A novel nanoelectrospray emitter was created by joining two separate pieces of fused silica with different dimensions. A nanospray probe was designed to incorporate the new emitters to a commercially available MS platform. The probe has a compact head profile which can accommodate both the prototype emitters and commercially available emitters which may or may not be coated. The probe has an option to apply a nanospray potential through a metal zero-dead volume union on nanospray emitters with varying length. The emitter/probe combination was tested on a Q-Tof system with nanoACQUITY UPLC™.In an initial test a 3.5µm Atlantis dC18 nanobore column was connected to a novel emitter using a metal zero-dead volume union. The stability of the emitter and the voltage connection was tested with nLC/MS. Good chromatographic data was generated through an injection of 50 fmol/µL Enolase tryptic digest sample over a 60 minute (2-60%B) gradient. Analysis of 7 relevant peptide peaks from the sample mixture yielded an average half-width of 0.11 mins and average peak capacity of 328.005. The nanospray appeared stable across the gradient and the emitter design limited the possible post column band broadening. Another study of the emitter spray stability across gradient with complex mixture of 4 tryptically digested proteins (Enolase, Bovine Serum Albumin (BSA), alcohol dehydrogenase and phospohorylase B) showed high reproducibility and peak symmetry.

(501) **Simultaneous determination of Polycyclic Aromatic Hydrocarbons (PAHs) and Chlorinated Pesticides (OCPs) in Sewage Sludge using Gas Chromatography - Tandm Mass Spectrometry**

Zainab Al-Ballam[1], Murad Helaleh[1], Ali Al-Omair[1], Nisar Ahmed[1], [1]Kuwait Institute for Scientific Research

Because of their low solubility in water and high hydrophobicity, polycyclic aromatic hydrocarbons (PAHs) and organochlorinated pesticides (Ocs) are quantitatively removed from the suldge and adsorbed on soil particles during sedimentation,the results is the formation of sewage sludges. Thus sludges which are spread on agricultural land as fertilizers are likely to contain such PAHs and Ocs that are persistent and develop high carcinogen and mutagenic toxicity. Therefore, there is arisk of soil contamination that must br reduced by developing analytical methods to allow routine monitoring of sludge matrices. A prerequisite to quantify the evolution of PAHs and Ocs in sludge is to develop sensitive and effective method to measure their concentrations. The method involve is accelerated solvent extraction and elimination of fats and sulfur in order to isolate PAHs and OCs. The method allows a simultaneous determination of PAHs and OCs in a single chromatographic run.

(502) **On Charge Exchange IonizatiAgents for Dopant-Assisted Atmospheric Pressure Photoionization for Reverse-Phase LC/MS**

Michael Blades[1], Derek Smith[1], Damon Robb[1], [1]University of British Columbia

In this study we investigate a variety of substituted-benzene compounds for their potential use as a dopant in Dopant-Assisted Atmospheric Pressure Photoionization under reverse-phase LC conditions. Numerous compounds were tested to determine the stability of their respective radical cations. A number of new candidate compounds were found to produce stable radical cations. One of the most promising is 3-(trifluoromethyl)anisole was found to be able to ionize many analytes by charge exchange and provides a substantially enhance signal relative to "usual" dopants.

(503) **Pyrolysis GC/MS Analysis of a Halophilic Bacterial Population in an Activated Sludge System**

John Glass Green[1]; [1]The Dow Chemical Company, Louisiana Operations

Pyrolysis GC/MS is a useful tool for comparing bacterial samples. Application of this method to following changes in the bacterial population in an activated sludge system was attempted for use in troubleshooting the system. Most of the pyrolysis products were determined to be typical products of protein, DNA and carbohydrate pyrolysis. One of the main pyrolysis products, 2-methylpyrimidine, was, however, not associated with any reported biological source in the literature. The pyrolysis product was identified by its mass spectrum, accurate mass values, and comparison to standards of isomeric compounds and authentic 2-methylpyrimidine. Pyrolysis of the supernatant from a diluted sludge sample showed essentially only the 2-methylpyrimidine pyrolysis product, indicating that it arose from some soluble cellular component. It was determined that a possible source for this pyrolysis product was a compound, ectoine, used by halophilic bacteria as a compatible solute for osmoadaptation. Ectoine is the common name for 2-methylpyrimidine-4-carboxylic acid. Pyrolysis of this compound in saline solution with iron present produced high yields of 2-methylpyrimidine. Proton NMR analysis of a fraction of the sludge showed ectoine in confirming its presence there. Pyrolysis GC/MS can be a useful tool to determine the presence of ectoine or perhaps other compatible solutes in halophilic bacteria.

(504) **Direct Analysis of Drugs and Their Metabolites by Infrared Atmospheric Pressure Matrix-Assisted Laser Desorption Ionization Mass Spectrometry**

Bindesh Shreath[1], Yue Li[1], Akos Vertes[1]; [1]George Washington University

Mass spectrometry is a well established tool for the analysis of the pharmaceuticals and their metabolites. Many of the traditional ion sources, however, slow down the analysis due to the need for extensive sample preparation. Infrared (IR) atmospheric pressure (AP) matrix-assisted laser desorption ionization (MALDI) mass spectrometry (MS) was successfully applied to the rapid and direct detection of formulated drugs and their metabolites in unprocessed urine. A Q-TOF Premier (Waters Co.) mass spectrometer was modified by replacing the electrospray source with a custom made AP-MALDI interface. To improve the ion collection efficiency, the ions produced by a Nd:YAG laser-driven optical parametric oscillator (running at 2.94 micrometer) were sampled into the mass spectrometer using pulsed dynamic focusing. A common generic cough medicine formulated as gelatin capsule was cut open for analysis. The active ingredients were acetaminophen, dextromethorphan, guaifenesin and pseudoephedrine. A few microliters of the unprocessed drug and the urine collected at different times after drug ingestion were analyzed directly without drying, extraction or any other preparation steps. Molecular ions and some fragments of all the active ingredients and an inactive ingredient, PEG, were detected in the direct MS analysis of the drug. The urine sample taken after 2.5 hours showed the presence of pseudoephedrine, acetaminophen and PEG. Structural identification of the individual ions, e.g., the protonated pseudoephedrine in urine, was obtained by MS/MS. The dried urine sample did not give any signal, thus its urea content could be excluded as a matrix. The mass spectra obtained after re-wetting the sample spot with water was similar to the original urine mass spectra. This indicated that water played an important role, perhaps as a matrix, in the IR laser desorption ionization process. Compared to the sample collected at 2.5 hours, the relative ion intensity of pseudoephedrine significantly decreased in the urine taken 24 hours after medication. Thus IR-AP-MALDI mass spectrometry has potential applications in the rapid semi-quantitative analysis of drugs and their metabolites as well as in pharmacokinetics investigations.

(505) **Levitated and Dried Droplet Sample Preparation Strategies with Ionic Matrix Compounds and Common Matrices Applied to Membrane Protein Sequence Coverage**

Diem Ly Van[1], Teresita M. Cruz Sanchez[1], George Agnes[1]; [1]Simon Fraser University

Membrane proteins are essential to life, being indispensable for intercellular communication, transport and energy generation, and a cell's response to its environment. Although MALDI-MS has become a preferred technique for peptide mapping due to its high sensitivity, speed, and relatively straightforward sample preparation, the characterization and identification of membrane bound proteins using MALDI-MS remains elusive due to their hydrophobic nature. In consideration of their physiological relevance, the focus of this study is to develop a protocol that will improve the sequence coverage of membrane bound proteins using MALDI-MS. In this work, we exploited ionic matrix compounds to increase sample homogeneity by more evenly distributing the analyte in a sample spot. Even when they are crystalline at room temperature, ionic matrix compounds still produce more homogeneous samples due to having smaller crystal size than common matrices (J. Am. Soc. Mass Spectrom. 2005, 16, 679). Furthermore, MALDI-MS sensitivity can be increased when a smaller, more concentrated sample spot is created using wall-less sample preparation method (Anal. Chem. 2002, 74, 489). Hence, our protocol combines a strategy for solute concentration plus the use of ionic matrix compounds. In comparing results obtained using this sample preparation strategy and the dried droplet method for a model membrane protein, bacteriorhodopsin, after chymotrypsin digestion in sodium dodecyl sulfate, the total sequence coverage was improved to 100% from 80% respectively.

(506) **Differential Protein Expression by MALDI-TOF-MS Following The Deposition of Organic Particulate Matter Mimics**

Alice Kardjaputri[1], George Agnes[1]; [1]Simon Fraser University

Inhalation of ambient particles can cause lung inflammation that leads to pulmonary and cardiovascular diseases. We are monitoring the secretion of pro-inflammatory mediators such as chemokine and cytokines in response to dosing lung cells with particles having different chemical composition. In this experiment we employ a methodology in which we are able to create PM10 mimics of known size and composition (Anal. Chem. 2005, 77, 3623-3628; Toxicology in Vitro. 2006, 20, 1030-1039). For instance, one particle type used was 11.3 nL in volume, and it was comprised of 42 pg of dodecyl aldehyde and 886 pg of elemental carbon. An

average of 73±13 particles in each experiment were delivered to an A549 cell culture consisting 105-106 cells. Followed a 30 minute incubation period, non-surface bound biomacromolecules are harvested from the supernatant and extracted using C18 ZipTip. The compounds extracted are analyzed by MALDI-TOF-MS using sinapic acid as a matrix. In comparing the spectra of the negative control and the injured cells, we observed up-regulation of biomacromolecules that were detected in the window of m/z from 7 to 20 kDa. Standard proteomic strategies to identify these compounds are being employed.

(507) **Evaluation of the Internal Temperature of Protein Cations Exposed to a Hot Dispenser Cathode Employed in Electron Capture Dissociation**

Yong-Hyeon Yim[1], Sunyoung Lee[2], Byungjoo Kim[1], Seonghee Ahn[1], Hun-Young So[1], Han Bin Oh[2]; [1]Korea Research Institute of Standards and Science, [2]Sogang University

The 'effective' internal temperature of an 8.6 kDa ubiquitin cation was estimated under electron capture dissociation (ECD) conditions, in which a dispenser cathode electron source was mounted just outside an ion cyclotron resonance (ICR) cell, i.e., axially displaced at a distance less than 1 cm from the rear trap plate of the ICR cell. In this ECD configuration, thermal activation of the molecular ions stored in the ICR cell was anticipated since the heated dispenser cathode emitted a large amount of (both visible and infrared) radiation as well as electrons. An evaluation of the internal temperature of ubiquitin 6+ and 7+ cations was made by comparing our ECD\r\nfragmentation patterns with those obtained by McLafferty et al. (J. Am. Chem. Soc. 2002; 124: 6407) as a function of the ion temperature. In McLafferty's configuration, the heating (or thermal activation) effect of their filament source was minimal since the filament was displaced by a distance as far as 70 cm from their ICR cell. A careful comparison reveals that the fragmentation patterns obtained in this work are very similar to those previously measured at T=125 oC. In terms of sequence coverage, our ECD configuration provides better results, and in particular without the aid of any other simultaneous activation method, such as thermal heating, infrared multiphoton irradiation, or collisional activation, except for the visible and infrared radiation from the heated cathode.

(508) **Conversion of Sertraline to N-methyl sertraline in Embalming Fluid, a Forensic Implication.**

Sai Prakash P.K[1], Suma Ramagiri[1]; [1]Osmania University,Department of Chemistry,India.

Zoloft (Sertraline hydrochloride) is one of the antidepressant medications used to treat depression, obsessive-compulsive disorder (OCD) and Social anxiety disorder (SAD). Taking antidepressants may increase suicidal thoughts and this significantly increases the probability of accidental or intentional death. The practice of embalming cadaver is common, yet it may create problems for forensic toxicologists if the case was not previously suspected. According to Eschweiler-Clarke reaction, drugs containing secondary amine group react with formaldehyde to give N-methyl derivatives. Sertraline has secondary amine group, therefore we predicted that it may react with formalin to give N-methyl derivative. On similar lines we initiated the stability study of sertraline in formalin solution at three different concentrations (5% 10% and 20%) and at three different pH levels (3.0, 7.0 and 9.5) for a total period of 30 days. Setraline and its degraded products were extracted by liquid-liquid extraction using chloroform and the concentrated extracts were analyzed by gas chromatography/mass spectrometry using electron impact ionization mode (GC/MS-EI). The rate of conversion of sertraline to its N-methyl derivative increased with increase in the concentration of formalin and pH of the solution. The rate of conversion is rapid at higher pH. Sertraline was totally converted to N-methyl derivative after 30 days in 10% and 20% formalin solutions at neutral and basic conditions. Therefore, forensic toxicologists should be cautious while performing death investigation, if formalin solution is the only sample available for analysis .This work shows that analysis for parent drug or its N-methyl derivative may provide data that will reduce the likelihood of false negatives and assists in feasibility of exhumation if Zoloft overdose is suspected.

(509) **Detection of Explosive Hexanitrohexaazaisowurtzitane (Cl-20) Residues by Surface Laser Photfragmentaion-Fragment Ionization Spectrometry**

R Sausa[1], J Cabalo[1]; [1]US Army Research Laboratory

Detection and monitoring of explosives is important in many civilian and military applications [2]. In this abstract, we report the detection of hexanitrohexaazaisowurtzitane (CL-20) by surface laser photofragmentation (SPF) with subsequent fragment detection (FD) at ambient conditions and in real time. We photolyzed or vaporized the energetic molecule with a low power, ultraviolet laser and then detected the characteristic NO photofragment by resonance-enhanced multiphoton ionization using the same or a second laser operating at 226 nm. NO is characteristic of the NO2 functional group that is present in the parent molecule and contributes to the selectivity of the analytical method. Our response plots show that the ion signal is linear over a wide range of concentrations, and yield a detection limit of about 15 ng/cm2 (S/N=3) for 0.01-0.02 mJ of photolysis and probe laser energy. This value is about five times greater than that observed for hexahydro-1,3,5-trinitro-1,3,5-triazine (RDX) and half the value observed for trinitrotoluene (TNT). The sensitivity of the SPF-FD technique depends on the photochemical and photothermal processes yielding NO, as well as the processes involved in its detection. These processes will be discussed and presented at the meeting. References: 1. J. Cabalo, past National Research Council Postdoctoral Associate; present address: US Army Edgewood Chemical Biological Center, Edgewood, MD 21010. 2. J. Cabalo and R. Sausa, "Trace Detection of Explosives with Low Vapor Pressure Emissions by Laser Surface Photofragmentation-Fragment Detection spectroscopy Using an Improved Ionization Probe," Applied Optics, Vol. 44(6), 1084-1091 (2005).

(510) **Analysis of Forensic Adhesive Tapes by ATR Infrared Spectroscopy**

Hsiu-Hsien Shis[1], Liling Cho[2]; [1]Forensic Science Center, Taipei City Police Depart, [2]Department of Forensic Science, Central

Adhesive tapes could be found in crime scene as evidences in many criminal cases. Duct tapes are used to seal boxes and fix part of guilty tools. Tape evidences could also be found in explosive cases, question document identification and even homicide or rape cases where tapes are used as a tool to plaster or control victims. In forensic science, tapes are examined to specify the product and its manufacturer. In this study, 32 adhesive tapes including 7 duct tapes, 5 semi-transparent tapes, 3 silver tapes and 17 transparent tapes are analyzed by optical and physical measurement. FTIR Spectroscopy was used in this study to analyze adhesive tapes. In this study, we set up a systemic non-destruction forensic analysis method to analyze adhesive tapes. The results showed that it is possible to characterize the sources of unknown tape samples by these techniques. 7 duct tapes, 5 semi-transparent tapes and 3 silver tapes can be individualized successfully. 17 transparent tapes can be identified into 7 groups. The results in this study could be of assistance in criminal investigation in Taiwan.

(511) **Analysis of Photocopy and Laser Toners by ATR Microspectroscopy**

Liling Cho[1], Chih Chicung Cheng[2]; [1]Dept.of Forensic Sci., Central Police University, [2]Taipei County Government Police Bureau

Photocopies could be found in crime scene as evidences in many criminal cases. The photocopier and printer have largely given way to the use of photocopyes, which offer certain adventages to the criminal. Analysis of toners from a photocopied document gives reproducible results and makes possible differentiation of toner samples obtained from different photocopying machines. In addition, banks, post offices, school, shopping centers, and department stores now make available photocopying machines for self-service use by clients. As a result of this increased ease with which documents can be copied, there has been a shift in the way falsified documents and anonymous letters are being constructed. I In this study, 49 photocopy toners are analyzed by ATR microspectroscopy. Photocopies from 140 different photocopying machines which can be classified into 49 different toners were obtained from different company representatives in Taiwan(Including toners used in 7-11, OK, FamilyMart, and Hi-Life convenient stores). In this study, we set up a systemic non-destruction forensic analysis method to analyze toners. The results showed that it is possible to characterize the sources of unknown toner samples by this technique. 49 toners can be identified into 25 groups. ATR technique gives reproducible results and makes possible differentiation of samples obtained from different photocopy machines or laser printers. Infrared database created from this research would be a valuable aid to document examiner in the increasing number of cases involving photocopies.

(512) **Determination of Storage Effects on Human Scent using SPME-GC/MS**

Davia Hudson[1], Allison Curran[1], Adee Schoon[2,3], Kenneth Furton[1]; [1]Florida International University, [2]University of Leiden, [3]Canine Unit, Netherlands National Police

Studies have shown the ability of canines to match both a freshly collected odor to a sample after a period of storage in glass container at room temperature. Currently, there are no optimized or standardized methods for the storage of human scent evidence obtained from objects or people. This paper will discuss the contributions of various storage materials to the headspace of analytically clean cotton materials including glass vials, polyethylene and polypropylene bags as well as both aluminized and heavy duty bags. The cotton materials used in this study were pre-treated with a methanol-modified supercritical fluid extraction (SFE) method to achieve analytical cleanliness. Storage studies conducted in triplicate for 1, 2 and 5 week periods, have shown glass to be the storage material which contributes the least amount of compounds to the absorbent materials analyzed through headspace SPME-GC/MS. Human scent is comprised of hundreds of components that can be classified into three main categories: primary odor which is stable over time regardless of diet or environmental conditions, secondary odor which is determined by diet and internal factors, and tertiary odor which is present due to the influence of external factors. Three intra-day hand samples were collected from a male subject though ten minutes of direct contact with pre-treated cotton materials and analyzed through headspace SPME-GC/MS. The stability of the primary odor components of collected hand odor samples for a subject when placed under different environmental stresses including room temperature, -80 0C, darkness, as well as UVA and UVB light exposure were studied over 1, 3, 5, and 7 week periods. The primary odor components of the subject were compared across the initial 12 samples using Spearman Ranking correlation and were found to correlate to each other above a match to no-match threshold of 0.8. The samples which were subjected to -80 0C storage and UV A and UV B light exposure showed the greatest decrease in correlation to the initial samples prior to storage after the first week. Determining the optimal storage materials and conditions for human scent evidence will lead to enhanced performance of canines in the field.

(513) **Analysis of Lipstick Smears by ATR Microspectroscopy**

Liling Cho[1], Kuo-Chao Hsui[2], Ming-Ju Chuang[3]; [1]Central Police University, [2]Keelung Police Department, [3]Taipei County Government Police Bureau

Smeared traces of a lipstick can be easily transferred from a female victim to an assailant during crime of violence. A small amount of lipstick smears are sometimes found as evidence on clothing, glass, cigarette butts, and other miscellaneous crime scene surfaces as a result of contact with such objects. Comparison of the recovered smear to a victim or suspected source has the potential to provide a link between the victim or suspect and the crime. Attenuated total reflection (ATR) microspectroscopy has been applied to the forensic examination of surface treatment. In this study, fifty lipstick samples were collected from cosmetic companies to establish lipstick infrared database. Five different types of lipsticks were selected to print on different surfaces such as cotton fabric, glass, cigarette butt, ceramics, paper cup, and tissue. Lip prints were left to dwell for different periods and were analyzed by micro-ATR. Lip prints were developed with intervals ranging from 2 hours from impression up to 30 days from impression. The results showed that identifiable lip prints can be obtained up to 30 days after being produced on different surfaces. The smear lip print spectra show a great intensity decreased at 2915cm-1 and 2848 cm-1 and 842 cm-1 on cotton fabric's surface. The smears on cigarette butt's surface showed that the amounts of the smears were decreased as the developing time increased. This study shows that the age of the lipstick smear could lead to variations in the intensity of the spectra but would not change the major peak of the lipstick spectra. Micro-ATR is a good non-destructive forensic identification method which can be used not only with lipsticks but also with most cosmetics.

(514) **Laser Photofragmentation Mechanisms of Nitro-Based Explosives**

Maria-Pamela Monterola[1], Benjamin Smith[1], Nicolo Omenetto[1], James Winefordner[1], [1]University of Florida

Laser photofragmentation followed by chemiluminescence detection have been developed to detect nitro containing explosives in various media. The photofragmentation process produced NO2 and/or NO fragments after mildly focusing a 193 nm ArF laser on a quartz window of a cell containing the explosive sample. The NO2 produced upon photofragmentation was subsequently detected by its chemiluminescence reaction with aerosolized luminol solution. The intensity of the chemiluminescence signal was detected by a thermoelectrically cooled photomultiplier tube.\r\nThe discussion focus on the understanding of the laser photofragmentation dynamics of highly energetic materials in terms of the amount of the sample ablated at varying laser parameters such as the total number of pulses and energy. The various possible mechanisms of interaction of the laser photons with both solid and vapor phase explosives are investigated. The photofragmentation efficiency of 4-nitrotoluene, 2, 4 dinitrotoluene and trinitrotoluene will be discussed and compared.

(515) **Development of Reliable, Contraband Mimics for Biological/Instrumental Training Aids/Calibration Standards Using SPME/GC-MS**

Micahel S. Macias, BS, BS[1], Kenneth G. Furton, PhD[1]; [1]Florida International University

Odor detection has become a focused area of research over the past number years because of its importance to the forensic, law enforcement, and legal communities. The use of biological detectors and instrumental detectors is highly researched both for the determination of the chemical signature of individual odors to which alerts are made and to whether or not there is a common element within different items to support the use of contraband mimics. Research results demonstrate that canines are generally not using the relatively low volatility parent compounds but instead use characteristic volatile headspace components (VOC) to accurately locate specimens. The implications of these results on the optimal selection of canine training aids and the tuning of instruments for these compounds are also discussed. In the work presented, headspace analysis of the parent compounds is performed by Solid Phase Microextraction / Gas Chromatography – Mass Spectrometry (SPME/GC-MS), and used to identify dominant odor chemicals seen at room temperature. The applicability of smokeless powders as mimics for high explosives is being investigated. Determination of the dominant odor chemicals in headspace of the smokeless powders can show the availability of training aid/calibration standard replacements for the high explosives. Additional field studies are underway to help improve the permeation devices currently being researched. This should allow for the creation of better training aids/calibration standards that are safer, easier to acquire, and more consistent that currently available. Overall, this will lead to improvements in the performance and standardization of biological and instrumental stand-off detection of targets.

(516) **Characterizing Illicit Drug Residues and Drug Odor Chemicals in Paper Currency**

Jo Nell Aarons[1,2], Ya-Li Hsu[1,2], Kenneth Furton[1,2]; [1]International Forensic Research Institute, [2]Florida International University

Numerous reports have indicated that the majority of paper currency in general circulation is contaminated with trace amounts of illicit drug residues. This fact has made extracting and identifying illicit drug residues on paper currency extremely important. Unfortunately this presents law enforcement personnel and forensic scientists with the challenge of distinguishing money related to drug trafficking from innocently contaminated currency. Although commonly used drugs include cocaine, heroin, methamphetamine and marijuana, most studies have only found trace quantities of cocaine on currency (~10µg). It has been established that certified law enforcement detector canines do not alert to the parent drug itself, rather they alert to by-products or decomposition products. These products are described as being odor signatures; they produce the odor canines are trained to alert to. Research into odor signatures of specifically cocaine and MDMA has reported their odor signature chemicals to be methyl benzoate and piperanol respectively. This presentation will demonstrate that these particular odor signatures are not present in paper currency in general circulation and will therefore not initiate an alert. Solvent extraction and solid phase microextraction (SPME) combined with gas chromatography mass spectrometry (GC-MS) were used to quantify and extract possible drug residues. SPME fibers were optimized by regulating the fiber chemistry in addition to the application of different extraction and sampling times. The optimal fiber was Carbowax Divinyl Benzene (CW/DVB), which has proven effective in removing volatiles from the headspace of illicit drugs. Headspace SPME sampling makes it possible to obtain consistent signature odor from very small quantities of drugs and paper currency. Studies have determined that by using solvent extraction only 15% of cocaine spiked in the uncirculated currency can be removed after 5 weeks. The potential presence and persistence of other widely abused illicit drugs will be examined and presented.

(517) **Pulsed Glow Discharge Mass Spectrometry Detection for Gas Chromatography: Explosives Analysis**

Megan DeJesus[1], James H. Barnes IV[1], Elizabeth P. Hastings[1], Fred L. King[2], Crist L. Lewis[1]; [1]Los Alamos National Laboratory, [2]West Virginia University

The detection and identification of explosive compounds has received large success by combining the separation power of gas chromatography (GC) and the accuracy of mass spectrometry (MS). In such detection schemes, ion sources such as Electron Impact (EI) or Chemical Ionization (CI) are used to identify different analytes based on either fragment ions or its intact molecular precursor ion. It is only through the combination of these two complementary ionization sources that positive identification can be achieved. The pulsed glow discharge ion source offers the distinct advantage of producing both fragment and molecular ions within a single pulse cycle. Thus, using time-gated detection both fragment and molecular ion spectra can be obtained within a single GC analysis. This paper will outline the utility of using a time-gated pulsed glow discharge ion source for the identification of different explosive mixtures. Results will be presented for a series of explosive compounds detailing the spectral differences arising from the various temporal glow discharge ion processes.

(518) **Explosive Recovery Off of Solid Matrices Over Time**

Julie Bitter[2], Kristi George[1,2], C. Douglas Clark[1], Michael Sigman[1,2]; [1]National Center for Forensic Science, [2]University of Central Florida

The lifetime of explosives on post-blast debris and spectator surfaces must be considered when recovering and storing evidence from a bombing scene. As a means of establishing the lifetime of trace residues of common explosives on such surfaces, the loss rates of RDX, PETN, and TNT were determined for four different matrices; glass, low density polyethylene, soft pine, and aluminum. The experiments were performed by placing 10 micrograms of each explosive on separate tokens, made of each matrix, and placing each individual token into a sealed plastic container. The samples were collected at set time points up to 240 hours, and quantitatively analyzed by ion mobility spectrometery (IMS) and gas chromatography – mass spectrometry (GC/MS). Standard solutions (1000 ng/microliter) of TNT, RDX, and PETN were obtained from commercial vendors. These standards were used for loading tokens and preparation of calibration standards. The samples were then stored in plastic containers for up to 240 hours. Extraction of the explosive residue was accomplished by placing a token into a beaker containing 3mL of acetonitrile, and placing the beaker into an ultrasonic bath for 5 minutes. This step was repeated three times, and the washings from each token were combined in a single 10mL volumetric flask and diluted to the mark with acetonitrile. Quantitative analysis of each sample was performed to determine the amount of recovered explosive. External standard calibration curves were created for each explosive on the IMS in the 0.05 to 1.0 ng/microliter range. The cumulative amplitude of the peak(s) for an explosive were summed and plotted as a function of explosive concentration. GC/MS analysis was performed by selected ion monitoring for each explosive, with calibration in the 0.1 to 1.0 ng/microliter range. The loss rate observed for TNT (lifetime of approximately 70 hours) was significantly higher than those of PETN and RDX, which displayed losses of approximately 5% and 10% respectively

over a 240 hour period. The TNT lost from the surface could not be recovered from the inside of the container. The effects of storage temperature, controlled surface air currents and method of explosive deposition are under investigation.

(519) **A Complete Set of Vibrational Assignment for 1,10-Phenanthroline-5,6-Dione**

Uche Udeochu[1], Toiya Jimerson[1], Charles Hosten[1], Alberto Vivoni[2]; [1]Howard University, [2]InterAmerican University,

This paper presents a complete set of Raman vibrational assignments (50 – 4000 cm-1) of 1,10-phenanthroline-5,6-dione. Clear and distinct Raman spectra of phendione with very intense peaks were obtained in the solid phase. Identification of the normal modes with appropriate symmetry representation symbols was achieved by employing the Density functional theory calculations. The calculation was done in close comparison to that already reported for analogous phenanthroline. Results of the B3LYP calculations were consistent and established that phendione possessed sixty fundamentals. FT-Raman of phendione in solution was characterized by low signal to noise ratio. The synthesis and crystal structures of the complex [Ag(L)2](CLO4) is also reported. We will present FT Raman spectra of the silver complexes along with DFT calculations and band assignments.

(520) **Raman Study of the Variability of the Cobalt Blue Pigment**

Danita de Waal; University of Pretoria,

Cobalt blue is the most common pigment used in the decoration of blue and white porcelains from the Ming period to the present. Raman identification of the cobalt compound as a ceramic pigment, is complicated by the interference from glazes and the ceramic matrix. Representative spectra extracted from various databases are generally unreliable because of unexplained variability. In order to obtain a standard reference Raman spectrum it has been necessary to conduct a comparative analysis of published spectra and the spectra of synthetic samples produced under a variety of experimental conditions. This analysis is complicated by the existence of three closely related spinel structures, CoAl2O4, Co2AlO4 and Co3O4. Only the first of these is used as a pigment, but the other two appear as by-products during the synthesis of cobalt blue, especially when produced from non-oxide precursors. The conditions for the synthesis of the authentic material will be presented. To correlate these results with the spectra of blue porcelains it was necessary to examine different techniques to record spectra of intact and fragmented objects of art. In the case of intact objects where exposed layers are not available for direct observation, a new technique to focus into the surface to various depths was required. In this way it is possible to separate the spectra of glaze, pigment and matrix. Representative spectra to demonstrate all of the observed effects will be discussed.

(521) **Probing the Effects of Trehalose on Protein Structure in Food Materials using FTIR-ATR and FT-Raman Spectroscopy**

Douglas L. Elmore[1], Sean Smith[1], Carrie Lendon[1], Allen Muroski[1]; [1]Cargill

Thermal processing alters the higher order structure of food proteins, which intern, often alters their functionality in an negative manner. In order to minimize undesirable functionality, it is helpful to understand how the protein structure changes with processing. It is well known that trehalose acts as an excellent stabilizer for protein structure and functionality during heating and spray drying. Our group is interested in identifying and understanding ways that trehalose can be used to improve functionality of thermal processed food proteins. The results of two studies will be presented. In the first study, FTIR-ATR and FT-Raman spectroscopy were used to investigate the effect of trehalose on the structure of spray dried soy and whey proteins. The results showed that trehalose protects the native secondary structure of these proteins and inhibits aggregation associated with intermolecular beta-sheet formation. In the second study, temperature-dependent FTIR-ATR and FT-Raman spectroscopy were used to investigate the effect of trehalose on protein structural changes that occurred during the cooking process of brine marinated roast beef. The experimental results revealed interesting relationships between beta-sheet content, hydrogen-bonding (at the protein backbone) and temperature. The results show that trehalose protects native secondary structure of the beef proteins (myosin and actin) during the cooking process and hydrogen bonding at the protein backbone decreases most rapidly at lower temperatures when trehalose is present. Results are consistent with the so called "Water-Layer Hypothesis" in which trehalose molecules cluster around the protein surface forming a trehalose shell that traps a thin layer of water. The trehalose molecules compete with the protein to form hydrogen bonds with the trapped water molecules, partially desolvating the protein. Results suggest that it may be possible to increase the amount of water retained in beef during the cooking process by using trehalose as a thermal stabilizer.

(522) **Comparative Performance of NIR Image Intensified Cameras and InGaAs Arrays for Raman Spectroscopy**

Leslie Tack[1], J. Bruce True[1], M. Bonner Denton[2]; [1]Intevac Corporation, [2]University of Arizona

The very recent availability of high performance Near-Infrared image intensified cameras with high responsivity between 950 and 1650 nm has significantly raised the sensitivity of NIR dispersive Raman systems that have previously used IngaAs focal plane arrays or NIR optimized CCD's. The MOSIR 950 Electron-Bombardment (EB) Gain sensor with Transfer-Electron (TE) photocathode provides greater then X100 gain with a very low noise penalty (excessive noise factor < 1.1). Comparative NIR Raman data with deeply cooled InGaAs arrays shows the MOSIR 950 NIR camera can provide sensitivity advantages ranging from X10 to X1000 depending on camera timing requirements.

(523) **Raman Spectroscopy – From Spectra to Knowledge**

Gene Hall[1], Michael Boruta[2]; [1]Rutgers University, [2]Advanced Chemistry Development, Inc.

As Raman spectroscopy continues to grow the need for tools to assist in the identification and interpretation of Raman spectra grows with it. The task of interpreting unknown spectra has always relied on experience, text books, reference spectra, software tools to assist with the interpretation and any prior knowledge of the chemistry of the sample. Although traditional databases have always been good at identifying exact matches, their ability to assist with interpretation of unknowns has been limited. Because of the limited size of reference collections for Raman spectroscopy, the possibly of finding exact matches is reduced and there is a greater reliance on interpretation skills. This limitation of using reference spectra for interpretation has been primarily due to a lack of spectra structure correlations associated with the reference spectra. Without this knowledge of spectra structure correlations, interpretation of an unknown spectrum from a set of reference spectra is very difficult. Recently work at Rutgers University has been undertaken to compile a database of Raman spectra along with accompanying structures and band assignments. This unique database should prove to be a valuable tool to assist spectroscopists in the interpretation of Raman spectra. The progress on this work will be reported.

(524) **Fluorescence Rejection in Resonance Raman Spectroscopy Using a Picosecond-Gated Intensified CCD Camera**

Freek Ariese[1], Evtim Efremov[1], Joost Buijs[1], Cees Gooijer[1]; [1]Laser Centre Vrije Univ. Amsterdam, Netherlands

Fluorescence interference, either from the analyte itself or from the matrix, is a major obstacle in Raman spectroscopy. The most common approach to reduce fluorescence is to use either very long (> 650 up to 1064 nm) or very short (< 250 nm; Asher approach) excitation wavelengths. The intermediate visible and near-UV range is seldom used because of the abovementioned fluorescence problem, although there would be several important advantages, such as wider possibilities to use resonance Raman for extra sensitivity and selectivity, and the availability of more sensitive photon detectors than in the near-infrared. Compared to the deep-UV region there would be a better spectral resolution, less photodegradation, and better transparency of the matrix. By making use of short laser pulses and time-gated detection, one could record the Raman signals during the pulse while blocking most of the fluorescence. Of course both the laser pulse and the detector response need to be short relative to the fluorescence lifetime (typically in the low ns range). A major breakthrough in this field was the application of picosecond Kerr gating. Here, we present an alternative approach, using an ultrafast intensified CCD camera. The fluorescence rejection efficiency depends mainly on the closing slope of the gate, which is about 80-100 ps. This allows us to improve the Raman/fluorescence ratio with typically two orders of magnitude. Other critical aspects are the uniformity of the gate pulse accross the spectrum, loss of spectral resolution compared to a non-intensified CCD, and the intensifier efficiency as a function of the gate width. For excitation we use a frequency-tripled or doubled Ti-sapphire laser with a pulse width of 3 ps; it should not be shorter in view of the required spectral resolution. The gated intensifier can be operated at 80 MHz, so low pulse energies can be used and photodegradation is minimized. The first results obtained with this new setup will be shown, and the effectiveness of fluorescence rejection will be demonstrated for a variety of samples.

(525) **UV Resonance Raman Examination of Concentration-Dependent Conformational Distributions in The Fs Peptide**

Jonathan Scaffidi[1], Zeeshan Ahmed[1], Alexander Mikhonin[1], Sanford Asher[1], [1]University of Pittsburgh

The Fs peptide has long been considered an excellent model for investigating the energetics and kinetics of the helix-coil transition in real-world biological systems. Recent steady-state UV resonance Raman studies examining helix-coil conformational distributions at Fs concentrations between 0.5 and 15 mg/mL (~0.3 to ~8.5 mmol/L), however, suggest that peptide-peptide interactions play a significant role in stabilizing helical conformations even at peptide concentrations as low as 1 mg/mL (~0.6 mmol/L). As studies in our and other laboratories have typically been performed at Fs concentrations anywhere between 1 and 15 mg/mL, the current results indicate that a reexamination of previous research with Fs may be in order.

(526) **Considerations for Raw Material Inspection and Authentication Using Intelligent Portable Raman Systems**

Christopher D. Brown[1], Masud Azimi[1], Peili Chen[1], Kevin Knopp[1], Greg Vander Rhodes[1], Peidong Wang[1], Daryoosh Vakhshoori[1]; [1]Ahura Corporation

The molecular selectivity of the Raman technique makes it an attractive option for a wide variety of chemical problems. Furthermore, recent advances in instrumentation have led improved performance, and portability that is difficult to match with NIR and FTIR methods. The latter characteristic has opened up a number of applications of the technology that were previously confined to laboratory environments or static instruments, such as unknown material identification, spot-measurements in reaction vessels, and raw material authentication. Handheld Raman technology is particularly attractive for raw material authentication in the pharmaceutical and chemical industries, as it enables non-contact verification of incoming materials and finished product with the excellent selectivity. In this presentation we discuss a handheld Raman system with several unique hardware modifications to address this specific need. One of the most labor intensive aspects of NIR raw material authentication is the initial method development, which entails the collection and measurement of a range of calibration samples and provisions for transfer of methods to slave instruments. We will also discuss data analysis approaches that are embedded in the handheld Raman system designed to minimize this traditional overhead. Examples will be given from deployed raw material authentication systems highlighting challenges and successes. We also discuss the utility of the system for field-portable pharmaceutical product authentication.

(527) **Development and Validation of Novel Raman Spectroscopic Methods for Assay of Polymorphic Content in Drug Products**

Xiaohua Zhang[1], Gregory Webster[1]; [1]Pfizer Inc.

International Conference on Harmonization (ICH) guidelines on validation of analytical procedures have been well applied in liquid chromatography method validation and occasionally used with near-infrared assays, but have not been widely applied to Raman spectroscopy. This paper discusses how the ICH guidelines can be applied for a Raman assay of different polymorphs in pharmaceutical products. Each of the validation elements (accuracy, precision, specificity, quantification limit, linearity, range and system suitability testing) are defined and compared the validation approach commonly understood for a LC method. Method development and validation of a Raman method was presented in this paper including both the protocol writing and the final validation results. Methods for calibration standards and sample preparation were also detailed demonstrated. Using this approach for Raman method validation, a suitable method for pharmaceutical applications can be validated.

(528) **Regarding Raman Spectral Intensity Calibration: (A) Cyclohexane Validation Measurements; (B) Treatment of Column-Summed CCD Data**

Wilbur Hurst[1], Steven Choquette[1], Edgar Etz[1],; [1]National Institute of Standards & Technology

Once the spectral intensity correction curve for a spectrometer has been determined and applied to Raman spectral data, the determination of the ratios of chosen band areas of the measured Raman spectra of a given compound can then provide validation that the intensity correction procedure has been correct, if those ratios have been previously determined and agreed upon. It is shown that band area ratios obtained from Raman spectra of cyclohexane with laser excitation wavelengths varying from 488 nm to 785 nm can have widely varying values. The effects of various measurement conditions upon the measured band area ratios will be shown and discussed. The collection of Raman spectra with spectrometer employing two-dimensional CCD array detectors is usually done by column-summing the stored charge in the pixels. The validity of the intensity-calibration procedure then depends upon certain requirements of the pixel photon-sensitivity and/or of the measured Raman light and the properties of the light from the source of known relative irradiance that is used. In most cases these requirements are adequately met so as to not present a

problem, but there can be exceptions. The requirements are discussed and examples given of problems that have been observed.

(529) **Rapid Raman Microspectscopy and Imaging: The Role of the Electron-Multiplied CCD (EMCCD)**

Mayank Tripathi[1], William Finney[2], Kurtulus Golcuk[2], Tso-Ching Chen[2], Michael Morris[2]; [1]Andor Technology, [2]Univ of Michigan

Poster Presentation: We demonstrate a 50X increase in speed of acquisition of Raman microprobe spectra and Raman hyperspectral images with use of an EMCCD in place of a conventional CCD. The EMCCD is a back-thinned device which uses a series of avalanche gain stages in place of conventional semiconductor amplifiers to amplify the signals from the serial register of the CCD itself. The camera operates at 2.5 MHz and enables more rapid data collection than is possible with the previous generation of CCD detectors. We show that the system can be used with green (532 nm) laser excitation. Depending on the Raman cross section of the material examined and on the laser power and wavelength, the time for acquisition of a line of 400 Raman spectra is as little as 1 sec if no binning is used, or 25 millisec if full vertical binning is used. We will demonstrate the use of this system with a variety of synthetic materials and animal tissue specimens, including musculoskeletal tissues. Both families of Raman spectra and images in which contrast is generated from spectral intensities will be presented.

(529a) **Enhanced Gas Phase Raman Scattering Using Silver Coated Hollow Waveguides**

William F. Pearman[1], S. Michael Angel[1], and J. Chance Carter[2]; [1]University of South Carolina; [2]Lawrence Livermore National Laboratory

This work presents early results of the use of silver coated hollow quartz capillaries for Raman analysis of gases. Initial experiments, focused on the detection of nitrogen using both the rotational and vibrational Raman spectra for nitrogen in ambient air, show order-of-magnitude or larger signal enhancements using the capillary waveguide. The technique utilizes a 6 around 1 fiber optic probe that is either placed flush against the capillary or coupled to the capillary using a lens system. In the latter experiments, the focusing of the fiber optic probe into a “cone of acceptance” of the capillary proved critical but is easily accomplished. In preliminary experiments the effect of key experimental parameters such as capillary length and inner diameter and launch optics were evaluated. This paper will focus on optimization of these key experimental parameters.

(530) **41 Years of Competition, Collegiality, and Collaboration**

Gary M. Hieftje; Department of Chemistry, Indiana University

Gary Horlick and I spent nearly four years together in graduate school and, not surprisingly, emerged with similar goals, aspirations, ideas, and philosophies. Our subsequent career paths, parallel in many ways, then naturally brought us into competition with each other, but always in the most positive sense. Although each of us had a number of research areas that were unique to our respective groups, the areas of overlap were stimulated by the frequent interaction that we enjoyed. In this presentation, some of these overlap areas will be identified and current research that emerged from them will be featured. Examples include fundamental studies in the inductively coupled plasma and the use of array detectors for multi-element analysis.

(531) **Improving Chemical Analysis With Advanced Detector Technology**

M. Bonner Denton; University of Arizona

Over the last fifteen years, focal plane array detectors have brought an amazing revolution to analytical spectroscopy. These devices have dramatically changed atomic emission spectroscopy by allowing simultaneous observation of the entire spectral region or selected subregions, providing increased sensitivity, requisite dynamic range, and greatly improved background correction. Focal plane arrays have also vastly increased sensitivity in many other areas of low-light spectroscopy, including fluorescence, phosphorescence, and Raman. Recent advances in utilizing these detectors for spectroscopy and spectroscopic imaging will be presented. Array detectors combined with other recent advances have allowed the development of a new generation of Raman instrumentation. The impact of recent technological breakthroughs in array detectors, optical components and geometries of optical systems employing both dispersive and imaging optics will be contrasted with more conventional approaches. How these advances are propelling Raman into the mainstream of routine chemical analysis will be discussed. New approaches for implementing advanced detectors for mass spectrometry and ion mobility spectrometry will be described. These detectors that have been implemented using technologies originally developed for advanced visible CCD's and infrared arrays hold great promise for vastly improving many areas of mass spectrometry. Initial results will be presented demonstrating significant advances over previous technology. Current trends will be assessed and utilized to predict future application of improved focal plane arrays to modern chemical analysis.

(532) **Application of Microfluidics for Elemental Analysis**

Eric Salin[1], Josiane Lafleur[1]; [1]McGill University

We will present work that uses laser ablation icp-ms to extract elemental composition information from a microfluidic system. The microfluidic system is on a CD sized disk operated centrifugally. Species are trapped and concentrated on the top of a small C18 column. The system can operate as many as 8 collection systems in parallel. The results from trapping experiments, including detection limits, will be presented as well as a discussion of the potential for elemental speciation.

(533) **Membrane Introduction Mass Spectrometry - Recent Advances and Applications**

Chris Gill[1,2], Alexander Thompson[1,2], Skye Creba[1,2], Robyn Ferguson[1,2], Derek Van Pel[1,2], Owen Stechishin[1,2], Erik Krogh[1,2]; [1]Malaspina University-College, [2]Applied Environ. Research Labs

The technique of membrane introduction mass spectrometry (MIMS) uses a membrane interface as a direct sampling strategy for mass spectrometry. MIMS has the advantages of high sensitivity (ppb-pptr without preconcentration), no sample preparation (for air and water), rapid analysis and real time monitoring capabilities. The interface is very robust (typically a polydimethylsiloxane, PDMS hollow fibre membrane), and can be used with relatively dirty and/or reactive samples. The use of tandem mass spectrometry (MS/MS) with this methodology allows rapid analytical separations of (volatile and semi-volatile) analyte species directly from environmental samples. Our group is focused upon both fundamental and applied MIMS research. Presented will be an overview of some of our recent work, including a range of applications such as process/effluent monitoring, real time environmental monitoring, as well as the extension of this technique to the prediction of physico-chemical properties in-situ for environmental systems. In addition, several exciting new MIMS developments that extend its usefulness for the

measurement of much less volatile analytes will also be discussed. These developments include derivatized membrane strategies (e.g. immobilized enzymes) as well as coaxially heated hollow fibre membrane assemblies.

(534) **Laser Particle Spectrochemistry**

Nicolo Omenetto[1], Xihong Wu[1], Benjamin Smith[1], James Winefordner[1]; [1]University of Florida, Gainesville, FL 32611 (USA)

Aerosol characterization as a result of the interaction of individual particles with laser radiation has been the subject of many theoretical papers, experimental measurements and instrumental developments. The panorama of laser-based techniques challenged for this task is vaste, encompassing different kinds of spectroscopic principles: extinction and scattering, plasma emission, molecular fluorescence, photo-fragmentation/ionization mass spectrometry. The information provided by each of these approaches, together with their basic instrumental requirements and their limitations, will be discussed. A general assessment of the current status of single particle analysis, the achievements obtained and the problems yet to be solved, will be attempted.

(535) **Ambient Mass Spectrometry in Forensics and Biology**

Andre Venter[1], R. Graham Cooks[1], Robert J. Noll[1], Ismael Cotte-Rodriguez[1]; [1]Purdue University

The rapid ambient ionization method, desorption electrospray ionization (DESI) is applied to the analysis of explosives, toxic compounds, environmental contaminants and to an array of biological compounds in complex matrices. The hallmark of this method is the lack of sample preparation and the short time required to take data. Newer instrumentation for DESI is described including smaller mass spectrometers. Results of studies of the mechanism of DESI ionization are presented. Related ambient methods, including desorption atmosheric pressure ionization (DAPCI), which employ gases rather than solvents are compared. The deliberate addition of reagents to the spray solution in DESI allows the highly selective "reactive DESI" experiment to be performed and examples of functional group specification are shown. Comments are also made on the future of this area of chemical analysis.

(536) **Analysis of Explosives Using Fast Separations and Fast Tandem Mass Spectrometry**

Glen P. Jackson[1], Matthias Beier[1], Olivier Collin[1], Unige A. Laskay[1], Carolyn M. Zimmerman[1]; [1]Ohio University

The aim of this work is to develop a fast, confirmatory technique for the identification of trace levels of high-explosives. We recently developed a fast screening method for a mixture of nine explosives, including nitrate esters, nitroaromatics and a nitramine using fast-GC coupled with a pulsed-discharge electron capture detector (PD-ECD) that provided on-column detection limits in the low femtogram range in less than 140 seconds. Although the PD-ECD provided extremely low limits of detection, it did not provide confirmatory evidence for the identification of explosives. For confirmatory analysis, GC-MS is the gold standard, but analysis times are typically longer than 20 minutes, excluding sample preparation. In order to speed up the confirmatory GC-MS analysis using a QIT-MS, certain modifications are required to the scanning speed and general operation of the QIT. This presentation will report on the benefits and shortfalls of fast-mass-scanning QIT-MS as a potential detection method for fast confirmatory analyses. To establish the data acquisition rate of a commercial instrument (Polaris Q with a Trace GC, Thermo Finnigan, Austin, TX), fast-GC was performed on a microbore capillary column with the default mass-scanning conditions of 0.18 ms/amu, in NICI mode. The mass spectrometer was able to store a maximum of five averaged (n=3) mass spectra per chromatographic peak (~2.6 Hz),which is at the limit for good quality peak definition. The latest eluting compound, tetryl, elutes in less than three minutes and was readily detected at 100 fg on-column (detection limits have not been established). By operating the mass spectrometer at twelve times the normal speed (0.015 ms/amu), the number of mass spectra per chromatographic peak is only increased by ~30% (to ~3.3 Hz). We explain the non-linear relationship between mass scan rate and sampling frequency, and demonstrate additional approaches to speed up the data acquisition rate, such as storing the data in centroid versus profile format. In addition to faster scanning, we will also report on our preliminary studies involving tandem mass spectrometry of explosives on the timescale required for fast-GC using the new method of collision-induced dissociation during mass acquisition.

(537) **Latent-Print Detection by Macro-Raman Imaging - SERS Active Fingerprint Components and Degradation Products**

Linda Lewis[1], Samuel Lewis[1], Maggie Connatser[2], Ellyn Schuette[1]; [1]Oak Ridge Natioonal Laboratory, [2]University of Tennessee

Fingerprints deposited on many surfaces often go undetected once latent prints age over a few hours, especially when exposed to UV radiation. The ability to develop latent fingerprints is often influenced by many factors including print-type (clean/eccrine through oily/sebaceous), humidity, light, surface matrix, etc. Recent findings on the fundamental chemistry of superglue fuming, a prominent method for developing prints on non-porous surfaces, revealed acetic acid regeneration methods capable of enhancing the ability to develop latent fingerprints that would otherwise go undetected. This enhancement, however, was not effective on fingerprints exposed to UV radiation from sun or fluorescent lighting, especially on surfaces containing iron (III). In the presence of iron (III), the major cyanoacrylate polymerization initiator, responsible for rendering prints visible by the superglue fuming method, is photodegraded into a volatile component. In addition, the enhancement method is complex and not easily amenable to field applications. Thus, a real need exists to efficiently and effectively detect latent fingerprints on all surfaces regardless of the print type or environmental exposure factors. To accomplish this goal, constituents and associated degradation products originating from fingerprint secretions deposited on a range of matrices were characterized via Electrospray-Ionization Mass Spectroscopy (ESI-MS). Through an understanding of time-related changes in fingerprint components, discrimination between fingerprint constituents and the deposition surface facilitated the development of enhanced friction ridge visualization methods. Simplistic methods that increase the detection sensitivity for macro-Raman Imaging through SERS techniques were targeted in this initiative to address these deficiencies in fingerprint detection. With the discriminatory power afforded by SERS imaging, we expect to develop a fingerprint detection method that increases the average-print area and quality, as well as in the differentiation between fresh and aged prints.

(538) **Analysis of Inorganic Oxidizer Salts by ESI-MS**

Michael E. Sigman; University of Central Florida

Inorganic oxidizer salts of nitrate, chlorate, perchlorate and others are readily analyzed by ESI-MS in both positive and negative ion modes. These salts form clusters which are readily distinguished by their mass spectrum. The complexes are not observed under the more harsh conditions that exist in an APCI interface. For example, in the ESI interface sodium nitrate will form clusters of the form [(NaNO3)nNa]+ in the positive ion mode, where the cluster size, n, ranges from one to greater than 10. Sodium nitrate solutions are

also observed to form doubly-charged clusters of the type [(NaNO3)n2Na]2+ and [(NaNO3)n2NO3]2-, where n = 11, 13, 15, etc., in addition to singly-charged cluster ions. The identity of the doubly-charged clusters has been determined by tandem mass spectrometry. Binary aqueous mixtures of NaNO3, KNO3 and NaClO4 oxidizers give more complicated clustering behavior. Two-component NaNO3 - KNO3 salt solutions form cluster ions of the type [(NaNO3)i(KNO3)jNO3]- in the negative ion mode and [(NaNO3)i(KNO3)jNa]+ and [(NaNO3)i(KNO3)jK]+ in the positive ion mode. Two-component solutions of salts which do not share a common cation or anion, such as KNO3 – NaClO4 , form ions of the type [(KNO3)i(NaClO4)j(KClO4)k(NaNO3)lK]+ and [(KNO3)i(NaClO4)j(KClO4)k(NaNO3)lNa]+ in the positive ion mode. Similar clusters around nitrate and perchlorate are formed in the negative ion mode. In each case, the maximum number of spectral lines for a cluster of size n can be calculated as the number of combinations of nth order (where n=i+j) of N different cation-anion pairs taken with replication and without regard for the ordering of the N cation-anion pairs. The actual number of lines observed may be reduced due to m/z degeneracy for some ions.

(539) **Characterization of Depleted Uranium Oxides Fabricated Using Different Processing Methods to Identify Key Signatures for Nuclear Forensics**

Elizabeth Hastings[1], Cris Lewis[1], John FitzPatrick[1], Lav Tandon[1]; [1]Los Alamos National Laboratory

In nuclear forensics, the ability to identify key signatures in interdicted Special Nuclear Materials (SNM) is essential to rapidly identify a sample's characteristics, such as origin, intended use, and route attribution. To determine what key signatures exist in nuclear materials processed by different methods, a series of depleted uranium oxides fired at various temperatures have been analyzed. Differences that are evident range from physical appearance to the particle size distribution. For example, upon initial observation of the uranium oxide powders, a distinct difference in their coloring is observed. In this study, depleted UO2, UO3, and U3O8 fired at three temperatures ranging from 350-1100 C are compared based on non-destructive and destructive techniques that include the material density, particle size distribution, optical microscopy, and elemental composition (Inductively Coupled Plasma – Mass Spectrometry). Each analysis is performed at the bulk sample level followed by particle fractionation (cascade impactor) and analysis of each individual size fraction. LA-UR 059562

(540) **Characterization of Explosives Compounds Using High-Field Asymmetric-Waveform Ion Mobility Spectrometry**

Richard A. Yost[1], Christopher K. Hilton[1], Jared Boock[1]; [1]University of Florida, Department of Chemistry

Introduction A major threat to national security of the United States is the continued use of explosives abroad and possible use of explosives by terrorists on the domestic front. As a result, there is a need for improved separation and detection technologies for explosives compounds. Research regarding the use of high-field asymmetric-waveform ion mobility spectrometry (FAIMS) offers new capabilities for real-time ion separation in conjunction with mass spectrometric detection. This could lead to vast improvements in explosives detection by FAIMS/MS. Method Data were collected using an Ionalytics Selectra Beta II prototype FAIMS apparatus as an ion separation device coupled to a Thermo-Finnigan LCQ quadrupole ion-trap mass spectrometer (ITMS). Compounds were ionized by atmospheric pressure chemical ionization (APCI). A set of eight explosives compounds was selected for characterization based on threat assessment, as listed below. Table 1. Compounds Undergoing Characterization TNT (2,4,6-trinitrotoluene) HMX (cyclotetramethylene tetranitramine) RDX (cyclotrimethylene trinitramine) 2,4-DNT (dinitrotoluene) 2,6-DNT (dinitrotoluene) 3,4-DNT (dinitrotoluene) PETN (pentaerythritol tetranitrate) TNB (trinitrobenzene) These compounds were diluted in a solution of 64.9% methanol, 35% water, and 0.1% carbon tetrachloride to a concentration of ~ 1-10 ppm. They are all chemically similar as they all have one or more nitro groups attached and all have a tendency for negative ionization under APCI conditions. Preliminary Data Optimal parameters were determined for high-field ion mobility separation of these compounds. These parameters include, but are not limited to, compensation voltage (CV), carrier gas composition, and carrier gas flow rate. In addition, data sets were taken based on both characterization of individual compounds and isolation of single compounds in a mixture. The mobility behavior of each of these compounds under varying electric field was also examined. Dispersion voltages (DV) were varied over the range from -4000V to +4000V. Four replicate CV scans were conducted for each DV setting. From these data, the relationship between CV and DV was determined. Preliminary data show that the majority of the explosives exhibited "A" type mobility behavior under high electric field, which corresponds to increasing mobility (increasing Kh/K ratio) as the field strength (E/N) increases. Some explosives demonstrated "B" type behavior, which corresponds to an initial increase in mobility as E/N increases followed by decrease. The performance of the FAIMS/MS system demonstrates the potential of this approach for sensitive and selective detection of explosive compounds in a variety of applications.

(541) **Electrical "Visualization" of Biomolecules to the Single Molecule Level with Silicon Nanowire Devices**

Ying Fang[1], Gengfeng Zheng[1], Fernando Patolsky[1], Charles M. Lieber[1]; [1]Harvard University

Nanoscale materials offer unique opportunities for detection of biological and chemical species central to many areas of healthcare and the life science, ranging from disease diagnosis to the discovery and screening of new drug molecules. We report a general platform using nanowire transistor arrays for real-time electrical detection of a variety of biomolecules ranging from small molecules, proteins, DNA to viruses to the single molecule level. The nanowire arrays consist of hundreds of individually addressable field-effect devices with reproducible electrical characteristics, and are controllably modified using antibodies, PNA probes or cell-surface receptors with precise device registration. Electrical measurements show conductance changes characteristic of selective binding and unbinding of target biomolecules, thus providing a high-throughput, real-time parallel detection of biomolecules. Studies show that proteins and viruses can be simultaneously detected at femtomolar concentrations with high selectivity even in undiluted serum samples. Furthermore, direct and real-time detection of single DNA oligonucleotides has been demonstrated. Electrical measurements on silicon nanowire devices modified with PNA probes showed discrete conductance changes characteristic of binding and unbinding of single DNA molecules. Dynamical information from statistical analysis of single molecule time trajectories is derived for both perfectly matched and mismatched PNA-DNA. This nanowire-based approach represents unique and new opportunity for direct and real-time studies of biological systems at single molecule level, and highlights the potential of the interface between nanoelectronics and the life sciences.

(542) **Single Conducting Polymer Nanowire Based Chemical and Biosensors**

Nosang Myung[1], Adam Wanakeya[1], Wilfred Chen[1], Ashok Mulchandani[1]; [1]University of California-Riverside

We present a simple method to fabricate, characterize and demonstrate the application of a single conducting polymer nanowire (CPNW) based sensors for chemical and biological analytes. A single conducting polymer nanowire was fabricated between pre-fabricated gold electrodes by an electropolymerization within e-beam patterned nanochannel. Since electropolymerization uses benign conditions, chemically or biologically functionalized CPNW was formed readily. Further post synthetic functionalization, alignment and positioning are therefore not necessary as is in the case with carbon nanotubes and silicon nanowires-based devices. Detection of various analytes was achieved by the extremely sensitive modulation of the electrical conductance of the CPNWs brought about by the change in the electrostatic charges from binding of the analytes to the receptors. This procedure led to a direct, real-time, sensitive, rapid and label free detection. The whole fabrication and detection procedure was carried out at ambient condition. Further, by using a third electrode in an electrolyte-gated approach, the sensitivities of the devices were tuned by the simple control of the gate potentials. A large modulation of up to three orders of magnitude in electrical conductivity was demonstrated as a result of variation in the electrochemical potential.

(543) **Localization and Detection of Oxidized LDL By MEMS Shear Stress Sensors and In_2O_3 Nanowire/Carbon Nanotube Based Fets**

Mahsa Rouhanizadeh[1], Hongyu Yu[1], Juliana Hwang[1], Eun Sok Kim[1], Chongwu Zhou[1], Tzung Hsiai[1]; [1]University of Southern California

Introduction– Coronary artery disease (CAD) preferentially develops at the arterial branching points or bifurcations areas where low density lipoprotein (LDL) can undergo oxidative modification to oxidized LDL (oxLDL). Hemodynamics, particularly wall shear stress, plays an important role in regulating the development of CAD and oxLDL is considered a biomarker for acute heart attack in patients with CAD. Knowing that oscillatory fluid shear stress induces oxidative modification of LDL particles in vascular endothelial cells, diagnosis device to integrate the measurement of temporal and spatial variations in shear stress with oxidized LDL sensing would be highly demanded. New research in nanotechnology has yielded evidence that nanowire based diagnostic and therapeutic methods may be the next stage in monitoring and regulating chemical and biological events inside the human body. Methods– MEMS shear stress sensor was fabricated and developed to resolve circumferential variations in shear stress using a three-dimensional symmetric bifurcation model in order to search for the accumulation site of the oxidized LDL particles. Then, we studied the complementary response of indium oxide (In2O3) nanowires network- and carbon nanotube network-based field effect transistors (FETs) to differentiate the LDL particles between the reduced (native LDL) and the oxidized state (oxLDL). LDL samples isolated from human plasma were exposed to In2O3 nanowire and carbon nanotube FETs, and conductivities and gating characteristics were compared as current versus drain-source voltage (ID–VDS), and current versus gate-source voltage (ID–VGS). The results were also validated by high performance liquid chromatography (HPLC). Specificity of the nanosensors to the oxLDL particles was evaluated by carbon nanotube network-based FETs conjugated with anti-copper oxLDL antibody. Results– Shear stress measurement with the MEMs sensor offers a feasibility to identify the oscillatory shear stress-exposed regions where LDL particles undergo oxidative modification. Application of nanowire-based field effect transistor, differentiate the oxidative modified LDL particles by revealing a higher conductivity in the LDL sample containing 15.1% oxLDL relative to the sample containing 4.4% oxLDL after exposure to In2O3 nanowires and a complementary response after exposure to carbon nanotubes.

(544) **Detection of DNA Oligonucleotides on Nanowire Array Electrodes**

Mahnaz El-Kouedi[1], Aja Andreu[1], Jon Merkert[1]; [1]UNC-Charlotte

We present the results of our studies on the chronocoulometric detection of DNA oligonucleotides on gold nanorod arrays. A template synthesis method was used to fabricate high surface area electrodes. The free-standing rod arrays were then derivatized with a mixed monolayer of thiolated DNA oligonucleotides and mercaptohexanol spacer molecules. A hexamine ruthenium (III) chloride redox marker was used to measure the charge associated with the electrode surface before and after hybridization of the complementary target DNA strand. Our data indicates that upon addressing the problems associated with miniaturization of the electrode system and the associated increase in surface area, we can detect low concentrations of our target DNA strands with good sensitivity and high selectivity.

(545) **Tuning the Chemical Selectivity of SWNT-FET and Polymer Nanojunctions for Selective Heavy Metal Ion Detection**

Larry Nagahara[3], Alvaro Díaz Aguilar[1], Erica Forzani[1], Xiulan Li[1], Peiming Zhang[2], Ruth Zhang[3], Islamshah Amlani[3], Raymond Tsui[3], Nongjian Tao[1], ; [1]Dep. of Electrical Engineering & CSSER, ASU, [2]Biodesign Institute, ASU, [3]ESPS, Motorola Labs, Tempe

We present two methods based on polymer nanojunctions (PNJs) and Single Wall Carbon Nanotubes Field Effect Transistors (SWNT-FETs) for selective detection of heavy metal ions in water. We electrochemically deposit peptide functionalized polymers to form nanojunctions as well as onto SWNT walls of the FET devices. Selective detection of the analytes is demonstrated by choosing different peptide sequences. In the case of the PNJs, conducting polymers of polyaniline are deposited in a 20-100 nm gap between pairs of gold nanoelectrodes and the signal transduction mechanism of sensor array is based on the change in the nanojunction conductance as a result of polymer conformational changes induced by the metal-ion chelating peptide. On the contrary, non-conducting peptides modified polymers are electrochemically deposited on SWNTs to functionalize and to retain the electronic properties of the SWNT-FET devices. The transduction mechanism of these sensors relays on the lost of chemical interactions between His residues from peptides and SWNT walls upon heavy metal ion chelation. Real time detection of heavy metal ions in the ppt-ppb range is demonstrated on both, peptide-modified PNJ and SWNT-FET sensors, and the use of PNJ arrays allow the quantification of copper ion concentration in drinking water.

(546) **Fundamental Aspects of Chemical Vapor Generation by Aqueous Tetrahydroborate(III) Derivatization**

Alessandro D'Ulivo; C.N.R., Inst. Chem. & Phys. Processes, Pisa, Italy

Fundamental aspects of chemical vapor generation by aqueous tetrahydroborate(III) derivatization Alessandro D'Ulivo National Research Council of Italy, Institute for Chemical-Physical Processes, Pisa, Italy E-mail dulivo@ipcf.cnr. Analytical application of chemical vapor generation (CVG) by aqueous tetrahydroborate(III) derivatization coupled with many spectrometric techniques represents one of most powerful method

for determination and speciation of trace and ultratrace elements. Fundamental aspects dealing with the mechanism of CVG of trace elements have scarce relevance in comparison with analytical applications and developments. \r\nCVG is widely employed generation of the volatile species of As, Sb, Bi, Ge, Sn, Pb, Se, Te, Hg, Cd, Zn, In, Tl and, more recently, volatile species of transition and noble metals. The main difference is in the stability of the final products that are: (i) hydrides for As, Sb, Bi, Ge, Sn, Pb, Se, Te, (ii) both free atoms and hydrides for Cd (iii) free atoms for Hg and (iv) volatile, not yet identified, species for transition and noble metals. In the case of stable hydrides the study of the mechanistic aspect of CVG can be performed by deuterium labeled reagents while in the other cases the studies are based mainly on the acquisition of indirect evidences. This presentation reports a discussion on the mechanisms involved in CVG, and on some recent studies on the hydride forming element As, Sb and Bi that are useful to improve the present status of knowledge. Among them: (i) the use of deuterium labeled reagents in competitive reaction experiments and use of advanced mass spectrometry approaches, which allow to gain new information on the mechanism of CVG of AsH3, SbH3 and BiH3;\r\n(ii) the positive effect of some transition metal compounds on the generation of BiH3 have been investigated by CVG-AAS and GC-MS, indicating a probable participation of the additives to the mechanism of hydride transfer from boron to bismuth.

(547) **Arsenic Speciation: An Evaluation of Their Determination by Various Techniques**

Ian D. Brindle[1], Roger McLaughlin[1], April Conn[1]; [1]Brock University

Vapour generation atomic spectrometry continues to develop. We shall present results from our laboratory using the Multimode Sample Introduction System (MSIS) (US Patent # 6,891,605) in three areas; 1: HPLC-ICP-MS for arsenic speciation - determination of vapour-forming species and non-vapour-forming species in a single run. 2: Internal standard for matrix correction and improved RSDs for vapour-phase element determination by ICP-AES3: Improvements in turnround time in the production laboratory using the MSIS for both conventional an vapour generated elements..

(548) **Generation of Volatile Drivatives with Borohydride-form Anion-exchangers: Possibilities for Simultaneous Determinations by ICP-OES**

Julian Tyson[1], Yustina Rodriguez[1]; [1]UMass Amherst

Abstract: There have been several reports of the simultaneous determination of hydride-forming elements. This is a potentially difficult analysis because of the possible need for oxidation state adjustment if an oxidative sample pretreatment is involved. For most flow-based procedures, the sensitivity for the higher oxidation state is considerably lower than that for the lower oxidation state (for Se the higher oxidation state gives no signal). Oxidation state adjustment is difficult if selenium is involved, as conditions that reduce AsV to AsIII will reduce higher oxidation states of selenium to Se0. A further problem is that the conditions for highest sensitivity for a given oxidation state of a given element are almost certainly not the best conditions for another element. We have found that hydrides can be generated simultaneously from a number of elements by passage of an acidified sample through a column containing a borohydride-form anion-exchanger, and that the optimum conditions apply to a number of elements. We have determined As, Bi, Hg, Sb, Se, and Sn in natural waters and a urine SRM. During the study of interferences, we discovered that volatile derivatives of Co, Fe, Mn, Ni, Pb and Zn were also formed.

(549) **Metal Vapor Generation - Radical Approaches to Mature Techniques**

Ralph Sturgeon[1], Scott Willie[1], Mariana Antunes Vieira[1], Anderson Schwingel Ribeiro[1]; [1]NRC-INMS, Ottawa

A resurgence of interest in the field of metal vapor generation has occurred over the past 5-8 years, potentially heralding revolutionary changes to historical approaches which have been in use for the past 40 years. Conventional chemical reduction may be augmented by radical-based procedures driven by ultraviolet and ultrasonic sources. An overview of these recent techniques, focusing primarily on, but not limited to, mercury as the analyte will be given. Figures of merit for the AAS detection of total mercury following reduction by either UV or ultrasonic fields will be presented as will speciation measurements of this element. Application of the techniques to ICP-MS detection will also be highlighted wherein advantage is taken of a new spray chamber specifically designed to efficiently take advantage of UV photogeneration.

(550) **Investigations of Photochemical Vapor Generation Atomic Absorption Spectrometry**

Neil Fitzgerald; Marist College

Recent reports of vapor generation of a number of elements accomplished by UV irradiation of an analyte in a low molecular weight organic acid in lieu of a separate chemical reductant (such as sodium borohydride), has renewed interest in vapor generation techniques for sample introduction to atomic spectrometry. The ability to remove the chemical reductant from a vapor generation system has a number of advantages including the simplification of the system, removal of vigorous moisture forming reactions and elimination of the need to purchase and freshly prepare chemical reductant solutions. In our work we have concentrated on the determination of mercury with detection by atomic absorption spectrometry. Initial studies have shown that total mercury can be determined at relatively low concentrations (ppb level) using simple and inexpensive equipment without the use of a chemical reductant. Both flow injection and batch systems will be discussed. Interferences were encountered in the flow system and methods for their elimination investigated. The batch system allowed samples to be determined without a separate sample preparation stage by UV irradiation followed single drop microextraction. Interferences in this system were overcome by using the method of standard additions. This presentation will summarize previous work and also consider other possible advantages of photolysis vapor generation including, the feasibility of speciation, application to other elements and simplification of sample preparation methods.

(551) **Spectral Resolution Effects on Calibration Quality and Calibration Transfer in Multivariate Optical Computing**

Michael Myrick[1], Luisa Profeta[1]; [1]University of South Carolina

Multivariate optical computing (MOC) is an approach to building application-specific measurement tools based on models expressed in the transmission and/or reflection spectra of an optical interference filter known as a multivariate optical element (MOE). MOEs are designed by refinement based on optimizing the prediction of calibration spectra, and judged by the MOE model prediction of validation spectra, similar to the process of building a model in conventional methods like principal components regression (PCR). To date, no systematic comparison has been made of MOE models to those that can be built by PCR. In addition, no discussion has been made of what is required of calibration and validation spectra to enable a MOE model to perform well in practice. This presentation will cover both topics using both experimental and theoretical approaches. We conclude that when spectral non-linearity is not too great, MOE models can

equal or be superior to PCR models based on the same spectral data. We also conclude that MOE models will show degraded performance in practical applications if the calibration spectra do not meet well-defined apodization and resolution requirements. In general, these requirements are that the apodization-limited FWHM of the instrument response function must be equal to or less than the FWHM of the collisional linewidth of Lorentzian absorption bands in the calibration spectra.

(552) **From Earth to Mars (and Back): Developing a Raman Analyzer Rugged Enough for Process Analysis**

Norman Wright[1], Robert Hegger[1], Bruce McIntosh[1]; [1]Hamilton Sundstrand

Raman Spectroscopy continues to gain awareness and mainstream acceptance of its capabilities in the analytical laboratory due to continuous technological advances to every component in the system. The advantages of obtaining chemical specificity comparable to mid infrared measurements and the ease of sampling using fiber optics and application specific probes have made Raman a compelling technique to consider and evaluate for on-line and process applications. This paper will describe a process monitoring system where the design considerations successfully incorporate the advantages of Raman spectroscopy in addressing process applications. Case studies will be presented.This talk will detail the design of a system rugged enough to be incorporated on the Mars Lander and used for planetary mineralogical investigation. The heart of that system is a unique spectrometer design based on a Dyson relay that provides wavelength dispersion for the full Raman shift region of 0-4000 cm-1. Additional features that have been incorporated for the process analytical workspace include the ability for real-time sample multiplexing as well as continuous reference monitoring for correction of both spectral axes. These features when added provide a stable and reliable process platform will also be discussed.

(553) **Optical Mass Flow Monitor for Pharmaceutical Freeze Drying**

Mark Druy[1], William Kessler[1], Mike Finson[1], Steve Davis[1], Phillip Mulhall[1], Henning Gieseler[2], Michael Pikal[3], David Debo[4], Vincent Bons[4], [1]Physical Sciences Inc., [2]University of Erlangen, [3]University of Connecticut, [4]BOC Edwards Pharmaceutical Systems

Physical Sciences Inc. and the University of Connecticut report on the use of tunable diode laser absorption spectroscopy (TDLAS) for the measurement of water vapor mass flow rates in the duct connecting a freeze-dryer chamber and condenser. The TDLAS instrument measures water vapor concentrations and gas flow velocities using near-IR spectroscopy. The concentration and velocity measurements are combined with the duct diameter to determine the instantaneous water vapor mass flow rate (grams/second) exiting the product chamber. The instantaneous measurements are integrated as a function of time during the drying process to provide a measurement of the total water removed (grams) from the product at any point during the process. The TDLAS measurements of total water removed are compared to gravimetric determinations to determine the sensor measurement accuracy. Sublimation and product freeze drying runs have been performed in both laboratory and pilot scale freeze dryers. The presentation includes an overview of TDLAS and the mass flux measurement technique. In addition we will show water vapor concentration, velocity and mass flux data recorded during laboratory and pilot scale freeze-drying operations. The integrated TDLAS-based mass flux measurements are compared to gravimetric determinations of the amount of water removed during the freeze-drying process to evaluate its use as a process endpoint monitor.

(554) **Application Of NIR Spectroscopy to the Real Time Monitoring of Pharmaceutical Blend Uniformity: A Mass Balance Approach.**

Kevin Bynum, Busolo Wabuyele, Joseph Zilenski, Rosario LoBrutto, Subash Patel, Richard Vivilecchia; [1]Novartis

Blend homogeneity is a critical parameter that can be monitored in real time, through the use of process analytical technology (PAT). One of the most common techniques utilized to monitor the homogeneity of a pharmaceutical blend is near infrared spectroscopy. Since the active and inactive pharmaceutical ingredients are typically mixed in a rotating blender, a number of technical constraints are placed on the spectrophotometer utilized for such an application. The spectrometer must be firmly affixed to the exterior of the rotating blender, which will impart significant mechanical stresses to the spectrometer. These stresses limit the design of the spectrometer to those which do not utilize moving components (diode array and AOTF). The rotation of the blender also makes it difficult to couple the spectrometer to external power sources and data systems. Power can be self contained in a battery, that is affixed to the blender, and a wireless link can be utilized to transmit data from the spectrometer to a control computer. This presentation will discuss the implementation, validation, and application of a blend uniformity monitoring system that utilizes a wireless photodiode array near infrared spectrophotometer to monitor and control the homogeneity of a pharmaceutical blend. The construction including DOE, validation, and maintenance of a chemometric model which enables the assay of all active and inactive components will be discussed as well as the appropriate reference analysis used to construct and validate the model. This "mass balance" approach, where all components are assayed simultaneously will allow for control of not only the content uniformity of the final dosage form, but also other properties such as drug release (dissolution) and hardness. This mass balance approach also provides critical insight and understanding into the drug formulation process. Finally the method transfer including the appropriate acceptance criteria and scale up of the methodology to a production environment will be discussed in detail.

(555) **The Application of Variable Filter Array (VFA) Mid Infrared Spectrometers in Process Monitoring**

Paul Wilks[1], Sandra Rintoul[1]; [1]Wilks Enterprise, Inc.

Mid-IR Fourier Transform spectrometers (FTIR) are widely used in quality control laboratories for many applications related to process management. However, these instruments are typically not suited for installation in plant environments adjacent to process streams. The time delay resulting from transporting samples from the production area to the laboratory can make process management difficult. Fixed wavelength, IR filter analyzers have been used both in-line (i.e. beverage monitors) and at line (i.e. hydrocarbon-in-water analyzers) for many years. The recent introduction of linear variable filters (LVF) and mid-IR detector arrays allow for a spectral range to be analyzed much like an FTIR and thus have greatly broadened the applicability of infrared analysis for process monitoring. VFA spectrometers are compact, have no exposed air path or moving parts and can operate in rugged plant environments. Specific applications of VFA spectrometers such as alcohol in wine and gasoline, biodiesel in diesel fuel, trans fatty acid in vegetable oil and others will be described in detail. With a simplified computer interface, displays can be modified for a specific application to make it friendly to non-technical operators by giving either a numeric readout or a pass/fail message.

(556) **A Miniature Raman Spectrometer Engine and Its Industrial Applications**

Richard Crocombe[1], Bill Ahern[1], Dale Flanders[1], David Coppeta[1]; [1]Axsun Technologies

Common visions for the ideal analytical instrument focus on the concepts of a deployable process spectrometer and a hand-held, intelligent device that gives specific analytical answers. Miniature X-ray fluorescence instruments have been available for some time for metals analysis, but miniature high-resolution, high-sensitivity molecular spectrometers (infrared, near-infrared, Raman) have remained a challenge. A number of portable, moderate cost, Raman spectrometers have been developed, but in general these have operated at either low resolution (~10 to 20 cm-1), or have compromised performance in other areas. Adaptation of technology developed for the telecommunications industry has allowed the construction of near-infrared spectrometers with simultaneous high resolution, high signal-to-noise and rapid data collection [1]. This technology has now been extended into Raman spectroscopy. Novel aspects of this Raman engine design include excitation at wavelengths longer than 785 nm to minimize fluorescence, high (~ 5 cm-1) resolution, good sensitivity, battery operation, all in a hand-held or deployable package. This engine is therefore well-suited for Raman spectroscopy of 'real-world' samples, whether in organic synthesis or crime scenes, where a combination of fluorescence avoidance and high specificity are required. This paper will describe the technology behind this Raman spectrometer engine, give examples of its performance and outline industrial application areas. [1] R. A. Crocombe, D. C. Flanders and W. Atia, "Micro-optical instrumentation for process spectroscopy", Proc. of SPIE, 5591, 11-25 (2004).

(557) **Linear, Nonlinear, and Excitation Anisotropy Spectroscopic Characterization of Efficient Multiphoton Absorbing Fluorine Derivatives**

Kevin Belfield[1], Mykhailo Bondar[2], Olga Przhonska[2], Sheng Yao[1]; [1]University of Central Florida, [2]Institute of Physics

The electronic structure of a number of two-photon absorpbing (2PA) fluorene derivatives, N-(7-benzothiazol-2-yl-9,9-bis-decyl-9H-fluoren-2-yl)-acetamide, (1), 9,9-didecyl-2,7-bis-(N,N-benzothiazoyl)fluorene, (2), 4,4'-[[9,9-bis(ethyl)-9H-fluorene-2,7-diyl]di-2,1-ethenediyl]bis(N,N-diphenyl)benzeneamine, (3), and 4,4',4''-[[9,9-bis(ethyl)-9H-fluorene-2,4,7-triyl]tri-2,1-ethenediyl]tris(N,N-diphenyl)benzeneamine, (4), were investigated by a steady-state spectral technique, quantum chemical calculations and a picosecond pump-probe method. These derivatives are of interest for their relatively high two-photon absorption (2PA). The steady-state excitation anisotropy spectra reveal the nature of the ground-state absorption bands. Semi-empirical quantum chemical calculations of the fluorene derivatives (AM1, ZINDO/S) show good agreement with experimental data. The spectral position and alignment of various electronic transitions of 1 – 4 were estimated by their excited-state absorption and anisotropy spectra. Linear and nonlinear spectroscopy analyses will be presented.

(558) **Spectroscopic Investigations of Binary Guanosine Gels**

Elizabeth Morgan[1], Darren Nakamura[1], Yuehua Yu[1], Linda McGown[1]; [1]Rensselaer Polytechnic Institute

Guanosine gels (G-gels) are self assembled aggregates of guanosine nucleotides. The building blocks of these gels are derived from Hoogsten hydrogen bonding between a nucleobase and its neighbors, resulting in the formation of G-tetrads. These relatively simple building blocks can further associate into more complex, extended structures, which we have been investigating for applications in separations, nano-solubilization, and bioencapsulation. Although G-gels formed by single guanosine compounds have been well studied, gels formed by mixtures of guanosine compounds are a new area of investigation. We have discovered that binary G-gels composed of guanosine and 5'-guanosine monophosphate exhibit interesting thermal properties that vary with the ratio of the two compounds as well as solution conditions such as pH, cation content, and buffer strength. UV-visible absorption and circular dichroism spectroscopies were used to investigate gel aggregation, melting behavior, and reversibility as a function of temperature. Fluorescent probe studies were performed to examine structural and microenvironmental characteristics as a function of gel composition and temperature.

(559) **Application of Dendritic and Hyperbranched Polymers to Chemical Sensing**

Sheryl Tucker[1], Lisa Norton[1], Katrina Kline[1]; [1]University of Missouri

Dendrimers are a unique, highly-diverse class of polymers that have well-defined macromolecular architectures. They are constructed by the iterative addition of branching unit layers, called generations (G), to a polyfunctional core atom or molecule. Dendrimers possess three distinct architectural regions: core, interior zone created by the branches, and exterior surface. Dendrimers are known sequestering agents and are described as unimolecular micelles. They are monodisperse, covalently-bound molecules at all concentrations. Hyperbranched polymers differ from their fully-branched dendritic cousins in the extent of branching – generally 55-75%. They can contain a central core, with the main difference being their polydispersity and lack of perfect symmetry. Using UV/Visible absorption and steady-state and dynamic fluorescence spectroscopic techniques, we have shown that the fluorophore phenol blue is sequestered at the core of both amine-terminated (-AT) poly(propyleneimine), PPI, and poly(amidoamine), PAMAM dendrimers in aqueous solution. We have also found that polycyclic aromatic hydrocarbons (PAHs), such as pyrene, also show a similar trend with them sequestered in the outermost branches of carboxylate-terminated PAMAM dendrimers. The entrapment of phenol blue in dendritic polymers is exceptionally robust. The dye does not leach out of the dendrimers in water or methanol. Furthermore, we have also discovered that the larger (G5+) PAMAM-AT dendrimers are capable of loading several dye molecules within a single dendrimer. In the presence of excess phenol blue, three and six dye molecules were loaded in G5 and G7 PAMAM-AT, respectively. Subsequent removal of the unassociated, surplus dye, via extraction, did not appear to affect the association of multiple dye molecules within these dendrimers. Ensnared phenol blue senses to the presence of other analytes. For example, the fluorescence emission intensity of phenol blue in G5 PPI decreases substantially with the addition of triethylamine, a fluorescence quenching agent. A similar response to quenching agents, in this case nitromethane, is also seen with PAHs, such as pyrene. Current work is extending to hyperbranched polymers, other fluorophore-analyte pairs.

(560) **Fluorescence Lifetime Enhancement of Organic Chromophores Attached to Gold Nanoparticles**

Florencio E. Hernandez; UCF

Through radiative decay engineering (RDE) in a hybrid system, we have experimentally proven, for the first time, the possibility to enhance the fluorescence lifetime of organic chromophores, attaching them to metal nanospheres with their molecular dipole parallel to the metal surface. The hybrid system was a modified "di-conjugated" molecular probe, 4-Acetamido-4'-maleimidylstilbene-2,2'-dithiol, covalently bound to the surface of ca. 5 nm diameter Au nanospheres by its two sulfur atoms, at a distance d < 1 nm, and with its molecular axis parallel to the

surface of the nanoparticles surface. We measured a fluorescence lifetime increase of a factor two. We also found that the fluorescence quantum yield of this hybrid system is not reduced, proof of a weak energy transfer between the molecular probe and the nanoparticle. These results demonstrate that a molecular dipole oriented parallel to the metal surface tends to be reduced by the coupling with its image.

(561) **One Step Closer to the IR Spectral Nose**

John Coates; Coates Consulting

This paper will describe a mid-IR concept that will provide both quantitative and qualitative measurement of gases. The system will come in a 4 x 4 x 2 inch package (approx.) and will perform all forms of ambient air and gas stream monitoring. The intended system will be powered by a dedicated mircoprocessor, and will be totally transportable with optional battery power (or 12VDC from a vehicle lighter connection). It will include wireless and GPS related communications. The system will use compact flash measurement modules which will provide for standard quantitative, chemometric and chemical ID algorithms. The target component cost will be under $750. A potential timetable for development is about 18 months.

(562) **Highly Accurate Trace Gas Measurements Using Cavity Ring-Down Spectroscopy and a Precision Optical Wavemeter**

Chris Rella[1], Serguei Koulikov[1], Sze Tan[1], Edward Wahl[1]; [1]Picarro, Inc.

Applications such as petrochemical process control, semiconductor gas purity, and atmospheric monitoring, have driven the need for field deployable optical analyzers with ppb sensitivity and high accuracy. Cavity ringdown spectroscopy (CRDS) and, in fact, all optical trace gas analysis techniques rely on the Beer-Lambert law relating the optical absorption coefficient to the molecular optical absorption cross-section, the optical path length, and the gas concentration. In general, the molecular optical absorption cross-section is wavelength dependent, and has the following important property: the total area (not peak maximum) of an isolated absorption line is proportional to the concentration of the gas for all pressures and broadening conditions. This simple principle has important ramifications for all spectroscopic gas sensing techniques. An instrument that uses the absorption peak maximum as a measurement of the gas concentration need only excel in the measurement of the absorption loss. However, this instrument will suffer systematic errors, due to pressure or temperature fluctuations, or changes in the background gas matrix which can affect the line broadening parameters. To take advantage of the improved accuracy provided by absorption line area measurements, the instrument must excel both in the measurement of absorption loss and the measurement of the absolute optical wavelength. To achieve a gas concentration accuracy of 1%, the line area must be measured to 1% as well, which in turn requires a spectral resolution of 0.0001 wavenumbers. Optical spectroscopies that employ incoherent light sources do not have anywhere near the required frequency resolution. Laser-based measurement methods, including CRDS, come close, with a typical resolution the order of 0.001 wavenumbers. The spectral resolution can be improved still further by incorporating a high-resolution optical wavemeter into the instrument. In this paper, we present results obtained with a commercial CRDS analyzer employing an in-line optical wavemeter with a resolution of better than 0.0001 wavenumbers. Using this analyzer we demonstrate accuracy as low as 0.1% on two complicated and challenging target gas systems: carbon dioxide for atmospheric monitoring, and hydrogen sulfide in vehicle exhaust.

(563) **Trace Gas Analysis Using Cavity Ring-Down Spectroscopy**

Wen-Bin Yan; Tiger Optics, LLC

Cavity Ring-Down Spectroscopy (CRDS) is becoming a widely used technique for detecting trace species. CRDS uses continuous wave (CW), single mode, near-infrared diode lasers that are readily available thanks to advancements in the telecommunications industry. CRDS is highly sensitive for detection of many important trace species, such as H2O, O2, CH4, C2H2, NH3, CO, CO2, NO2, N2O, HF, HCl, etc. The CRDS technique has proven particularly useful for measuring moisture in semiconductor process gases, including bulk, specialty and corrosive gases. Since moisture in these widely used gases can cause significant damage in semiconductor manufacturing, its detection is critical to yield enhancement. The current development of CRDS gas analyzers at Tiger Optics will be presented.

(564) **Designing a MEMS-scale Photoacoustic Sensor Using a Interband Quantum Cascade Laser**

David Heaps[1], Paul Pellegrino[1]; [1]Army Research Laboratory

Photoacoustic spectroscopy is a useful monitoring technique that is well suited for trace gas detection. A sensitive differential photoacoustic method for trace gas measurements is proposed. The technique also possesses favorable detection characteristics when the system dimensions are scaled to a micro-system design. The objective of present work is to incorporate two strengths of the Army Research Laboratory (ARL), Interband Quantum Cascade Laser (ICL) source development and chemical and biological sensing into a monolithic micro-electromechanical systems (MEMS) photoacoustic trace gas sensor. Previous data have show that reducing the size of the photoacoustic cell can produce a very sensitive sensor using a CO2 laser. Recent work has shown that with further reduction in the size of the photoacoustic cell and using an ICL as the source a detection limit of ~600 ppb for Dimethyl Methyl Phosphonate (DMMP) a precursor to a nerve agent. These studies involve the incorporation of an ICL source operating at ~3.45 ìm. Past experiments have begun directing the creation of a MEMS photoacoustic sensor.

(565) **Near-Infrared Optical Sensor for Monitoring NH3 using Wavelength Modulation Spectroscopy**

Mohammadreza Gharavi[1], Steven G Buckley[1]; [1]University of California at San Diego

A near-infrared optical sensor for measuring gas phase NH3 using Wavelength Modulation Spectroscopy (WMS) is discussed. The optical sensor is operated around 1512 nm in a region far from H2O absorption transitions. Due to the complexity of NH3 transitions in the absorption region, spectroscopic parameters such as line strengths, transitional frequencies, and pressure broadening coefficients are not available in the literature for several of the transitions. A method for measuring these spectroscopic parameters at different temperatures is developed and employed with a variety of collision partners over a range of temperatures. In addition, spectroscopic parameters of the H2O absorption transition closest to the selected NH3 absorption region are measured. Following this measurement, the interference of the H2O absorption on the NH3 spectra is studied. The measured parameters allow the use of Wavelength Modulation Spectroscopy to make very sensitive NH3 measurements. Based on these parameters, a detailed mathematical model for quantification of 2f signal of NH3 is developed. The results of the model for quantification of 2f signal are validated by comparing with experimental results and a very good agreement is observed.

(566) **Trace Gas Analysis With Miniaturized Mid-Infrared Sensors: From Ft-Ir To Quantum Cascade Lasers;** B. Mizaikoff[1], C. Young[1], C. Charlton[1], B. Temelkuran[2], G. Dellemann[2], L. Mechold[3], J. Kunsch[3]; [1]Georgia Institute of Technology, School of Chemistry and Biochemistry, Atlanta; [2]OmniGuide Communications, [3]Laser Components GmbH

Trace gas sensor technology in the mid-infrared (MIR) spectral range (3-20 μm) is gaining importance in process monitoring, environmental analysis, security/surveillance applications, and the biomedical field due to the increasing demand for robust sensor devices with inherent molecular specificity. Interfacing IR-transducers with continuous measurement situations in the gas and liquid phase becomes increasingly feasible with the advent of appropriate waveguide technology (e.g. MIR transparent optical fibers and planar waveguides), protective surface coatings (e.g. diamond-like carbon, sol-gels, polymers, etc.), and the availability of advanced light sources such as room-temperature operated quantum cascade lasers (QCLs) leading to miniaturized IR diagnostics.

Mid-infrared gas sensing utilizing hollow waveguides as miniaturized gas cells has been demonstrated as an effective approach for monitoring trace gases in real-time in combination with conventional FT-IR spectrometers [1]. State-of-the-art infrared sensor systems for target analysis take advantage of the unique properties of quantum cascade lasers as a light source [2,3]. The use of single mode distributed feedback (DFB) QCLs allows for the creation of wavelength-tailored waveguides matched to the laser emission frequency. Integrated mid-infrared sensing system for trace level (ppb) gas analysis combining quantum cascade lasers with an emission frequency of 10.3 μm with a frequency matched photonic bandgap hollow core waveguide have recently been developed, demonstrating the first sensing application of photonic bandgap fibers [4]. The photonic bandgap fiber simultaneously acts as a wavelength selective waveguide and miniaturized gas cell. The laser emission wavelength corresponds to the vibrational C-H stretch band of ethyl chloride gas. This sensing system enables the detection of ethyl chloride at concentration levels of 30 ppb (v/v) with a response time of 8 s probing a sample volume of only 1.5 mL in a transmission absorption measurement within the photonic bandgap hollow core waveguide. Based on this new generation of compact IR sensing platforms utilizing integrated waveguide technology for gas phase analysis, selected application examples for trace gas phase sensing in combination with FT-IR and QCLs useful for process analysis and breath monitoring will highlight today's state-of-the-art.

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(567) **Spectroscopic Monitoring of Polymerization in Microfluidic Channels**

Susan Barnes[1], Zuzanna Cygan[1], Jesse Yates[1], Kathryn Beers[1]; [1]Polymers Division, National Institute of Standards

There have been significant advances in the use of microfluidic devices for performing chemical analysis and reactions on the micrometer scale. Technology development in this field has been driven by the rewards gained from the use of microanalysis in replacement of its conventional macro-scale analogues. The small sample volumes associated with microfluidics demand application of sensitive analytical techniques for on-chip characterization of chemical species. This study demonstrates the application of fiber optic Raman and near-infrared (NIR) spectroscopy's as relatively inexpensive, portable techniques for characterization and monitoring of polymeric reactions inside microchannels. Results are presented from the application of Raman spectroscopy for combinatorial analysis of a gradient of methacrylate-based droplets formulated in a microfluidic device. Raman data have been acquired for accurate quantification of monomer composition in each droplet and degree of conversion of the particles following photopolymerization. Results have been related to optical analysis of droplet size before and after polymerization as a measurement of volumetric shrinkage. Transmission NIR is demonstrated as a suitable technique for non-invasive, high-throughput measurement of degree of double bond conversion as a function of reaction time. NIR data are presented from analysis of the solution polymerization reactions carried out in an integrated microchannel reactor. The results obtained are in agreement with those acquired from off-chip measurements of conversion acquired by NMR. The results presented from both applications demonstrate that vibrational spectroscopic techniques are effective analytical tools for screening and quantitative analysis of polymeric materials on the micrometer scale in microfluidic devices.

(568) **Environmental Monitoring of Deep Sea Hydrothermal Vents using Raman Spectroscopy**

Michelle Meighan[1], Tina Battaglia[1], Karl Booksh[1]; [1]Arizona State University

Hydrothermal vents along oceanic ridges were not discovered until the late 1970s, so much of their chemistry has yet to be elucidated. These black smokers reach temperatures of up to 400ºC and release a plethora of chemicals into their surrounding environment, especially sulfides. Studying these vents is of consequence because several different organisms utilize chemosynthesis as opposed to photosynthesis as they thrive off of the sulfides released. Raman spectroscopy is ideal to monitor different ions because of its ability to detect many compounds simultaneously, as well as the weak signal from water. In the present study, black smoker vents on the Juan de Fuca ridge in the Pacific Northwest were investigated using Raman spectroscopy. Signal enhancement was achieved through the use of silver nanoparticles.

(569) **Fluidic Devices Integrated with Uniquely Fabricated Nanocomposite SERS Features**

Michael Sepaniak, R. Maggie Connatser[1], Jenny Oran[1], Nahla AbuHatab[1], Marco DeJesus[2]; [1]University of Tennessee, Department of Chemistry, [2]University of Puerto Rico

The addition of vibrational spectroscopies to the arsenal of detection modes for microfluidics (MF) offers benefits afforded by structurally descriptive identification of electrokinetically delivered and/or separated solute bands. To create these MF-SERS devices, silver-polydimethylsiloxane (Ag-PDMS) substrate regions are integrated into the architecture of a fluidic chip also fabricated from PDMS or glass. In this talk, we investigate and improve the analytical figures of merit for integrated MF-SERS devices by

implementing improvements in fluidic and SERS substrate fabrication as well as data collection strategies. Improvements are achieved by chemical modification and physical manipulation of the PDMS channels. Additionally, a method is developed to exploit the inherent concentration profile of analyte material within an electrophoretic band in order to extend the linear dynamic range of detection of the SERS technique via spatial interrogation of the profile. Finally, we will describe approaches to create SERS substrates created via electron beam lithography (EBL) with rationally optimized enhancement factors to increase sensitivity. The effects on SERS activity of varying the sizes, shapes, and proximities of silver nanoparticles created by physical vapor deposition of the metal onto periodic polymer nanostructures will be demonstrated. These structures are fabricated directly on e-beam resist using EBL. Efforts assessing the feasibility of using these EBL created nanostructures with MF and the nanoimprint transferring of the structures will also be presented.

(570) **Surface Enhanced Raman Spectroscopy of Dipicolinic Acid on Silver Colloids Generated by Flow Injection Analysis**

Joy Guingab[1], Young Seok Kim[2], Benoit Lauly[1], Benjamin Smith[1], Nicolo Omenetto[1], James Winefordner[1]; [1]Department of Chemistry, University of Florida, [2]Department of Chemical Engineering

Surface Enhanced Raman Spectroscopy (SERS) has been explored as a tool to study biological agents. The anthrax attack in the US postal system in October 2001 intensified the need for a rapid and accurate detection of bacterial spores. Dipicolinic acid (DPA) an important biomarker used for detection of bacterial spores. The feasibility of using SERS in a continuous flow mode as a detection technique for DPA is evaluated in this study. A Raman system is employed to investigate DPA on silver colloid dispersions prepared under controlled conditions of Flow Injection Analysis (FIA). The study evaluates the experimental conditions required to obtain reproducible SERS signal from DPA molecule. Characterization of the FIA-generated silver colloids is done by absorptiometric method and Scanning Electron Microscopy (SEM). The developed SERS-FIA system will be used for silver colloid generation, sample introduction and detection of DPA in various Bacillus species.

(571) **Smart Combinatorial Operando Spectroscopy Catalytic System**

Fran Adar[1], Israel Wachs[2], Sukwon Choi[2], Nicholas Burke[1], Sergey Mamedov[1]; [1]Horiba Jobin Yvon, [2]Lehigh Univ

Introduction – There is a pent up demand in catalysis research to develop characterization methodologies that can provide molecular and electronic structural information under relevant reaction conditions with simultaneous online product analysis (termed operando spectroscopy in the literature in past few years). Only from such fundamental information will it be possible to establish molecular/electronic structure – activity/selectivity relationships for catalytic systems and to molecularly engineer advanced catalytic materials for specific targeted applications. The operando spectroscopic approach requires that the spectroscopic and catalytic information be able to provide the following: real-time generation of spectroscopic and catalytic data •molecular structures of catalytic active site telectronic structures of catalytic active sites molecular structure of surface reaction intermediates rate-determining-step surface reaction mechanism surface kinetics overall reaction kinetics spatial resolution temporal resolution (on the order of seconds or less). Experimental Methods –Optical characterization techniques can satisfy all of the operando spectroscopy (Raman, IR and UV-Vis) and microscopy requirements. There are no temperature and pressure limitations on Raman spectroscopy and current technology allows for rapid data acquisition (as fast as 1 second) and spatial resolution better than a micron. Visible Raman spectroscopy is limited to ~800 oC by black-body radiation, but this is circumvented by UV Raman spectroscopy. Raman provides molecular structural information of the catalytic active sites, surface reaction intermediates and their location on the catalyst surface. Complementary information is provided by IR, but thermal broadening limits the reaction temperature to less than ~500 oC and the strong absorption of gas phase molecules needs to be spectroscopically subtracted to enhance the vibrations originating from the catalyst surface. The IR spectroscopy acquisition time is currently better than 1 second and spatial resolution of ~10 microns can be achieved. In contrast to Raman and IR spectroscopy, UV-Vis diffuse reflectance spectroscopy (DRS) provides electronic information (oxidation states and degree of aggregation of catalytic active sites). The current temperature limit on UV-Vis DRS spectrometer systems is ~750 oC with spectral acquisition time in milliseconds and spatial resolution of ~10 microns. Temperature programmed surface reaction (TPSR) spectroscopy provides the surface mechanistic and kinetic details. Finally, real-time online product analysis with a mass spectrometer or a micro-GC can provide the desired overall catalytic activity, selectivity and kinetics.

(572) **Evaluation of Raman Spectrometry for Monitoring Powder Blending**

Pamela Allan[1], David Littlejohn[1], Alison Nordon[1], Luke Bellamy[1]; [1]University of Strathclyde

During the blending of powders, there is a need to establish in real-time, and without manual sampling, when the blend has reached homogeneity. Techniques that can be employed non-invasively are of particular interest, as it is possible that an invasive probe may contaminate the powders and/or affect the dynamics of the mixing process. Optical techniques such as near infrared spectrometry and Raman spectrometry can be employed non-invasively, but only if there is an appropriate viewing window present in the vessel. The ability to monitor the mixing of Avicel (excipient) and aspirin (active) of varying particle sizes in a high-shear laboratory-scale blender using Raman spectrometry has been investigated. Raman signals were collected using the Raman PhAT probe, which has a 6 mm diameter sample spot, larger than that of a conventional process Raman spectrometer. To investigate the effect of particle size and mass of solids on the signals obtained with a Raman PhAT probe, the analyte peak intensities were measured for pure powders and powder mixtures. During agitation of mixtures of aspirin in Avicel, the Raman intensity did not change with increasing particle size of aspirin. Also, the Raman scattering intensity of the analyte peak increased linearly with concentration during mixing. The depth of sample contributing to the Raman PhAT probe signal was also examined for both pure powders and powder mixtures, as a function of particle size. As the particle size of pure powders increased, the depth of information increased. However, both particle size and shape influenced the penetration depth. For two-component powder mixtures the information depth is influenced by the main component.

(573) **Developing New Tools for Analytical Measurements - A Horlick Legacy**

Michael Blades[1]; [1]University of British Columbia

This talk will describe the development of a novel single particle mass spectrometer for laboratory studies of aerosol aging and chemical reactivity. The system consists of an aerocol lens, TOF sizer, a tunable, short pulse IR laser for vaporization, and a stable,

high powered, broadly tunable VUV source for photoionization that can be triggered off of the TOF signal generated from sampled areosols with sizes in the 300 - 800 nm range. The analysis is carried out in an ion trap mass spectrometer allowing MS/MS characterization of the aerosol.

(574) **Individual Particle and Correlation Based Measurements: Insight into Elemental Fractionation and Particle Composition**

John Olesik; Ohio State University

Time-resolved signals measured from single particles and correlations between time-varying signals can provide insight that simply cannot be gained from time-integrated measurements. Gary Horlick demonstrated new ways to use correlation related to atomic spectroscopy for both particle analysis and processing of Fourier transform spectrometer signals. Here, the use of time resolved measurements and correlation of individual particles including particles produced from signal droplets and nanoparticles will be presented. The implications for understanding elemental fractionation and particle composition will be discussed.

(575) **Speciation with Field-Flow Fractionation Inductively Coupled Plasma Mass Spectrometry**

Ramon Barnes[1], Atitaya Siripinyanond[2]; [1]University Research Institute for Analytical Chem, [2]Mahidol University

Field flow fractionation (FFF) has become an important tool capable of separating and characterizing materials in macromolecular and colloidal size ranges. The combination of flow FFF (FlFFF) with inductively coupled plasma mass spectrometry (ICP-MS) is a powerful technique for the detailed characterization of metals in macromolecules and particles. Most applications of FFF-ICP-MS have been to natural suspended particles and colloid systems, humic substances, and clay materials. Relatively few investigations have explored biological and botanical macromolecules. Investigation of biological fluids (e.g., milk proteins, plasma proteins) and botanical fluids (e.g., food and fruit extracts) will be explored in this presentation. FlFFF-ICP-MS can characterize elemental size distributions of macromolecules in various fruit and food samples including fresh orange, fresh strawberry, tomato, mushroom, seaweed, and spinach extracts. In addition, bovine liver, fish homogenate, oyster tissue, and whole egg extracts, as well as milk and cocoa extracts, have been investigated. Unique analytical information obtained from these studies will be described. A fraction of 100 kDa) were observed in milk and cocoa samples. These applications illustrate the feasibility of FlFFF-ICP-MS for elemental size characterization of biological and botanical samples and size-based elemental speciation of macromolecules. Comparison of FFF techniques and parameters affecting separation efficiency will be described. Lastly, the capability of FlFFF-ICP-MS for providing complementary or confirmed information with the currently used techniques (e.g., CE-HPLC-, SEC-ICP-MS, and off-line ultrafiltration with element specific detection) will be discussed.

(576) **The Pro-inflammatory Potential of Ambient Particle Types**

George Agnes; Simon Fraser University

Epidemiology studies have associated particulate matter concentration in the troposphere (PM10) with increased incidence of respiratory and cardiovascular disease. The connection between the adverse health effects and inhalation exposure to elevated concentrations of PM10 is local and systemic inflammation. A developing area of interest regarding this relationship is the understanding of how particle chemical composition influences different biological outcomes. Described will be the development and application of an apparatus wherein a known number of particles of tropospherically relevant chemical composition are designed and levitated in an ac trap followed by their controlled deposition directly from the ac trap onto air-liquid interface cultured lung cells. The particle deposition process mimics particle-cell interaction as it occurs in vivo and as such it affords the capability to query the inflammation potential as a function of particle composition where the design of the particle ranges from several components to opportunities to investigate both health and climate change effects due to heterogeneous and multiphase tropospheric particle chemistry. The cellular response to dosage with numerous different particle compositions will be discussed. Several particle types exhibit synergy with respect to the extent of the downstream biological response as determined using fluorophore-labeled antibodies in a fluorescence assay. We have observed that, for a given particle type, there is a threshold particle dose regarding the extent of cellular injury, as indicated by a switching of the differential expression of intercellular adhesion molecule (ICAM)-1 from being localized at the site of particle deposition to widespread upregulation of ICAM-1 across the entire cell-culture. This finding suggests there is potential to investigate local versus systemic thresholds in vitro using this technology. In addition, we are incorporating standard as well as non-standard proteomic methodologies into our procedures to enable the measurement of multiple downstream biological responses, specifically pro-inflammatory cytokines, secreted from lung cells dosed with particles.

(577) **Looking for Many Elements in Small Samples With a Complex Matrix: It Doesn't Have to be Painful**

James A. Holcombe; The University of Texas

With the advent of time-of-flight mass spectrometers (TOFMS) coupled to ICPs, multimelement analysis no longer requires a trade off of masses monitored and duty cycle, viz., loss in S/N. Partially as a consequence of this capability, successful coupling of transient sources to ICPMS also becomes much more viable. Thus, introduction techniques such as HPLC, GC, CE, FIA etc. provide millisecond time resolved signals with temporal synchronization of all masses monitored as well as improved isotopic ratio measurements. Electrothermal vaporization (ETV) also benefits from the simultaneous mass detection and permits multielement analysis from microsamples with complex matrices. The thermal program of the ETV can be combined with the time resolved MS signal from an ETV-ICPTOFMS to minimize many isobaric interferences that can plague many analyses.

(578) **Ideal Analytical Spectroscopy**

Gary Horlick; University of Alberta

At the 1994 Pittcon symposium entitled "Pioneers in Analytical Chemistry", Howard Malmstadt commented that new developments "...often start with a simple question or comment. Why wouldn't this work? There must be a better way! What would be the 'ideal' way? It takes too much time to do it that way! How can we make it available to others?" These questions and comments, particularly, "What would be the 'ideal' way", were often the driving force of many "blue-sky discussions" that occurred during Malmstadt research group seminars at the University of Illinois. These blue-sky discussions primed his students to be early participants in many of the developments that occurred in analytical spectroscopy over the last four decades. In this presentation I will briefly review some of our own work dealing with photodiode arrays, Fourier transform spectroscopy, inductively coupled plasma atomic emission and mass spectrometry and electrospray mass spectrometry that was inspired by the elusive goal of developing the ideal analytical spectroscopy technique.

(579) **Microfluidic Bioanalysis Systems Formed Using Sacrificial Layer Methods**

Adam Woolley[1], Bridget Peeni[1], Milton Lee[1], Aaron Hawkins[1]; [1]Brigham Young University

Microfluidic systems are being applied increasingly in the analysis of biological molecules. However, the construction of high-performance devices remains an obstacle to the widespread utilization of microchips in protein analysis. Although simple fabrication is possible in materials such as poly(dimethylsiloxane), protein separation performance in this elastomer is suboptimal; on the other hand, glass microdevices provide much higher separation quality, but microchip manufacturing is more cumbersome. Thus, we have focused on developing improved methodologies for assembling microdevices, to enhance protein and peptide characterization. We have recently demonstrated a phase-changing sacrificial layer approach that allows facile solvent bonding of polymer microchips.1 Moreover, this same sacrificial layer technique can be applied in interfacing ionically conductive hydrogels with microfluidic channels, to enable on-chip protein preconcentration or electric field gradient focusing.2 We have also developed a thin-film sacrificial layer method for making glass microdevices for electrophoretic analysis of amino acids.3 We report here a tenfold improvement in the separation performance of these thin-film microfluidic systems and a six-fold decrease in analysis times, relative to our earlier work. In addition, we have applied these thin-film microchannels in peptide and protein separations. Advances in microchip fabrication using sacrificial layers should facilitate the rapid characterization of proteins and peptides. References Kelly, R.T.; Pan, T.; Woolley, A.T. Phase-Changing Sacrificial Materials for Solvent Bonding of High-Performance Polymeric Capillary Electrophoresis Microchips. Anal. Chem. 77, 3536-3541 (2005). 2.\tKelly, R.T.; Li, Y.; Woolley, A.T. Phase-Changing Sacrificial Materials for Interfacing Microfluidics with Ion-Permeable Membranes to Create On-Chip Preconcentrators and Electric Field Gradient Focusing Microchips. Anal. Chem. 78, 2565-2570 (2006). 3. Peeni, B.A.; Conkey, D.B.; Barber, J.P.; Kelly, R.T.; Lee, M.L.; Woolley, A.T.; Hawkins, A.R. Planar Thin Film Device for Capillary Electrophoresis. Lab. Chip. 5, 501-505 (2005).

(580) **Understanding the Utility of Fluorescent Dyes as Noncovalent Labels for Protein Assays by Capillary Electrophoresis with Laser-Induced Fluorescence Detection.**

Christa Colyer[1], Weiying Yan[2], Amy Sloat[1], Anthony Gerardi[1], Jennifer Lubbeck[1]; [1]Department of Chemistry, Wake Forest University, [2]Dept of Physiology and Pharmacology, WFU

Noncovalent interactions between fluorescent probe molecules and protein analyte molecules, which typically occur with great speed and minimal sample handling, form the basis of many high sensitivity analytical techniques. Understanding the nature of these interactions and the composition of the resulting complexes represents an important area of study that can be facilitated by capillary electrophoresis. Specifically, we will present how frontal analysis and Hummel-Dreyer methods can be implemented with CE to determine association constants and stoichiometries of red luminescent squarylium dyes Red-1c and Red-3 with various model proteins. By adjusting solution conditions, such as pH or ionic strength, it is possible to selectively modify the binding process. For example, reducing the pH of the separation buffer from 9.5 to 6.5 reduces the association constant for bovine serum albumin with Red-1c by more than two orders of magnitude, thus illustrating the important role of electrostatic interactions in these noncovalent dye-protein complexes. Dyes such as these or even longer wavelength near-IR dyes can be used to effectively label a mixture of proteins in on-column derivatization procedures. On-column derivatization is generally simpler and more sensitive than pre-column methods. LODs ranging from 10-7 to 10-10 M are routinely achieved by on-column labeling of model proteins with Red-3 and Red-1c dyes in our CE-LIF studies. Although the use of high salt buffers in these methods has afforded some improvements in separation efficiencies, we have also studied the utility of various surfactant coatings with this goal in mind. Specifically, two-tailed, cationic surfactants, such as 2C14DAB, 2C16DAB, or 2C18DAB, have been shown by others to produce simple, robust capillary coatings, and we have found that they can be used even in the presence of fluorescent probes to improve separation efficiency without adversely affecting background fluorescence and sensitivities. Electroosmotic flow is reversed in these coated columns, but they are compatible with acidic buffer systems, such as formate and acetate, which have previously been used for the resolution of noncovalently labeled protein mixtures in uncoated columns in our laboratory, and so modifications to separation methods are minimal upon adoption of surfactant coated columns in this work.

(581) **Non-SELEX Selection of Aptamers with Kinetic Capillary Electrophoresis**

Maxim Berezovski[1], Michael Musheev[1], Andrei Drabovich[1], Sergey Krylov[1]; [1]York University

Aptamers are typically selected from libraries of random DNA (or RNA) sequences by SELEX, which involves multiple rounds of alternating steps of partitioning and PCR amplification. Here we report, for the first time, Non-SELEX selection of aptamers – a process, which involves repetitive steps of partitioning with no amplification between them. A highly efficient affinity method, non-equilibrium capillary electrophoresis of equilibrium mixtures (NECEEM), was used for partitioning. We found that three steps of NECEEM-based partitioning in the Non-SELEX approach were sufficient to improve the affinity of a DNA library to a target protein by more than four orders of magnitude. The resulting affinity was higher than that of the enriched library obtained in three rounds of NECEEM-based SELEX. Remarkably, NECEEM-based Non-SELEX selection took only one hour in contrast to several days or several weeks required for a typical SELEX procedure by conventional partitioning methods. In addition, NECEEM-based Non-SELEX allowed us to accurately measure the abundance of aptamers in the library. Not only does this work introduce an extremely fast and economical method for aptamer selection but it also suggests that aptamers may be much more abundant than they are thought to be. Finally, this work opens the opportunity for selection of drug candidates from libraries of small molecules, which cannot be PCR-amplified and thus are not approachable by SELEX

(582) **Analysis of Environmentally Important Phenolic Compounds by Capillary Electrophoresis using Fused Silica Capillaries Coated with Montmorillonite.**

Maria Fernanda Mora[1], Carlos Garcia[1]; [1]Univ. of Texas at San Antonio

Recently, there has been a growing concern regarding the consequences of exposure of wildlife and humans to phenolic pollutants. Phenolic compounds are widely used in industrial processes, in pharmaceutical products, as antiseptics, and in agriculture. Due to its toxicity, phenols have been included in the US Environmental Protection Agency (EPA) list of priority pollutants. Different analytical methods have been proposed to analyze phenols, among them, capillary electrophoresis (CE) has proven to be a very attractive technique offering speed, small sample and solvent volumes, low cost and the possibility of miniaturization. Different approaches have been used to improve separations in CE by using coatings of the capillary surface. In this

work, a simple procedure for coating of fused silica capillaries with poly(diallyldimethyl ammonium chloride) (PDDA) and K+-montmorillonite (MMT) is presented. The coated capillaries were characterized measuring the EOF as function of the pH of the background electrolyte, the number of layers of PDDA and K+-montmorillonite and the stability. The PDDA-MMT coated capillaries were used for the effective separation of nine environmentally important phenolic compounds showing a significant improvement in the resolution compared to bare fused silica capillaries. The coated capillaries were very stable allowing repetitive analysis for several days. The electroosmotic flow (EOF) of the coated capillaries is pH-independent which offers the possibility of optimizing the pH for the separation without altering the EOF.

(583) **Characterization of Selected Aptamer Binding Affinity towards Campylobacter Jejuni Employing Capillary Electrophoresis**

Sun McMasters[1], Dimitra Stratis-Cullum[1]; [1]US Army Research Laboratory

Biological molecules that are capable of recognizing whole bacteria cells with high affinity and selectivity have been identified and evaluated. Specifically, molecular recognition abilities of DNA aptamers, screened against Campylobacter jejuni via a systematic evolution of ligands using the exponential enrichment process in vitro, have been examined using capillary electrophoresis with laser induced fluorescence detection. To enhance the sensitivity of the analysis, these aptamers and Campylobacter jejuni were labeled with 6-carboxyfluorescein and stained with SYTO9, respectively. The relative binding affinity of each aptamer was assessed using nonequilibrium capillary electrophoresis of the equilibrium mixture (NECEEM) immunoassay. Preliminary data indicated that these three aptamers possess differing binding affinities, one of which presents a promising candidate as an anti-Campylobacter jejuni aptamer. Furthermore, cross-reactivity of these aptamers with other food-borne pathogens including Escherichia coli O157:H7, Listeria genus, Borrelia burgodorferi, and Salmonella typhimurium were examined by fluorescence microscopy, along with capillary zone electrophoresis. This presentation will include a discussion of the selectivity and specificity of the aptamers towards Campylobacter jejuni suggesting the potential for integrating and selecting aptamers for use in a variety of biosensing applications.

(584) **Study of Electroosmotic Flow and Electrophoretic Mobility in Discontinuous Solutions in Capillaries Using Periodic Photobleaching of Neutral and Negative Fluorophores**

Yohannes H. Rezenom[1], Gervas E. Assey[1], Funda Kizikaya[1], S. Douglass Gilman[1]; [1]Louisiana State University

We report experimental studies of electroosmotic flow (EOF) dynamics in capillaries filled with zones of solutions that are discontinuous in pH, ionic strength, and composition. Electroosmotic flow was monitored in a capillary using a method based on periodic photobleaching of a neutral dye (coumarin 334) added to a separation buffer. A negatively charged fluorophore (fluorescein) was added to the separation buffer to study changes in the potential field based on the electrophoretic mobility of fluorescein while simultaneously monitoring the electroosmotic flow rate using coumarin 334. Both coumarin 334 and fluorescein were separated and detected using capillary electrophoresis with laser-induced fluorescence (LIF) detection. Using this method, effects of injected zones of different buffer concentrations and pHs other than the separation buffer were studied. This research will serve as a basis for comparing experimental studies to theoretical models that will lead to improved models describing EOF and electrophoretic mobilities.

(585) **Developments and Applications of Low and Medium Flow Nebulization for ICP-MS and ICP-AES**

Fred Smith; CETAC Technologies

Over the last decade low-flow nebulizers have proved very useful for sample introduction, particularly with ICP-MS instrumentation. Important benefits have included the analysis of volume-limited and highly corrosive (ex. HF-containing) samples in areas such as geology and semiconductors. The first part of this paper will describe recent improvements in the use of low-flow nebulizers with membrane desolvation coupled to ICP-MS. Benefits have included signal enhancement and the reduction of solvent-based interferences. Nonetheless, care must be taken to reduce electrostatic effects from polymer components and the buildup of solvent vapor from the use of higher (> 100 microliter/min) uptake rates. The latter is especially desired for even higher analyte sensitivity. The second part of the paper will describe the use of a medium flow (400 microliter/min) nebulizer for ICP-AES. The aim is to match the analyte sensitivity of a higher flow (1.5 to 2.0 mL/min) conventional nebulizer with a minimum amount of sample waste.

(586) **Nano-HPLC-Plasma Mass Spectrometry for Arsenic Speciation**

Akbar Montaser[1], Maryam Farmand[1], Jessica Gray[1], Kaveh Kahen[1], Sue-Ann O'Brien-Murdock[1], Ryan Brennan[1], [1]The George Washington University

Arsenic has important applications in industry such as smelting, glass making, semiconductor manufacture, and mining, but it is also a dangerous pollutant. When introduced into the environment, arsenic takes different forms that vary in toxicity from harmless organic compounds to hazardous inorganic species. Exposure to the inorganic species may lead to several illnesses, including cancer, neurological disorders, and cardiovascular diseases. Distinguishing different forms of arsenic is therefore important. Conventional high performance liquid chromatography (HPLC) coupled to inductively coupled plasma mass spectrometry (ICPMS) offers high sensitivity and element specific selectivity in arsenic speciation, but it requires a large amount of sample and expensive mobile phases. A nano-HPLC-ICPMS method is developed, using a demountable direct injection high efficiency nebulizer, to reduce sample and mobile phase consumption, minimize organic waste generation, reduce analysis time, and enhance separation efficiency.

(587) **The Roles of Evaporation and Aerosol Charging in Approaching 100% Aerosol Utilization from Sub-Microliter Samples in Elemental Analysis and CE-ICP-MS**

Noel Casey[1], John W. Olesik[1]; [1]Ohio State University

Elemental speciation analysis of sub-microliter samples by Capillary Electrophoresis ICP-MS requires high aerosol transport efficiency and minimal band broadening in order to quantitatively determine sub-ppb concentrations. Sample introduction system optimisation has minimised band broadening but the impact of such changes on aerosol transport has not been directly assessed. Sample transport efficiency approaching 100% can be only obtained if nebulisation occurs at a low total solution flow rate (~10 µL/min) and if the aerosol evaporates before impacting the walls of the spray chamber. If the aerosol does not have sufficient time to evaporate, analyte will be lost to the spray chamber walls while decreasing analyte transport efficiency into the ICP. Recent results indicate that when a high voltage is applied for CE, the nebulised aerosol becomes highly charged. The charged aerosol impacts the spray chamber walls much more readily than when no voltage is applied to the CE capillary inlet. This results in a three to five-fold decrease in analyte transport efficiency and analyte signal. Once the spray chamber becomes wet, evaporation of water from the

walls competes with evaporation of aerosol entering the spray chamber thus decreasing the overall evaporation rate. This happens even when the total solution flow rate to the nebuliser is 10 μL/min and the Ar gas is not fully saturated with water vapour at room temperature. Then the analyte transport efficiency into the ICP falls far below 100%. Excess charge on the nebulised aerosol can be effectively neutralised by using a radioactive Po-210 source. Alpha particles, produced by the source, ionise the surrounding nebuliser gas into highly charged bipolar ions which are neutralised by combining with charges of opposite polarity on the aerosol. This is independent of the voltage polarity used in CE. Experimental results show that the Po-210 source can neutralize the charged aerosol, and if the spray chamber walls remain dry, then analyte transport efficiency greater than 50% can be obtained. Signals are then independent of the voltage applied to the electrophoresis capillary which means that only minor improvements in sensitivity are possible by using lower total solution flow rates in a CE-ICP-MS interface.

(588) **Ion Chemistry and Conformation Change with Spraying Modes in Electrosprays**

Peter Nemes[1], Ioan Marginean[1], Akos Vertes[1]; [1]George Washington University

Based on spray current measurements in 1998, Juraschek and Röllgen identified three main axial modes I (burst regime), II (pulsating Taylor cone regime) and III (cone-jet regime), in electrosprays. These modes have been shown to correspond to different electrohydrodynamics at the electrified meniscus but their correlation with the chemistry of the spray plume in largely unexplored. Here we report on some relationships between the electrospray modes, the spray characteristics and the chemistry of the produced ions. Solutions of 50% (v/v) methanol, 3-methoxybenzylpyridinium chloride (3MO-BP), reserpine, cytochrome c and ubiquitin were electrosprayed against a stainless steel counter electrode. Spray current measurements and fast Taylor cone imaging were used to characterize the established spraying modes. The electrospray emitter voltage and the flow rate were adjusted to induce particular spraying regimes, and the size and the velocity distributions of the corresponding droplets were measured by phase Doppler anemometry. Simultaneously, mass analysis of the produced ions helped to reveal their yield and chemical composition. Depending on the flow rate and the applied voltage on the needle, multimodal droplet size distributions were observed along the axis of the spray. Upon changing these parameters, profound changes were observed in the droplet size distributions. Under certain operating conditions production of small droplets with uniform size distribution was observed. A magnitude higher ion counts were detected in axial III spraying mode, showing improved ionization efficiency. Survival yield measurements of the thermometer molecule and reserpine showed that in this spraying regime gentler fragmentation conditions was achieved and the electrochemical oxidation was suppressed. A change in the spraying regime from axial II to axial III was followed by a noticeable shift in the charge state distribution of proteins indicating slight conformational changes.

(589) **A Dual-Source Inductively-Coupled Plasma/Electrospray Ionization Time-of-Flight Mass Spectrometer for Comprehensive Elemental Speciation.**

Steven Ray[1], Gary Hieftje[1], Duane Rogers[1], David Koppenaal[2]; [1]Indiana University, Department of Chemistry, [2]Pacific Northwest National Laboratory

The importance of elemental speciation analysis derives from the fact that the toxicity, bioavailability, and environmental impact of metals and metalloids are determined by both the concentration and the chemical form of an element. Thus, the successful application of modern analytical atomic spectrometry to many biochemical and environmental studies requires a method that is capable of directly quantitating elements amongst their various chemical forms. Here, a unique time-of-flight mass spectrometer (TOFMS) capable of analyzing ions from two (or more) ion sources in a simultaneous fashion is examined as a means of comprehensive elemental speciation. These sources take the form of one 'atomic' ionization source and one 'molecular' ionization source. The atomic source, here an inductively coupled plasma (ICP), produces exclusively atomic ions from the sample, establishing the identity, isotopic distribution, and concentrations of elements with high sensitivity and wide dynamic range. The 'molecular' ionization source, here electrospray ionization (ESI), provides chemical information concerning the metal, metalloid, or non-metal-containing species in the sample. The parent-ion mass, and potentially structural information provided through m/z-fragmentation can then be used to elucidate the chemical form, covalent and non-covalent associations, and even detect those species that are not associated with a particular element at all. Because both sources of information are concurrently monitored by a common TOFMS, complete atomic, isotopic, and molecular mass-spectral information is available simultaneously. The use of TOFMS in this role also permits the entire mass range to be observed with high temporal resolution, without spectral skew, and with spectrometer conditions that can be rapidly modulated. Coupling this system with chromatographic separations is particularly advantageous, as run-to-run variations are eliminated, and unknown or unexpected components within a sample can be directly identified. Thus, the atomic and molecular speciation information that is conventionally collected by multiple analyses is obtained in a single step. Design criteria, current experimental capabilities, and future embodiments of this novel instrument will be discussed.

(590) **LIBS for Quantitative Aerosol Analysis: Plasma Interactions and Analyte Response**

David Hahn[1], Bret Windom[1], Prasoon Diwakar[1]; [1]University of Florida

The application of LIBS for aerosol analysis is discussed, including quantitative analysis of individual submicron-sized particles. Single-shot LIBS analyses of aerosols raises new questions regarding the precision of the analyte signal, the calibration response and the dependency of analyte phase, and analyte homogeneity within the laser-induced plasma. These issues are all related to the fundamental interactions between the laser-induced plasma and individual aerosol particles. Recent experiments exploring the temporal evolution of the plasma-particle interaction are presented, including direct measurement of atomic diffusion with in the plasma, along with single-pulse and dual-pulse methodologies as related to understanding and improving the analyte response of single-aerosol particles within laser-induced plasmas. The latter topic is investigated in detail using both gas-phase and aerosol species. In consideration of a range of spectroscopic and plasma transmission data, the plasma-analyte interactions realized with a dual-pulse methodology are explained in terms of the interaction with the initially expanding plasma shock wave, which differs between gaseous and particulate phase analytes.

(591) **Infrared Spectra of Gaseous Ions**

John Eyler[1]; [1]University of Florida

Mass spectrometry (particularly Fourier transform ion cyclotron resonance - FTICR - mass spectrometry) can easily distinguish ions of different mass, even those with extremely small mass differences. However, differentiation of isomeric ions has

traditionally relied on indirect methods based on differing reactivity or fragmentation patterns. A much more direct approach is to obtain the infrared spectra of isomeric ions, since different isomers are expected to have a number of normal modes of differing frequencies. With support from the National High Field FT-ICR Facility at the National High Magnetic Field Laboratory (NHMFL) we have recently coupled an FTICR mass spectrometer (4.7 T magnet) with a free electron laser (FEL) which produces continually tunable infrared radiation in the mid-infrared range from ~250 – 2000 cm-1. Using the approach of infrared multiple photon dissociation (IRMPD), spectra of a number of interesting ions have been obtained. These range from small, metal-attached cyclic compounds through mono- and di-saccharides and peptides to intact, multiply-charged proteins. The important features of the FTICR-FEL instrumentation will be presented and results from the laboratories of both the author and a number of other collaborators/users will be described.

(592) **Development of nLC-dualESI-FT-ICR MS and it Applications in Cancer and Cardiovascular Plasma Proteomics**

David Muddiman[1], Adam Hawkridge[1], Yuko Ogata[2], William Cliby[3], John Burnett[3]; [1]North Carolina State University, [2]Seattle Biomedical Institute, [3]Mayo Clinic College of Medicine

This presentation will describe our efforts at developing nLC dualESI-FT-ICR Mass Spectrometry for discovering novel biomarkers for Ovarian Cancer in Plasma in conjunction with orthogonal techniques including 2D-PAGE, PTM specific stains and Western Blots. This presentation will also describe our efforts at developing FT-ICR MS for understanding and quantifying specific protein biomarkers used in cardiovascular research.

(593) **Rapid de-novo Terminal Domain Assignment of CAD Fragments from Intact Proteins**

PaulSpeir[1], Michael Easterling[1], Christian Berg[1]; [1]Bruker Daltonics, Inc.

Top-down sequencing of proteins combines information from measurements of intact protein molecular weight with fragmentation from a variety of dissociation techniques. For known proteins, fragments can be compared against the putative sequence to localize modifications. The difficulty of this approach increases if the nature of the modification is either unknown or occurs in the presence of other modifications or mutations. Sequence verification of either the N or C termini of proteins is quite useful for this type of analysis and can concurrently verify the protein identification and localize modifications to a specific terminus. Without chemical modification, intact protein dissociation methods generally cannot localize fragments to either side of the protein without using sequence information. Our experiments test the effectiveness of a new approach that combines CAD in the ion funnel source region of a hybrid Qq-FTICR followed by fragment isolation in the Q-region and ECD in the ICR cell. Since 'b' type ions are known to lose a CO group from the C terminus during ECD, we can quickly generate domain assignments based on a 28 Da neutral loss tag without using sequence information. Observation of the 28 Da shift is used as a tag to indicate a particular fragment originates from the N terminus of the intact protein. A statistical treatment of this methodology will be reported as well as several examples relevant to biological interest.

(594) **Mass Spectral Studies of Bioactive Chromium Peptides**

Carolyn Cassady[1], Jungie Gao[1]; [1]The University of Alabama

Chromium-containing peptides, such as chromodulin, are important in the carbohydrate metabolism of mammals. These peptides are believed to play a role in diabetes, which is a major human health concern. However, chromodulin and its analogs have defied amino acid sequencing by both solution-phase techniques and mass spectrometry. Sequencing of these peptides is complicated by their high percentage of acidic residues, the multiple attachments of covalently bound chromium(III) ions via oxygen linkages, and the presence of disulfide bonds. This presentation will discuss our efforts to use electrospray ionization/Fourier transform ion cyclotron resonance (ESI/FT-ICR) and matrix-assisted/time-of-flight (MALDI/TOF) mass spectrometries to sequence chromodulin. Tandem mass spectrometry (MS/MS) involving both collision-induced dissociation (CID) and post-source decay (PSD) has been employed. Chromodulin has been isolated from the livers of cow (bovine), chicken, and alligator. Bovine chromodulin has been our focus because it is believed to most closely resemble human chromodulin. Bovine chromodulin yields MS/MS spectra that are not readily interpretable, probably due to the presence of four bound chromium ions. The parent ion signal with chromium present in chromodulin is also of low intensity. Solution-phase procedures for removing chromium from the peptide are under development in collaboration with the group of Dr. John Vincent at the University of Alabama. Also, two model peptides that are believed to have peptide sequences very similar to that of bovine chromodulin have been synthesized in our laboratory. When chromium is not present, these peptides give easily interpretable MS/MS spectra by both CID and PSD. The additional of chromium causes the ion signals to drop dramatically by both ESI and MALDI and complicates the resulting mass spectra. However, MS/MS studies on these compounds with chromium bound to known peptide sequences have assisted our understanding of how chromium ions affect mass spectral fragmentation.

(595) **Memory of Hydrophobic Component in Lipid-Peptide Binding as Observed by Nano-ES-FT-ICR**

Richard Cole[1], Yan Li[1], Frédéric Heitz[2], Christian Le Grimellec[3]; [1]University of New Orleans, [2]CRBM CNRS-FRE, [3]CBS INSERM

Nano-electrospray Fourier Transform – Ion Cyclotron Resonance mass spectrometry (nano-ES-FT-ICR-MS) has been used to investigate noncovalent associations between lipids and fusion peptides (subunits of viral proteins that insert into the lipid-rich host cell membrane to initiate disease propagation). While the electrostatic component of noncovalent binding is known to be strengthened upon passage from solution into the gas phase, any hydrophobic component will be weakened as the final solvent molecules depart. Nevertheless, strong evidence has been compiled to demonstrate the importance of the initial hydrophobic interaction to the observation of lipid-peptide binding by nano-ES-FT-ICR-MS. To establish that the association is hydrophobically driven, binding is shown to: 1) be disrupted by addition of organic solvents, 2) exhibit a temporal component, and 3) be strengthened by an initial increase in ionic strength. Memory of the solution-phase hydrophobic interaction is thus preserved in the gas phase, and we demonstrate the possibility to employ nano-ES-FT-ICR-MS for the study of such hydrophobic associations. These findings regarding lipid-peptide binding establish that mass spectrometry may contribute to the detailed understanding of viral infections that are initiated via insertion of fusion peptides into a healthy cell membrane.

(596) **Single Molecule Detection and Spatial Multiplexing: Detection of Rare Events for Clinical Diagnostics**

Steven Soper, Louisiana State University

We are developing systems that can molecularly count low abundant markers from mixed populations, which can provide diagnostic information for a number of different diseases. Since the effective clinical assessment of most diseases requires a panel of markers that must be simultaneously interrogated, spatial

multiplexing is being employed during readout using a single molecule detection format to provide high sensitivity and specificity. In this presentation, we will give examples of polymer-based microfluidic systems for performing LDR/spFRET, which uses an allele-specific ligation reaction (Ligase Detection Reaction, LDR) coupled to single pair Fluorescence Resonance Energy Transfer (spFRET) to score the presence of mutations in genomic DNA. Using a clinically relevant system, point mutations in K-ras oncogenes, which provide high diagnostic value for colorectal cancers, were evaluated. A flow-through biosensor assembly was fabricated, which consisted of two different microfluidic chips; a polycarbonate, PC, chip for performing the LDR and a poly(methyl methacrylate), PMMA, chip for the detection of the LDR products using spFRET. Previous work in our laboratory demonstrated the ability to couple LDRs with single-pair fluorescence resonance energy transfer (LDR-spFRET) using molecular beacons to detect point mutations in DNA in a microchip (Wabuyele et al., Journal of the American Chemical Society 125, 2003, 6937). To expand the readout into a multiplexing format, a micro-fluidic device was designed to test for 19-point mutations simultaneously by imaging laser excitation zones onto an array of pixels of a CCD camera. The fluorophores are illuminated using a diode laser launched into an embedded waveguide that irradiates a series of flow cells. The waveguide consists of SU-8, a negative tone resist, which was embedded in PMMA. The waveguide also contains a free-standing microlens to couple light from one waveguide into another across a series of microchannels, with each channel looking for a single mutation (spatial multiplexing). For single molecule detection, the CCD is operated in a time-delayed integration mode to build the signal to noise ratio as well as the duty cycle for single molecule readout.

(597) **High-Resolution, Low-Temperature Fluorescence Methods: What Can We Learn From Them?**

Freek Ariese[1], Arjen N. Bader[1], Joost de Klerk[1], Cees Gooijer[1]; [1]Laser Centre Vrije Univ. Amsterdam, Netherlands

Fluorescence spectroscopy is widely regarded as a sensitive technique, but in solution the spectra are generally featureless. Inhomogeneous broadening from the surrounding solvent or matrix obscures the underlying information. This means that fluorescence spectra are not very useful for identification, and mixtures of compounds cannot be analyzed without separation. Similarly, spectral broadening is a problem when studying photophysical phenomena, conformational changes, or the interaction between a fluorescent probe and the matrix. There are two cryogenic approaches that we can use to obtain high-resolution spectra in the condensed phase: matrix-induced narrowing in polycrystalline n-alkane lattices (Shpol'skii spectroscopy), and fluorescence line-narrowing (FLN) spectroscopy in which a narrow-banded laser source is employed to select a subset of molecules with equal S0-S1 energy differences from an inhomogeneously broadened population. This subset or isochromat will yield narrow-banded emission since in the frozen matrix at 5 K conformations are unlikely to change during the lifetime of the excite state. Examples from several recent studies will demonstrate the power of these cryogenic techniques. Photophysical experiments were carried out in n-octane matrices and provided insight into the mechanisms and rates of proton transfer reactions in several systems. As regards life science applications: FLN spectroscopy does not require special solvents and is therefore often the method of choice. Matrix-induced changes in FLN spectra were used to study ligand-receptor and probe-protein interactions.

(598) **Low-Temperature Luminescence Studies of Europium Complexes with Humic Acids and Well-Defined Model Ligands**

Michael Kumke[1], Bettina Bettina Marmodee[1], Freek Ariese[2], Joost de Klerk[2], Cees Gooijer[2]; [1]University of Potsdam, [2]Vrije Universiteit of Amsterdam

The transport and fate of metal ions in the environment is to a large extent determined by complexation equilibria with humic substances (HS), i.e., mixtures of degradation products from plant or animal origin. In order to investigate the metal complexation with these heterogeneous ligands, the application of luminescence probes is very promising. Lanthanide ions such as Eu3+ are especially valuable since they show an intrinsic luminescence and the accompanying parameters (e.g., decay time, quantum efficiency, and wavelength of the luminescence transitions) are strongly dependent on the molecular environment. At low temperature, the spectral bandwidth of the luminescence is reduced and a more detailed picture of energetically different binding sites of Eu3+ to HS can be obtained. In addition to Eu-HS complexes, suitable model compounds with well-defined binding sites such as salicylic acid and various hydroxylated benzoic acids, representing substructures of HS binding sites, were also investigated to help interpret the results and derive structural information. Luminescence line-narrowing spectroscopy (LLNS) were carried out at 5 K, in which the laser was scanned through the 5D0 - 7F0 transition of Eu3+ ion and emission to the 7F1 levels was recorded. Surprisingly, high-resolution excitation-emission contour plots with positive or negative slopes showed an unusual line-narrowing effect, indicating non-random correlations between the different F levels in the inhomogeneous matrix. Indicating strong effects of the ligand field on the energy splitting of F and D levels. Due to symmetry and charge effects the obtained luminescence pattern was characteristic for different complexes. From the comparison with the model compounds it is concluded that in the complexes of HS and Eu3+ the carboxylic groups are dominating the metal binding. Contributions from chelate binding like it is found in complexes with salicylic acid were not observed. Furthermore, the LLNS measurements also revealed that a considerable time (in the order of days) is needed for the distribution of complexes formed to reach equilibrium.

(599) **New Experimental and Instrumentation Measuring Fluorescence and Phosphorescence Quantum Yields at Liquid Nitrogen and Helium Temperature**

Andres Campiglia[1], Shenjiang Yu[1], Huiyong Wang[1]; [1]Dept. of Chemistry University of Central Florida

We present a unique approach to measuring fluorescence and phosphorescence quantum yields at 77K and 4.2K. Measurements are performed with a single instrument capable to recording absorption, fluorescence and phosphorescence spectra at low temperature. Excellent reproducibility of measurements is obtained with the aid of a cryogenic fiber optic probe. Absorption measurements are performed by monitoring the scatter intensity of a pulsed tunable dye laser with a spectrograph and an intensified charge-coupled device (ICCD). Time-resolution and luminescence (fluorescence and phosphorescence) lifetime measurements are accomplished with the aid of a pulsed delay generator. An experimental procedure is presented to determine fluorescence and phosphorescence quantum yields of polycyclic aromatic hydrocarbons in Shpol'skii matrixes.

(600) **Terahertz Attenuated Total Reflection Spectroscopy**

David Newnham[1], Axel Zeitler[1, 2, 3], Philip Taday[1]; [1]TeraView Limited, [2]University of Cambridge, England, [3]University of Otago, New Zealand

Terahertz pulsed spectroscopy (TPS) is a novel spectroscopic technique for characterizing crystalline materials. It provides sensitive detection of subtle differences in the crystalline structures of materials and readily distinguishes and quantifies polymorphic forms. In this paper terahertz attenuated total reflection (ATR) hardware and techniques are described. Terahertz ATR has the advantage of minimal sample preparation for rapidly recording absorption spectra. The performance characteristics of ATR modules with different angles of incidence are reported with example terahertz spectra of solid, powder, and liquid samples.

(601) **Terahertz Attenuated Total Reflection Spectroscopy for Pharmaceutical Analysis**

J Axel Zeitler[1,2,3], Mike Claybourn[4], David A. Newnham[3], Philip F. Taday[3], Michael Pepper[2,3], Keith C. Gordon[5], Thomas Rades[1]; [1]School of Pharmacy, University of Otago, NZ, [2]Cavendish Lab, University of Cambridge, [3]TeraView Limited, Cambridge, UK, [4]AstraZeneca, Macclesfield, UK

Utilising pulsed coherent radiation in the far-infrared region of the electromagnetic spectrum (2 cm-1 to 133 cm-1), terahertz pulsed spectroscopy (TPS) has proven to be a very versatile novel spectroscopic technique to characterize crystalline materials. Radiation at this energy level is probing phonon modes and hydrogen bonding vibrations, linked directly to the crystal structure. In the pharmaceutical setting TPS has been demonstrated to distinguish and quantify polymorphic forms and different hydrate forms. It has been used for the study of solid state reactions and a number of other applications have been demonstrated. However, all this experiments were performed in transmission setup. Here, we describe how attenuated total reflection (ATR) can be used as a new sampling technique to acquire terahertz spectra of pharmaceutical materials. For different crystalline forms of pharmaceutical drugs the sample preparation and spectral acquisition is described. A comparison of the ATR spectra with transmission spectra is presented and the specific differences between the two sampling techniques are discussed.

(602) **Terahertz Spectroscopic Imaging for Non-Destructive Pharmaceutical Film Coating Analysis**

Ryanne N. Forcht[1], Robert P. Cogdill[1], Richard Creekmore[2], James K. Drennen[1]; [1]Duquesne University, [2]AstraZeneca

Besides providing the mechanism for the safe and convenient delivery of accurate dosage, tablets are coated for the protection of a drug substance from the destructive influences of atmospheric oxygen or humidity, or from the destructive influence of gastric acid after peroral administration, etc. However, if coatings are nonuniform or contain surface defects, the desired dose delivery and bioavailability may be compromised. In this study, coating thickness uniformity at both the tablet and batch levels, were explored. Two coating types were considered, Opadry White and Opadry II Pink; each tablet type had representative samples from both coating types at five reference coating levels. Near-infrared (NIR) single-point reflectance data were collected, and data were regressed with respect to reference batch percent weight gain. This method was used as a filter to choose a smaller subset of samples for terahertz pulsed imaging (TPI), and was also used as a secondary method for validation of TPI results. The features in TPS time-domain spectra result when an incident THz plane wave meets a refractive index interface, which may be converted to an absolute distance. Therefore, assuming a discernible difference in refractive index between coating material and core exists, coating thickness can be determined non-destructively. Partial least-squares regression showed good correlation between TPI average predicted thickness and NIR. TPI was considered advantageous, as like results were obtained and no costly calibration was needed. Additionally, optical microscopy was employed on a subset of samples to validate absolute thickness values, and correlations between the three methods were obtained.

(603) **Hyperspectral Imaging of Obliterated Writing**

Diane Williams[1], Hina Ayub[2]; [1]Federal Bureau of Investigation, [2]ORISE

The forensic questioned document community has encountered difficulty visualizing obliterated writing using conventional methods. Cases have been reported in which pencil obliterated by ink, and ink obliterated by ink, cannot be discerned visually. Conventional methods for visualization of obliterated writings do not adequately visualize writing when obliteration is made with the same color ink, or when graphite pencil writings are obliterated by ink. We report the use of hyperspectral imaging to successfully view obliterated writings in which a “true black” ink obliterated graphite as well as graphite/graphite and ink/ink obliterations.\r\n\r\nHyperspectral imaging (HSI) is a novel technique in which hundreds of narrow contiguous bands, over a large range of wavelengths, can be viewed to yield a complete spectral profile at each pixel in the image. HSI has evolved as the product of conventional two-dimensional imaging and spectroscopy. The resultant image of HSI is a three-dimensional data cube, with the pixels constrained to a single plane, and the complete reflectance spectra seen along the orthogonal axis. We used three types of hyperspectral imaging systems, which provided a wavelength range spanning approximately 300 to 1700 nm, to visualize the obliterated writing samples. Additionally, we will present data obtained from the use of thermal imaging to successfully view obliterated writings.

(604) **Imaging-Based Algorithms for Determining the Uniformity of Drug Products and Blends**

Mazen L. Hamad[1], Christopher D. Ellison[1], Mansoor A. Khan[1], Robbe C. Lyon[1]; [1]Food and Drug Administration/CDER/OTR/DPQR

Spectroscopic and imaging techniques for chemical and physical analysis of pharmaceutical products and processes offer significant advantages over traditional analytical methods. However, representative sampling of heterogeneous pharmaceutical materials and products during process monitoring is challenging. For the most accurate results with optical measurements, such as Raman spectroscopy, it is necessary to determine the minimum appropriate spot size to measure a representative sample. Intuitively, an image is homogeneous at a given resolution if most pixels are representative of the whole. The goal of this study is to explore imaging-based algorithms that produce quantitative descriptions of heterogeneity. Near-infrared chemical images were acquired from sets of pharmaceutical tablets which fall into three different regimes: 1) uniform tablets, 2) slightly heterogeneous tablets, and 3) very heterogeneous tablets. Preprocessing and chemometric techniques were applied to each NIR image to create an API concentration image (120x120 pixels). In one algorithm, “macropixels” of varying sizes were constructed by concatenating neighboring pixels. The macropixels, representing sub-samples of the original image, were evaluated to determine how well they represented the entire image. In all cases, homogeneity improved as the macropixel size increased. Coupling the information from the macropixels with a specified accuracy range yielded a minimum appropriate spot size for a given image. Additional imaging-based algorithms, including co-occurrence matrices and

Markov Random Fields, were evaluated for their ability to characterize local and regional image homogeneity. These algorithms will serve as useful tools for providing quantitative assessments of the spatial characteristics of drug products and pharmaceutical blends. Additionally, these methods of analysis can be used to predict the sampling requirements of heterogeneous materials undergoing analysis with spectroscopic and non-spectroscopic techniques.

(605) **Advances in Vibrational Spectroscopic Spatial Resolution and Measurement Speed Using Raman Microscopy and AFM Tip-Enhanced Raman Spectroscopy (TERS);** Andrew Whitley[1], Eunah Lee[1], Fran Adar[1], [1]Horiba Jobin Yvon, Inc.

The recent trend in Raman microscopy field demands higher spatial resolution than ~0.5 μm that diffraction limited far-field Raman microscopy can provide. This can only be achieved by employing advanced technology such as coupling of atomic force microscopy (AFM) and surface-enhanced Raman scattering (SERS), and measuring near-field Raman signals. In the process of integrating AFM with SERS, the AFM tip is coated with one of the SERS active metals such as gold or silver. Under the control of AFM, the coated tip is moved 'close' to sample surface, which then produces a surface-enhanced Raman signal around the tip (TERS, tip enhanced Raman scattering). Even though the signal is measured with conventional far field optics, the enhanced signal from AFM tip will overwhelm the ordinary Raman signal and allow the near-field signal to be observed. The spatial resolution of AFM coupled TERS microscopy is approximated by the dimension of the tip, and currently is 100 nm with expectation to improve by at least a factor of 2 to 4. Unlike bright field microscopic images, Raman images contain vibrational spectral information based on individual spectra. The measurement time of a Raman image cube using point mapping technique relies not only on speed of stage movement and signal readout but also on spectral quality such as S/N ratio and spectral resolution. The impact of the quality of spectra on the data measurement time and information content of Raman imaging as well as the strategy for designing the most efficient data measurement, data processing and information extract compared to time invested will be explored.

(606) **Raman Microscopy and Raman NSOM: Chemical Imaging on the Nanometer Length Scale**

Alan Campion; The University of Texas at Austin

Raman spectroscopy has long been known to be a very powerful tool for chemical analysis and for materials characterization. Recent developments in instrumentation have made it possible to characterize materials with submicron spatial resolution using Raman microscopy and sub-100 nm resolution using Raman near field scanning optical microscopy (NSOM). I will review progress made recently in our laboratory in instrument development as well as present results of our studies in the application of these techniques to problems of interest in microelectronics. In particular, we have been focusing on the characterization of the three-dimensional chemical composition and strain in Si and SiGe alloys on the submicron length scale.

(607) **Scanning Nano-Raman Spectroscopy of Silicon and Other Semiconducting Materials**

Alexei Sokolov[1], Nam-Heui Lee[1], Ryan Hartschuh[1], Disha Mehtani[1], Alexander Kisliuk[1], Mark Foster[1], John Maguire[2]; [1]University of Akron, [2]AirForce Research Laboratory

Characterization of materials at the nanoscale remains a great challenge in modern nanoscience and nanotechnology. Scanning probe (SPM) and electron microscopy are extensively used to obtain topographical images at the nano-scale. However, analysis of chemical composition, conformational states, stresses and many other parameters with nanoscale lateral resolution remains essentially out of the reach. The use of traditional optical techniques is still restricted by the diffraction limit and no significant progress is achieved with aperture-limited near-field optics (SNOM). The main challenge with traditional SNOM is extremely low transmission of the optical signal. Development of apertureless near-field optics is an alternative way that already proved to be very efficient for materials characterization with lateral resolution ~10-20 nm [1-3]. It is based on enhancement of an optical signal in the nanoscale vicinity of a metal or metallized probe of the SPM (the so-called tip-enhanced spectroscopy). Tip-enhanced Raman spectroscopy (TERS), a combination of SPM and Raman spectroscopy, is a new technique for nano-scale chemical and stress imaging. We overview TERS results accumulated to date by various groups. Advantages and challenges of various optical schemes designed for the TERS are discussed and compared. The overview focuses mostly on application of TERS to analysis of silicon based and other semiconducting materials. Two-dimensional topographic and chemical/stress images of the nanostructures with the spatial resolution ~20 nm are presented. Future of the apertureless near-field optical spectroscopy and its main challenges are discussed at the end. N. Anderson, et al., J. Am. Chem. Soc. 127, 2553 (2005). 2. T. Ichimura, , et al., Phys. Rev. Lett. 92, 220801 (2004) 3.tD. Mehtani, et al., J. Raman Spectrosc. 36, 1068 (2005).

(608) **Tip enhanced Raman spectroscopy - applications for life science**

Volker Deckert; SAS - Institute for Analytical Sciences

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 to obtain highly enhanced Raman signals together with a high lateral-resolution of around 20 nm. Only the very small area of molecules close to the tip apex will experience the field enhancement. Commercially available AFM tips with apex diameters of 2 to 10 nm coated with silver have been used. The lateral resolution of the spectroscopic investigations is predicted to be in a same range as the probe dimensions. In order to optimise the TERS experiments, various probe geometries (e.g. coatings, shapes and layers) are have been modelled and experimentally tested. Obtaining the highest enhancement factors and resolutions of the probes is still a major challenge, our goal is the application of this method to problems in life science. Standard SERS and Raman spectra of various DNA components are used as a spectroscopic database. We are working in parallel on TERS of the deoxynucleotides of nano crystals of DNA monomers and on the combination with topographical analyses from atomic force microscopy (AFM) of DNA immobilised on solid surfaces. These studies can be used towards TERS studies of single molecule DNA. TERS measurement of thymine and cytosine crystals and the comparison with standard Raman spectra of the bulk polycrystalline compounds will be shown. Another subject is the study of cell membranes or cell walls in-vivo by TERS. First results of spectra and implications of the measurements with respect to lateral resolution will be discussed. References [1] R. M. Stöckle, Y. D. Suh, V. Deckert, and R. Zenobi, Chem Phys Lett, 318,131 (2000). [2] A. Rasmussen and V. Deckert, J Raman Spectrosc., 37, 311 (2006).

(609) **Raman/AFM - TERS: Understanding and Optimizing Measurement Conditions to Obtain High Spectral Contrast**

Razvigor Ossikovski[1], Quang Nguyen[1], Joachim Schreiber[2] ; [1]Ecole Polytechnique, [2]Horiba Jobin Yvon

We present the design and performance of a novel tip-enhanced-Raman equipment based on the coupling of an atomic force microscope and a micro-Raman spectrometer in oblique backscattering mode. Examples of applications of the system to the characterization of different materials and structures are reported. Optimization of the measurement conditions, in particular those related to the polarization of incident and scattered radiations, is presented and discussed. Perspectives of further developments and potential applications are also given.

(610) **Investigation of Apertureless NSOM for Measurement of Stress in Strained Silicon**

Robert Geer[1], Colin McDonough[1], Jacob Atesang[1]; [1]College of Nanoscale Sci & Eng, UAlbany

Illumination of a nanomachined tip in the immediate vicinity of a Raman-active surface exhibits enhancement of Raman scattered light similar to so-called surface-enhanced Raman scattering (SERS). Such effects have given rise to the development of apertureless near-field scanning optical microscopy (a-NSOM) for which a metallic or metal-coated nanoprobe is utilized to generate local (< 50nm) scattering enhancement at a surface. This approach has been investigated as a route to provide high spatial resolution profiling of stress in strained-Si device structures. We present investigations of tip-enhanced Raman scattering (TERS) on unstrained and strained Si samples to determine the efficacy of this approach. For these measurements a Veeco Aurora-3 NSOM has been integrated with a Renishaw Raman spectrometer. In place of conventional coated optical fibers eletropolished W wire has been used as an apertureless probe. For Ag-coated and Au-coated W tips an inverse power-law relationship has been observed between tip radius and enhancement factor. The smallest tip radii investigated (~ 17 nm) demonstrated an enhancement factor exceeding 5000. Similar experiments have been undertaken on blanket and patterned strained silicon-on-insulator (sSOI) test structures incorporating a strained (0.75%), 50nm Si device layer. Preliminary analysis has been carried out to investigate the depth profile of enhanced Raman scattering on blanket sSOI samples. Similarly, patterned sSOI structures have been investigated to characterize lateral profiling capabilities.

INDEX OF AUTHORS

INDEX OF AUTHORS

INDEX OF AUTHORS

INDEX OF AUTHORS

INDEX OF AUTHORS

INDEX OF AUTHORS

INDEX OF AUTHORS

INDEX OF AUTHORS

INDEX OF AUTHORS

INDEX OF AUTHORS

INDEX OF AUTHORS

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