

American Chemical Society
DIVISION OF ANALYTICAL CHEMISTRY
ABSTRACTS

220th ACS National Meeting

Washington, DC
August 20-24, 2000

B. Chase, C. L. Wilkins, Program Chairs

SUNDAY AFTERNOON

- **Analytical Chemistry: A Broad Spectrum of Career Opportunities**
C. Larive, Organizer; C. Larive, Presiding Papers 1 - 6

SUNDAY EVENING

- **General Papers**
B. Chase, Presiding Papers 7 - 122

MONDAY MORNING

- **Awards Symposium**
T. R. Williams, Presiding; D. B. Chase, Organizer Papers 123 - 126

MONDAY AFTERNOON

- **Frontiers in Chemical Instrumentation**
D. Muddiman, Organizer; D. Muddiman, Presiding Papers 127 - 131

TUESDAY MORNING

- **Detection of Explosives: Challenges for Chemists**
R. Q. Thompson, Organizer; F. T. Fox, Presiding Papers 132 - 137
- **Distinguished Service in the Advancement of Analytical Chemistry**
H. Blount, Organizer; R. Marianelli, Presiding Papers 138 - 143

TUESDAY AFTERNOON

- **Detection of Explosives: Challenges for Chemists**
D. D. Fetterolf, Presiding; R. Q. Thompson, Organizer Papers 144 - 149
- **Frontiers in Spectrochemical Analysis**
R. K. Marcus, Organizer; R. K. Marcus, Presiding Papers 150 - 155

WEDNESDAY MORNING

- **Proteomics and genomics in the 21st century**
W. G. Kuhr, Organizer; S. J. Lillard, Organizer, Presiding Papers 156 - 159
- **Frontiers in Electrochemistry**
T. Kuwana, Organizer; T. Kuwana, Presiding Papers 160 - 164

WEDNESDAY AFTERNOON

- **Proteomics and genomics in the 21st century**
W. G. Kuhr, Organizer; S. J. Lillard, Presiding Papers 165 - 168
- **Frontiers in Electrochemistry**
T. Kuwana, Organizer; T. Kuwana, Presiding Papers 169 - 171

THURSDAY MORNING

- **Quantification of Measurement Uncertainty**

T. Vetter, Organizer; T. Vetter, Presiding

Papers 172 - 176

THURSDAY AFTERNOON

- **Quantification of Measurement Uncertainty**

T. Vetter, Organizer; T. Vetter, Presiding

Papers 177 - 183

DIVISION OF ANALYTICAL CHEMISTRY

1. CAREER OPPORTUNITIES FOR ANALYTICAL CHEMISTS AT THE GRADUATE RESEARCH UNIVERSITY: *NON MINISTRARI SED MINISTRARE*. *Patricia Ann Mabrouk, Chemistry, Northeastern University, 111 Hurtig Hall, Boston, MA 02115, Fax: 617-373-8795*

Many exciting career opportunities exist today for talented young people in the field of analytical chemistry. One alternately exhilarating and and infuriating vocation is that of a university professor. This job requires many different skills (e.g., technical, communications, managerial) and can take a variety of different forms depending on a person's interest and abilities. In this talk, I will share how my scholastic experiences led me to a career as a teacher and scholar in bioanalytical chemistry and chemical education at Northeastern University, an urban graduate research university. I will describe what an academic career teaching and doing research at a graduate institution might look like. Finally, since a Ph.D. degree is an important requirement for this career path, I will also discuss graduate school as an option after completing an undergraduate chemistry degree.

2. SUCCEEDING AS A FACULTY MEMBER AT AN UNDERGRADUATE INSTITUTION. *Thomas J. Wenzel, Department of Chemistry, Bates College, Lewiston, ME 04240*

A faculty position at a primarily undergraduate institution (PUI) can be a rewarding career path. The majority of one's time is spent in direct contact with undergraduates, either in the context of classes or research. Most PUIs are supportive of faculty efforts to implement curricular reform, a process facilitated by the smaller class sizes. Excellence in teaching is usually the primary factor that PUIs use in evaluating people for tenure and promotion, although most PUIs expect faculty to be active scholars and do not grant tenure without evidence of scholarly success. Scholarly activity is valued because it maintains vitality of the faculty member and, when done in conjunction with undergraduate students, provides an outstanding educational opportunity. Most PUIs have teaching loads that enable faculty to be active scholars. Sufficient grant opportunities exist in chemistry to maintain an externally supported research program at a PUI. Faculty positions at a PUI provide considerable freedom and flexibility, however, they do require an enormous commitment. Advice about how to get such a position and how to enhance one's chances of getting tenure will be provided.

3. ONE WOMAN'S VIEW OF ANALYTICAL CHEMISTRY IN A U.S. FEDERAL (AND MILITARY) LABORATORY. *Debra R. Rolison, Surface Chemistry Branch, Naval Research Laboratory, Code 6170, 4555 Overlook Avenue, SW, Washington, DC 20375, Fax: 202-767-3321, rolison@nrl.navy.mil*

In 1915, in an interview in the New York Times, Thomas Edison said: "The Government should maintain a great research laboratory . . . In this could be developed . . . all the technique of military and naval progression without any vast expense." From this seed grew the U.S. Navy's corporate laboratory: the Naval Research Laboratory (NRL), which was commissioned by Congress in 1923. With over 1900 research staff, NRL conducts a multidisciplinary program of scientific research and advanced technological development directed toward the Navy's environment of sea, sky, and space, including maritime applications of new and improved materials. In that an experimentalist in chemistry or materials science cannot understand her (or his) results unless analytical chemistry is part of the process, NRL offers analytical chemists opportunities in areas beyond traditional paths, while analytical chemists provide perspective to NRL and the Navy across a range of S&T research issues.

4. INDUSTRIAL RESEARCH OPPORTUNITIES FOR B.S., M.S., AND PH.D. ANALYTICAL CHEMISTS. *D. Ronald Webb, Senior Manager, Doctoral Recruiting, Procter & Gamble Company, Miami Valley Laboratories, P.O. Box 538707, Cincinnati, OH 45253-8707, Fax: 513-627-2266, webb.dr@pg.com*

Industrial research opportunities for B.S., M.S., and Ph.D. analytical chemists exist, but each presents its own unique set of opportunities and related challenges. Not surprisingly, these pros and cons often are diametrically opposed across the B.S.-Ph.D. degree range, and pose a real dilemma to the graduating chemist. This presentation will discuss these pros and cons, and look at past employment hiring trends relative to Ph.D. hiring projections over the coming year.

The presentation will also highlight the attributes and characteristics industrial hiring managers look for in the successful industrial research candidate.

5. CAREER PATHS FOR BS/MS LEVEL CHEMISTS IN INDUSTRY: MAKING THE MOST OF YOUR DEGREE. *Thea K. Barbarakis, Business Group Diagnostics, Bayer Corporation, 511 Benedict Avenue, Tarrytown, NY 10591-5097, Fax: 914-524-3323, thea.barbarakis.b@bayer.com*

Abstract text not available.

6. TRANSITION ZONE: FROM ACADEMIA TO START-UP TO INSTRUMENT SALES. *Dean L. Olson, Capillary LC-NMR Group, MRM Corporation, 101 Tomaras Avenue, Savoy, IL 61874, Fax: 217-352-6655, dolson@microNMR.com*

In navigating through a career in analytical chemistry, change is an important phenomenon to recognize and expect. For instance, the development of a technological advance from its inception in academia to its sale as a commercial product is marked by a steady series of transitions. For a given technology to make the leap from academia to industry, at least three main features must be incorporated into it during its progression from research project to sale: robustness, ease-of-use, and wide applicability. A case study involving the transition of microcoil NMR from an academic effort to a commercial product will be presented and used as the basis of discussion for exploring some of the issues of establishing and working at a start-up company (which in this case originated at the University of Illinois). One important lesson learned is that people in academia and industry often don't fully appreciate the forces that motivate each group. However, each group has much to learn from and offer to the success of the other.

7. STUDY OF A THERMAL ELIMINATION REACTION OF A POLY(P-PHENYLENE VINYLENE) PRECURSOR. *Yolanda Liszewski, and Georgia Arbuckle-Keil, Chemistry Department, Rutgers University, 315 Penn St, Camden, NJ 08102, Fax: 856-225-6506, yyl@clam.rutgers.edu*

Poly(p-phenylene vinylene), or PPV, has many useful properties including high electrical conductivity upon doping, electroluminescence, and photoluminescence. PPV in its final form is highly insoluble and difficult to process. PPV and its derivatives can be synthesized using precursor routes. An advantage of these routes is that the precursor polymer is processible. The precursors are investigated to provide a thorough understanding of the thermal elimination reaction which converts the precursor to the final PPV polymer. Typical precursor routes include the sulfonium precursor route (SPR), the xanthate precursor route (XPR), and the chlorine precursor route (CPR). We will be focusing specifically on the thermal elimination reaction mechanism of the xanthate precursor route. Results obtained from thermogravimetric analysis (TGA), differential scanning calorimetry (DSC), evolved gas analysis (EGA), and thermogravimetric mass spectroscopy (TGA-MS) will be discussed. A compilation of this data will reveal the intriguing mechanism of the xanthate precursor route.

8. ANALYSES OF VALUED CHINESE MEDICINES, GANODERMA AND CORDYCEPS SINENSIS: COMPARISON OF BOTH QUALITATIVE AND QUANTITATIVE RESULTS FROM HIGH PERFORMANCE LIQUID CHROMATOGRAPHY (HPLC) AND THIN LAYER CHROMATOGRAPHY (TLC) STUDIES. *Tsz-Pun Chan, King-Wah Ma, and Foo-Tim Chau, Department of Applied Biology and Chemical Technology, Hong Kong Polytechnic University, Hong Kong, Hong Kong, Fax: (852)-23649932*

Chinese medicines (CMs) have about four thousand years of therapeutic history. Ganoderma and Cordyceps Sinensis are two of the most valued herbs in Chinese medicines and have been widely used for a long time. Recently, ganoderma was used for hyperlipemia, hypertension and coronary heart diseases. On the other hand, Cordyceps can improve inspiration to relieve dyspnea, eliminate phlegm and stop bleeding. Therefore, it is desirable to have good quality control of these valued Chinese medicines. In Mainland and Hong Kong, many of commercial products of these medicines, such as capsules and tablets, are available on the market. All of them claimed that they have high contents of ganoderma or Cordyceps Sinensis but the prices varies from ten to over fifty U.S. dollars. In this work, one of the classes of active ingredients in ganoderma and Cordyceps Sinensis, nucleosides, were investigated and used as the indicator to determine the quality of these CM commercial products. The concentrations of nucleosides in individual products under study were obtained and then compared with those from the herbs. Nowadays, qualitative and quantitative analyses of Chinese medicines are mainly carried out by using thin layer chromatography (TLC) and high-performance liquid chromatography (HPLC). In this investigation, we employed a HPLC instrument coupled with a diode array detector system (HPLC-DAD) and two TLC image analysis systems of CAMAG and a low cost system coupled with the software package TLCQA developed by us. The qualitative and quantitative results obtained from these techniques are compared. We found that the performance of our software, TLCQA, is comparable with the CAMAG software and the HPLC method. This may lead to the development of a low-cost, fast and reliable method for quality control of the two Chinese medicines.

9. CYCLIC VOLTAMMETRY DETERMINATION OF CHELATION CONSTANTS USING COMPETITIVE REACTION. *Charles O. Ngowe, and Kris A. Berglund, Department of Chemistry, Michigan State University, East Lansing, MI 48824, Fax: 517-432-2430, ngowecha@msu.edu*

Cyclic voltammetric responses of p-nitrophenol were used to determine chelation constants for compounds that are not electrochemically active. EDTA, nitroacetic acid, and citric acid were used to chelate Ca²⁺ and Mg²⁺ and the electrochemical response of p-nitrophenol as a function of ligand concentration was monitored. The binding kinetics and the time and pH dependence studies will be presented. A plot of the electrochemical potential of p-nitrophenol vs the log[ligand] was obtained. The slope and the intercept of the graph were used to determine the stoichiometry of complex and the formation constant, respectively. This novel method eliminates the need to monitor the equivalence point, the free metal concentration, and is applicable to all divalent cations.

10. EXTREME UV SPECTROSCOPIC STUDIES OF HYDROGEN EMISSION FROM INCANDESCENTLY HEATED HYDROGEN GAS WITH CERTAIN CATALYSTS. *Randell L. Mills, Ying Lu, Jinquan Dong, and Nelson Greenig, Blacklight Power Inc, 493 Old Trenton Road, Cranbury, NJ 08512, Fax: 609-490-1066, rmills@blacklightpower.com*

Typically the emission of extreme ultraviolet light from hydrogen gas is achieved via a discharge at high voltage, a high power inductively coupled plasma, or a plasma created and heated to extreme temperatures by RF coupling (e.g. 10E6 K) with confinement provided by a toroidal magnetic field. We report the observation of intense EUV emission at low temperatures (e.g. <10E3 K) from atomic hydrogen and certain atomized pure elements or certain gaseous ions which ionize at integer multiples of the potential energy of atomic hydrogen.

11. FORMATION OF A PLASMA AND NOVEL HYDRIDES FROM INCANDESCENTLY HEATED HYDROGEN GAS WITH CERTAIN CATALYSTS. *Randell L. Mills¹, Bala Dhandapani¹, Nelson Greenig¹, Jiliang He¹, Jinquan Dong¹, Ying Lu¹, and Johannes P. F. Conrads². (1) Blacklight Power Inc, 493 Old Trenton Road, Cranbury, NJ 08512, Fax: 609-490-1066, rmills@blacklightpower.com, (2) Institute of Nonthermal Plasma-Physics*

Typically the emission of extreme ultraviolet light from hydrogen gas is achieved via a discharge at high voltage, a high power inductively coupled plasma, or a plasma created and heated to extreme temperatures by RF coupling (e.g. 10E6 K) with confinement provided by a toroidal magnetic field. We report the observation of intense EUV emission at low temperatures (e.g. <10E3 K) from atomic hydrogen and certain atomized pure elements or certain gaseous ions which ionize at integer multiples of the potential energy of atomic hydrogen. The products of the EUV emitting reaction were novel inorganic hydride compounds which comprise high binding energy hydride ions. The novel hydride compounds were identified by time of flight secondary ion mass spectroscopy, X-ray photoelectron spectroscopy, proton nuclear magnetic resonance spectroscopy, Fourier transform infrared spectroscopy, electrospray ionization time of flight mass spectroscopy, liquid chromatography/mass spectroscopy, thermal decomposition with analysis by gas chromatography, and mass spectroscopy, and elemental analysis. Hydride ions with increased binding energies may form many novel compounds with broad applications.

12. GRADIENT CHROMATOFOCUSING: THE EFFECT OF INORGANIC SALT CONCENTRATION AND COMPOSITION ON PROTEIN SEPARATION. *Lian Shan, and David J. Anderson, Department of Chemistry, Cleveland State University, 1983, E.24th Street, Cleveland, OH 44115, Fax: 216-687-9298, l.shan@popmail.csuohio.edu*

Gradient Chromatofocusing is a chromatographic technique developed by our research group which addresses the limitations of conventional chromatofocusing. In conventional chromatofocusing, a linear pH gradient is generated on an anion-exchange column by a stepwise change from a high pH mobile phase buffer to a low pH mobile phase buffer (usually a polymeric ampholyte buffer). Disadvantages of the conventional technique include: the high cost of mobile phase, difficulty in controlling pH gradient slope, limitation of the mobile phase to low buffer concentration conditions, and contamination of the proteins by the polymeric ampholytes, making purification difficult. Gradient chromatofocusing overcomes these limitations by using low molecular weight buffer components that are mixed through a HPLC gradient system to generate a linear pH gradient, making it cheaper and flexible for protein separation.

In conventional chromatofocusing, the combination of ionic strength and pH gradient effects for optimizing protein separations is not possible because the technique is limited to low buffer concentrations (i.e. low ionic strength). The versatility of gradient chromatofocusing allows for the use of a wide range of ionic strengths in the mobile phase, does adding a powerful new parameter to chromatofocusing optimization. In the present study, five proteins (conalbumin, ovalbumin, BSA, Beta-lactoglobulin A and B) were chromatographed on a Mono P column (from Amersham Pharmacia biotech) using the same linear pH gradient but different inorganic salt concentrations. Results show a significant effect of salt concentration on protein separation, demonstrating the unique capability of combining pH gradient and ionic strength parameters in chromatofocusing protein separation. Different inorganic salts were studied.

13. HEADSPACE GC/MS ANALYSIS OF VOLATILE ORGANIC COMPOUNDS IN PATHOLOGY SPECIMENS AND CONSUMER PRODUCTS. *Diane M. Wong-Verelle, Steven C. Cordero, Benjamin Moeller, and V. F. Kalasinsky, Department of Environmental and Toxicologic Pathology, Armed Forces Inst of Pathology, 6825 16th Street, Washington, DC 20306-6000, Fax: 202-782-9215*

Headspace analysis is a useful technique for the rapid assessment of volatile compounds. Minimal sample preparation is required, and a variety of sample matrices can be accommodated. When coupled with a gas chromatography mass spectrometer (GC/MS) system, headspace analysis is a powerful tool for identifying trace chemicals in blood, tissue, or commercial chemical products. Inhalation of propellants or other volatile compounds may result in acutely toxic effects. A rapid screen by headspace GC/MS has been used to confirm the

presence of halocarbons and hydrogen sulfide in biological specimens following accidental and occupational exposures. The cause of death in each case was attributed to inhalation of volatiles. Unregulated personal care products (such as bath oils, medicinal oils, and alternative medications) are often complicated chemical mixtures, and some contain volatiles that are detrimental to human health. Headspace GC/MS can readily detect the presence of such volatiles in these complicated mixtures.

14.

NOVEL INORGANIC HYDRIDE. *Randell L. Mills, Blacklight Power Inc, 493 Old Trenton Road, Cranbury, NJ 08512, Fax: 609-490-1066, rmills@blacklightpower.com*

A novel inorganic hydride compound KXKHCO_3 which is stable in water and comprises a high binding energy hydride ion was isolated following the electrolysis of a K_2CO_3 electrolyte. Inorganic hydride clusters $\text{K}[\text{XKHCO}_3]_n^+$ were identified by Time of Flight Secondary Ion Mass Spectroscopy. Moreover, the existence of a novel hydride ion has been determined using X-ray photoelectron spectroscopy, and proton nuclear magnetic resonance spectroscopy. Hydride ions with increased binding energies may be the basis of a high voltage battery for electric vehicles.

15.

REPLICA MOLDING OF LIQUID CHROMATOGRAPHY (LC) COLUMN MICROSTRUCTURES IN POLY(DIMETHYLSILOXANE). *Emilia Lugowska¹, Mary Tang², and Fred E. Regnier¹. (1) Department of Chemistry, Purdue University, 1393 BRWN, West Lafayette, IN 47907, Fax: 765-494-0359, (2) Stanford Nanofabrication Facility, Stanford University*

The ability to produce an efficient micro-LC column is a major problem which limits progress toward LC separation systems on a chip. Among different approaches to manufacturing of LC columns on a chip, open-tubular columns and particle packed bead columns do not show the expected separation capabilities. In our approach, we fabricate a column particles directly on the chip through the creation so-called collocated monolith support structures (COMOSS). A LC column based on COMOSS can be further derivatized in different ways offering alternative separation systems in the same well controlled format. We will present the results and SEM images of the COMOSS-based LC columns microfabricated in poly(dimethylsiloxane). The microstructure has monolith particles of $5 \mu\text{m}$ (W) \times $5 \mu\text{m}$ (L), separated by channels of $0.5 - 1.5 \mu\text{m}$ wide. The channels were cast 5 to $50 \mu\text{m}$ deep. This paper will discuss problems specific to the feasibility of replica molding of COMOSS. The quality of column microstructure using different technologies for microfabrication of masters, different ways of surface preparation of masters and different kind of release agents will also be presented.

16.

SENSITIVE DETECTION OF ANALYTES USING LASER WAVE MIXING. *William G. Tong, Mirna M. Lopez, and Julia A. Schafer, Department of Chemistry, San Diego State University, 5500 Campanila Drive, San Diego, CA 92182, Fax: 619-594-2442, william.tong@sdsu.edu, baker2@rohan.sdsu.edu*

Degenerate four wave mixing based on nonlinear optical phase conjugation has been demonstrated as a sensitive optical absorption detection method for a wide range of samples and applications, including liquid chromatography and capillary electrophoresis. Collection of the wave-mixing signal is very efficient since it is a coherent laser beam with all the properties of the laser used to generate it. The signal beam has a cubic dependence on laser power and a quadratic dependence on sample concentration. Since wave mixing is an optical absorption method, both fluorescing and non-fluorescing analytes can be detected, eliminating the need for chemical labeling. Other advantages of this method include excellent signal to noise ratio, virtually zero background noise, ease of alignment, and convenient sample introduction. This method can be applied to study chemical, biomedical, geological and environmental samples.

17.

SPECTROSCOPIC STUDIES ON NOVEL ALKALI AND ALKALINE EARTH HYDRIDES. *Randell L. Mills, Bala Dhandapani, and Jiliang He, Blacklight Power Inc, 493 Old Trenton Road, Cranbury, NJ 08512, Fax: 609-490-1066, rmills@blacklightpower.com*

Novel inorganic alkali and alkaline earth hydrides which comprise high binding energy hydride ions were synthesized in a high temperature gas cell by reaction

of atomic hydrogen with certain catalysts and alkali and alkaline earth halides. For example KHxly , KHxCly , SrHBr and CaHBr compounds were isolated and characterized with various state of the art techniques. The compounds were primarily identified by time of flight secondary ion mass spectroscopy, thermal decomposition with analysis by gas chromatography, and mass spectroscopy. X-ray photoelectron spectroscopy show that the metal core level binding energies shift to higher energies relative to metal halides. Solid state proton nuclear magnetic resonance spectroscopy indicated such new hydrides have different chemical shifts and have a shorter inter-nuclear spacing compared to normal metal hydrides. Hydride ions with increased binding energies form novel compounds with potential broad applications such as a high voltage battery.

18.

UV-VIS DRS ANALYSIS FOR THE IDENTIFICATION OF INTRA- AND EXTRA-FRAMEWORK GALLIUM SPECIES IN [GA]-MFI ZEOLITE. *Hyun-Sik Hahm, Jinu Park, Sang-Beom Kim, and Tae-Ok Kim, Department of Chemical Engineering, Myongji University, San 38-2, Nam-Dong, Yongin, Kyonggi-Do 449-728, South Korea, Fax: 0335-337-1920, hahm@wh.myongji.ac.kr*

The gallosilicate, [Ga]-MFI, can be prepared by template-assisted hydrothermal synthesis at atmospheric pressure. Incorporation of gallium into the zeolite framework has been confirmed by means of powder X-ray diffraction, solid state NMR and IR spectroscopy. But extra-framework gallium species that stems from the residues of the synthesis, burning of the template and subsequent thermal treatments and is known to be a bifunctional catalyst in the aromatization of light hydrocarbons, has not been observed by means of these tools. The aim of this presentation is to show a very simple method for the identification of intra- and extra-framework gallium species in [Ga]-MFI zeolite using UV-vis diffuse reflectance spectroscopy.

19.

DYNAMIC ARTIFICIAL STOMACH AND INTESTINE MODEL TO EVALUATE THE BIOAVAILABILITY OF DRUGS AND FORMULATIONS. *David C. Sperry, and Michael Hawley, Pharmaceutical Development, Pharmacia Corporation, 4831-259-175, 7000 Portage Rd., Kalamazoo, MI 49001-0199, Fax: 616-833-6262, David-cons.Sperry@am.pnu.com*

We have developed and tested an artificial stomach and intestine model that will provide quantitative *in vitro* solubilization data and qualitative bioavailability for solid drug forms and formulations. The apparatus consists of two chambers (representing the stomach and duodenum in a human) connected by computer controlled pumps that regulate the flow of fluid through the system. Ultraviolet fiber optic probes in each chamber provide data on aqueous drug concentration in real time, and pH probes constantly monitor the pH. The design of the model and the fact that it is computer controlled allow one to easily change and control "biological" conditions in the GI tract, thereby subjecting a drug sample to a wide range of biopharmaceutical conditions. The results of our experiments and the bioavailability predictions will be presented.

20.

A FEW APPLICATIONS OF THE QUARTZ CRYSTAL MICROBALANCE/HEAT CONDUCTION CALORIMETER (QCM/HCC), A NOVEL THERMOGRAVIMETRICAL TOOL. *Allan L. Smith, Hamid M. Shirazi, S. Rose Mulligan, Justine M. Ciruolo, Anna Ayrapetova, Betty Jacob, and David Schneider, Department of Chemistry, Drexel University, 32nd and Chestnut Streets, Philadelphia, PA 19104, Fax: 215-895-1265, hamid_shirazi@drexel.edu*

The QCM/HCC is a novel scientific instrument equipped with two very sensitive sensors: a 5MHz "AT cut" QCM, which measures mass changes with high sensitivity ($\pm 2\text{ng/cm}^2$); and a thermopile measuring very small heat flows ($\pm 50\text{nW}$). In one experiment the QCM/HCC was used to study the sorption process of selected organic vapors into thin aliphatic poly(ether)urethane (TecoflexTM) films (~ 0.7 to $2\mu\text{m}$). The mass change and heat flow during sorption cycles were measured, while the partial pressure of each organic vapor above the TecoflexTM film was changed periodically. Two electrodeposited thin films of palladium (54nm and 141nm) were also exposed to different partial pressures of hydrogen at 298.13K. During the hydrogen sorption/desorption cycles fast mass changes were accompanied by relatively large heat flows ($\sim 15\text{kJ/molH}_2$). The energetics of hydration/dehydration of a spray-coated thin film of lysozyme ($\sim 1\mu\text{m}$) was measured at various relative humidities. Important

potential applications of this new thermogravimetric technique in the areas of chemical sensors, separation sciences and surface catalysis are discussed.

21.

GENERAL SFC METHOD: CONQUERING THE REQUIREMENTS. *Joan M. Stevens*, Technical Support, Gilson, Inc, 3000 W. Beltline Hwy, Middleton, WI 53562, Fax: 608-831-4451, jstevens@gilson.com, and *Alan Hamstra*, Customer Support, Gilson, Inc

Supercritical fluid chromatography is a method of analysis that holds many advantages over HPLC; namely, less solvent consumption, faster column equilibration, and pressure gradients. In semi-preparative mode (flow rates up to 25 ml/min), SFC also offers non-aqueous fraction collection in a substantially smaller volume. Compared to RP-HPLC under the same running conditions we have a drastic decrease in the time required for fraction dry down. Although SFC seems to be a viable alternative or complementary to RP-HPLC, many chromatographers are unfamiliar with SFC and the conditions to employ as a general SFC method. The purpose of this application is to present to the chromatographer a table of results based on a mixture of three compounds (neutral, basic, and bifunctional) in which the mixture was chromatographed under various conditions. The conditions that were used consist of various chromatographic media, organic solvents, addition of modifier, pressure and temperature. Based on the results presented in the SFC table conditions will be offered that can be employed as a general chromatography method for SFC.

22.

NEW CLASS OF HIGHLY FLUORESCENT IMIDAZOLE DYE CONTAINING POLYMERS FOR POTENTIAL ANALYTICAL APPLICATIONS. *Javier Santos*, Xiu R. Bu, and Eric A. Mintz, Department of Chemistry, Clark Atlanta University, Atlanta, GA 30314, Fax: 404-880-6890, jsantos@chemist.com

Organic fluorescence materials are expected to find many analytical applications. In particular, there is considerable interest in the development of fluorescence techniques for metal trace detection or for the recognition and measurement of metal components in various systems. Although many investigations have been focused on heterocyclic compounds such as coumarins, bipyridines, rhodamines, and pyrrole derivatives, little is known for imidazole-based sensing materials. A series of monomeric and polymeric based fluorescent dyes were prepared containing a thiophene unit at the 2- position of the imidazole ring. Dependence of fluorescence efficiency on parameters of solvent polarity and substituent groups has been investigated. It was found that the formyl group at the 2- position of the thiophene ring dramatically increased the fluorescent properties. Responsive interaction with metal ions indicated their potential as sensor materials. These fluorophores have flexibility for introduction of versatile substituent groups that could improve the fluorescence efficiency and sensor properties.

23.

NEW STANDARD REFERENCE MATERIAL FOR LC COLUMN EVALUATION. *Lane C. Sander*, and Stephen A. Wise, Analytical Chemistry Division, National Institute of Standards and Technology, 100 Bureau Dr. MS 8392, Gaithersburg, MD 20899, Fax: (301) 977-0685

One of the single most important topics influencing the theory and practice of liquid chromatography is the nature of the stationary phase. Central to any discussion of retention processes are the physical and chemical properties of the stationary phase, and column selection is one of the first and most important decisions made in method development. Recent advances in solid state nuclear magnetic resonance spectroscopy and other analytical techniques have improved the level of understanding of chemically modified surfaces. Despite these advances, column selection in method development is often based on trial-and-error approaches that may not result in optimal or even satisfactory separations. SRM 870, "Column Performance Test Mixture for Liquid Chromatography" has been developed as a tool for column characterization and classification, to assist the analyst in column selection, and as quality controls in column manufacturing. The use of this material will be discussed for a variety of commercial columns.

24.

NOVEL HPLC DETECTOR: GENERATING ON-THE-FLY FLUORESCENCE LIFETIMES CONCURRENTLY AT MULTIPLE EMISSION WAVELENGTHS. *Pamela Ramage*¹, *Scott Reeve*¹, *Michael A. Dvorak*², and *Gregory D. Gillispie*². (1) Department of Chemistry, Arkansas State University, PO Box 419, State University, AR 72467, sreeve@navajo.astate.edu, (2) Dakota Technologies, Inc

We describe the construction and performance of a novel liquid chromatography (HPLC) detector that simultaneously generates fluorescence decay curves at multiple emission wavelengths. The fourth harmonic (266 nm) excitation light from a pulsed Nd:YAG laser is focused into a Bethune cell prism modified for use as an HPLC flow cell. A small spectrograph disperses the fluorescence. Fiber optic delay lines positioned in the exit focal plane time the arrival of photons at the PMT detector. Four wavelength channels with 50 ns channel spacing were used in this study. The intensity-decay time waveform is averaged with a digital phosphor oscilloscope. Temporal overlap between adjacent wavelength channels is removed during the post-processing of the data. System performance was characterized by chromatographic elution of polycyclic aromatic hydrocarbons (PAH). We have determined sub 100 ppb detection limits for a variety of representative polycyclic aromatic hydrocarbons. We also demonstrate the resolution of coeluting analytes on the basis of differences in their lifetimes and spectral distributions.

25.

NOVEL MOLECULAR CONTROLLED SEMICONDUCTOR DEVICE: A NEW SENSOR FOR METAL IONS. *Ronnie Benshafrut*¹, *David Cahen*², *Avner Haran*³, *Ron Naaman*³, *Benjamin Schneider*¹, *Abraham Shanzer*⁴, and *Dmitry Shvarts*¹. (1) AMOS, Ltd, Weizmann Institute of Science, Rehovot 76100, Israel, Fax: 972-8-9344123, ronnie.benshafrut@weizmann.ac.il, (2) Department of Materials and Interfaces, Weizmann Institute of Science, (3) Department of Chemical Physics, Weizmann Institute of Science, (4) Department of Organic Chemistry, Weizmann Institute of Science

We present a new highly selective sensor for metal ions based on a novel organic-semiconductor hybrid structure. This *Molecular Controlled Semiconductor Resistor* (MOCSESR) is based on having a doped GaAs layer on top of a semi-insulating layer. It may be used as a sensor when it is coated with specially synthesized bifunctional organic molecules, which are bound to the surface of the device and contain receptor functionalities for selective binding of various molecules or ions. The sensor can be applied for a wide range of analytes, i.e. gases or various metal ions, by simply changing the nature of the organic monolayer. It is a real-time sensor characterized by high sensitivity (better than 30 ppb of the analyte), selectivity and a wide dynamic range of more than four orders of magnitude. It is inexpensive to produce, and suffers relatively little interference from the surrounding media because its functioning does not require transfer of the electrical current through the solution.

26.

NOVEL ONLINE OIL CONTENT MONITORING SYSTEM: ULTRAVIOLET FLUORESCENCE AND LIGHT SCATTERING AS INPUTS TO AN ARTIFICIAL NEURAL NETWORK CALIBRATION ALGORITHM. *Li-Ming He*¹, *Lora L. Kear-Padilla*², *Stephen H. Lieberman*¹, and *John M. Andrews*¹. (1) Environmental Sciences Division D361, San Diego State University, Space and Naval Warfare Systems Center, 53475 Stroh Road, San Diego, CA 92152, Fax: 619-553-2876, lhe@spawar.navy.mil, (2) Computer Sciences Corporation

Ultraviolet fluorescence and light scattering are two methods used for online measurement of oil-in-water content. A major technical challenge for these methods is to maintain quantitative accuracy in the presence of various oil types and chemical and physical interferences. Four types of oils, each consisting of a dozen subtypes of oil samples, were examined to compare fluorescence and scattering intensity at different oil concentrations. The significant variations in intensity with oil types and subtypes make it difficult to calibrate the analytical instrument using traditional methods; hence a nonlinear calibration of instrumental response was implemented through an artificial neural network (ANN). The combined use of fluorescence and scattering data significantly improves quantitative prediction accuracy. The trained ANN successfully predicts the concentrations of single oils and their mixtures. The novel technique permits the online monitoring of oil spills and the accurate determination of oil concentrations in wastewater discharged from ships and oil refinery industry.

27.

RAPID, SIMPLIFIED SPME PROCEDURE FOR THE DETERMINATION OF MODERATELY HYDROPHOBIC HERBICIDES IN AGRICULTURAL RUNOFF. *John Schaumloffel¹, Richelle M. Allen-King², and David Talmage².* (1) Chemistry and Biochemistry Department, University of Massachusetts, 285 Old Westport Road, 11-310, North Dartmouth, MA 02747, jschaumloffel@umassd.edu, (2) Department of Geology, Washington State University

Traditional pesticide extraction procedures are time and equipment intensive. A SPME (solid phase micro extraction) procedure was developed to complete relatively rapid analyses of selected chlorinated herbicides in water using standard laboratory equipment. Samples can be processed at a rate of > 3/hr. Detection limits for lindane (g-HCH), triallate (S-2,3,3-trichloroallyl diisopropylthiocarbamate) and other selected compounds are in the low part per trillion range when determined using gas chromatography (GC) with electron capture detection (ECD). Simplified procedures employing direct exposure of the fiber and enhanced mass transport are utilized. Mass uptake was proportional to exposure time for the relatively short exposure periods and an internal standard has improved accuracy and precision of the procedure. The development of this method has facilitated study of temporal variability of the target analyte in groundwater and stream samples at the field scale. The method could be easily adapted for use by students in a lab setting because of the relatively low equipment demand and short extraction times.

28.

ACCELERATING THE RATE OF PROCESS SCREENING AND OPTIMIZATION USING THE OPTIMATE WORKSTATION™. *Joan M. Stevens, Technical Support, Gilson, Inc, 3000 W. Beltline Hwy, Middleton, WI 53562, Fax: 608-831-4451, jstevens@gilson.com, Mark Harding, Product Manager, Anachem Ltd, and Veronica Watson, Technical Specialist, Anachem Ltd*

The goal of this workstation is to help accelerate the rate at which processes can be screened and optimized. In 1998 the SK233 Workstation™ was launched following extensive consultation with leading pharmaceutical companies. The SK233 was designed to automate the screening of catalysts, reagents and solvents, as well as the optimization of processes in regards to reactant volume, addition rates, order of addition and stoichiometry. The workstation was based on an industry standard XYZ sampler fitted with chilled or heated reaction stations. The addition of the patented REACTarray™, provided the ability to perform both inert and reflux chemistries. The design of the REACTarray™ allows for good visibility and permanent probe access to the reaction content. Chemistries performed in the reaction stations versus those carried out in more traditional glassware showed a high degree of correlation. The SK233 is equipped to sample from the reactions at user defined intervals for on-line analysis. Consultation with key members of the pharmaceutical industry has resulted in a flexible software interface that is easy to use in the hands of the synthetic chemist. The summer of 2000 saw the release of the second generation SK233, called the OptiMate Workstation™. This product introduced many new hardware enhancements (such as the REACTivate multiple temperature zone reaction station) and software features requested by users of the SK233. Application and examples to support the versatility, convenience and ease of use of the OptiMate™ coupled with on-line HPLC analysis data and reaction profiles will be presented.

29.

ADVANCEMENTS IN DETERMINATION OF ALUMINUM IN ENVIRONMENTAL AND BIOLOGICAL MATERIALS BY ²⁷Al NUCLEAR MAGNETIC RESONANCE SPECTROMETRY. *Shuping Bi, Xianlong Wang, and Gongwei Zou, Department of Chemistry, Nanjing University, Nanjing 210093, China, Fax: 011 86 25 3317761, bisp@nju.edu.cn*

²⁷Al nuclear magnetic resonance (NMR) spectrometry, as a rapid, direct, and non-destructive analytical tool, has been used to investigate the hydrolysis process of aluminum (III) in the presence and absence of some organic and inorganic ligands, to study the structure and reactivity of Al(III) complexes with environmentally and biologically important ligands, to quantitatively determine and speciate the Al(III) species present in environmental and biological samples and to monitor the transport process of aluminum in plants, animals, yeast, and other organisms during the last twenty years. In this paper, the advances of these applications are reviewed and a lot of ²⁷Al chemical shift data of species

present in aqueous solution are summarized. More than 70 references are involved. (No. 49831005 NFSC).

30.

ADVANCES IN THE APPLICATION OF RPP AND SSV TO THE STUDY OF TRACE METAL BINDING BY HETEROGENEOUS LIGANDS. *Montserrat Filella, University of Geneva, CABE, Quai Ernest-Ansermet 30, CH-1211 Geneva 4, Switzerland, Fax: 41-22-702-6069, montserrat.filella@cabe.unige.ch, and Raewyn M. Town, School of Chemistry, Queen's University of Belfast*

We have developed a new approach for the interpretation of Reverse Pulse Polarography (RPP) and Scanning Stripping Voltammetry (SSV) data that overcomes some limitations of direct SV. The heterogeneity of complexants is considered through two parameters which are inherent properties of the ligand and which allow complexation parameters to be calculated for other metal loading conditions. Application to Pb(II) and Cu(II) complexation by Suwannee River fulvic acid (SRFA) reveals that (i) complexation of Pb(II) is less heterogeneous than that of Cu(II), and (ii) complexes are less labile under conditions of greater ligand excess. Both, Pb(II)-SRFA and Cu(II)-SRFA were labile under RPP conditions. Pb(II)-SRFA approached non-lability by SSV and the binding parameters obtained are probably influenced by some loss of lability. For Cu(II)-SRFA, considerable loss of lability occurred and binding parameters could not be calculated. Adsorption effects were more evident for Cu(II). Our experimental observations are consistent with recent theoretical predictions.

31.

ANALYTICAL EVALUATION OF A TRACE, BIOACTIVE CONSTITUENT IN LODENOSINE, A NEW ANTI-AIDS DRUG. *Manohar L. Sethi¹, Harry Ford¹, Jeri S. Roth¹, Riad Agbaria², David G. Johns¹, and James A. Kelley¹.* (1) Laboratory of Medicinal Chemistry, National Cancer Institute, Building 37, Room 5C02, NIH, Bethesda, MD 20892-4255, Fax: 301-402-2275, SethiM@mail.nih.gov, (2) Department of Clinical Pharmacology, Ben-Gurion University of the Negev

Lodenosine (2'-β-fluoro-2',3'-dideoxyadenosine, F-ddA) is a synthetic, sugar-fluorinated dideoxynucleoside analogue (ddN) with a greatly enhanced acid and enzymatic stability, which makes it ideally suited for oral administration. These properties, coupled with an anti-HIV activity and potency as a reverse transcriptase inhibitor that is comparable to that of the FDA approved drug didanosine (2'-3'-dideoxyinosine), have prompted its clinical development. Oral dosage forms of lodenosine, either alone or as a component of triple combination therapy, have been evaluated in limited Phase I and Phase II clinical trials in adult and pediatric AIDS patients. Because lodenosine is synthesized by coupling 2-deoxy-2-fluoro-1,3,5-tri-O-benzoyl-D-arabinofuranose with adenine followed by deoxygenation and deprotection, there is the potential of producing 2'-β-fluoro-2'-deoxyadenosine (2'-F-dA) as a byproduct. LC/MS/MS has been used to confirm that trace amounts of 2'-F-dA do indeed occur in lodenosine. A reversed-phase HPLC method capable of measuring 0.005% 2'-F-dA in bulk F-ddA has been employed to determine that amounts of this constituent are less than 0.2% in all drug currently analyzed. The anabolic and catabolic metabolism of 2'-F-dA has been investigated singly and in the presence of lodenosine. The differential phosphorylation of [³H]-2'-F-dA and [³H]-F-ddA to potentially active metabolites has been determined and quantified in MOLT-4 cells, a human lymphocyte line, by anion exchange HPLC with radiochemical detection. The relative rate of deamination of 2'-F-dA to 2'-β-fluoro-2'-deoxyinosine has been measured and the susceptibility of this latter compound to enzymatic depurination has been evaluated. The implications of these results for the observed toxicity profile of lodenosine will be discussed.

32.

ANALYSIS OF D/L-AMINO ACIDS IN NERVE TISSUE SAMPLES. *Yi-Ming Liu, Shulin Zhao, and Willa Williams, Chemistry, Jackson State University, 1400 Lynch Street, Jackson, MS 39217, Fax: 601-973-3674, ymliu@stallion.jsums.edu*

Quantification of amino acid enantiomers present in nerve tissue samples using chiral capillary electrophoresis (CE) and gas chromatography-mass spectrometry (GC-MS) is described. In the chiral CE procedure, amino acid enantiomers are fluorescently tagged with naphthalene-2,3-dicarboxaldehyde (NDA). Enantioseparation is achieved by cyclodextrin modified micellar electrokinetic chromatography (MEKC) in the presence of methanol as an organic modifier. The separation is coupled with laser induced fluorescence detection. In the GC-MS procedure, amino acids are extracted from the sample matrix by SPE,

derivatized, and then separated on a val-sil chiral column. Rat brains and ganglia of *Aplysia californica* are analyzed. D-Asp, D-Leu, and D-Phe both free and bonded in small peptides, soluble proteins, and non-soluble proteins/tissues are determined.

33.

ANALYSIS OF STREAM FULVIC ACIDS USING TERBIUM FLUORESCENCE SPECTROSCOPY. *Donald J. Nelson, Sean Dunn, Gemma Rolle, and Kelly M. Elkins, Department of Chemistry and Biochemistry, Clark University, 950 Main Street, Worcester, MA 01610, Fax: 508-793-8861, dnelson@clarku.edu*

Humic substances derive primarily from dead plant material. They are the residue that remains after the organic material has been attacked by microorganisms and other processes. Humic substances affect the pH of natural waters, trace metal aquatic chemistry and bioavailability and the degradation and transport of hydrophobic organic molecules. The fulvic acids are the lowest molecular weight substances with the highest oxygen content in the complex humic group. In this study we have investigated the interaction of the trivalent lanthanide, Tb³⁺, with fulvic acids in a standard (Suwannee River) fulvic acid sample, obtained from the International Humic Substances Society. We have found that the Tb³⁺ ⁵D₄ → ⁷F₅ fluorescence emission (545 nm) is *strongly quenched* by fulvic acids at low pH values (pH < 5) but is *strongly enhanced* at slightly higher pH values. The Tb³⁺ fluorescence emission enhancement, measured at pH 6.3 for example, is quite dramatic: 309 % greater emission intensity at 545 nm observed in the presence of fulvic acid over that observed in its absence. The “blue-shifting” of the ⁵D₄ → ⁷F₅ fluorescence emission transition is consistent with Tb³⁺ going into a less polar environment. These results suggest that Tb³⁺ fluorescence may serve as a valuable tool for investigating fulvic acids. The affect of Tb³⁺ on the fluorescence behavior of the fulvic acids, as monitored by excitation-emission matrix (EEM) contour plots, is in full support of the conclusions drawn from the affect of fulvic acids on Tb³⁺ fluorescence behavior.

34.

ANALYSIS OF THE MICROHETEROGENEITY OF PSP COATINGS VIA FLUORESCENCE MICROSCOPY. *Joanne Bedlek-Ansow¹, Kirk S. Schanze¹, J. Paul Hubner², Bruce F. Carroll², and Weihong Tan¹. (1) Department of Chemistry, University of Florida, PO Box 117200, Gainesville, FL 32611-7200, Fax: 352-846-0296, bedlek@chem.ufl.edu, (2) Department of Aerospace Engineering, Mechanics & Engineering Science, University of Florida*

An anomaly of PSP (pressure sensitive paint) coatings is the microheterogeneity of luminescence distribution through out the polymer coating. A common characteristic of these coatings is the negatively deviating Stern-Volmer quenching plots. A possible explanation for the curvature exhibited by the plots is the microheterogeneous nature of the luminophore distribution. Fluorescence microscopy has been employed to investigate the quenching characteristics of discrete regions across a coating surface. Statistical analysis of the quenching characteristics of these coatings will enhance the understanding of the effects of heterogeneity exhibited in a single coating as well as in comparison to other coating formulations.

35.

ANALYTICAL CHEMISTRY OF FINDING EXPLOSIVES WITH HONEYBEES. *M. E. Sigman¹, G. C. Smith², R. H. Ilgner¹, D. C. Jones², and C. Y. Ma¹. (1) Chemical and Analytical Sciences Division, Oak Ridge National Laboratory, PO Box 2008, MS 6100, Oak Ridge, TN 37831-6100, Fax: 865-574-4902, sigmanme@ornl.gov, (2) Department of Chemistry, University of Montana*

Honeybees are known to function as environmental sampling tools as they forage for food and other hive resources in the area surrounding their hive. Chemicals that the bees encounter in the environment may be monitored within the hive, provided the appropriate technology and analytical methodology are available. We will report on new methods developed at ORNL for collecting and analyzing organic explosives from the vapor phase. Field applications demonstrating the detection of explosives within honeybee hives will be discussed. Research sponsored by the Defense Advanced Research Projects Agency (DARPA) DOE No. 1868-HH09-X1, U.S. Department of Energy, under Contract DE-AC05-00OR22725 with Oak Ridge National Laboratory, managed and operated by UT-Battelle, LLC.

36.

APPLICATIONS OF HIGH RESOLUTION SURFACE PLASMON RESONANCE SPECTROSCOPY. *Shaopeng Wang, Salah Boussaad, Sergio Wong, and Nongjian Tao, Department of Physics, Florida International University, 11200 SW 8th Street, CP 204, Miami, FL 33199, Fax: 305-348-6700, wangs@fiu.edu*

We have recently developed a high-resolution Surface Plasmon Resonance (SPR) Spectroscopy setup. By using a bi-cell photodetector, the resolution of ~10⁻⁵ degrees and a response time of ~1 μs were achieved. The setup has good linearity, is compact and immune to noise from the ambient light. By using a white light source and a monochromator, we expanded the capability of the setup to multi-wavelength measurements, which has been used to study the electronic states of the molecules. When the wavelength is tuned to the absorption bands, the resonant angle oscillates at the wavelengths and provides an electronic signature of the molecules. By modulating the applied potential, SPR based Stark spectroscopy of organic adsorbates on electrodes was also obtained by using the Kramers-Kronig relation. In addition, information about the conformation of molecules following an electron transfer reaction was determined. The kinetic of electron transfer reaction induced conformational changes in native cytochrome c were measured. The thickness change of ~0.3 Å due to the conformation change of protein with a time constant of ~200 ms was easily detected.

37.

APPROACHES TO ON-LINE API MASS SPECTROMETRY: KINETICS OF THE BASE HYDROLYSIS OF ISATIN. *Jeffrey Brum¹, Philip Dell'Orco¹, Jon Littell², Sarah Lapka², and Kenneth Muske². (1) Analytical Sciences, SmithKline Beecham Pharmaceuticals, 709 Swedeland Rd., King of Prussia, PA 19406, Fax: 610-270-7510, jeffrey_brum@sbphrd.com, (2) Dept. of Chemical Engineering, Villanova University*

We have previously demonstrated the utility of reaction monitoring by on-line mass spectrometry (OLMS) utilizing electrospray ionization (ESI) in various contexts. A wealth of mechanistic and qualitative kinetic information can be obtained from a variety of reactions. Detailed kinetic models require a refined understanding of the ionization process within the context of ion production and signal quantification. Previous work by Tang and Kebarle did much to expand the understanding of the ESI process. We have used this work as a basis to extend our understanding of ion formation from multi-component mixtures. As a test case we examine the base induced hydrolysis of isatin (70:30 MeOH:water), monitoring the reaction in both positive ([M+H]⁺, [M+Li]⁺) and negative ion mode ([M-H]⁻). The utility of both approaches is examined. Hydrolysis kinetics are modeled using OLMS data.

38.

ASSESSMENT OF STRUCTURAL CHANGES IN HUMAN HAIR BY NEAR IR MICROSCOPY. *Louis J. Kirschenbaum, Luciana Coutinho, Scott W. Huffman, and Chris W. Brown, Department of Chemistry, University of Rhode Island, Kingston, RI 02881, Fax: 401-874-5072, kirschenbaum@chm.uri.edu, lcoutinho@chm.uri.edu*

Undamaged and damaged human hair fibers have been analyzed by near infrared microscopy. This technique provides a simple, rapid and non-destructive method for monitoring the structural changes in the fibers caused by environmental exposure (aging) and cosmetic treatments (permanent waving and bleaching). The infrared microscope allows the acquisition of spectra as a function of position along intact hair fibers with minimal preparation. Even samples containing moisture give satisfactory results. Our studies employ a Bio-Rad UMA 300 A microscope coupled to a Bio-Rad Model FTS-40 NIR Spectrometer. Bands between 3800 and 5300 cm⁻¹ are monitored: they represent combination and overtone bands of the N-substituted amide groups of the peptide linkages. The absorption mode is applied, yielding spectra representing not only the hair cuticle, but also the cortical cells. Results reveal that besides damage to the disulfide bonds, the peptide backbone is significantly affected by photoirradiation and chemical treatment. Damaged hair shows an increase in the relative intensities in the C-H bands and the structural transformation from alpha-helices to beta-sheets is observed. Application of antioxidants and sunscreens as a trial to minimize hair damage will also be presented.

39.

BIOSENSOR FOR SALMONELLA DETECTION. *Yuanping Tang*¹, *J. Barbaree*², *V. Vodyanov*³, *B. Chin*¹, *B. Fiebor*¹, *C. Bailey*¹, *W. Yan*¹, *H. Chen*², and *K. Krome*¹. (1) *Material Engineering, Auburn University, 104 Beech, Apt# 16, Auburn, AL 36830, tangyua@mail.auburn.edu*, (2) *Biological Science, Auburn University*, (3) *College of Veterinary Medicine, Auburn University*

A rapid & sensitive surface acoustic wave biosensor was developed for the detection of Salmonella bacteria. The Langmuir Blodgett method was used to apply a polyvalent Salmonella antibody to the surface of a quartz crystal transverse shear mode (TSM) quartz crystal. The resonance frequency of the quartz crystal was found to decrease due to attachment of bacteria to the sensor surface. The change in resonance frequency is due to both mass and viscoelasticity changes of the surface upon attachment of the bacteria. The biosensor has a response time of less than 100 seconds and a lower limit of detection of a few hundred cells per ml. Data are presented on the effect of solution viscosity and temperature on the response of the biosensor.

40.

CADMIUM(113) NMR STUDIES OF CADMIUM-FULVIC ACID COMPLEXES.

*William H. Otto*¹, *W. Robert Carper*², and *Cynthia K. Larive*¹. (1) *Department of Chemistry, University of Kansas, Lawrence, KS 66045, Fax: 785-864-5396, wotto@ukans.edu*, (2) *Department of Chemistry, Wichita State University*

Humic substances are a complex heterogeneous mixture of decomposition products of natural organic materials. Aquatic fulvic acids, an operationally defined subset of humic substances, are environmentally important in pollution transport because they are known to effect the transport and bioavailability of metal ions. The complexation of the toxic heavy metal Cd(II) with fulvic acid is examined in this study through the use of ¹¹³Cd NMR. ¹¹³Cd chemical shift, spin-lattice (R1) and spin-spin (R2) relaxation rates are examined to probe of Cd(II)-fulvic acid binding. A range of Cd(II)-fulvic acid ratios is examined at pD 6.4. The ¹¹³Cd chemical shift shows fast exchange between free and complexed Cd(II) species on the NMR time scale. Competition of Cd(II) with Ca(II) is also investigated by observing displacement of Cd(II) upon Ca(II) addition using ¹¹³Cd NMR.

41.

CHARACTERIZATION OF BIOPOLYMERS BY SIZE EXCLUSION CHROMATOGRAPHY EQUIPPED WITH RIGHT-ANGLE LASER LIGHT SCATTERING AND VISCOSITY DETECTORS.

Chikako Yomota, *Tamaki Miyazaki*, and *Satoshi Okada*, *Division of Drugs, National Institute of Health Sciences, 1-1-43 Hoenzaka, Chuo-ku, Osaka, Japan, Fax: +81-6-6942-0716, yomota@nihs.go.jp*

Characterization of biopolymers by size exclusion chromatography equipped with right-angle laser light scattering (RALS) and viscosity detectors has applied to characterize the water-soluble biomedical polymers, such as pullulan, dextran and hyaluronate. A series of narrow molecular weight pullulan standard and broad molecular weight distribution dextran standards was measured, and the obtained values of M were in good agreement with the proposed values. In the case of a series of hyaluronate sample, the results are accurate up to a million. At the molecular weight of over three millions of hyaluronate, the peculiar behavior can be revealed that after the usually measured decrease of the molar mass and the intrinsic viscosity with increasing elution volume the molar mass increased at even higher elution volume similar to the report for polystyrene microgels.

42.

CHARACTERIZATION OF COMPLEXATION BETWEEN METAL IONS AND ORGANIC CHROMOPHORES.

J. J. Tulock, and *G. J. Blanchard*, *Chemistry, Michigan State University, E. Lansing, MI 48824, Fax: 517-353-1793, tulock@photon.cem.msu.edu*

We report on the complexation of 1-pyrene carboxylic acid (PCA) with Zr⁴⁺ in aqueous solution. We are interested in the interaction of this chromophore with metal ions, both for its potential in sensing applications and because the issue of changes in chromophore dynamics upon complexation are not well understood. When complexed with Zr⁴⁺, PCA exhibits a 10nm red-shift in its absorption maximum and a pronounced change in both steady state and

time-resolved emission responses. The emission spectrum of Zr⁴⁺-complexed PCA is featureless and red-shifted by -40 nm with respect to the un-complexed chromophore, and the fluorescence lifetime decreases from 40 ns to 4.6 ns upon complexation. These data, in conjunction with rotational diffusion information, provide a more complete understanding of metal ion interactions with organic chromophores in solution.

43.

CHARACTERIZATION OF IRON-CONTAINING PROTEINS IN HUMAN SERUM.

David M. Bunk, and *Michael J. Welch*, *Analytical Chemistry Division, National Institute of Standards and Technology, 100 Bureau Drive, Stop 8392, Gaithersburg, MD 20899-8392, Fax: 301-977-0685, david.bunk@nist.gov*

Serum iron determination is an important clinical measurement. Low serum iron levels are indicative of diseases such as anemia, rheumatoid arthritis, and certain infections. Hemochromatosis, the most common form of iron overload disease, is an inherited disorder that causes the body to absorb and store too much iron, and often results in failure of the liver, heart, or pancreas. Typically, for the purpose of medical diagnosis, the total serum iron concentration is measured. However, in many iron-related diseases, the distribution of iron bound to serum proteins is altered. For improved medical diagnosis, it would be beneficial to determine the speciation of iron among serum proteins as well as the total serum iron concentration.

A variety of chromatographic techniques have been utilized in conjunction with mass spectrometry to characterize several iron-binding proteins in human serum. Protein structure, concentration, and iron binding saturation have been investigated and these results will be presented.

44.

CHARACTERIZATION OF POLYMER-BASED REVERSED-PHASE LIQUID CHROMATOGRAPHIC PHASES USING MULTIVARIATE RESOLUTION METHODS.

Shyroine R. Anthony, *Shalini Nigam*, and *Sarah C. Rutan*, *Department of Chemistry, Virginia Commonwealth University, P. O. Box 842006, 1001 W. Main Street, Richmond, VA 23284-2006, Fax: 804-828-8599, wonder08@aol.com*

The solvatochromic method has been used to probe the solid/solution interface of a polymer-based stationary phase in mobile phase mixtures of methanol-water and acetonitrile-water. UV-visible spectral measurements of solvatochromic dye solutions at different mobile phase compositions and of slurries wetted by these same solutions have been recorded. Two solvent-sensitive dyes, N-methyl-2-nitroaniline (NM2NA) and N,N-dimethyl-4-nitroaniline (NDMNA), have been used. In order to resolve the spectra into the contributions due to the different solvated species, multivariate curve resolution-alternating least squares (MCR-ALS) has been used.

45.

CHARACTERIZATION OF RETENTION ON OCTADECYLSILICA PHASES USING PRINCIPAL COMPONENTS ANALYSIS.

*Lawrence A. Lopez*¹, *Sarah C. Rutan*¹, *Lloyd Snyder*², *John Dolan*², and *John Dorsey*³. (1) *Department of Chemistry, Virginia Commonwealth University, P. O. Box 842006, 1001 W. Main Street, Richmond, VA 23284-2006, Fax: 804-828-8599, s2lalo@titan.vcu.edu*, (2) *LC Resources*, (3) *Florida State University*

Reversed-phase chromatography (RPC) is a popular technique for analytical separations. A large variety of (RPC) stationary phase materials based on octadecyl silica are currently available. Differences in sample retention for these distinct but related columns exist and can be taken advantage of during RPC method development. However, there is a need for a better understanding of how separation selectivity depends on the column and sample. In this study, principal component analysis (PCA) is used to analyze the retention variation of a large set of compounds on ten different octadecyl phases. These results are used to better understand the underlying chemical interactions and to identify "key solutes" that best represent the retention process.

46.

CHARACTERIZATION OF TETANUS TOXIN PROTEIN-LIGAND NON-COVALENT COMPLEXES USING MASS SPECTROMETRY.

Sharon J. Shields, *Chemistry and Materials Science, Lawrence Livermore National Laboratory, 7000 East Avenue, L-231, Livermore, CA 94550, Fax: 925-422-1336, shields9@llnl.gov*, and *Rodney L. Balhorn*, *Biology and Biotechnology Program, Lawrence Livermore National Laboratory*

Tetanus toxin C-fragment is a 51 kDa fragment of tetanus neurotoxin (150 kDa) that initiates binding to gangliosides on the surface of neuronal cells. There is a

significant effort to identify small molecules that non-covalently bind to proteins, such as tetanus toxin C-fragment. Understanding the nature of the protein-inhibitor interaction is a critical part of the drug discovery and drug design process. Electrospray (ESI) mass spectrometry (MS) has demonstrated great utility for the rapid detection of specific non-covalent interactions between tetanus toxin C-fragment and small molecule ligands. This technique is useful for screening a large set of potential ligands that bind to proteins; however, it does not offer information about the ligand binding site. Kinetic studies of the rate of proteolysis of the ligand free protein and the protein-ligand complex using MALDI-MS have been developed to determine the protein-ligand binding site. This work was performed under the auspices of the U.S. Department of Energy by University of California Lawrence Livermore National Laboratory under contract No. W-7405-ENG-48.

47. CHROMATOGRAPHIC ANALYSIS OF ORGANIC INTERMEDIATES IN PHOTOCATALYTICALLY TREATED AQUEOUS SOLUTIONS OF LINDANE IN THE PRESENCE OF $PW_{12}O_{40}^{3-}$. Ch. Nezis, A. Hiskia, S. Boyatzis, and E.

Papaconstantinou, Institute of Physical Chemistry, NCSR "Demokritos" 15310 Athens, Greece, Agia Paraskevi, 15310 Athens, Greece, Fax: +301-651-1766

Homogeneous aqueous solutions of the organometallic insecticide lindane undergo effective photodegradation upon photolysis with UV and near visible light in the presence of a characteristic polyoxometallate catalyst $PW_{12}O_{40}^{3-}$. These substrates remained practically intact under similar conditions in the absence of catalyst. All indications are that the system proceeds through the formation of OH radicals from the reaction of the excited polyoxometallate with water. The system is comparable with the widely published system based on TiO_2 . In this study, Gas Chromatographic-Mass Spectrometric analysis of the photocatalytically treated solution containing lindane were carried out for identification of intermediates in the presence of the polyoxometallate catalyst. Some conclusions concerning the lindane degradation pathways are also presented.

48. COMBINATORIAL SCREENING OF ELECTROCATALYSTS FOR AMPEROMETRIC GLUCOSE SENSORS. Yipeng Sun¹, Benny C. Chan¹, Thomas E. Mallouk¹, and Harvey Buck². (1) Department of Chemistry, Pennsylvania State University, University Park, PA 16802, Fax: 814-863-8403, ysun@chem.psu.edu, (2) Roche Diagnostics Corporation

Recently, combinatorial methods have been used to search for new materials ranging from zeolites to heterogeneous catalysts. We have developed a rapid combinatorial synthesis and screening method for the discovery of new electrocatalysts. This paper reports the extension of this method to the search for improved anode materials for amperometric glucose sensors. Preliminary results show that active alloy compositions containing Pt, Pb, Rh, Au and/or Pd oxidize glucose at substantially more negative potentials than pure platinum in enzyme-free voltammetric measurements. The improvement can be interpreted in terms of a decrease of electrode poisoning. Interference from ascorbate, urate, and other reducing agents found in serum or blood can be largely eliminated by operating the sensor at potentials negative of -100 mV vs. SCE.

49. COMPARISON OF APPROACHES TO CONFIDENCE INTERVALS OF LINEAR CALIBRATION. Yuzuru Hayashi¹, Rieko Matsuda¹, Mari Katsumine², Kazuo Iwaki², Yoko Tagashira³, and Chikako Yomota³. (1) National Institute of Health Sciences, 1-18-1 Kami-Yoga, Setagaya, Tokyo 158-8501, Japan, Fax: 03-3707-6950, fumi@nihs.go.jp, (2) Center of Technology Department, Ebara Research Co., Ltd, (3) Osaka Branch, National Institute of Health Sciences

The 95% confidence intervals of a calibration line can be calculated by the well-known statistical method and a probabilistic approach called FUMI theory. The former method is applicable to any problem, without knowledge of the causality of the errors accompanied with analytical procedures used, but the resulting confidence intervals are not so reliable. On the other hand, the FUMI theory needs the probabilistic model of error including preparation and measurement, but can provide more precise estimates of the 95% confidence intervals than the statistical method. The determination of pesticide (quisalofop), polysaccharide (pullulan) and K ion are taken as an example of reversed-phase chromatography and ion chromatography. About 9 calibration lines are prepared

and superimposed on the 95% confidence intervals of the calibration lines to demonstrate the exact intervals can be obtained theoretically from the error estimates of the preparation (dilution) and measurement. The reliability of the two methods is compared.

50. COMPLEXATION IN AQUEOUS SOLVENT MIXTURES: RAMAN SPECTROSCOPY AND CHEMOMETRIC ANALYSIS. Carol A. Holden, Sally S. Hunnicutt, and Sarah C. Rutan, Department of Chemistry, Virginia Commonwealth University, 1001 W. Main St., P.O. Box 842006, Richmond, VA 23284-2006, Fax: 804-828-8599, cholden@vcu.org

Methanol-water and acetonitrile-water mixtures are widely used in liquid chromatographic separations. Hydrogen bonding complexation in these mixtures can be observed using Raman spectroscopy. Mathematical analysis is required to resolve the experimental spectra into profiles corresponding to the individual species in the mixtures.

Raman spectra of methanol-water and acetonitrile-water mixtures were recorded and analyzed by evolving factor analysis and alternating least squares. The results indicate three chemical species are present in methanol-water mixtures: one pure methanol, one pure water, and one methanol-water complex. In acetonitrile-water mixtures the results suggest four chemical species are present: one pure acetonitrile, one pure water, and two different acetonitrile-water complexes. These results will be compared to results from similar studies of the same mixtures using infrared spectroscopy. Mathematical analysis of the infrared spectra indicates two distinct pure water species. Additional results using acetone as a model solute in acetonitrile-water mixtures will be presented.

51. COMPLIMENTARY PURIFICATION OF A NEW PEPTIDE BY USING ION-EXCHANGE AND REVERSED-PHASE CHROMATOGRAPHY. Jack Liu, and Peter C. Rahn, Biotage, a Division of Dyax Corp, 1500 Avon Street Extended, Charlottesville, VA 22902, JLiu@biotage.com

This paper presents a technique to purify a new peptide by using the combination of ion-exchange and reversed-phase chromatography. The peptide contains 27 amino acids and has a molecular weight 2749 dalton. To remove impurities, the crude peptide was fractionated with BIOFLASH 12M Macro-Prep Q. The results show the ion-exchange method resolved the peptide from impurities better than reversed-phase chromatography. However, reversed-phase technique was used to remove salts and buffers resulting from the ion-exchange step. Once the peptide was loaded on the C18 column, it was eluted with isopropanol to recover the peptide. The reversed-phase procedure was very selective to quickly remove the non-volatile solvents and buffers with high peptide recovery. This study demonstrates the advantages of combining ion-exchange and reversed-phase chromatography is synergistic to obtain high purity peptides.

52. CRYOGEN-FREE MEASUREMENT OF AMBIENT C2-C12 VOLATILE ORGANIC COMPOUNDS. Jia-Lin Wang, Weih-Li Chen, and Moor Lin, Department of Chemistry, National Central University, Chungli 320, Taiwan, Fax: 886-3-4277972, cwang@cc.ncu.edu.tw

An automated gas chromatographic system was constructed for measuring ambient volatile organic compounds (VOCs). Preconcentration of the VOCs was performed by using two separated sorbent traps of different combinations with each designated for either low or high boiling VOCs. Both traps and their associated valve systems were integrated as a complete system sharing a common sample inlet. No additional cryo-focusing stage prior to the column was needed owing to the flash heating capability for desorption. Other than the cryogen free preconcentration and focusing, the separation of VOCs of large volatility difference was also performed without cryogen. The system employed a Al_2O_3/KCl PLOT column for separating C2-C7 compounds; and a DB-1 column for C6-C12. Our study reveals that flash heating as well as proper plumbing were the key factors to optimize resolution under cryogen free condition.

53.

DETECTION OF NITROAROMATIC COMPOUND VAPORS USING AN OPTICAL SENSOR ARRAY AND PATTERN RECOGNITION. *Gregory A. Bakken¹, Gregory W. Kauffman¹, Peter C. Jurs¹, Keith J. Albert², Shannon S. Stitzel², and David R. Walt².* (1) Chemistry Department, Pennsylvania State University, 152 Davey Lab, University Park, PA 16802, gab@zeus.chem.psu.edu, (2) Department of Chemistry, Tufts University

A cross-reactive sensor array with optical detection is used to determine the presence or absence of nitroaromatic compound (NAC) vapors in pure samples and in variable backgrounds of volatile organic compound vapors. The array is composed of four bead-based sensor types, with 50 replicates of each bead type. Presentation of vapor to the array produces time-dependent fluorescence profiles. After autoscaling, the profiles for each sensor type are signal-averaged, and numerical descriptors are calculated to encode the average response. Models are developed using training observations, and prediction ability is verified with an external prediction set. Information-rich subsets of descriptors are identified using a genetic algorithm and k-nearest neighbor analysis. A five-descriptor model capable of correctly classifying all prediction set observations as containing or not containing an NAC vapor is presented. Additionally, models developed using a training set that did not contain all NAC vapors that are in the prediction set are discussed.

54.

DETECTION OF P450 METABOLITES BY MALDI-TOF WITH APPLICATION OF A BINARY PHASE EXTRACTION. *Mark Olson, and Dan Fabris, Department of Chemistry and Biochemistry, University of Maryland, 1000 Hilltop Circle, Baltimore, MD 21250, Fax: 410-4552608*

MALDI-TOF mass spectrometry is capable of providing accurate mass analysis not only for medium and large molecules (in excess of 500 kDa molecular weight), but also for relatively small analytes (below 1000 Da). In this work, MALDI-TOF mass spectrometry is applied to characterize the metabolites produced by *in vitro* reaction of P450 with tamoxifen (a chemotherapeutic agent used in breast cancer treatment), promethazine and diphenhydramine (antihistamine drugs). A correct choice of matrix is crucial in order to obtain good sensitivity and avoid overlapping with analyte peaks in the low mass range. The use of a binary phase extraction has been investigated to eliminate the small mass components present in the microsomal preparations of P450, which may interfere with the detection of the analyte of interest. This approach offers several advantages over alternative methods, which employ radioactive tracers and/or lengthy separation procedures to monitor the P450 reaction. Analysis can be performed in a very expedite way and using minimal sample volumes (less than 200 nL).

55.

DETERMINATION OF CAPSAICINS IN HOT CHILI PEPPERS WITH MICELLAR ELECTROKINETIC CHROMATOGRAPHY. *Angela H. Wu, and David C. Locke, Department of Chemistry and Biochemistry, Queens College of the City University of New York, 65-30 Kissena Blvd., Flushing, New York, NY NY11367, Fax: 718-997-5531, wxhqc@qcunix1.qc.edu*

A simple and rapid method using capillary electrophoresis (CE) was developed for the determination of capsaicin and dihydrocapsaicin. The capsaicins were extracted from various capsicum fruits such as chipotle, ancho, mulatto, pasilla, and jalapeno peppers using acetonitrile. Extracts were analyzed using micellar electrokinetic capillary chromatography (MECC), the CE technique in which an ionic surfactant is used above its critical micelle concentration (CMC) to produce micelles that solubilize neutral species and allow them to be separated electrophoretically. The method was optimized for surfactant concentration, buffer composition and concentration, organic modifier, and sample matrix. Validation of the method was carried out in terms of precision, linearity, limits of detection and quantitation, accuracy, and ruggedness. The MECC results for the hot pepper samples compare favorably with those using HPLC.

56.

DETERMINATION OF CYCLOOXYGENASE-2 SPECIFIC INHIBITORS (ROFECOXIB AND CELECOXIB) IN DOSAGE FORM AND PLASMA USING CHROMATOGRAPHIC/SPECTROMETRIC METHODS. *Salah M. Blaih, Department of Chemistry, Kent State University, 4314 Mahoning Ave. NW, Warren, OH 44483, Fax: 330-847-6610, blaihs@trumbull.kent.edu*

Rofecoxib and celecoxib are new non-steroidal anti-inflammatory drugs (NSAIDs). Both compounds are known to inhibit cyclooxygenase-2 enzyme (COX-2) without affecting COX-1. In therapeutic anti-inflammatory dose, both drugs lack the gastrointestinal side effects that are common to compounds that inhibit both isoforms of cyclooxygenase. Chromatographic techniques, namely reversed-phase HPLC with or without derivatization along with parameters such as choice of mobile phase, chromatographic conditions, detection limit, and selectivity will be presented. Spectrometric techniques and color formation with certain chromogenic reagents will also be discussed. The above methods are used for the determination of these drugs in their dosage forms and in plasma. Optimization of the assay conditions in order to determine both drugs in presence of other interfering substances, degradation products, and/or metabolites is included.

57.

DETERMINATION OF SULFONAMIDE IN MEAT BY LIQUID CHROMATOGRAPHY-ELECTROSPRAY-MASS SPECTROMETRY. *Ming-Ren Fuh, and Shun-An Chan, Department of Chemistry, Soochow University, P.O. Box 86-72, Taipei, Taiwan, Fax: +886-2-2881-2685, msfuh@mail.scu.edu.tw*

A liquid chromatography-electrospray-mass spectrometry (LC-ES-MS) method was developed to determine nine sulfonamides (sulfadiazine, sulfapyridine, sulfamerazine, sulfamethazine, sulfamonomethoxine, sulfisoxazole, sulfadimethoxine, sulfaquinoxaline, sulfaphenazole) in meat product. A reversed phase LC with gradient elution was utilized for the separation of these chemicals. Selected ion monitoring was employed for quantitative measurement. Phenyl-13C6-sulfamethazine was used as an internal standard. Good linearity (0.1 to 10 ppm) and detection limit (-0.03 ppm) of each compounds were determined. A solvent extraction method was developed to extract analyte compound from meat. Satisfactory recovery (80%) of each compound was determined. The application of this newly developed LC-ES-MS method was demonstrated by examining the sulfonamide spiked meat samples.

58.

DEVELOPMENT OF REAL-TIME DNA HYBRIDIZATION ASSAYS USING FIBER OPTIC SENSORS. *Richard H. Smith¹, Bradford Henderson¹, Wayne D. Lancaster², Alan P. Hudson³, James G. Downward IV¹, and Judith L. Erb¹.* (1) IA, Inc, 6109 Jackson Ave, Ann Arbor, MI 48103, Fax: 734-995-6869, downward-rsmith@ic.net, (2) Center for Molecular Medicine & Genetics, Wayne State University School of Medicine, (3) Department of Microbiology and Immunology, Wayne State University School of Medicine

Current methods to determine DNA from pathogenic organisms requires the use of laboratory scale equipment for amplification and measurement of hybridization to oligonucleotide probes. We are using fiber optic sensors to develop DNA hybridization assays for pathogens, such as human papilloma virus (HPV) and Chlamydia trachomatis (CT), whose confirmed presence is a significant indication for patient therapy. Oligonucleotide probes (about 30-mers) for specific HPV and CT strains are coupled to optical fibers. Binding of complementary fluorophore-labeled oligonucleotide probes is determined in real time using an evanescent fiber optic fluorometer, and sample values are estimated from calibration data obtained on each fiber, with data collection occurring typically over a 3 minute period. Kinetic data indicate that we can detect <10 pmol of amplified HPV or CT DNA. These assays, coupled to DNA amplification methods, may provide a solution to the need for point of care testing for human pathogens.

59.

DEVELOPMENT OF REDOX PROBES FOR REAGENTLESS BIOSENSORS. *Scott A. Trammell¹, Leonard M. Tender¹, David W. Conrad², and Homme W. Hellinga².* (1) Center for Bio/Molecular Science & Engineering, Naval Research Laboratory, 4555 Overlook Ave., Washington, DC 20375, Fax: 202-404-7946, trammell@ccs.nrl.navy.mil, (2) Department of Biochemistry, Duke University Medical Center

Polypyridyl-amine and polypyridyl-cyano complexes of Ru(II) exhibit environmentally sensitive spectroscopic and electrochemical properties. We have initiated an investigation to incorporate these dependencies into reagentless transduction schemes for determination of analyte binding to proteins that undergo large conformational changes upon analyte binding (such as glucose binding protein). In these schemes, ammine or cyano polypyridyl complexes of Ru(II) are conjugated to sites allosterically coupled to analyte binding so as to induce a localized change in the environment of the conjugate. We will report on the synthesis and characterization of thiol-reactive polypyridyl-amine and polypyridyl-cyano complexes of Ru(II) and preliminary transduction observations.

60.

DNA ANALYSIS BASED ON A MICROFABRICATED CAPILLARY ELECTROPHORESIS DEVICE. *Masanori Ueda, CREST, Japan Science and Technology Corporation, 1637 Yana, Kisaradzu 292-0812, Japan, Fax: +81-438-52-0130, uedam@fc.ph.tokushima-u.ac.jp, and Yoshinobu Baba, Department of Medicinal Chemistry, Faculty of Pharmaceutical Sciences, University of Tokushima*

Laser-induced fluorescence detection system coupled with highly sensitive silicon intensified target (SIT) video camera is successfully applied to the imaging of a band for DNA fragment labeled with fluorescence dye and the visualizing of a separation process in the microchannel fabricated on a chip. We demonstrated that the imaging of the sample injection process is a powerful method for the optimizing the electric potentials. Moreover, in microfabricated capillary electrophoresis ($f\hat{E}$ -CE) devices, the continuous observation for the sample separation process is available. This direct imaging method is useful for the study of separation dynamics on $f\hat{E}$ -CE devices.

61.

EFFECT OF THE TEMPERATURE AND POLAR SOLVENTS IN THE SEPARATION OF POLYETHOXYLATED SURFACTANTS BY HPLC. *Nelson Marquez, Fredy J. Ysambertt, Gerson E. Chavez, and Belgica B. Bravo, Departamento de Quimica-Facultad de Ciencias, Universidad del Zulia, Maracaibo 526, Venezuela, Fax: 5861598099*

Non-ionic surfactants are of the polyether-type synthesized by the addition of ethylene oxide to substances with a reactive hydrogen atom, such as alkylphenol. During the ethoxylation process, the adduction randomness results in a mixture of oligomers with a variable degree of ethoxylation, which is often Poisson distributed. The oligomer distribution in polyethoxylated surfactants was determined by normal-phase HPLC on amino column using a mixture of apolar and polar mobile phase. The addition of polar solvent to the mobile phase improved the separation of hydrophilic oligomers without affecting the retention time of lipophilic oligomers. Consequently, both the absolute retention and selectivity are lower using a mixture of apolar and polar mobile phase. However, polar mobile phase increased the column pressure and reproducibility problems arrived because of the interaction of the mobile phase with the stationary phase. These problems can be overcome by increasing the temperature of the column. As we increase the temperature of the column, the surfactant oligomers become more lipophilic and migrate to the non-polar mobile phase, decreasing the interaction with the polar stationary phase. Therefore, the resolution and elution times for the surfactant oligomers can be easily adjusted by simply changing the temperature.

62.

EFFECTS OF DILUENT MONOMERS ON PROPERTIES OF EXPERIMENTAL DENTAL POLYMERS. *Cynthia J. E. Floyd, and Sabine H. Dickens, Paffenbarger Research Center, American Dental Association Health Foundation, Polymers Building (224), Room A153, National Institute of Standards and Technology, Gaithersburg, MD 20899-8546, cfloyd@nist.gov*

Deficiencies in degree of cure and hydrophilicity of dental BisGMA/TEGDMA resins lead to polymers with inferior properties and leachable monomers.

Diluent monomers, benzyl- or lauryl-methacrylate, (0-20) mass fraction %, were added to BisGMA/TEGDMA mixtures to improve cure and polymer crosslinking, and to decrease water sorption and leachable monomer content. Three (20 × 0.5) mm visible light-cured polymer disks were prepared from each formulation. The bulk cure was studied using near-infrared (NIR) spectroscopy (C=CH₂ peak at 6164 cm⁻¹). Disks were exposed to 75% relative humidity and water sorption was determined from the NIR water absorption envelope at 5200 cm⁻¹. The disks were extracted with dichloromethane and then cyclohexane, and the eluates analyzed by ¹H NMR. The diluent monomethacrylate generally improved properties measured over those of BisGMA/TEGDMA resins. The addition of the monomethacrylate increased conversion and crosslinking while reducing water uptake and leachables. Supported by ADAHF, NIST, NIDCR DE09322.

63.

ELECTROLESS DEPOSITION AND CORROSION STUDIES OF AMORPHOUS NI-RE-P ALLOYS DEPOSITED FROM ACIDIC HYPOPHOSPHITE SOLUTIONS.

Donald E. Mencer, Department of Chemistry, Pennsylvania State University, Hazleton, PA 18201, Fax: 570-450-3182, dxm53@psu.edu

Amorphous Ni-Re-P alloys of varying composition (atomic percent rhenium 0.0 to 7.5 %) were prepared using electroless deposition from acidic solutions of Ni²⁺, perchlorate, hypophosphite, and succinic acid/succinate. A pH of 4.5 produced deposits more readily than other pH values. The composition of each alloy was determined using Electron MicroProbe Analysis (EMPA) and varies as a function of solution composition. The alloys were also characterized using X-ray diffraction (XRD) and Differential Scanning Calorimetry (DSC). All of the alloys prepared in this study were amorphous and the crystallization temperatures of the alloys increased with increasing rhenium (decreasing phosphorus) composition. The mole ratio of rhenium to nickel in the alloys is approximately one half the value for that ratio in the solution from which it is deposited. Corrosion resistance of the alloys is enhanced by the addition of rhenium.

64.

ENHANCED RETENTION AND SENSITIVITY IN THE ANALYSIS OF CYANURIC ACID IN WATER USING POROUS GRAPHITIC CARBON AND UV DETECTION IN HPLC. *Ricardo Cantu¹, Otis Evans¹, Fred K. Kawahara², and Alfred P. Dufour¹.* (1) National Exposure Research Laboratory, United States Environmental Protection Agency, 26 West Martin Luther King Dr, Cincinnati, OH 45268, Fax: 513-569-7757, Cantu.Ricardo@epa.gov, (2) National Risk Management Research Laboratory, United States Environmental Protection Agency

Cyanuric acid (CA) has found application as a chlorine stabilizer in pool waters. The National Swimming Pool Foundation recommends CA levels between 30-50 ppm and a chlorine residual of 1.0-3.0 ppm. These chlorine levels are needed to destroy harmful pathogenic organisms. Developing a rugged method to monitor CA in water is crucial in maintaining adequate chlorine levels that do not pose undue hazards to human health. Existing methodology employing HPLC has proved ineffective because of the lack of CA retention imposed by the use of silica based columns. A rugged method has been developed using porous graphitic carbon (PGC) to analyze real world water samples. The analysis employed 95% phosphate:5% methanol at pH 7.4 with UV detection at 213nm. The CA retention factor (k') using PGC was 8 while for C18, C8, C6H5, NH2, and CN silica columns it was unsuitable (< 0.1). Raising the pH to 9.2 resulted in practical retention ($k'=4$) and gave 20 % more sensitivity due to optimum UV detection.

65.

EXAFS INVESTIGATION OF LA0.6CA0.4CO03 PEROVSKITE CATALYST IN BIFUNCTIONAL OXYGEN ELECTRODES. *Otto Haas¹, Stefan Müller¹, Franziska Holzer¹, James McBreen², X. Sun², and X. Q. Yang².* (1) General Energy Research, Paul Scherrer Institute, Villigen CH-5232, Switzerland, Fax: 0041 310 4415, otto.haas@psi.ch, (2) Applied Science, Brookhaven National Laboratory

The chemical stability of the La_{0.6}Ca_{0.4}CoO₃ perovskite as an electrocatalyst for bifunctional oxygen electrodes has been studied using ex-situ and in-situ EXSAFS investigations. The catalyst was investigated in bilayered bifunctional oxygen electrodes which contained 50 wt% of La_{0.6}Ca_{0.4}CoO₃ perovskite in the active layer mixed with graphitized and activated Vulcan XC72 and 15% Teflon as a binder. EXSAFS spectra were measured before and after and while using the electrodes as an oxygen electrode to reduce or evolve oxygen in alkaline solutions. Although the catalyst keeps its activity for more than thousand hours,

changes in the XANES region of the XAS spectra can be observed after short operation times. The Co-edge is shifted to higher energies if the electrode potential is changed from oxygen reduction to oxygen evolution potential, which indicates a increase of the valence state of the Co in the catalyst. The oxidation state of the Co in the electrode depends also on the heat treatment of the composite electrode during preparation.

66.

EXTRACTION OF ESSENTIAL OIL OF THYMUS CAPITATUS AND JUNIPERUS PHOENICIA L OF TUNISIA: INFLUENCE OF THE PRESSURE ON THE COMPOSITION AND THE KINETICS OF THE EXTRACTION OF THE ESSENTIAL OIL. *Manef Abderrabba¹, Lassaad Hedhili¹, Mehrez Romdhane², and Abdellatif Gadri².* (1) *Laboratoire de Physico-chimie des matériaux IPEST, Tunis II University, IPEST Route Sidi Bou Said, 2070 La Marsa, Tunisia, Fax: 00 216 1 746 551, manef.abderrabba@ipest.rnu.tn,* (2) *Ecole Nationale d'Ingenieur de Gabes-Tunisia*

In this paper we are dealing with the extraction of essential oil by vapodistillation from a few Tunisian plants (Juniperus Phoenicia L, Thymus Capitatus, . . .). For this purpose we have used the installation developed in our laboratory and described hereafter. It is essentially made up of a 50-liter column, with five baskets whose bottoms are pierced trays which can hold a mass of solid plant matter of approximately 5Kg. The water steam produced by a furnace goes through the trays and drags the essential oil with it. The installation also includes electrovanne that regulates the pressure of steam in the column. In this paper we have studied: -The influence of the pressure of water steam in the column on the kinetics and the output of the extracted essential oil. -The interest of supplying plants to the column by the top and by the bottom. -The effect of the condensation temperature on the retrieval of the essential oils. -The essential oil composition according to the time (kinetics) and to the pressure.

67.

FAST GC-ECD ANALYSIS FOR DECODING LARGE COMBINATORIAL LIBRARIES. *Ying Jin¹, Joan Guo¹, Nicole Volpe¹, and Roland E. Dolle².* (1) *Department of Analysis, Pharmacoepia, Inc, CN5350 Princeton, NJ 08543-5350, CN5350 Princeton, NJ 08543, Fax: 732-422-0156, yjin@pharmacop.com,* (2) *Department of Chemistry, Pharmacoepia, Inc*

Capillary GC-ECD decoding technology has been used to identify individual organic compounds as potential drug leads from large diverse small molecule combinatorial libraries. It is one of the key components of Pharmacoepia's proprietary ECLiPS (Encoded Combinatorial Libraries on Polymeric Supports) technology. Traditionally, capillary GC-ECD decoding was performed on a Hewlett Packard 5890/ECD system with a 15 minute run time and sensitivity level at 0.2 pmol. Recently, we have developed a fast GC-ECD method on a Hewlett Packard 6890 GC/micro-ECD system. This method has reduced the GC run time from 15 minutes to 2.5 minutes without sacrificing any resolution for the 18 polychlorinated-phenoxyalkyl-based tags, which we use to identify the structures of individual compounds from our libraries. The micro-ECD improved the sensitivity to 2 fmol (100-fold increase). Our decoding throughput has been increased up to 4500 runs per month. This paper will describe the parameters optimized and different approaches used in order to achieve the success.

68.

FAST GRADIENT LIQUID CHROMATOGRAPHY/MASS SPECTROMETRY FOR HIGH THROUGHPUT QUALITY CONTROL OF ENCODED COMBINATORIAL LIBRARY. *Kevin J. Bowman¹, Wenni Li¹, and Roland E. Dolle².* (1) *Analytical Chemistry Department, Pharmacoepia, Inc, CN5350, Princeton, NJ 08543-5350, kb Bowman@pharmacop.com,* (2) *Department of Chemistry, Pharmacoepia, Inc*

Combinatorial techniques in the drug discovery field have enabled the synthesis of large numbers of compounds in a relatively short time, creating an ever increasing demand for high throughput analytical approaches to characterize the compounds. This poster describes a fast gradient liquid chromatography/mass spectrometry (LC/MS) method for high throughput quality control of an encoded combinatorial library. A statistical sampling of beads was arrayed in single bead per well. The cleaved products from single beads were pooled together in groups of five and were analyzed by HPLC/UV/MS to confirm the structures. This pooling method allows for a high-throughput assay similar to flow-injection MS (FIA/MS) while maintaining the resolution of single bead LC/MS. Discrete compounds are capable of being characterized at the rate of 1 compound per

minute by fast gradient LC/MS. This pooling method was validated by evaluating each cleaved compound by single bead LC/MS and pooling LC/MS. Matrix effects of plate type and beads after the pooling were also investigated.

69.

FLUORESCENCE LIFETIME IMAGING OF ORGANIC THIN FILMS IN NEAR-FIELD SCANNING OPTICAL MICROSCOPY. *Eun-Soo Kwak, TaiJong Kang, Julie Teetsov, and David A. Vanden Bout, Department of Chemistry and Biochemistry, University of Texas, A5300, Austin, TX 78712, ekwak@mail.utexas.edu*

Near-Field Scanning Optical Microscopy (NSOM) is a high resolution scanning probe technique capable of obtaining simultaneous optical and topographic images with spatial resolution of tens of nanometers. We have integrated Time-Correlated Single-Photon Counting (TCSPC) and NSOM to obtain images of fluorescence lifetimes with high spatial resolution. A pulsed Ti:Sapphire laser was used for sample excitation and fluorescent photons are sorted into two time delay bins. Using this technique, near-field fluorescence images of photons in two time windows (short and long) can be collected while scanning the surface. A sample consisting of two phase-separated incompatible polymers that were tagged with different dyes was used to demonstrate the technique. In addition, thin films of dialkylfluorene were studied to determine the spatial extent of intra- and inter- polymer emitting species. The fluorescence lifetime measurement technique was expanded to allow for full time correlated histograms at each pixel of the NSOM image.

70.

FORMATION AND STRUCTURE OF SELF-ASSEMBLED MONOLAYERS OF N-OCTADECYLTRICHLOROSILANE ON FUMED AND COLLOIDAL SILICA.

Rongwei Wang, and Stephanie L. Wunder, Department of Chemistry, 016-00, Temple University, Norris and 13th Sts, Philadelphia, PA 19122, Fax: 215-204-1532, rwang@astro.temple.edu

The saturation adsorption of octadecyltrichlorosilane (OTS) on fumed silicas of 7 nm, 40 nm primary particle sizes and 106 nm colloidal silica particles was investigated as a function of their hydration state. TGA and FTIR spectroscopy were used to characterize the silanol distribution and amount of water adsorbed on the silica. The coverage of OTS on the silica was affected by the hydration state of silica, which in turn affected the intrachain and interchain order of OTS self-assembled monolayers (SAMs). Ordered OTS SAMs were formed on "super-hydrated" silicas. Raman spectra showed that the ordered SAMs on larger size silica particles were conformationally and thermally more stable than that on smaller size particles after heat treatment. This was attributed to the effects of the underlying substrate and free volume in the monolayer.

71.

FT-RAMAN STUDIES OF PORPHYRIN MACROCYCLES. *Muthusamy Mylrajan, Regional Sophisticated Instrumentation Center, Indian Institute of Technology, Chennai 600036, India, Fax: 044-2350509, mylrajan@eth.net*

Fourier transform Raman studies were carried out for octaethyl, tetraphenyl and protoporphyrins with near-infrared YAG laser with 1064nm excitation. Near-infrared excitation shows Raman spectra similar to 514.5 nm excited resonance Raman spectra. A comparative analysis was carried out between resonance Raman with visible excitation and FT-Raman with near-infrared excitation. In addition to resonance Raman bands of macrocycle non-resonant Raman bands of peripheral substituents and C-H stretching modes were also seen in FT-Raman. FT-Raman spectra of hemoglobin and myoglobin were also compared with model compounds. Various normal modes were assigned and compared with calculated values. Various advantages and analysis will be presented.

72.

FULLY AUTOMATED FIA-MS/LC-MS ANALYSIS OF COMBINATORIAL LIBRARIES UTILIZING SWITCHING VALVES. *Catherine Meyer Hicks, Lawrence W. Dillard, and Roland E. Dolle, Department of Chemistry, Pharmacoepia, Inc, CN 5350, Princeton, NJ 08543, Fax: 732-422-0156, chicks@pharmacop.com*

The confirmation of a product synthesized combinatorially can be readily obtained by high-throughput flow-injection analysis mass spectrometry (FIA-MS). However, the FIA-MS technique is not generally applicable to purity analysis or by-product identification. Gradient reversed-phase high-performance liquid chromatography with UV and MS detection has established itself as the complementary counterpart to FIA-MS analysis, providing information about

purity and reaction by-products. Through the use of switching valves, direct control of the Waters Alliance 2690, and the Thermoquest Xcalibur software package, we have developed a system to analyze combinatorial library products and intermediates in order to assess the progress of chemical reactions. A system was devised which would allow a chemist to select a flow injection run or a LC/MS run (with or without MSⁿ). If it is so desired, both a flow injection and LC/MS result can be obtained for the same sample. This set-up provides mass spectra as well as PDA data. The type of data obtained depends entirely on the experimental method chosen. Methods are available for all types of separations currently used throughout the company. A generic gradient LC/MS method has been found to be useful for greater than 90% of the compounds studied and provides considerable information about the compounds studied. Both positive and negative ion analyses can be performed with or without fragmentation. With the use of the Finnigan LCQ, fragmentation can be with source CID or MSⁿ. This poster describes the design and configuration of this system.

73.

GLUCOSE SENSORS BASED ON REDOX BIOPOLYMER-ENZYME FILMS.

Waldemar Gorski, and **Ning Guo**, Division of Earth and Physical Sciences, University of Texas, 6900 N. Loop 1604 W, San Antonio, TX 78249, Fax: 210-458-4469, wgorski@utsa.edu, guo@jetson.uh.edu

The integrated biosensing films were prepared on the surface of glassy carbon electrodes by immobilizing the enzyme glucose oxidase and osmium, or ruthenium, complexes into the host matrix of the natural polymer chitosan. The electrode-supported films were used in the development of a new line of reagentless electrochemical biosensors for glucose, i.e. biosensors that could operate in anaerobic samples containing no enzyme. The kinetic analysis showed that the transition metal complexes in the films acted as efficient artificial mediators of the enzymatic reaction between the glucose oxidase and glucose. The biosensors were tested in a flow system to determine their operational stability, response time, linear dynamic range, detection limit and reproducibility of the preparation procedure. The analytical performance of the biosensors depended on the amount of the enzyme and the mediator in the chitosan film, degree of the film crosslinking and film thickness.

74.

HIGH PERFORMANCE LIQUID CHROMATOGRAPHY OF 5-AMINO-1,3,2-DITHIARSENANE DERIVATIVES USING PHOTODIODE-ARRAY AND PARTICLE BEAM MS DETECTION. Fu-Lian Hsu, and **Paul C. Bossle**, AMSSB-RRT-TC, U.S. Army, Edgewood Chemical & Biological Center, 5183 Blackhawk Road, Aberdeen P.G., MD 21010-5424, Fax: 410-436-2107, fulian.hsu@sbccom.apgea.army.mil

The 2,5-cis/trans isomers of 5-(phenylamino)-2-phenyl- and 5-(1-naphthyl-acetamido)-2-phenyl-1,3,2-dithiarsenane adducts of the lewisite simulant, phenyl dichloroarsine, were separated on a C-18 column using an acetonitrile-water eluant and were identified/characterized by both PDA and particle beam MS detection. Limits of detection were in the 2-5 nanogram range for both compounds.

75.

HIGH SENSITIVITY DETECTION OF BACTERIAL ENDOSPORES. **Nicholas F. Fell Jr.**, Paul M. Pellegrino, and James B. Gillespie, Optics Branch, U.S. Army Research Laboratory, 2800 Powder Mill Road, Adelphi, MD 20783, Fax: 301-394-0310, nfell@arl.mil

Detecting bacterial endospores is a critical challenge to bioanalytical chemistry, since a number of serious diseases and health problems are caused by members of the genera Bacillus and Clostridium. We have developed a highly sensitive method for their detection and have demonstrated detection limits of less than 5000 CFU/ml. Our method is based on the presence of a marker compound in bacterial endospores, dipicolinic acid (dpa). When complexed with Tb and excited in the UV, the dpa enhances the photoluminescence emission of Tb by several orders of magnitude. Since only 10% or less of the dpa is released when the endospores are suspended in aqueous buffer, we have also examined methods for enhancing the release of dpa. We have achieved a 20 fold increase in dpa release from *B. globigii* endospores through the addition of dodecylamine and heating to 80 °C.

76.

HIGH-PERFORMANCE LIQUID CHROMATOGRAPHIC DETERMINATION OF COCAINE AND ITS METABOLITES IN SERUM MICROSAMPLES WITH FLUORIMETRIC DETECTION AND ITS APPLICATION TO PHARMACOKINETICS IN RATS.

Lei Sun, Department of Psychology, Rutgers University, 152 Frelinghuysen Road, Piscataway, NJ 08854, Fax: 732-445-5147, leisun@rutchem.rutgers.edu

A sensitive, selective and simple HPLC method with fluorimetric detection is described for quantitating cocaine and its three metabolites in rat serum microsamples (50 ul). Chromatographic separation is achieved on a Hypersil BDS C18 column (100 * 2.1 mm, 5 um) with an isocratic mobile phase consisting of methanol-acetonitrile-25.8 mM sodium acetate buffer, pH 2.6, containing 1.0*10⁻⁴ M tetrabutylammonium phosphate (14:10:76, v/v/v). The detection limit was 0.5 ng/ml for all the compounds using direct fluorometric detection operated at excitation and emission wavelengths of 230 and 315 nm, respectively. The effects of ratio of alcohol to chloroform in an extraction solvent on the recovery and precision for cocaine and its metabolites are systematically examined. The method was used to study the pharmacokinetics of cocaine after administration of intravenous 2 mg/kg and oral 20 mg/kg doses.

77.

HPLC METHOD VALIDATION FOR ASSAY AND DEGRADATION PRODUCTS OF EFAVIRENZ ORAL SOLUTION.

Lisa A. Gearhart, Jessica M. Garcia, Robert W. Woodeshick, James Segretario, and Paul K. Hovsepian, Analytical Research & Development Section, DuPont Pharmaceuticals Company, Experimental Station, E353/304, P.O.Box 80353, Wilmington, DE 19880, Fax: 302-695-9802, lisa.a.gearhart@dupontpharma.com

Efavirenz is a non-nucleoside reverse transcriptase inhibitor used in the treatment of HIV. Efavirenz oral solution is a novel dosage form being developed as a solution of efavirenz in a non-aqueous medium. The interactions between the sample solvent, mobile phase, and sample medium provided challenging method development issues. A single, stability-indicating reversed-phase gradient HPLC method has been developed and validated for assay and quantitation of degradation products. Data demonstrating the accuracy, precision, specificity, linearity, and ruggedness of the method will be presented.

78.

INDIRECT DETERMINATION OF ALUMINUM IN SURFACE WATERS BY COULOMETRIC BACK TITRATION.

Shuping Bi, Junrong Weng, Jun Xu, and Lihua Huang, Department of Chemistry, Nanjing University, Nanjing 210093, China, Fax: 011 86 25 3317761

There has been a growing interest for detecting aluminum content in natural waters by electrochemical techniques during the last decade. In this paper, a novel electroanalytical method, indirect determination of aluminum in surface waters by coulometric back titration (Br₂/8-hydroxyquinoline{8-HQ}), is presented. Under the optimal experimental conditions (0.15 M KBr, pH 3-3.5, I=1 mA), the linear working curve is established within 1.4*10⁻⁶ to 2.7*10⁻³M and the detection limit can be down to 10⁻⁶ M. This method is simple and sensitive. It has been applied to the practical analysis for Al in various surface waters (Tai Lake, Nantong well and mineral waters) and the recoveries are found to be 100+/- 12 %. This project is supported by the NAF of China No. 29777013 and No. 49831005.

79.

INTER-CORE AND INTER-SHELL STRUCTURES AND REACTIVITIES FOR NANOPARTICLE THIN FILM ASSEMBLING AND CHEMICAL SENSING.

Li Han, Frank L. Leibowitz, Mathew M. Maye, David R. Daniel, and Chuan-Jian Zhong, Department of Chemistry, State University of New York, P.O. Box 6000, Binghamton, NY 13902, bi90341@binghamton.edu

Many applications of nanometer-sized particles rely on the preparation of macroscopic materials with isolated nano properties. This work explores the spontaneous core-shell and shell-shell reactivities of thiolate-capped nanoparticles for assembling such nanomaterials as thin films. Gold nanoparticles of two different core sizes (2 and 5 nm) and functionalized thiols of two types of functionalities (thiol and carboxylic acid) were studied. Such systems involve inter-core or inter-shell reactivities leading to covalent Au-thiolate bonding or non-covalent hydrogen-bonding. Spectrophotometric and quartz-crystal microbalance measurements provide kinetic assessments of core-shell exchange,

nucleation and crystallization in the film formation and growth. The films are exploited as coatings of interdigitated microelectrode and microbalance devices for gas-phase sensing. The correlation of the sensor responses with surface and electronic properties will be discussed for developing strategies in designing highly sensitive and specific sensing interfaces in terms of nanosized binding sites, core sizes and shell structures.

80.

INTERACTIVE COMBINATIONS OF TAMOXIFEN AND 9-CIS RETINOIC ACID AND THEIR ROLE IN HUMAN BREAST CANCER CHEMOPREVENTION. *Michelle M. Haghpanah, Elise J. Branca, and John J. Mitnick, Department of Chemistry, Laboratory of Physical Biochemistry, Fairfield University, 1073 North Benson Road, Fairfield, CT 06430, Fax: 203-254-4034*

Tamoxifen is a nonsteroidal triphenylethylene derivative that is a mixed estrogen agonist and antagonist. Competing with estradiol for estrogen receptors (ER) protein, tamoxifen binds to cytoplasmic estrogen receptors in the breast. Tamoxifen demonstrates a good ability to suppress the anchorage-independent growth of breast cancer cells. A retinoid most frequently associated with growth inhibition of neoplastic cells is 9-cis retinoic acid (9-cis RA). Responsible for performing major function as hydrophobic signaling molecules, retinoids such as 9-cis RA acknowledge intracellular receptor sites in order to classify and control cell differentiation and proliferation. Retinoic acid receptor (RAR- α) has been shown to be involved in the inhibition of anchorage-independent growth by retinoids in ER- positive human breast cancer cell lines. The chemopreventative action of 9-cis RA and tamoxifen has been linked to their ability to bind to ER proteins thereby inhibiting estrogen dependent cancer cell lines. Our laboratory efforts seek to examine the activity of various combinations of 9-cis RA and tamoxifen. Concern lies in the particular molecular mechanisms which regulate the yielding competence of 9-cis RA and tamoxifen in human breast cancer chemoprevention.

81.

INVESTIGATION OF A PHARMACEUTICAL DRUG SUBSTANCE DEGRADATION PRODUCT PROFILE BY HPLC USING HIGH PH MOBILE PHASES. *Mary Ann Quarry, Christine Gau, and David Buckley, Analytical R&D, DuPont Pharmaceutical Company, Experimental Station E353/227A, Wilmington, DE 19880-0353*

Typical degradation product methods for pharmaceutical drug substances involve HPLC using gradient elution with mobile phases in the pH range of 2-7 for column stability. While investigating the selectivity of a method, a new HPLC column that was developed for use at high pH was used. This led to the discovery of a related substance which had co-eluted with the drug substance peak in the original method. Method parameters and column stability will be discussed.

82.

INVESTIGATION OF NEAR-IR FLUORESCENT DYES FOR USE AS CELL STAINS IN CYTOTOXICITY STUDIES. *Richard J. Williams, Department of Chemistry, Morgan State University, 1700 East Cold Spring Lane, Baltimore, MD 21251, Fax: 410-319-3778, rwillia6@morgan.edu*

The use of chromophores from the ultraviolet (uv) and visible regions as stains and dyes is a very effective tool in several bio-analytical techniques. While conventional uv-visible spectroscopy techniques can provide good sensitivity and specificity, they are often limited in sensitivity by interference from the background spectral properties of non-targeted components in the uv-visible region. Bio-analytical techniques that incorporate fluorescent near-infrared (near-IR) dyes offer several advantages as an alternative to techniques that utilize chromophores in the uv-visible region. In the near-IR region, background interference is minimized, since few biological compounds naturally exhibit near-IR spectral properties. Near-IR dyes typically exhibit strong molar absorptivity coefficients and good quantum yields. In this study, several near-IR dyes are compared to standard visible fluorophores as possible stains and labels for use in cell toxicity monitoring techniques. Comparisons of detection sensitivity and cell loading ability are reported.

83.

ION-INDUCED INTERFACIAL DYNAMICS OF PHOSPHOLIPID MONOLAYERS. *Shaowei Chen, and Kui Huang, Department of Chemistry, Southern Illinois University, Neckers Building m/c 4409, Carbondale, IL 62901-4409, Fax: 618-453-6408, schen@chem.siu.edu*

Ion-induced interfacial dynamics of phospholipid monolayers were studied by various electrochemical techniques. The lipid monolayers were constructed by using the mercapto-derivatives of natural lipids that were self-assembled directly onto gold electrode surfaces in a tails-down fashion. The supported lipid assemblies appeared to act as rather effective electron-tunneling barriers with K₃Fe(CN)₆ as the redox probe, despite a relatively low surface coverage and/or disordered surface structure. Upon the stimulation by alkaline-earth ions, the lipid layers appeared to undergo surface reorganization, exposing part of the electrode surface which resulted in the formation of microscopic mass-transfer lipid channels. The dimensions and/or the number of these channels increased with increasing ion concentrations, and this ion-gate effect appeared to be quite selective, with the most pronounced effects observed with Ca²⁺ among the series of alkaline-earth ions.

84.

ISOLATION OF AMPHETAMINES FROM HUMAN HAIR USING ON-LINE DERIVATIZATION/SUPERCritical FLUID EXTRACTION. *Janet F. Morrison, and Alison L. Rada, Department of Chemistry, Trinity College, 300 Summit Street, Hartford, CT 06106, Fax: 860-297-5129, janet.morrison@mail.trincoll.edu*

This project investigates the development of a screening method for the rapid detection of drugs of the amphetamine class from human hair. The increasing illicit use of these synthetic psychoactive drugs, including methamphetamine and 3,4-methylenedioxymethamphetamine (MDMA, "Ecstasy"), has prompted increased efforts aimed at the development of more rapid and reliable methods for their isolation and detection in biological samples. Hair expands the time window for drug detection compared with urine and blood, and thereby provides a relatively non-invasive testing medium for evaluating chronic drug use. While traditional analytical methods typically involve liquid-liquid or solid-phase extraction followed by lengthy derivatization procedures to convert the drugs to chemical analogs suitable for GC-MS analysis, the method reported here combines into a single step the extraction and derivatization steps by incorporating the derivatization reagents directly into the supercritical fluid extraction (SFE) solvent. A variety of acyl derivatization reagents and SFE operating parameters are investigated for efficiency of on-line derivatization and extraction, and examples of the application of optimized methodology to drug-fortified and drug user hair will be presented.

85.

LARGE VOLUME STACKING USING AN ELECTROSMOTIC FLOW PUMP AT HIGH PH. *Man-Seog Chun, and Doo Soo Chung, School of Chemistry, Seoul National University, Seoul 151-742, South Korea, Fax: +82-2-889-1568, manstone@bachem.snu.ac.kr*

Large volume stacking using an electroosmotic flow pump (LVSEP) is known to be an efficient on-column preconcentration method in capillary electrophoresis. Since analytes should move against the electroosmotic flow (EOF), LVSEP has been applied for inorganic anions at low pH of reduced EOF. We report two new schemes of extending the applicability of LVSEP to higher pH ranges. By increasing the run buffer concentration, the EOF is suppressed and LVSEP is accomplished at medium pH with a bare fused silica capillary. When a coated capillary is used, LVSEP of amino acids such as phenylalanine, tyrosine, and tryptophan at pH 10 yields the detection limits as low as 50 nM with conventional UV detection.

86.

LASER ABLATION OF POLYMER SUBSTRATES FOR THE FABRICATION OF MICROFLUIDIC DEVICES. *Emanuel A. Waddell¹, Susan L. R. Barker², David J. Ross², Laurie E. Locascio¹, and Gary W. Kramer¹. (1) Analytical Chemistry Division, National Institute of Standards and Technology, 100 Bureau Dr, MS8394, Gaithersburg, MD 20899-8394, Fax: 301-975-6587, emanuel.waddell@nist.gov, (2) Process Measurements Division, National Institute of Standards and Technology*

We have successfully fabricated and characterized microchannels in polymeric materials using laser ablation. The laser-ablated channels were fabricated with

the use of a KrF laser (248 nm). We examined the physical, chemical, and electroosmotic flow characteristics of the microchannels formed in copolyester, polystyrene, polycarbonate, and poly (methylmethacrylate) using this technique. Microchannel surface chemistry was also modified by deposition of polyelectrolyte multilayers (PEMS) on the channel walls. The multilayer was created by exposing a surface to alternating solutions of positively and negatively charged polyelectrolytes. Although the layers are merely adsorbed onto the substrate or previous layer, the resulting multilayers have multiple bonds and are very stable and uniform. The efficacy of the surface modification has been evaluated using XPS. This presentation will compare the differences observed in each polymer as characterized by optical profilometry, contact angle measurements, and chemical mapping of ablated polymers.

87. LIQUID-LIQUID-LIQUID EXTRACTION AS A PRECONCENTRATION METHOD IN CAPILLARY ELECTROPHORESIS. *Kihwan Choi¹, Yongseong Kim², and Doo Soo Chung¹.* (1) School of Chemistry, Seoul National University, Seoul 151-742, South Korea, Fax: 82-2-889-1568, genmania@plaza1.snu.ac.kr, (2) Division of Fine Chemistry, Kyungnam University

A small drop of run buffer (pH 9.0) on the inlet of a capillary was covered with a thin film of octanol. By dipping the capillary into a dilute sample solution of pH 1.0, the drop on the capillary was enriched with the samples. Since a thin organic film separated the two aqueous phases, the enrichment process was much faster than usual liquid-liquid-liquid extraction methods. Preconcentration of at least two orders of magnitude was achieved for sodium fluorescein and fluorescein isothiocyanate isomer I within 30 min.

88. MEASUREMENT OF DNA-PROTEIN INTERACTIONS BY CE. *Ram P. Singhal,* Department of Chemistry, Wichita State University, Wichita, KS 67260, Fax: 316-978-3431, Singhal@twsu.edu

Specific interactions between DNA and its protein, complementary base pairing between the two DNA strands, and movement and conformation of dsDNA in free solution are examined. Results indicate that annealing of short ssDNA can be accomplished in minute capillary columns. Procedures involving CE technique have been developed. They allow binding of the dsDNA with its specific protein, without interference or competition with other proteins present in the reaction mixture. In the binding reaction, unlike gel electrophoresis method, nuclease inhibitors, the non-specific DNA competitors, and other additives are not needed in CE. The results indicate DNA-protein interactions are weak in nature. It revealed a very high dissociation constant, i.e. K_d values of mM for a protein, serum-response factor and its DNA probe. CE offers easy quantification, experimental flexibility, speed, small sample size, and very high sensitivity of detection. This work shows that the nature of interactions among different macromolecules can be studied at very sensitive (femtomolar) scale.

89. METAL COATINGS ON FUSED SILICA AND THE EFFECTS OF SURFACE FEATURES ON THE TRANSMITTANCE OF OPTICAL FILTERS. *Paul C. DeRose,* John C. Travis, Melody V. Smith, and Gary W. Kramer, Analytical Chemistry Division, National Institute of Standards and Technology, 100 Bureau Dr., MS8394, Gaithersburg, MD 20899-8394, paul.derose@nist.gov

Metal thin films on fused silica are widely used as transmittance filters and related standards for UV and visible light. Large changes in transmittance between different batch coatings of Cr, produced by optical glass and coatings manufacturers, are reported. Atomic force microscopy and scanning electron microscopy are used to measure the surface roughness and thickness of the films. Measurements of reflectance, absorbance and transmittance of UV and visible light by the films is then used to correlate interactions of light with metal coatings to their surface characteristics.

90. METHYLATION OF HOMOCYSTEINE TO METHIONINE BY 5-METHYLTETRAHYDROFOLATE. *Heather A. Green, Shannon L. Ballard, Donald J. Ross, and John J. Mitnick,* Department of Chemistry, Laboratory of Physical Biochemistry, Fairfield University, 1073 North Benson Road, Fairfield, CT 06430, Fax: 203-254-4034, jmitnick@fair1.fairfield.edu

Homocysteine is an amino acid naturally synthesized in the body. Studies have indicated that elevated serum levels of homocysteine correspond to the

development of coronary heart disease. Homocysteine, like cholesterol, has been known to increase coagulation of blood and deplete vasodilator nitrous oxide levels, ultimately leading to blood vessel damage. A deficiency in folic acid, Vitamin B12, and Vitamin B6 accompany abnormally high levels of serum homocysteine.

Homocysteine is an intermediate in the conversion of methionine to succinyl-CoA. Methionine differs from homocysteine in that it has a terminal methyl group attached to a sulfur atom, while homocysteine just has a terminal sulphydryl group. Our studies focus on the reduction of homocysteine levels by rapid conversion of homocysteine to methionine via methylation. 5-methyltetrahydrofolate is used to methylate the homocysteine. Methyl transfer is catalyzed by methionine synthase using methylcobalamin prosthetic group. 5-methyltetrahydrofolate methylates with cobalamin prosthetic group to form tetrahydrofolate and CH₃-cob(III)alamin. This then reacts with homocysteine to form cob(I)alamin and methionine. Measurement of the absorbance of methyltetrahydrofolate indicates the methylation of cob(I)alamin and thus, the methylation of homocysteine.

91. MOLECULAR MODELING STUDY OF DOPED AND UNDOPED OLIGOMERS OF POLY(VINYL)FERROCENE USING THE EXTENSIBLE SYSTEMATIC FORCE FIELD (ESFF), MSI INC. *Emmanuel Aouad, and Stanley Bruckenstein,* Department of Chemistry, State University of New York, 276 Travers Circle, Amherst, NY 14228, Fax: 716-691-8815, aouad@acsu.buffalo.edu

Molecular modeling using InsightII 97, was used to model the equilibrium conformational states of oligomers of poly(vinylferrocene). Initially, a study of the ferrocene molecule was made with respect to the interionic and steric interactions between the ferricenium cation and model monovalent spherical anions formed from group VIII atoms. The modeling procedure was then extended to undoped (neutral) and doped (partially or fully oxidized) oligomers of (vinylferrocene)_x. for x=2,3, 4 and 16. The results indicate the existence of a variety of oligomeric configurations that have similar energy minima. These correspond to quasi stable structures resulting from coulombic, van der Waals, bonding and non bonding interactions between ferricenium oligomers and anionic species.

92. NMR DIFFUSION CHARACTERIZATION OF SURFACTANT VESICLES USED IN VESICULAR ELECTROKINETIC CHROMATOGRAPHY. *Benjamin J. Cutak,* Jennifer L. Razak, Craig E. Lunte, and Cynthia Larive, Department of Chemistry, University of Kansas, 2010 Malott Hall, Lawrence, KS 66045, Fax: 785-864-5396, bencutak@eagle.cc.ukans.edu

Vesicles formed from cetyltrimethylammonium bromide (CTAB) and sodium n-octyl sulfate (SOS) were characterized with respect to size and polydispersity by pulsed-field gradient NMR (PFG-NMR) measurements. The vesicle PFG-NMR data were analyzed with CONTIN software to yield a diffusion coefficient distribution. From the distribution, three weighted-average diffusion coefficients and a polydispersity index were calculated. Using an average diffusion coefficient, the average vesicle diameter was determined to be 42 nm. The polydispersity index was 1.5-1.6, indicating a fair degree of polydispersity. The PFG-NMR results showed that the surfactants had both a rapidly diffusing component and a slowly diffusing component, monomers and vesicles, respectively. This presented the possibility of ion pairing. Further PFG-NMR measurements showed that ion pairing between monomer surfactant and analyte did not occur to an appreciable extent.

93. ON-LINE TRACE ANALYSIS OF HUMAN HAIR: FORENSIC AND HEALTH-RELATED APPLICATIONS. *Bruce A. Benner,* Chemical Science and Technology Laboratory, Analytical Chemistry Division, National Institute of Standards and Technology, 100 Bureau Drive, Stop 8392, Gaithersburg, MD 20899-8392, Fax: 301-977-0685, bruce.benner@nist.gov, and Jeffrey A. Degrasse, Department of Chemistry, George Washington University

Hair and fibers are routinely collected at crime scenes for subsequent forensic analysis. Hair is typically inspected by microscope techniques to determine color, thickness and morphology (straightness). On-line supercritical fluid extraction - gas chromatography/ mass spectrometry (SFE-GC/MS) has been proposed as a method for characterizing small samples (microgram - mg of

sample material). The method offers a number of benefits including increased sensitivity compared with liquid extraction methods because the entire extractable mass is transferred to the analytical system, compared with only a few percent from a conventional liquid extraction/injection. This presentation discusses the results of an SFE-GC/MS study of small samples (100 micrograms to 1 mg) of human hair, with the goal of distinguishing individuals based on the chemical profiles of extracts of their hair. Recent results concerning the detectability of specific health-related components (e.g., hormones) as well as the results of analyses of archived samples will also be discussed.

94. OPTICAL ANION SENSING OF INDIUM-PORPHYRIN AND LIPOPHILIC DICHLOROFLUORESCEIN DOPED FILMS.

Enju Wang, Carlos Romero, and Darran Santiago, Chemistry, St. John's University, 8000 Utopia Parkway, Jamaica, NY 11439, Fax: 718-990-1876, Wange@stjohns.edu

The anion optical sensing characteristics of thin plasticized poly(vinyl chloride) (PVC)/polyurethane membranes doped with anion selective ionophore indium porphyrins and a dichlorofluorescein (DCFE) derivative were investigated. The response mechanism is based on ion extraction of anions into the bulk organic film and a simultaneous coextraction of hydrogen ions. This results in protonation of the pH chromophore and hence a change in the optical absorbance of the polymeric film. When In(OEP) was used, anions such as chloride, thiocyanate and salicylate increased absorption of the red band more than 2 times. Anion sensors based on In(OEP)-DCFE is fully reversible with response times of 30 seconds and life time of more than a month. When the phthalocyanine indium porphyrin was used as the ionophore, anions including dichlorofluorescein do not change the red band significantly. Highly selective sensor for acetic acid can be made with the indium phthalocyanine porphyrin.

95. OPTICAL ELECTRON TRANSFERS IN ELECTROCHEMICALLY GENERATED MIXED VALENT FILMS OF MOLTEN RUTHENIUM TRIS-BIPYRIDINE.

Enders Dickinson V, Jason E. Ritchie, and Royce W. Murray, Kenan Laboratories of Chemistry, University of North Carolina, CB#3290, Chapel Hill, NC 27599, Fax: 919-962-0458, enders@email.unc.edu

We have electrochemically generated mixed valent gradients in neat polyether melts of Ru(bpy)₃ and observed NIR bands consistent with optical electron transfers. These melts are synthesized by exchanging the outer sphere counterions of Ru(bpy)₃²⁺ with polyether tailed counterions. The resulting hybrid polyether melt is fluid at room temperature with a Ru(bpy)₃ concentration of approximately 0.8M. Utilizing a conductive ITO sample cell, the [Ru(bpy)₃](SO₃-MPEG)₂ melt can be electrochemically disproportionated while simultaneously analyzed with NIR spectroscopy. This approach allows us to view transfer bands for mixed valent materials that are otherwise quite difficult to synthesize and preserve. Including a second redox-active moiety in the melt allows us to assign bands to specific couples by observing changes in the spectrum.

96. OPTICAL FIBER SENSORS USING THE DYNAMIC MODIFICATION PROCEDURE.

Darrell Ray Fry, and Donald R. Bobbitt, Department of Chemistry, University of Arkansas, Chemistry Building, Room 101, Fayetteville, AR 72701, Fax: 501-575-4049, dfry@comp.uark.edu

One challenge facing those involved in the development of optical fiber sensors has been the development of strategies for immobilization of probe molecules at, or near the optical fiber surface. With the recent commercial introduction of a wide variety of easily modifiable probe molecules, this challenge is being addressed. These include haptens, IgG's, and antibodies. One immobilization approach that is versatile and generally applicable for a range of chemical sensing probes, is dynamic modification. In this approach, an optical fiber surface is modified with octadecylsilane, which renders the optical fiber surface hydrophobic. Probe molecules which are either inherently hydrophobic, or which are rendered hydrophobic through the addition of a carbon chain can be effectively immobilized onto the optical fiber. This presentation will discuss the details of probe modification, evaluate various protocols for immobilization of a probe on the optical fiber, and describe the quantitative characteristics of these dynamically modified sensors.

97. PARTICLE SIZE METHOD DEVELOPMENT OF A DRUG SUBSTANCE USING LASER DIFFRACTION WITH COMPARISON TO VISUAL ANALYSIS.

Susan A. Lerke, Jennifer L. Addison, and Paul K. Hovsepian, Analytical R&D, DuPont Pharmaceuticals Company, Experimental Station, P.O. Box 80353, Wilmington, DE 19880, Fax: 302-695-9802, susan.a.lerke@dupontpharma.com

Particle size analysis provides an excellent means by which to evaluate and control the physical attributes of pharmaceutical solids. Particle size determinations can be made using a variety of instrumental techniques such as electrical zone sensing, sieving and laser diffraction. Although laser diffraction allows rapid analysis, it does not permit direct observation of the particles, as with visual analysis techniques. Therefore, direct visual analysis with a microscope was used as a reference in developing laser diffraction methods of particle size analysis. The results obtained using wet and dry methods for particle size analysis of DMP 777 drug substance, comparison with visual analysis and the advantages of each technique, will be presented.

98. PERFORMANCE-BASED QUALITY ASSURANCE PROGRAM FOR THE ANALYSIS OF PAHS, PCB CONGENERS, AND CHLORINATED PESTICIDES IN MARINE TISSUE AND SEDIMENT SAMPLES.

Michele M. Schantz, Reenie M. Parris, and Stephen A. Wise, Analytical Chemistry Division, National Institute of Standards and Technology, 100 Bureau Dr, Stop 8392, Gaithersburg, MD 20899, Fax: 301-977-0685, michele.schantz@nist.gov

Since the beginning of the National Oceanic and Atmospheric Administration (NOAA) National Status and Trends (NS&T) Program in 1987, the National Institute of Standards and Technology (NIST) has coordinated annual intercomparison exercises for the determination of polycyclic aromatic hydrocarbons (PAHs), polychlorinated biphenyl (PCB) congeners, and chlorinated pesticides in marine tissue and sediment samples. These intercomparison exercises have become an excellent tool for assessing the comparability of analytical measurements among the marine environmental measurement community. In the most recent exercise, over 40 federal and state government, private, and university laboratories reported results on 18 PCB congeners, and 24 chlorinated pesticides in a fresh frozen fish tissue homogenate and on 23 PAHs, 18 PCB congeners, and 24 chlorinated pesticides in a frozen marine sediment material. The results from the most recent exercise will be summarized in this paper.

99. PERMANENT CHEMICAL MODIFIER FOR THE DETERMINATION OF SELENIUM BY TUNGSTEN COIL ATOMIC ABSORPTION SPECTROMETRY.

Xiandeng Hou, Zheng Yang, and Bradley T. Jones, Department of Chemistry, Wake Forest University, Winston-Salem, NC 27109, Fax: 336-758-3889, houx@wfu.edu

Iridium was used as a chemical modifier in the determination of selenium by tungsten-coil atomic absorption spectrometry. The chemical modifier was first coated onto the W-Coil by running a temperature program used for the determination of selenium. After the initial coating, the W-coil can be used indefinitely without further application of the modifier for up to 400 measurements. The coil can be re-coated for further use. This "permanent" chemical modifier prolonged the lifetime of the tungsten coil (over 800 heating cycles), elevated the char temperature, and improved the sensitivity and limit of detection of the method. The permanent chemical modifier approach also reduces the analysis time and conserves the precious metal solutions. Therefore the analysis cost can be significantly reduced. In an attempt to understand the mechanism of the chemical modification, SEM (scanning electron microscopy) was used for a closer look at the surface of the W-Coil with and without the chemical modifier, both before and after the prolonged use.

100. PH DEPENDANT KINETIC STUDIES OF E. COLI LIPOAMIDE DEHYDROGENASE: SUBSTRATE INHIBITION OF THE WT AND H444Q ENZYME FORMS.

Andrea Van Gilder, and Nancy Hopkins, Department of Chemistry, Rutgers University, 315 Penn St., Camden, NJ 08102, Fax: 856-225-6506, vangil@clm.rutgers.edu

E. coli Lipamide Dehydrogenase (LipDH) was assayed in potassium ferricyanide and NADH in concentrations varying from 2.0-0.33 millimolar and 200-37.5 microM, respectively. The activity of the enzyme was measured in terms of the absorbance change at 420nm. The pH of the assay cocktail was varied from 8.5-4.5. Inhibition by potassium ferricyanide was also noted, but to a lesser extent

compared to that of NADH. The current theory that NADH binds on one side of the flavin group of the active site, away from the area in which the mutation was made, suggests that there should not be any difference in activity between WT and H444Q enzymes. However, we found that while varying the pH of the assay the WT enzyme always had a larger activity when compared to H444Q enzyme. Increasing the pH of the assay resulted in decreased inhibition by NADH for both H444Q and WT, but to a diminished amount, for the WT enzyme. The degree of substrate inhibition by NADH was found to be larger for H444Q than that found in the WT enzyme. Decreasing concentrations of potassium ferricyanide resulted in increased substrate inhibition by NADH, possibly suggesting that both substrates bind at the same site. These results will be discussed during this presentation.

101. PHENOTHIAZINE OMEGA-FUNCTIONALIZED MONOLAYER-PROTECTED CLUSTER MOLECULES.

Deon T. Miles, and Royce W. Murray, Kenan Laboratories of Chemistry, University of North Carolina, CB #3290, Venable Hall, Chapel Hill, NC 27599-3290, Fax: 919-962-2542, deon@unc.edu

This paper describes the synthesis and electrochemical reactivity of monolayer-protected Au clusters (MPCs) where the alkanethiolate ligands have been exchanged with omega-alcohol thiolates, and then functionalized with phenothiazine molecules through an ester coupling reaction. The mixed monolayer MPC can contain as many as 10 phenothiazine sites/MPC, which are all electroactive in rapid, successive one-electron reactions. Double-potential step chronocoulometry was used to determine the amount of adsorption on the electrode surface as well as introduce a novel method to determine the change in electronic potential for single electron transfers. Double-layer charging of the gold core was observed with these MPCs as well. The increase in ordering of the MPC thiolate chains that have been functionalized with alcohol, carboxylic acid, or phenothiazine molecules was observed using infrared spectroscopy.

102. PREDICTION OF PROTEIN SIGNAL SEQUENCES AND THEIR CLEAVAGE SITES.

Kuo-Chen Chou, Computer-Aided Drug Discovery, Pharmacia & Upjohn, 301 Henrietta Street, Kalamazoo, MI 49007-4940, Fax: 616-833-9183, kuo-chen.chou@am.pnu.com

Protein signal sequences play a central role in the targeting and translocation of nearly all secreted proteins and many integral membrane proteins in both prokaryotes and eukaryotes. The knowledge of signal sequences has become a crucial tool for pharmaceutical scientists who genetically modify bacteria, plants, and animals to produce effective drugs. However, to effectively use such a tool, the first important thing is to find a fast and effective method to identify the "zipcode" entity; this is also evoked by both the huge amount of unprocessed data available and the industrial need to find more effective vehicles for the production of proteins in recombinant systems. In view of this, a sequence-encoded algorithm was developed to identify the signal sequences and predict their cleavage sites. The rate of correct prediction for 1937 secretory proteins and 1440 non-secretory proteins by self-consistency test is 90.15% and that by jackknife test is 90.13%. The encouraging results indicate that the signal sequences share some common features although they lack similarity in sequence, length, and even composition, and that they are predictable to a considerably accurate extent.

103. PREPARATION AND CHARACTERIZATION OF POLYLACTIC ACID (PLA)-POLYMALEIMIDE (PMI) BLENDS.

Parminder Agarwal, and Kris A. Berglund, Depts. of Chemistry and Chemical Engineering, Michigan State University, Chemistry Building, East Lansing, MI 48824, param@cem.msu.edu

Interest of scientists in polymers derived from lactic acid is primarily due to their environmental degradability. Polylactide (PLA) are now entering high volume areas such as packaging industry. Ability to tune the physical properties of these polymers is obtained by a number of approaches. These include copolymerization, blending and the manipulation of stereochemistry. Like PLA, polymaleimide (PMI) is also biodegradable. PMI is made by anionic polymerization of maleimide, which in turn, is obtained from corn syrup through a series of chemical reactions. PLA-PMI blends show good compatibility as shown by microscopy results. Thermal analysis (DSC and TGA) studies show that these blends have good thermal stability till 225 C. Mechanical properties of blends

show that they can be processed by molding, vacuum forming, film blowing or extrusion.

104. PROPERTIES OF NOVEL NITRIC OXIDE SENSITIVE POLYMERS. *Karen M. Padden¹, John F. Krebs¹, Robert Scarrow², and A. S. Borovik¹. (1) Department of Chemistry, University of Kansas, Malott Hall, Lawrence, KS 66045, Fax: 785-864-5396, kmpadden@eagle.cc.ukans.edu, (2) Department of Chemistry, Haverford College*

Nitric Oxide (NO) has been implicated in numerous physiological functions as inducing protective, regulatory, and deleterious effects. It is evident that materials, which both release and scavenge NO, would be desirable for clinical applications. Studies involving nitric oxide have thus become increasingly important in order to develop sensors and synthesize NO releasing compounds. We have found that template co-polymerized metal complexes can selectively and reversibly bind nitric oxide resulting in a dramatic color change, from orange to green. Characterizations of the physical and structural properties of the active site indicate that NO directly binds to the metal centers immobilized in the highly porous organic host. This talk will discuss efforts to determine binding event kinetics, as well as attempts in utilizing polymers in films and coatings for sensor applications of biologically relevant molecules.

105. QUANTIFICATION OF IMPURITIES MIGRATION AND CONCENTRATION FOR SEMICONDUCTOR LITHOGRAPHIC MATERIALS. *Fu-Hsiang Ko, Research and development, National Nano Device Laboratories, 1001-1, TA-HSUEH RD, Hsinchu, Taiwan, Fax: 886-35713403, fhko@ndl.gov.tw*

The migration and concentration of metallic impurities in semiconductor lithographic materials (e.g. resist, anti-reflective coating) are essential to ensure circuit yield. This work first develops the radioactive tracer method to determine the amount of impurities migration from lithographic material into underlying substrate. The effects of baking temperatures and substrate types are investigated. Our results indicate the anti-reflective material has significantly higher migration ratios than photoresist. The substrate type does not have strong effect on impurities migration. After the extent of impurities migration is quantitatively obtained, the new analytical method combining the microwave digestion and ICP-MS analysis for determining the ultratrace metals in lithographic materials is also established. The analytical reliability and throughput show the applicability of the developed method.

106. QUANTITATIVE ENANTIOMERIC ANALYSIS OF DRUGS VIA FT-ICR MS. *Gabriela Grigorean, and Carlito B. Lebrilla, Department of Chemistry, University of California, 1 Shield Ave, Davis, CA 95616, Fax: 530-752-8995, ggrigore@ucdavis.edu*

A general and rapid method for determining enantiomeric composition of drugs and other chiral analytes using strictly mass spectrometry is presented. Technique is based on the following gas-phase ligand exchange reaction: [Host:Analyte H]⁺ + Base=[Host:Base H]⁺ + Analyte Chiral recognition is achieved because the ligand exchange reaction occurs at different rates for the differing analyte enantiomers. Intensities of reactant, [Host:Analyte H]⁺, and the product, [Host:Base H]⁺ peaks are monitored as a function of reaction time. For a particular analyte, a calibration curves is made by analyzing several enantiomeric percentages. Once calibration curve is constructed, only one mass spectrum of an unknown enantiomeric mixture is necessary. Data from it is fit in the curve's equation and the enantiomeric composition of the unknown is deduced. Analytes analyzed in this manner include the 21 common amino acids, drugs (DOPA, amphetamine, penicillamine, ephedrine) and some peptides.

107. RAMAN SPECTROSCOPY OF TUMORIGENIC CELLS. *Kristin M. Omberg, James P. Freyer, and Jon R. Schoonover, Materials Science and Technology Division, Los Alamos National Laboratory, MS E544, Los Alamos National Laboratory, Los Alamos, NM 87545, Fax: (505) 665-2185, komberg@lanl.gov*

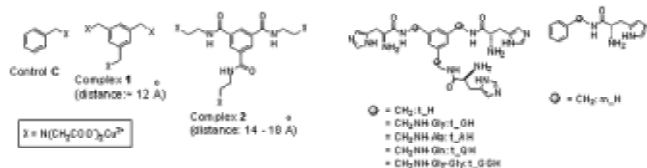
Raman spectra have been obtained for nontumorigenic and tumorigenic cells from the rat fibroblast M1 and MR1 model cell lines. Care was taken to assure the cells remained viable throughout the experiment, and both samples contained cells in the same growth phase. Interesting features are observed in

the spectra of both cell lines which can be interpreted as arising from differences in the cells' DNA:protein ratio.

108.

RECOGNITION OF FLEXIBLE PEPTIDES IN WATER BY TRANSITION METAL COMPLEXES. *Sanku Mallik, Md. Abul Fazal, Shuguang Sun, and Bidhan C. Roy, Chemistry, North Dakota State University, Ladd Hall, Fargo, ND 58105, Fax: 701-231-8831*

This presentation describes the design, synthesis and evaluation of transition metal complexes capable of recognizing to flexible histidine containing peptides in aqueous medium (25 mM HEPES buffer, pH=7.0, 25 OC). When the pattern of metal ions on a complex (2) matched with the pattern of histidine moieties on the peptide, strong interaction ($K=1.2 \times 10^6 \text{ M}^{-1}$) can be achieved. The complex was highly selective (200:1) in discriminating similar flexible peptides differing only by one glycine unit.



109.

RELATIVE TRANSFER RATES OF WATER AND POTASSIUM ION DURING THE REDOX SWITCHING OF PRUSSIAN BLUE. *Ketack Kim¹, Irena Jureviciute², and Stanley Bruckenstein¹. (1) Department of Chemistry, State University of New York, 607 Natural Science Complex, Buffalo, NY 14260-3000, Fax: 716-645-6963, kk10@acsu.buffalo.edu, (2) Institute of Chemistry*

The composition of a Prussian Blue (PB) film changes with potential cycling. The literature is in agreement that cation transfer and water transfer between the PB film and the solution occur in opposite directions. However, the reported mole ratio of water/cation varies with the author. Here we present a kinetic study, using cyclic voltammetry and the electrochemical quartz crystal microbalance, of the PB switching process in 0.1 M and 1.0 M potassium salt solutions at different potential scan rates. Our results show that the water/cation ratio depends markedly on the fraction of PB that is oxidized and the potential scan rate. After the first potential cycle in 0.1 M potassium sulfate solution, the average mole ratio of water/potassium is ~ 0.5 at 10 mV/s and is ~ 0 at 100 mV/s. Our results demonstrate that the potassium ion and transfer of water does not occur simultaneously.

110.

REMOTE QUERY ANALYSIS OF BLOOD CLOTting UTILIZING MAGNETOELASTIC SENSORS. *Mervat Issa¹, Craig A. Grimes², and Leonidas G. Bachas¹. (1) Department of Chemistry, University of Kentucky, Rose Street, Lexington, KY 40506-0055, Fax: 859-323-1069, mhissa0@pop.uky.edu, (2) Electrical Engineering, University of Kentucky*

The use of Metglas films has been demonstrated in engineering practices to detect fluctuations in viscosity and temperature. We have previously established the applicability of these methods in detecting surface mass fluctuations in enzyme-substrate reactions. Metglas is a magnetoelastic material that resonates at a specific frequency under the influence of an external magnetic field. The frequency, dependent on the film dimensions and physical environment, is susceptible to change dependent on mass loading at the surface interface. In this way, the use of Metglas as a sensing element is analogous to mass sensitive techniques such as surface plasmon resonance and quartz crystal microbalance. We have utilized this effect in the examination of the mammalian blood clotting mechanism under the influence of various inhibitory factors. The Metglas system requires no physical connections and does not require direct line of sight, allowing the complete immersion of the sensing film within the blood sample.

111.

SELECTION OF CHIRAL SELECTORS FROM A SMALL PARALLEL COMBINATORIAL LIBRARY. *Tingyu Li, and Yan Wang, Department of Chemistry, Vanderbilt University, Box 1822-B, Nashville, TN 37235, Fax: 615-343-8466, tingyu.li@vanderbilt.edu*

As part of our efforts towards more efficient chiral chromatography, we have developed an efficient method to screen parallel combinatorial libraries for chiral selectors. The method does not require the immobilization of analyte. The feasibility of this method was demonstrated with a model study of the chiral resolution of a naphthyl-leucine ester. Application of parallel combinatorial libraries to the development of other chiral selectors is currently being investigated and the results will be presented.

112.

SELENIUM-77 NUCLEAR MAGNETIC RESONANCE STRUCTURAL ANALYSIS OF SELENOMETHIONINE OXIDATION PRODUCTS. *Elizabeth M. Carey, and Patricia A. Pleban, Department of Chemistry & Biochemistry, Old Dominion University, Norfolk, VA 23529, Fax: 757-683-4628, ecarey@odu.edu*

Selenoproteins are reported to protect against oxidative damage from reactive oxygen species. Since large chemical shifts are produced by small changes in the ⁷⁷Se environment, NMR analysis should allow characterization of selenomethionine, SeMet, and its oxidation products. Using a Varian 400 MHz Unityplus NMR, we observed the ⁷⁷Se signal of SeMet at 75 ppm (versus dimethyl selenide at 0 ppm, pD=5, T=18°C, 80 mmoles SeMet). Addition of excess H₂O₂ gave two peaks at 708 ppm and 844 ppm. The original 75 ppm SeMet peak could be regenerated by addition of excess reduced glutathione suggesting that no cleavage of SeMet occurred. We tentatively identified two oxidation products with peaks at 708 ppm and 844 ppm as the hydrate and the monoxide species, respectively. Dispersive Raman analysis using a CCD detector confirmed the identification of the hydrate (Se-OH, 668-679 cm⁻¹) and the monoxide (Se=O, 785 cm⁻¹).

113.

SIMULTANEOUS DETERMINATION OF TRACE AMOUNTS OF SIX ELEMENTS IN CERTIFIED RIVER WATER REFERENCE MATERIALS BY GRAPHITE FURNACE AAS. *T. Shoji¹, T. Seki¹, and K. Oguma². (1) Central Research Institute, Nissan Chemical Industries, Ltd, Tsuboi-cho, Funabashi, Chiba 274-8507, Japan, (2) Faculty of Engineering, Chiba University*

In this work, we optimized the sample injection volume and the furnace-heating program to determine six elements (Cd, Ni, Fe, Pb, Cu, and Cr) simultaneously by using a Perkin Elmer SIMAA6000, which was developed for the simultaneous multi-element determination. The established experimental conditions were successfully applied to the determination of the six elements in the river water certified reference materials (JAC-0031 and JAC-0032 provided by The Japan Society for Analytical Chemistry). The relative standard deviation for four repeated measurements of peak area was found to range from 0.3% (5ppb Cr) to 2.8% (5ppb Ni).

114.

SOLID REDOX MEDIATORS FOR ENZYME ELECTRODES. *Waldemar Gorski, and Liang Chen, Division of Earth and Physical Sciences, University of Texas, 6900 N. Loop 1604 W, San Antonio, TX 78249, Fax: 210-458-4469, wgorski@utsa.edu, lichen@utsa.edu*

A mediated electron transfer of the enzyme glucose oxidase in the presence of inorganic redox crystals was investigated. The model system consisted of a solid mediator made of ruthenium complexes in close contact with the enzyme. The enzyme electrodes were prepared by immobilizing the mediator and the enzyme either in a biopolymer chitosan onto the surface of a glassy carbon electrode or in the bulk of the carbon paste electrode. Both designs resulted in stable amperometric biosensors for glucose. The sensing mechanism relied on reoxidation of the enzyme by redox active mediator. The biosensors could operate at a potential as low as -0.10 V vs. Ag/AgCl(3 M NaCl) which eliminated the influence of common interfering species such as ascorbic acid, uric acid and acetaminophen. The possible mechanisms of electron transfer between the reduced enzyme and the solid-state redox mediator were probed using electrochemical methods.

115. STUDY OF INTERACTION OF ACETONE WITH METHANOL-WATER MIXTURES USING IR SPECTROSCOPY AND CHEMOMETRICS. *Joani E. Hayman, Sally S. Hunnicutt, and Sarah C. Rutan, Department of Chemistry, Virginia Commonwealth University, P. O. Box 842006, 1001 W. Main Street, Richmond, VA 23284-2006, Fax: 804-828-8599, Joani_Hayman@Ethyl.com*

Methanol-water mixtures are commonly used as the mobile phase in reverse-phase, high-performance liquid chromatography. These systems are often described as binary, despite evidence that complexes are formed via hydrogen bonding interactions. Infrared spectroscopy can be used for studying these systems because observed spectral shifts can be related to structural changes in the molecule due to complexation. However, mathematical analysis is required to resolve the experimental spectra into the spectra corresponding to the individual species.

In the present study, a model solute, acetone, is added to a series methanol-water mixtures. The infrared spectra were recorded and analyzed to probe the formation of complexes in these mixtures. The spectra were resolved mathematically using singular value decomposition, evolving factor analysis and alternating least squares. Results will be presented that demonstrate the interactions in these solutions

116. TACKLING PURIFICATION AND FRACTION COLLECTION VIA SUPERCRITICAL FLUID CHROMATOGRAPHY. *Joan M. Stevens, and Alan Hamstra, Technical Support, Gilson, Inc, 3000 W. Beltline Hwy, Middleton, WI 53562, Fax: 608-831-4451, jstevens@gilson.com*

There are unique advantages to using SFC with modified carbon dioxide and standard (packed) HPLC columns up to 20 mm ID to produce a purified substance. Fractionation is one, because CO₂ is gaseous under normal ambient conditions leading to the separation of analytes from the mobile phase by pressure reduction. Collection solvent is added to keep the solutes dissolved after decompression of the mobile phase. The use of CO₂ drastically reduces the volume of organic solvents often used in semi-preparative HPLC. Therefore, time required for concentration of the fractions is significantly reduced. Last but not least semi-preparative SFC is faster than semi-preparative HPLC and the former has a wider range than gas chromatography. An SFC system that would allow for the semi-preparative separation of compounds under conditions that could be employed as a general method for a large range of compounds with fraction collection, would be extremely advantageous in combinatorial purification and positively effect sample throughput. Automatically injecting the collected fractions under analytical conditions to confirm the purity contributes to the overall flexibility of the SFC system. This presentation will address the aspects associated with the automated semi-preparative/analytical SFC including instrumentation, conditions, fractionation and data to support its performance.

117. TAIL-TAIL DYNAMICS OF POLYMERS DISSOLVED IN SUPERCRITICAL FLUIDS AT INFINITE DILUTION. *Maureen A. Kane, Gary A. Baker, Siddharth Pandey, and Frank V. Bright, Department of Chemistry, State University of New York, Natural Sciences Complex, Buffalo, NY 14260-3000, Fax: 716-645-6963, makane@acsu.buffalo.edu*

It is well known that most polymer behavior and dynamics can be controlled by the physicochemical properties of the solvent it is dissolved in. For example, the mean conformation of a polymer in a "good" solvent is significantly different than the same polymer in a theta or "bad" solvent. The extent of these conformational changes from solvent to solvent can be described by differences in the tail-tail cyclization dynamics. Unfortunately, many of the favored liquid solvents used in polymer science and technology are environmentally unfriendly. Supercritical fluids are an attractive alternative to liquid solvents. Their liquid-like densities and gas-like mass transfer make supercritical fluids appealing for applications such as extractions, chemical reactions, and separations. Since the physicochemical properties (solvent strength, density, etc.) of supercritical fluids are strongly dependent on the system pressure, they can be tuned between liquid and gas-like characteristics by simply changing pressure. Carbon dioxide is especially attractive because it has modest critical conditions, it is relatively inexpensive, nonflammable and non-toxic, it can be easily separated from the system, recycled and reused, and it is environmentally benign/responsible. In this presentation we report on the tail-tail dynamics of poly(dimethylsiloxane)

(PDMS) end-labeled with Pyrene (Py) (Py-PDMS-Py) in supercritical carbon dioxide. This presentation will discuss our most recent results comparing the Py-PDMS-Py system in liquid solvents to supercritical carbon dioxide at infinite dilution.

118. TOTAL MERCURY DETERMINATION IN CRUDE OIL BY MICROWAVE DIGESTION AND COLD-VAPOR ATOMIC ABSORPTION SPECTROSCOPY. *Jenny Q. Sun, Carolyn M. Lillemoen, Thomas A. Erickson, and Marc D. Kurz, Energy & Environmental Research Center, University of North Dakota, 15 North 23rd Street, Grand Forks, ND 58203, Fax: 701-777-5181, jsun@eec.und.nodak.edu*

The analysis of most trace metals in a solid matrix requires complete dissolution of the solid to produce a representative liquid sample containing a quantifiable level of the analyte of interest. This is the most critical step for accurate trace metal analysis in a solid matrix. Incomplete desorption of the analyte from the solid or analyte volatilization during digestion can lead to poor accuracy in the analytical results. The main advantages of using a microwave-assisted acid digestion for the analysis of mercury in crude oil are the ability to heat the oil under elevated pressure and temperature, the superiority of microwave-induced heating, and the use of a closed vessel, which prevents loss of volatile elements such as mercury. The microwave digestion method presented in this study proved to be a rapid and accurate means for the complete digestion of fossil fuel samples to determine trace amount of mercury in crude oil.

119. TOWARD PRACTICAL BIOSENSORS: INTERFACING ENZYMES AND ELECTRODES USING CHITOSAN. *Waldemar Gorski, and Juan Cruz, Division of Earth and Physical Sciences, University of Texas, 6900 N. Loop 1604 W, San Antonio, TX 78249, Fax: 210-458-4469, wgorski@utsa.edu*

A bio-compatible approach to integration of enzymes and electrodes is presented. An amperometric glucose biosensor was designed by immobilizing the enzyme glucose oxidase into a thin film of the biopolymer chitosan on the surface of a platinum electrode. Spectroscopic and electrochemical studies showed that a polysaccharide host matrix of chitosan provides good enzyme immobilization efficiency, a high level of biocompatibility and an efficient protection against fouling of the electrode surface. These properties translated into improved operational stability of the electrochemical biosensor, e.g. a response of the sensor in a flow system was stable for several days under continuous polarization and continuous flow of glucose solution. An extra level of selectivity against common interfering species (e.g. ascorbate, urate) was achieved by modifying the chitosan with Lucifer Yellow VS dye molecules. The application of chitosan for interfacing enzymes and electrodes is a promising step toward the development of practical electrochemical biosensors.

120. USE OF AFM FOR THE STUDY OF STRUCTURAL CHANGES IN COAL AND CHAR DURING PYROLYSIS. *Osamu Yamada, Mokhtar Zabat, Hajime Yasuda, and Mamoru Kaiho, Energy Resources Department, National Institute for Resources and Environment, 16-3 Onogawa, Tsukuba 3058569, Japan, Fax: 81298618408, oy@nire.go.jp*

Atomic force microscope (AFM) equipped with an environment-controlled chamber is used for the analyses of morphology, surface properties and mechanical properties of coal and char surfaces under inert atmosphere. In coal surface, three components are recognized; a layered structure at several microns, unstructured and soft component, and fibrous and electrostatic charged texture. In char obtained from pyrolysis at 1073K, layered structure at several microns and deposit of nanospheres are observed. Layered structure in coal seemed to be unchanged in its shape during pyrolysis and it became dominant in char. After pyrolysis, charged and soft components found in raw coal could not be observed. The difference of mechanical properties detected by force curve may be corresponding to heterogeneity in coal known as macerals. Changes in coal structure during pyrolysis is also clearly detected by scanning images and by mechanical property analyses.

121.

UV-VIS SPECTROMETER AND γ COUNTER FOR STUDYING THYROIDAL**CHANGES. Revathi Kasturi, Ethiraj College, No:6 / 8, 10 th Street, Nandanam Extension, Madras 600035, India, Fax: 763-764-3865**

The effect of light on thyroid metabolism was studied by UV-VIS spectrometry and Gamma Counter. Attempts were made to study thyroid physiology of *Heteropneustes fossilis*. Photo period induced thyroid changes were studied from serum tri iodothyronine, T3 level, serum thyroxine, T4 level and protein binding Iodine 131 uptake. The Radio Immuno Assay (RIA) kit was used for Iodine 131. The serum tri iodothyronine, T3 and serum thyroxine, T4 levels were monitored by the Gamma counter. The protein binding Iodine 131 uptake was monitored by UV-VIS specrometer at 420 nm. Iodine 131 uptake was measured during short and long photo periods. The duration of a short photo period is exposure of light for eight hours and darkness for 16 hours whereas a long photo period is light exposure for sixteen hours and darkness for eight hours. In a completely dark environment the Iodine 131 uptake was greatly reduced. The fish exposed to light had significantly high levels of protein bound Iodine. The serum T3 and T4 levels were increased in the fish exposed to light. The method and the mechanism will be discussed in the presentation. The thyroid metabolism has thus been studied by UV-VIS spectrometer and Gamma counter. The methods are simple and easy to use.

122.

VIBRATIONAL SPECTROSCOPIC STUDIES OF CHROME-TANNED LEATHER.**Dennis C. Shelly, Leather Research Institute, Texas Tech University, Box 41061, Dept. of Chemistry and Biochemistry, Lubbock, TX 79409-1061, Fax: 806-742-1005, kzdc@ttu.edu**

A vibrational spectroscopic study of chrome-tanned leather has been performed. Absorption in the mid and far infrared (2000-50 cm^{-1}) showed typical protein features and some environmental contributions, largely from salts. These results were obtained from both attenuated total reflection and diffuse reflection sampling of raw, pickled and in-process wet-blue hides. Very little chromium-based vibrations were seen. Raman scattering spectroscopic studies were performed in order to access the very weak organo-chromium vibrations, expected in the 600-50 cm^{-1} region. Indeed, such peaks have now been observed. This presentation is an overview of the instrumental and sampling requirements leading to these observations. Implications for protein microstructure and process analysis applications will be presented.

123.

SPECTROCHEMICAL ANALYSIS: DOES THIS RAINBOW HAVE A POT OF GOLD?**Joseph A. Caruso, Department of Chemistry, University of Cincinnati, P.O. Box 210037, Cincinnati, OH 45221-0037, joseph.caruso@uc.edu**

This talk will trace our involvement trace element analysis over the past two decades. It will begin with the furnace AA experiments and initial plasma studies with microwave induced plasmas. GC and ETV coupling for plasma sample introduction will follow plus experiments with hydride generation and halogenated hydrocarbons for chromatographic sample introduction into low power plasmas. The earliest plasmas were argon based and were formed in microwave fields. These lead to beginning experiments with helium plasma mass spectrometry, followed by LC and SFC method development. Future projections spring from current work with selenoaminoacids in selenium food supplements and selenium enriched yeasts. Selenoaminoacids are present as enantiomers in yeasts and in yeast based food supplements and their further characterization will be discussed. We have also begun studies of organoarsenicals in seaweed and edible algae. The uptake of arsenic by plants has high phytoremediation potential. The importance of elemental speciation studies using spectrochemical detection will be highlighted.

124.

ANALYTICAL SCIENCE AT THE CENTER OF CHEMISTRY AND BEYOND ITS**FRINGE. Roland F. Hirsch, Medical Sciences Division, SC-73, U.S.****Department of Energy, Office of Biological & Environmental Research, 19901 Germantown Road, Germantown, MD 20874-1290, Fax: 301-903-0567, roland.hirsch@science.doe.gov**

This talk will present reflections on changes in analytical chemistry over the past forty years and ideas about where the field is headed. Analytical chemistry has

since its beginnings enabled progress both in the fundamental sciences and in the wider world, for example in medicine, agriculture and public policy. However, where once it was unusual for an analytical chemist to become directly involved in the fields outside chemistry, today many of the best in our field are at the same time full participants in a second specialty. The integration of analytical science into fields outside chemistry will likely accelerate as the need for chemical information to understand the fundamental questions in these fields continues to increase. A once common definition of our field was "analytical chemistry is what analytical chemists do". As we continue to expand our horizons perhaps the motto of our discipline should be Chesterton's "we do not know enough about the unknown to know that it is unknowable".

125.

CAL GIDDINGS AND TEMPERATURE PROGRAMMING. Harold M. McNair, Dept of Chemistry, Virginia Tech, Blacksburg, VA 24061, Fax: 540-231-3255, hmcnair@vt.edu

Prof Cal Giddings is famous for many things, primarily his understanding and publications on chromatographic theory. Today I would like to pay homage to one of his less well known publications in the Journal of Chemical Education 39 569 (1962). This publication is, to my knowledge, one of the most useful and clear presentations of temperature programming for gas chromatography. I hope to do him justice in my presentation today.

126.

STRUCTURE AND REACTIVITY AT CARBON ELECTRODES: IS CARBON FINALLY**YIELDING TO OUR COLLECTIVE SCRUTINY?. Richard L. McCreery, Department of Chemistry, Ohio State University, 100 W 18th Avenue, Columbus, OH 43210, Fax: 614-688-5402, mcreery.2@osu.edu**

Despite the wide use of carbon materials in electroanalytical applications, the performance of carbon electrodes is often unpredictable due to differences in both bulk and surface properties. The goal of a comprehensive understanding of effects of carbon surface structure and electrochemical reactivity has been elusive, largely because of the difficulty in fabricating and characterizing reasonably well defined carbon surfaces, as well as their propensity toward oxidation and adsorption. Efforts from several research groups over the last two decades have revealed some of the major secrets of carbon surfaces, and made specialized electrodes with known reactivity possible. Our contribution to this large effort is based on Raman spectroscopy to characterize carbon surfaces, and novel methods for modifying carbon surface structure. Examples to be discussed include unenhanced Raman spectroscopy of monolayers on glassy carbon, preparation of modified carbon surfaces with unusual reactivity, and new methods for stabilizing and restoring electron transfer reactivity. The long range objective of this work is shared by several other research groups: the fabrication of carbon electrode structures with predictable, stable, and possibly selective reactivity, which are ultimately useful for broadly important electroanalytical applications.

127.

TWENTY-THREE YEARS FOLLOWING JOHN FENN: MOLECULE INERTIA AND**MULTIPLY CHARGED ELECTROSPRAY CLUSTERS. Juan Fernandez de la Mora, Department of Mechanical Engineering, Yale University, 9 Hillhouse Ave., New Haven, CT 06520-8286, Fax: 203-432-7654, juan.delamora@yale.edu**

Seeded molecular beams first made John Fenn famous. I will discuss the related debate on whether or not heavy species inertia rather than pressure diffusion is the source of the intense heavy species enrichment effects often exploited in GC-MS. Other important but less known analytical lessons following from Fenn's insight will be illustrated in relation to aerodynamic focusing and electrostatic ion guides at medium pressure. I will then briefly visit Fenn's 15 years of failures with electrospray ionization (ESI). 15 more years after his first published ESMS (inorganic) spectra, the debate on what is the source of ESI is far from settled. I will argue that Dole's charged residue mechanism is the main source of large multiply charged ES ions, that ion evaporation is the most common source of small ES ions, and that, most often, it also fixes the charge remaining on multiply charged ions.

128.

IMPACT OF ELECTROSPRAY IONIZATION ON INDUSTRY. *Barbara Larsen, Corporate Center for Analytical Science, DuPont, DuPont Experimental Station, Wilmington, DE 19880-0228, Fax: 302-695-1351, barbara.s.larsen@usa.dupont.com*

Advances in science are frequently preceded by developments in measurement technology. The introduction of electrospray as a viable means to introduce charged analytes into the vacuum system of a mass spectrometer by Professor John Fenn revolutionized mass spectrometry and had a profound effect on progress in many areas of science. The ability to analyze nonvolatile as well as high-mass materials at sub-micromolar levels, and the simple, reliable and highly sensitive interface electrospray provides with liquid separation methods has enabled advances in many fields of science. The rapid progress in the biological sciences over the past decade has especially been impacted by electrospray ionization especially when combined with MS/MS. In technology dependant industry, ESI-MS has become the most important analytical method for analyzing a wide range of materials. The method is an essential analytical technique in such industrially important areas as proteomics, metanomics, pharmacokinetics, environmental analyses, synthetic polymer characterization, combinatorial chemistry, and reaction screening. The impact of ESI-MS in industry is enormous and will be discussed along with examples of its utility in support of both product analysis and research and development.

129.

FOURIER TRANSFORM ION CYCLOTRON RESONANCE MASS SPECTROMETRY: A CELEBRATION OF THE POWER OF ELECTROSPRAY IONIZATION. *Alan G. Marshall, Christopher L. Hendrickson, and Mark R. Emmett, Center for Interdisciplinary Magnetic Resonance, Florida State University, National High Magnetic Field Laboratory, 1800 East Paul Dirac Drive, Tallahassee, FL 32310, Fax: 850-644-1366, marshall@magnet.fsu.edu*

Electrospray ionization (ESI) can generate molecular ions from almost all components of a complex mixture. Following John Fenn's lead, we show that FT-ICR MS can resolve and identify thousands of distinct elemental compositions of the heteroatom-containing components of heavy crude oil electrosprayed directly into the mass spectrometer. From the elemental compositions, we identify the "type" (number of rings plus double bonds) for each compound family, as well as the distribution of number of methylene groups appended to each family. In other experiments, we have resolved all possible mass-distinguishable peptides differing by 1-3 amino acids, including two peptides differing in mass by less than the mass of one electron (i.e., <0.0005 Da). We have also mapped contact surfaces between two or more proteins by solution-phase H/D exchange, followed by peptic cleavage before ESI FT-ICR MS.

130.

IN HONOR OF JOHN FENN: MOLECULAR BEAM STUDIES OF INTERFACIAL REACTIONS OF HCL WITH LIQUID GLYCEROL. *Gilbert Nathanson, and Bradley Ringeisen, Department of Chemistry, University of Wisconsin, 1101 University Ave, Madison, WI 53706, Fax: 608-262-9918, nathanson@chem.wisc.edu*

Molecular beam scattering, gas uptake, and residence time measurements are used to explore dissociation and D-H exchange in collisions of DCI with liquid glycerol. Gas-phase DCI molecules that thermalize upon collision with surface glycerol follow one of three pathways: longtime solvation and D-H exchange followed by desorption of HCl, trapping and immediate desorption without exchange, and interfacial exchange and desorption of HCl. We provide evidence that DCI can dissociate and become reprotonated within a cage of glycerol molecules in the near interfacial region, followed by HCl desorption within 2 μ s of the initial collision. These studies owe much to the experiments of John Fenn and his students, who 25 years ago, first investigated the scattering of argon atoms from liquid glycerol in vacuum.

131.

IN THE FOOTSTEPS OF A GREAT MASTER: FREE JETS AND COMMON SENSE. *Giacinto Scoles, Department of Chemistry, Princeton University, 2 Washington Road, Princeton, NJ 08544, Fax: 609-258-6665, gscoles@princeton.edu*

Some of the pioneering contribution of John B. Fenn to the study of supersonic free jet expansions and to their application to many areas of chemistry will be reviewed showing how they stand at the basis of much of today's chemical physics research and, in particular, of the research in progress in the author's laboratory. Two areas will be discussed in some detail: a) the role of the internal

degrees of freedom in surface chemistry and b) the presence and utilization of clusters in free jet expansions.

The seeds planted by John Fenn in many disciplines have produced uncountable fruits. There is however also another contribution of methodological nature that should not be overlooked. This is the clear demonstration of the superiority of common sense over complicated thinking which is present in all of his work. We should all be grateful to him for showing that the combination of simplicity and depth is still doing well in modern science.

132.

APPLICATION OF EXPLOSIVE DETECTION METHODS TO AIRLINE PASSENGER LUGGAGE. *Frank T. Fox, Federal Aviation Administration, 590 Herndon Parkway, Herndon, VA 20170-5232, Fax: 703-707-5675, frank.fox@faa.gov*

Following the terrorist bombing of Pan Am flight 103 Congress passed Section 107 of the Aviation Security Improvement Act of 1990 (Public Law 101-604) that requires the Federal Aviation Administration (FAA) to establish and carry out a program to accelerate the development and implementation of technologies and procedures to counteract terrorist acts against civil aviation. The Gore Commission in September 1996 developed recommendations to deploy such technologies in US airports to prevent explosive devices from being placed on civil passenger aircraft. The FAA has been the lead Federal agency for that purpose. Equipment has been installed in airports that can detect trace explosives as in a fingerprint and bulk amounts secreted inside luggage. Non-scientific operators are able to obtain fast and reliable analyses.

133.

AVAILABILITY AND ANALYSIS OF EXPLOSIVES RESIDUE. *Jimmie C. Oxley¹, James L. Smith¹, Elmo Resende¹, and R. Thomas Chamberlain². (1) Department of Chemistry, University of Rhode Island, Kingston, RI 02881, Fax: 401-874-2103, joxley@chm.uri.edu, (2) FAA Technical Center, Federal Aviation Administration*

Conventional explosives residue analysis will be discussed. Included will be swabbing techniques, extraction, gas and liquid chromatographic methods, and estimates on the amount of explosives residue which may be available. This tutorial will include an international survey of analytical techniques and a recent study of explosive stickiness and "sloppiness".

134.

ATF EXPLOSIVES DETECTION RESEARCH AND DEVELOPMENT EFFORTS.

Richard A. Strobel, and Mary Lou Fultz, Forensic Science Laboratory, Bureau of Alcohol, Tobacco and Firearms, 1401 Research Blvd., Rockville, MD 20850, Fax: 301-413-2466, rastrobel@atfhq.atf.treas.gov

Funding through the Antiterrorism and Effective Death Penalty Act of 1996 has spurred Federal efforts toward developing effective means for the detection of explosives. Recommendations from studies such as "Containing the Threat from Illegal Bombings" by the National Academy of Science's National Research Council has suggested future strategies toward which Federal efforts should be directed. ATF has concentrated its research and development efforts in a number of existing and conceptual detection "technologies". Among the areas being explored: enhanced canine explosives detection; feasibility of desensitizing or rendering ammonium nitrate inert; ammonium nitrate identification based upon crystallographic and chemical properties; determining survivability and retrieveability of identification tags in large scale vehicle bombs; development of advanced sensor technologies such as microcantilevers and microthermal analysis.

135.

DETECTION OF LANDMINES BY NUCLEAR QUADRUPOLE RESONANCE. *Allen N. Garroway, Michael L. Buess, and Joel B. Miller, Chemistry Division, Naval Research Laboratory, Code 6122, Washington, DC 20375, Fax: 202-767-0594, garroway@nrl.navy.mil*

Pure nuclear quadrupole resonance (NQR) of ¹⁴N nuclei is quite promising as a method for detecting bulk explosives, in quantities of interest. Because the NQR frequencies of different compounds are quite distinct, we do not encounter false alarms from the NQR signals of other benign materials; only explosives of interest yield a signal. In contrast, other detection methods detect ancillary features of the landmine and can suffer high false alarm rates. We first outline the basics of the NQR approach, highlighting strengths and weaknesses, and

then present representative results for explosives detection. We discuss some of the approaches specific to the detection of the explosives RDX, TNT, and tetryl with a surface coil. This work is sponsored in part by the US Federal Aviation Administration, Office of Special Technology (US Department of Defense) and the Defense Advanced Research Projects Agency.

136.

EXPLOSIVES DETECTION USING ION MOBILITY SPECTROMETRY: WHAT'S NEXT? *David A. Atkinson, C. J. Miller, K. A. Daum, and R. G. Ewing, Idaho National Engineering and Environmental Laboratory, Idaho Falls, ID 83415, Fax: 208-526-5327, bigdog@inel.gov*

Ion mobility spectrometry (IMS) has essentially become the detector of choice for the onsite analysis of explosives. The high sensitivity, ruggedness, and the field deployable nature of the instrument have driven the use of this technique in security applications where screening for explosives is required. Although well suited for the task, IMS still has a number of issues to be resolved. A better understanding of the gas phase ion chemistry which defines IMS response to explosives needs to be further developed. Also, the sampling methodologies and sample transfer efficiencies should be evaluated in more detail before IMS can be considered the best possible solution to the problem.

137.

EXPLOSIVES DETECTION: CASE STUDIES. *Steven G. Burmeister, Laboratory Division, Federal Bureau of Investigation, Washington, DC 20036, labcu@fbi.gov*

The Federal Bureau of Investigation often is involved in situations where explosive devices are found. Several cases are described to illustrate the methods and procedures used in explosives detection and analysis.

138.

SCIENCE AT THE INTERFACE. *Ari Patrinos, Biological and Environmental Research, Department of Energy, Office of Science, 19901 Germantown Road, Germantown, MD 20874, ari.patrinos@science.doe.gov*

For over fifty years the Biological and Environmental Research (BER) program has been promoting research at the interfaces of scientific disciplines long before it was trendy to do so. The results of that research have been a series of initiatives and discoveries that have had a great impact on science and society. Interdisciplinary scientific pursuits will continue and intensify into the new century and BER is positioning itself to continue the tradition of enabling research at the disciplinary interfaces. Studies of the greenhouse effect, human and microbial genomics, bioremediation research, and nuclear medicine have been some of the BER successes. They were made possible by the unique resources of the DOE National Laboratories and the marriage of several scientific disciplines, including biology, physics, engineering, and information science. The development of scientific "tools," broadly defined, has also figured prominently in the BER research portfolio. Looking ahead to the future, it is worth speculating on the frontiers of biological and environmental research and on the role that BER can play in pushing them as hard as possible.

139.

ANALYTICAL INSTRUMENTATION IN THE CENTURY OF BIOLOGY. *Lee Makowski, Division of Materials Research, National Science Foundation, 4201 Wilson Blvd, Arlington, VA 22230, Fax: 703-306-0902, lmakowsk@nsf.gov*

The intersection between biology, chemistry, physics and mathematics is both an expanding territory and a new frontier. Progress in unraveling the complexity of biological systems at all levels is driving the development of improved analytical instrumentation. The success of such development efforts is dependent on advances in chemistry, optics, electronics and computer science. Instruments capable of high throughput chemical and physical analyses, including nucleic acid sequence determination and mass spectroscopy of macromolecular complexes, are increasingly central to mainstream biological research. Advances in the study of the three-dimensional structure of biological molecules are tied to the development of synchrotron beam lines and other sophisticated national resources previously the mainstays of physics and materials science. The need to acquire, store and analyze the large amount of data produced by such instrumentation presents formidable challenges to applied mathematics and computer science. The development of methods for direct chemical synthesis of biomimetic macromolecules, analysis of their physical and chemical properties, and study of their assembly into ordered

structures will continue at the forefront of chemical and materials science. As the sophistication of these studies increases, they will begin to inform the understanding of dynamic biological phenomena such as the assembly of cellular organelles and recycling of membranes. In addition, the organizational principles derived from these studies are likely to improve our understanding of organization of biological systems at scales extending from the atomic to that of ecosystems.

140.

CHARACTERIZING ENVIRONMENTAL CONTAMINATION: THE HARDEST PART IS STILL AHEAD. *Mark Gilbertson, Office of Basic and Applied Research, Department of Energy, Office of Environmental Management, Washington, DC 20585, mark.gilbertson@em.doe.gov*

The cleanup of the nuclear weapons complex is estimated to cost \$200 billion or more through the year 2070. An accurate determination of the hazardous and/or radioactive contaminants in the environment and in waste forms is key to informed decision making. New techniques for nondestructive examination of complex waste forms and real-time remote monitoring of the performance of cleanup will plan an important role in the long-term stewardship of these problems.

141.

BIOLOGY AT THE LEVEL OF THE CELL. *James C. Cassatt, National Institute of General Medical Sciences, National Institutes of Health, 4500 Center Drive, Bethesda, MD 20892-6200, Fax: 301-480-2004, cassattj@nigms.nih.gov*

As stated in the draft of the NIGMS Planning and Priorities Document (<http://www.nigms.nih.gov/news/reports/planning.html#mission>) "A major goal of the Institute is to arrive at a complete understanding of the normal functioning of the living cell. This would include all the aspects mentioned above—the catalog of structure and function, the understanding of intermolecular linkages that lead to a wiring diagram, and ultimately the understanding of intracellular behavior and intercellular interactions in time and space." Such an understanding will require the marriage of classical biological disciplines with the disciplines of chemistry, physics, engineering, computer science and mathematics. In this context chemistry has an especially important role to play by providing and developing the tools to probe the inner working levels of the cell, even at the level of the atom. Recent advances and opportunities in this area will be discussed.

142.

ENVIRONMENTAL AND BIOMEDICAL SEPARATIONS USING POLYMERIC SURFACTANTS IN MICELLAR ELECTROKINETIC CAPILLARY CHROMATOGRAPHY. *Isiah Warner Sr., Department of Chemistry, Louisiana State University, Baton Rouge, LA 70803, Fax: 225-388-3971, isiah.warner@chem.lsu.edu*

Capillary Electrophoresis (CE) is an important analytical tool for separation of charged analytes. This is because of the enhanced separation efficiency of the CE method. The CE method when used in combination with a micellar pseudostationary phase will also allow separation of neutral analytes such as polycyclic aromatic hydrocarbons (PAHs). More recently, it has been demonstrated that CE offers a number of advantages for separation of racemic analytes when used with a chiral mobile additive. We have recently employed a new type of mobile phase additive, i.e. polymeric surfactants. The advantages of these polymeric surfactants over conventional micelles include 1) increased stability, 2) zero critical micelle concentration, 3) no deleterious monomer interactions, and 4) demonstrated selectivity in micellar electrokinetic capillary chromatography (MECC). We have recently shown that polymerized surfactants are broadly applicable to PAH analysis. We have also recently examined several enantiomeric separations by use of chiral polymeric surfactants. Both studies have shown that these polymers are more suitable than conventional micelles in MECC. We have also explored the utility of combining these polymers with γ -cyclodextrin (g-CD) for chiral separations. A mixture of four enantiomeric pairs was successfully resolved by use of this combination. The resolution of these enantiomers using this approach is superior to that obtained by the use of either the polymeric surfactants or the g-CD alone. The effects of polymeric surfactant concentration, -CD concentration, buffer concentration, and organic modifiers on chiral separations are also examined. In this talk, I will focus on the use of CE as a separation tool. The advantages of increasing the position and number of

chiral centers will also be discussed. A comparison of the use of polymerized micelles for separations will be made directly to separations by use of conventional (unpolymerized) micelles. The advantages of combining CE with polymerized surfactants to achieve improved analytical measurements will be discussed.

143.

ANALYTICAL CHEMISTRY AT THE INTERFACE OF MULTIDISCIPLINARY SCIENCE. *Michelle V. Buchanan, Oak Ridge National Laboratory, P.O. Box 2008, Oak Ridge, TN 37831-6124, Fax: 865-574-3036, buchananmv@ornl.gov*

Analytical chemists have traditionally been trained across the various sub-disciplines of chemistry, including organic, inorganic and physical, and even outside of classical chemistry, in the fields of biology, computer science, engineering, and physics. This breadth in training is most certainly why many analytical chemists find themselves working at the intersection of different scientific disciplines. Many of the scientific challenges before us will require a shift from small-scale, single investigator projects towards larger, multi-disciplinary programs. Teams of scientists are already working together to investigate complex problems, and analytical chemists are key contributors to these programs, as we have seen with the Human Genome Program. Many of the scientific challenges in the future will require new capabilities in analytical measurements to provide increased information, higher sensitivity, and real-time analysis. Rather than extending capabilities of current tools, new concepts in analytical instruments will be needed. This talk will discuss the role of analytical chemists in multi-disciplinary teams and how these teams will meet the scientific challenges of the future.

144.

DETECTION OF EXPLOSIVES RESIDUE. *Mark L. Miller, Forensic Science Research Unit, Federal Bureau of Investigation, FBI Academy, Quantico, VA 22135, Fax: 703-632-4557, mmiller@fbiacademy.edu*

The determination of whether a bombing has occurred is centered around investigative information, damage assessment, and the detection of explosives residue. The difficulty of finding labile compounds in trace quantities in various matrices is an analytical challenge for modern science. Numerous approaches using different technologies have been attempted to solve the problem of residue detection. This overview will examine bombing materials, the aftermath of bombing sites, approaches to sample collection, and analytical techniques used to detect explosives residue.

145.

INVESTIGATING BOMBING INCIDENTS: CASE STUDIES. *Kelly Mount, Laboratory Unit, Federal Bureau of Investigation, Washington, DC 20036, kmount@leo.gov*

The Federal Bureau of Investigation often investigates bombing incidents in the United States and around the world. Several cases are described to illustrate the methods and procedures used in explosives investigations.

146.

LIQUID CHROMATOGRAPHY/MASS SPECTROMETRY OF EXPLOSIVES: MECHANISTICS AND APPLICATIONS. *Jehuda Yinon¹, J. E. McClellan², and Richard A. Yost². (1) Weizmann Institute of Science, Rehovot 76100, Israel, Fax: 972-8-9344124, cijinon@wisemail.weizmann.ac.il, (2) Department of Chemistry, University of Florida*

Trace analysis of explosives is of major importance in detection and identification of residues from post-explosion sites and in forensic analysis of extracts from suspects and personal effects. LC/MS has already been established as a sensitive and selective method for such trace analysis, especially for thermolabile explosives. We have investigated electrospray ionization (ESI) mass spectra of a series of explosives including TNT, DNT, RDX, HMX and PETN, and determined the mechanistics of ion formation. Parameters of particular interest were limits of detection and linearity for each one of the explosives, as function of concentration and mobile phase modifier. LC/MS, using both ESI and APCI ionization modes, was used to determine impurities in TNT samples, in order to characterize the investigated explosives and determine their origin.

147.

ANALYSIS OF LOW EXPLOSIVES BY CAPILLARY ELECTROPHORESIS AND ION CHROMATOGRAPHY. *Bruce R. McCord, Department of Chemistry, Ohio University, Athens, OH 45701, Fax: 740-593-0148, mccord@ohio.edu*

Low explosives such as black powder, smokeless powder, and improvised energetic mixtures are commonly used as fillers in improvised explosives devices such as pipe bombs. The materials used to manufacture these devices are readily available throughout the United States from gunshops and hardware stores. These devices are easy to construct and responsible for the vast majority of explosives incidents in this country. For inorganic explosives, ion chromatography and, more recently, capillary electrophoresis are the methods of choice for the analysis of the explosives residue. When properly implemented, these methods provide sensitive and specific information on the products and reactants that remain from the rapid deflagration of an improvised explosive device. Techniques such as liquid chromatography and micellar electrokinetic capillary electrophoresis permit the analysis of explosive devices containing organic fillers such as smokeless powders.

148.

APPLICATION OF SOLID-PHASE MICROEXTRACTION TO THE RECOVERY OF EXPLOSIVES RESIDUE FROM POST-BLAST DEBRIS. *José R. Almirall, and Kenneth G. Furton, Department of Chemistry and International Forensic Research Institute, Florida International University, Miami, FL 33199, Fax: 305-348-3772, almirall@fiu.edu*

Solid-phase microextraction (SPME) is shown to be an inexpensive, rapid and sensitive method for the extraction of high explosives residue from solid debris samples and from aqueous samples. SPME of explosives allow for the detection of these compounds in sub part per billion concentrations when coupled with GC/ECD and LC/UV techniques. A current review of the application of SPME to the analysis of explosives residue is presented along with experimental results demonstrating the relative effects of controllable variables. Variables discussed include fiber chemistry, adsorption and desorption temperatures, extraction and desorption times, fiber sampling placement (direct, headspace, and partial headspace) and matrix effects, including water content.

149.

DETERMINATION OF EXPLOSIVES BY GAS CHROMATOGRAPHY. *Marianne E. Walsh, Thomas F. Jenkins, Alan D. Hewitt, and Thomas A. Ranney, Geological Sciences Division, Cold Regions Research and Engineering Laboratory, 72 Lyme Road, Hanover, NH 03755-1290, Fax: 603-646-4785, marianne@crrel.usace.army.mil*

Nitroaromatic (e.g., TNT), nitramine (e.g., RDX), and nitrate ester (e.g., NG) explosives are thermally labile, yet they can be quantitatively determined by gas chromatography (GC) if certain precautions are taken. Of particular importance is the cleanliness and deactivation of the injection port liner. Other considerations are the length of the capillary column and carrier gas linear velocity. Recoveries of the most thermally labile analytes are improved by shortening the column and increasing the carrier gas linear velocity. Detectors such as the electron capture detector and thermionic detector respond to the nitro group common to explosives and are suitable for determination of trace concentrations. We have used GC in the laboratory and recently to supplement field analyses where colorimetric and enzyme immunoassay on-site methods cannot quantify individual analytes among the suite that often coexist in explosives residue.

150.

USE OF GEL ELECTROPHORESIS AND CAPILLARY ELECTROPHORESIS COUPLED TO ICP-MS FOR HIGH RESOLUTION SPECIATION MEASUREMENTS. *Cameron W. McLeod, Department of Chemistry, University of Sheffield, Sheffield S1 1WB, United Kingdom, Fax: 44-114-222-3650, c.w.mcleod@sheffield.ac.uk*

Information on metal-protein interaction is increasingly required to understand transport, distribution, and toxicity of trace metals in biological systems. Most strategies to this end have involved the use of inductively-coupled plasma mass spectrometry (ICP-MS) as a highly sensitive element-specific detector for a variety of powerful separation approaches to perform these speciation analyses. Examples include the use of high pressure liquid chromatography (HPLC) or capillary electrophoresis (CE) separation modes prior to ICP-MS analysis.

Recently, characterization of metal-serum protein complexes has been achieved by combining gel electrophoresis with laser ablation ICP-MS. We describe here a new, high resolution speciation strategy employing gel electrophoresis with CE-ICP-MS. Serum samples are subjected to native polyacrylamide gel electrophoresis (PAGE) and protein-bound metals are then remobilized by electroelution and finally separation and analysis by CE-ICP-MS. Results will be presented showing metal distribution patterns for human serum samples.

151.

ELEMENTAL SPECIATION BY CAPILLARY ELECTROPHORESIS -INDUCTIVELY COUPLED PLASMA MASS SPECTROMETRY. *Gary Horlick, and Jianqi Wang, Department of Chemistry, University of Alberta, Edmonton, AB T6G 2G2, Canada, Fax: 780-492-8231, gary.horlick@ualberta.ca*

There is increasing demand for the development of analytical procedures for trace element speciation. In this study a system is presented that is applicable to the measurement of both cationic and anionic inorganic species. The system consists of a capillary electrophoresis (CE) sub-system coupled to an inductively coupled plasma-mass spectrometer (ICP-MS) using a laboratory constructed direct injection nebulizer (DIN). The CE-capillary is incorporated directly into the DIN, which is a unique demountable quad-concentric design providing front-end electrical contact along with nebulization and sheath flow containment all inside an ICP torch. The CE system is actually run in the electrostacking mode. This involves "injection" of a large sample plug that occupies about one-third of the CE capillary. When the CE voltage is applied, cations are stacked at the leading edge of the sample plug/background electrolyte boundary and anions are stacked at the trailing edge of the sample plug/background electrolyte boundary. This mode functions as a pre-concentration step and allows for the easy determination of cations and anions in a single run. The characteristics of this stacking mode along with multiple stacking modes of operation for CE will be illustrated. The determination of chromium, vanadium, antimony and arsenic species will be presented.

152.

AEROSOL INTERFACING OPTIONS WITH MICRO- AND NANO- NEBULIZATION FOR SPECIATION STUDIES WITH LC/ICP/MS AND LC/MS. *Richard F. Browner, Tiffany H. Cao, Wilson Z. Shou, Victor deJesus, Christine M. Nolan, Charlene W. Bayer, and Sheldon W. May, School of Chemistry and Biochemistry, Georgia Institute of Technology, Atlanta, GA 30332-0400, Fax: 404-894-1646, rick.browner@chemistry.gatech.edu*

The process of nebulization when interfacing low-flow liquid streams, such as with micro-LC and capillary-electrophoresis, at μL to nL/min flows, appears to differ significantly from that observed when using more typical macro-flows, e.g. mL/min flows. In many instances, a concentric buffer flow is added to the primary low-flow separation medium, in order to raise the net flow to a more convenient level. This paper will discuss some of the basic processes that occur under these interfacing condition, and attempt to demonstrate how critical control of gas and liquid flows used in the nebulization process can improve the quality and the efficiency of the nebulization process.

153.

SAMPLE INTRODUCTION INTO PLASMAS: THE HEART OF THE MATTER. *Akbar Montasser, Department of Chemistry, George Washington University, Washington, DC 20052, Fax: 202-994-2298, Montaser@gwu.edu*

Plasma-based techniques, particularly, inductively coupled plasma atomic emission spectrometry (ICP-AES) and ICP mass spectrometry (ICP-MS) are the standards in multielement analysis. The latter has become the most powerful technique for elemental and isotopic ratio analysis because it offer rapid multielement determinations over a wide concentration range and down to parts-per-trillion levels. However, sample introduction is still a major source of imprecision and inaccuracy in certain applications. In this presentation, we address advances in sample introduction research for nebulization at micro- and nano-liter levels. The emphasis is placed on speciation of difficult samples or materials that are toxic or expensive. The role of novel imaging techniques in advancing the area is discussed. The report then focuses on several applications of optical patterning for the rapid and non-intrusive elucidation of sources of noise and imprecision in the generation and whole-field characterization of aerosols for analytical spectrometries.

154.

TRUE ELEMENTAL SPECIATION IN GASEOUS SPECIMEN ANALYSIS THROUGH BRUTE SIMPLICITY: PULSED GLOW DISCHARGE MASS SPECTROMETRY.

Vahid Majidi, CST-9, Los Alamos National Laboratory, Mail Stop K484, Los Alamos National Laboratory, Los Alamos, NM 87545, Fax: 505-665-5982, majidi@lanl.gov

While there are a number of ionization methods for performing mass spectrometric analysis of gas-phase organic species, there is a need for sources of far greater versatility. A glow discharge ionization source pulsed on the millisecond time scale (ms-pulsed GD) is used for elemental, structural, and molecular analysis. Samples are continuously introduced into the pulsed plasma and allowed to interact with energetic gas-phase species. The analyte species may undergo soft ionization or may be completely atomized and ionized yielding elemental information. Detection of ions is done by a time-of-flight mass spectrometer (ToF-MS), which is the most suitable for complete mass spectrometric analysis of time-gated transient events. Toluene, p-xylene, ethylbenzene, and tungsten hexacarbonyl are among the molecules analyzed by the time-gated ms-pulsed GD-ToF-MS to illustrate the nature of the mass spectra. Extension of the basic method to applications involved in continuous process monitoring, environmental monitoring, and GC/MS applications will be suggested.

155.

TRUE ELEMENTAL SPECIATION IN HPLC ANALYSIS THROUGH BRUTE SIMPLICITY: PARTICLE BEAM GLOW DISCHARGE MASS SPECTROMETRY. R.

Kenneth Marcus, Department of Chemistry, Clemson University, Clemson, SC 29634-0973, Fax: 864-656-6613, marcusr@clemson.edu

While there are a number of promising approaches for speciation employing gas-phase sample introduction, methods for HPLC speciation are lacking. We describe here the combination of a particle beam LC/MS interface with a glow discharge ionization and excitation sources (PB-GDMS and AES) to affect comprehensive elemental speciation analyses. The PB interface is an effective means of introducing dry analyte particle to the glow discharge source, with transport efficiencies of over 20% for pure water flows up to 1 mL/min. As such, coupling with standard reverse phase or ionic separations is straightforward. The key to the elemental speciation application is the fact that the low pressure/low power glow discharge produces electron impact-type mass spectra for a very wide range of inorganic, organic, and organometallic species. As such, a separation of mixed aqueous (free metal) and organometallic analytes via reverse-phase LC produces mass spectra characteristics of the eluting metal ions and the organic molecules.

156.

HIGH-DENSITY OPTICAL SENSOR MICRO AND NANO ARRAYS FOR GENOMICS AND PROTEOMICS.

David R. Walt, Caroline Schauer, Jason Epstein, and Jane Ferguson, Department of Chemistry, Tufts University, 62 Talbot Ave, Medford, MA 02155, Fax: 617-627-3443, dwalt@emerald.tufts.edu

High-density fiber optic micro and nano array sensors have been developed using optical imaging fiber arrays. The micro and nano wells are etched into the end of an imaging optical fiber and the resulting wells are filled with micro and nano spheres. Each sphere contains a unique sensing chemistry such as an oligonucleotide probe or a protein-binding surface. Arrays are fabricated in a random fashion and require a decoding step to positionally register the array. Because fabrication requires multiple sensing beads of each type to be present in all the arrays, there are intrinsic sensitivity advantages of these arrays.

157.

GENETIC ANALYSIS BY MASS SPECTROMETRY. *Lloyd M. Smith, Department of Chemistry, University of Wisconsin-Madison, 1101 University Avenue, Madison, WI 53706-1396, Fax: 608/265-6780, smith@chem.wisc.edu*

In the last decade two powerful new tools for the mass spectrometric analysis of biomolecules have been developed, Matrix-Assisted Laser Desorption Mass Spectrometry (MALDI-MS), and Electrospray Ionization Mass Spectrometry (ESI-MS). The power of these methods lies in their ability to produce and mass analyze intact gas phase ions from very large molecules such as proteins and

nucleic acids. The speed, accuracy, and sensitivity of the technologies make them well-suited to address a number of problems in genetic analysis, including the analysis of DNA sequence, genetic variations, and gene expression. Results in these areas will be presented, including recent work in which single nucleotide polymorphisms (SNPs) in genomic DNA may be analyzed without need for a prior PCR amplification step.

158.

IDENTIFICATION OF UP-REGULATED PROTEIN IN *E. COLI* BASED ON SIGNATURE PEPTIDES APPROACH. *Asish Chakraborty, and Fred E. Regnier, Department of Chemistry, Purdue University, 1393 Brown Building, West Lafayette, IN 47907, asishc@omni.cc.purdue.edu*

Signature peptide proteomics is based on the fact that the properties of single tryptic peptides can be unique to a specific protein. In fact, most proteins have many signature peptides. The objective in proteomics is to identify all the protein species in a complex mixture of proteins. Based on the broad availability of DNA databases, proteins are now widely identified through mass spectra of their tryptic peptides that are then compared to the mass of peptides predicted from sequence databases. This paper describes how to identify a protein, which has been over expressed by an environmental stimulus. Following tryptic digestion of control and experimental proteins, the resultant peptides were labeled isotopically. Primary amino groups and lysines in peptides from experimental and control samples were derivatized with acetate and trideuterioacetate, respectively. After mixing the labeled control and experimental samples, the resulting peptides obtained mixture was separated by reversed phased chromatography and the fractions collected. The relative concentration of peptides was determined by isotope ratio analysis with MALDI-MS. Peptide masses and sequences were used to identify protein.

159.

MEASUREMENTS OF NUCLEIC ACIDS AND PROTEINS IN INDIVIDUAL CELLS. *Sheri J. Lillard, Futian Han, Shujun Chen, Jennifer L. Zabdyr, Christopher E. McCoy, and Rimon Shaker, Department of Chemistry, University of California, Riverside, CA 92521, Fax: 909-787-4713*

The study of nucleic acids and proteins during the latter part of the 20th century underwent explosive growth with regards to throughput and sensitivity of the assays. Efforts in our laboratory are directed towards devising and optimizing such assays for individual cells, with the significance being in the fields of biology and medicine. To achieve these goals, capillary electrophoresis (CE) with laser-induced fluorescence (LIF) detection is used to separate and quantitate intracellular species. In-situ sampling and separation of nucleic acids (e.g., RNA) has been obtained at the single-cell level, with excellent resolution obtained for both the larger and the smaller molecular weight components. Individual prostate cells have been analyzed to determine chemical signatures that might reveal early indications of cancer. We have also developed high-throughput instrumentation that permits continuous sampling and separation of intracellular proteins, from individual cells, at a rate of ~ 1 cell/minute.

160.

CONTROLLING CARBON SURFACES FOR ELECTROANALYSIS. *R. Mark Wightman, Chemistry, University of North Carolina, CB#3290, Venable Hall, Chapel Hill, NC 27599-3290, Fax: 919-962-2388, rmw@unc.edu*

Carbon electrodes have long been favored for electroanalytical applications in aqueous solutions. This is because carbon electrodes have low charging currents and stable background currents. However, it has long been clear that the chemical functionalities on the surface of carbon affect the electrochemical behavior, and, through McCreery's research, considerable progress has been made in harnessing this chemistry to optimize electroanalysis. Our own work employs carbon fiber electrodes. Many of the surface treatments shown to be useful on glassy carbon electrodes will be shown to be useful on microelectrodes as well.

161.

ELECTRON TRANSFER REACTIONS AT CONDUCTIVE MICROCRYSTALLINE AND NANOCRYSTALLINE DIAMOND FILM ELECTRODES. *Greg M. Swain, Department of Chemistry and Biochemistry, Utah State University, Logan, UT 84322-0300, Fax: 435-797-3390, gmswain@cc.usu.edu*

Conductive diamond thin films are new electrode materials for a variety of electrochemical systems. These materials are challenging to investigate because

they are typically polycrystalline with multiple crystallographic orientations exposed, contain high levels of incorporated dopant atoms (e.g., boron), and consist of extended and point defects, grain boundaries and low levels of nondiamond carbon impurity phases. Several factors can influence the electrochemical response of polycrystalline films: (i) nondiamond carbon impurity phases, (ii) the surface termination (H vs. O), (iii) the dopant type, level and distribution, (iv) grain boundaries and other morphological defects, and (v) the primary crystallographic orientation. The degree to which one or more of these factors influence the response will depend on the charge transfer mechanism of the redox analyte, as shown by the McCreery group in recent years for sp² carbon electrodes. In this presentation, electron transfer reactions at conductive microcrystalline and nanocrystalline diamond film electrodes will be discussed. The microcrystalline films have nominal grain sizes of 2-4 μm, are doped with boron (ca. 2000-5000 ppm B/C) and have in-plane film resistivities of 0.01 ohm-cm or less. The nanocrystalline films have nominal grain sizes of 10-50 nm, have nitrogen incorporated (ca. 10,000 ppm N/C) and have in-plane film resistivities of 0.01 ohm-cm or less. The influence of nondiamond carbon impurity phases, the surface termination, impurity incorporation, and the primary crystallographic orientation on the electrode reaction kinetics for several inorganic and organic aqueous-based redox analytes will be discussed.

162.

SCANNING KELVIN PROBE FORCE MICROSCOPY STUDIES OF CORROSION. *Patrick Schmutz, Derik Devecchio, Valerie Guillaumin, and Gerald S. Frankel, Fontana Corrosion Center, Ohio State University, 477 Watts Hall, 2041 College Rd., Columbus, OH 43210, Fax: 614-292-9857, schmutz@er6.eng.ohio-state.edu, frankel.10@osu.edu*

Scanning Kelvin Probe Force Microscopy (SKPFM) is a powerful technique to characterize the corrosion processes on passive surfaces. The topography and potential distribution of a surface can be simultaneously mapped with sub-micron spatial resolution by this technique. A linear relation has been found for a range of pure metals between the corrosion potential of in aqueous solution and the Volta potential measured in air upon emersion, indicating that this potential is a measure of the practical nobility of the surface. However, various observations indicate that the interpretation of the Volta potential measured in air is much more complicated. For instance, both the Volta potential and the OCP are both offset along the calibration line depending upon the ions in the solution. This talk will discuss the meaning of the potential measured by the SKPFM technique.

163.

APPLICATION OF RAMAN MICROSCOPY ON CORROSION STUDY OF AIRCRAFT ALUMINUM ALLOY AND STEEL. *Jun Zhao¹, Richard L. McCreery², Gerald S. Frankel³, and Fritz Allen¹. (1) Chromex, Inc, 2705 Pan American Freeway, NE, Albuquerque, NM 87107, Fax: 505-344-6095, chromex@nmia.com, (2) Department of Chemistry, Ohio State University, (3) Fontana Corrosion Center, Ohio State University*

Raman microscopy and spectral imaging were used to study the corrosion protection mechanism of a chromate conversion coating (CCC) on the aluminum aircraft alloy 2024-T3, and to identify the corrosion products of a steel sample. On aluminum alloy, the self-healing property of CCC against corrosion was attributed to the slow release of chromate species from the CCC film in aqueous environment and the subsequent migration and deposition of it at exposed, actively corroding regions, such as pits. Combined with electrochemical analysis, it was found that the released chromate, although at very low concentrations, inhibits the oxygen reduction, raises the polarization (corrosion) resistance by two orders of magnitude, reduces the corrosion potential of the alloy to the passive region, and therefore stops aluminum dissolution. On steel, microscopic Raman imaging readily identifies the various corrosion products and their spatial distributions.

164.

MODULATION TECHNIQUES IN IN SITU UV-VISIBLE SPECTROELECTROCHEMISTRY. *Daniel Scherson¹, Yuriy V. Tolmachev², and Ionel C. Stefan¹. (1) Department of Chemistry, Case Western Reserve University, 2074 Adelbert Road, 211N Millis Science Center, Cleveland, OH 44106-7078, Fax: 216-368-3006, dxs16@po.cwru.edu, (2) Materials Science Division, Argonne National Laboratory*

A mathematical framework is presented for the quantitative analysis of in situ potential modulation spectroelectrochemical techniques based on phase-

sensitive detection for the study of solution-phase redox systems under strict diffusion control. In the case of arrangements in which the probing beam is parallel to the electrode surface, the phase was found to be proportional to $(y/2D)^{1/2}$, where y is the distance normal to the electrode, w is the frequency of the perturbing signal and D the diffusion coefficient of the species responsible for absorption or refraction. Good agreement was found between theoretical predictions and the few available experimental results for both absorption and probe-beam deflection-type experiments. In particular, in the case of solutions containing the chromophore trianisylamine (TAA) and non-absorbing *p*-benzoquinone the phase angle difference between absorption and diffraction calculated from theory and measured experimentally yielded a common value of ca. 30°.

165. HIGH SPEED HIGH THROUGHPUT MUTATION DETECTION BASED ON CAPILLARY ELECTROPHORESIS. *Edward S. Yeung, and Qiuqiang Gao, Ames Laboratory-USDOE and Department of Chemistry, Iowa State University, Ames, IA 50011, Fax: 515-294-0266*

Single-point mutation detection has attracted much attention recently. Though many methods have been reported, low-cost, high-throughput and high-speed methods are still in demand. We present a fast and reliable mutation detection scheme based on temperature gradient capillary electrophoresis. A large temperature gradient (10 °C) was applied. A precision of 0.02 °C was set while a temperature ramp of 0.7 °C/min was performed. Multiple unlabeled samples from PCR reaction were injected and analyzed. Ethidium bromide was used as the intercalating dye for laser-induced fluorescence detection. Mutations were identified by comparing the electropherogram pattern of a heteroduplex with that of a homoduplex reference in continuous runs. All five mutations were successfully detected with high confidence. This scheme is suitable for applying multiple capillary array electrophoresis to the efficient screening of single-point mutations without prior knowledge of the exact sequences involved.

166. PLASTIC MICROFLUIDIC CHIPS FOR MULTIPLEXED GENETIC ANALYSIS. *Stephen J. Williams¹, Ingrid Cruzado¹, Pin Kao¹, Alexander Sassi¹, Sharat Singh², Hongdong Tan¹, and Maureen Cronin¹. (1) Genomics Applications, ACLARA BioSciences, Inc, 1288 Pear Avenue, Mountain View, CA 94043, Fax: 650-210-1210, swilliams@aclara.com, (2) Advanced Technologies, ACLARA BioSciences, Inc*

ACLARA BioSciences is developing plastic microfluidic LabCard™ devices for use in high-throughput drug screening and genetic analysis applications. Low manufacturing costs potentially allow these devices to be single use. Disposability can be of crucial importance where cross-contamination during sequential sample analysis is of concern, for example, in genotyping for forensic identification. Previously, we have demonstrated rapid 4-color DNA sequencing up to 640 bases on single channel cards. To address demand for sample throughput, we have recently built a system capable of loading, running and detecting multi-channel plastic LabCard™ devices. We will present results from this system. We are also working to develop microfluidic based-systems capable of high-throughput, multiplexed mRNA expression analysis and SNP genotyping. Multiplexing is made possible using specific signal molecules with distinct electrophoretic mobilities (eTAGS™), which can be rapidly separated in arrays of plastic microchannels. We present preliminary data from model, multiplexed gene expression assays.

167. PROTEOMICS AND MASS SPECTROMETRY: READING PROTEIN EXPRESSION BY HIGH RESOLUTION MASS SPECTROMETRY OF WHOLE CELL LYSATES. *Zee-Yong Park, and David H. Russell, Department of Chemistry, Texas A&M University, College Station, TX 77842-3012, Fax: 979-845-9485, park@mail.chem.tamu.edu, russell@mail.chem.tamu.edu*

Proteomics has benefited greatly from recent developments in mass spectrometry and from the accelerated construction of genomic databases. The information from mass spectral analysis is searched against protein or DNA databases for protein identification and characterization. Conventional approaches such as 2D-PAGE/ in-gel digestion combined with mass spectrometry is lengthy and labor-intensive. To overcome the limitations of 2D-PAGE/ in-gel digestion, we developed a simple separation/ in-solution digestion combined with high-

resolution MALDI TOF mass spectrometry method. High resolution MALDI TOF mass spectrometry can be used to analyze complex protein mixtures, thus complete protein separation is not required. Microtip column separation/ in-solution digestion minimizes time and effort required for sample preparation. Moreover, significantly fewer numbers of mass spectra are used to identify major proteins in whole cell lysates. The whole procedure from protein extraction to analysis of mass spectral data can be completed in a day and several hundreds proteins can be identified.

168. SINGLE CELL PROTEOME PROJECT. *Norman J. Dovichi, Zheru Zhang, Sergey Krylov, Edgar Arriaga, Shen Hu, and David Michels, Department of Chemistry, University of Alberta, Edmonton, AB T6G 2G2, norm.dovichi@ualberta.ca*

A simple proteome map was obtained from single HT29 human colon adenocarcinoma cells. The cell of interest was introduced into a fused-silica capillary, lysed, and the protein content was fluorescently labeled. The labeled proteins were separated by capillary zone electrophoresis in a sub-micellar buffer and detected by laser-induced fluorescence in a post-column sheath-flow cuvette. Several dozen components were resolved. One component was identified as a 100 kD protein by co-injecting the purified protein obtained from an SDS-PAGE gel. Protein expression varied significantly between cells. This expression difference was correlated with cell cycle.

169. ELECTROCHEMICAL ATTACHMENT OF FUNCTIONAL GROUPS TO CARBON SURFACES FOR CONTROLLING PROTEIN ADSORPTION. *Mark T. McDermott, James K. Kariuki, Truong C. Ta, and Ryan Chowdhury, Department of Chemistry, University of Alberta, Edmonton, AB T6G 2G2, Canada, Fax: 780-492-8231, mark.mcdermott@ualberta.ca*

Carbon materials are an important set of biomaterials in implant medicine. For example, low temperature isotropic carbon (LTIC) is used either partially or wholly to construct mechanical prosthetic heart valves. However, patients receiving carbon heart valves must often take anticoagulant drugs to reduce the risk of clot formation on the implant. When a foreign material comes into contact with blood, it is generally accepted that a complex biomolecular film containing plasma proteins forms rapidly at the interface. Thus, the ability to control the adsorption of proteins to carbon surfaces is vital to the development of more compatible implant devices. In this work, we are attempting to gain control of protein adsorption at carbon surfaces through the covalent attachment of functionalized aryl groups via the reduction of the corresponding diazonium salts. Due to the ease of synthesizing diazonium salts with different functional groups, this method allows the grafting of a broad spectrum of substances. We report our electrochemical, scanning force microscopic (SFM) and infrared reflectance absorbance spectroscopic (IRRAS) characterizations on the growth of aryl films on highly oriented pyrolytic graphite (HOPG) and pyrolyzed carbon surfaces. We then investigate the influence of aryl modification on the adsorption of albumin and fibrinogen. We will use our results as a guide for studies on LTIC with a view of developing a more biocompatible carbon surface.

170. SELECTIVITY MANIPULATION OF SEPARATION BY ELECTROCHEMICALLY-MODULATED LIQUID CHROMATOGRAPHY (EMLC). *Marc D. Porter, Jennifer Harnisch, Zhongmin Hu, Hajime Takano, Daniel Gazda, and David Keller, Chemistry Department, USDOE-Ames Laboratory, Microanalytical Instrumentation Center, Iowa State University, 42 Spedding Hall, Ames, IA 50011, Fax: 515-294-3254, mporter@porter1.ameslab.gov*

Electrochemically-modulated liquid chromatography (EMLC) provides a novel pathway to manipulate the efficiency of analytical separations. The strength of this technique derives from electrochemically-induced changes in the effective composition of a conductive stationary phase that acts as the working electrode in an electrochemical cell. Using an EMLC column, applications of applied potentials (E_{app}) negative of the potential of zero charge (pzc) generate an excess negative surface charge on the electrode. In contrast, at values of E_{app} positive of the pzc, the surface of the electrode will have an excess positive charge. This presentation describes the chromatographic separations of several classes of compounds: pharmaceutical agents, peptides, amino acids, and various chiral systems using porous graphitic carbon. For pharmaceutical

compounds, the modification of the selectivity of stationary phase chirality exploits the ability to alter the excess surface charge, which can also be viewed as changing the donor-acceptor interaction between the analytes and the column, and therefore the amount of a chiral selector adsorbed onto PGC. In each example, mechanistic aspects of the separation are discussed. The general design of the column is also detailed.

171.

CV AND FIA STUDY OF IONS AND MOLECULES PARTITIONING INTO FRACTURED CARBON FIBER ELECTRODES. *Theodore Kuwana¹, Brian Coleman¹, Tina H. Huang², Richard S. Kelly³, and James E. Flynn³.* (1) Department of Chemistry, University of Kansas, Lawrence, KS 66045, *tkuwana@ukans.edu*, (2) Process Measurements Division, Chemical Science and Technology Laboratory, National Institute of Standards and Technology, (3) Department of Chemistry, Merrimack College

A 10-um diameter carbon fiber (DuPont E120) can be electrochemically fractured to produce ultra-high surface areas, as a consequence of opening micro- to nano-porous interior. The partitioning of ions and molecules into the fiber has been studied by cyclic voltammetry (CV) and flow injection analysis (FIA). With FIA, the fractured fibers are affixed in a micro-flow channel and the electrochemical currents are measured at fixed potentials during injections of known amounts of ions and molecules. With cations, extent of partitioning increases with larger charge-to-size ratios and is concentration dependent. With a 0.025 M KNO₃ background, the injection of nanopure water results in an anodic followed by a cathodic peak (i.e., K⁺ out and in as fiber equilibrates with the background KNO₃). With a buffer background, injection of buffers with pH less or greater than the background results in a cathodic or anodic peak, indicative of protons partitioning in or out of the fiber. The currents are much larger if ions are electroactive. Partitioning of organics depends on charge (+ or -), size, shape and hydrophobicity. CV and FIA results will be compared to ions and molecules partitioning into polymer film electrodes.

172.

IMPACT OF A UNIFIED APPROACH TO ESTIMATING MEASUREMENT UNCERTAINTY ON THE INTERNATIONAL COMPARABILITY OF MEASUREMENTS AND STANDARDS. *Robert L. Watters Jr., Technology Services, National Institute of Standards and Technology, 100 Bureau Drive, MS2000, Gaithersburg, MD 20899-2000, Fax: 301-975-2183, robert.watters@nist.gov*

A Mutual Recognition Arrangement (MRA) signed by representatives of National Metrology Institutes (NMIs) now facilitates international comparability of measurements and standards that support international trade and regulation. The MRA establishes the technical basis for the mutual acceptance of calibration and measurement certificates of the NMIs. The two principal components of the MRA are measurement results from comparisons of national measurement and calibration standards (Appendix B) and a compilation of calibration and measurement (CMC) services offered by the NMIs (Appendix C). The claims in Appendix C must be qualified with specific reference to estimated uncertainties for each service. When such claims reference the results of comparisons, uncertainties in the results must be estimated in a consistent manner. The metrology community (including analytical chemistry) has embraced a uniform approach to estimating uncertainty as published by ISO in the "Guide to the Expression of Uncertainty in Measurement". The use of this guide will be described with examples of how the results may be used to ensure worldwide acceptance of measurements.

173.

QUANTIFYING UNCERTAINTY IN ANALYTICAL MEASUREMENT: THE NEW EURACHEM/CITAC GUIDE. *Thomas Vetter, Analytical Chemistry Division, NIST, 100 Bureau Drive, Mail Stop 8393, Gaithersburg, MD 20899-8393, Fax: 301-975-8392, thomas.vetter@nist.gov*

The Eurachem/CITAC Guide "Quantifying Uncertainty in Analytical Measurement" is an interpretive guide to the ISO document "Guide to the Expression of Uncertainty in Measurement," commonly referred to as "GUM." The Eurachem/CITAC guide has been explicitly written as a practical guide for the analytical chemist.

It includes extensive discussion of the use of existing data from method validation, proficiency testing, collaborative studies, and historical data for the quantification of uncertainty components. Detailed examples of uncertainty budgets for problems in analytical chemistry are used to illustrate the concepts.

This paper will present the 2nd edition of the guide, in voting draft form at the time of abstract submission, and will promote it as a tool for analytical chemistry.

174.

INTERPRETATION OF THE GUIDE TO THE EXPRESSION OF UNCERTAINTY IN MEASUREMENT. *Raghu N. Kacker, Statistical Engineering Division, National Institute of Standards and Technology, 100 Bureau Drive, Mail Stop 8980, Gaithersburg, MD 20899-8980, Fax: 301-990-4127, raghu.kacker@nist.gov*

The Guide to the Expression of Uncertainty in Measurement (GUM) is intended for all scientific and technological measurements in science, engineering, commerce, industry, and regulation. So the GUM must have an unambiguous interpretation. But it mixes up concepts from frequentist and Bayesian statistics in seemingly incompatible ways. Therefore, as presented, the GUM is ambiguous and liable to be applied in more than one way leading to more than one way of expressing uncertainty in measurement. This paper attempts to clear up the ambiguity of the GUM, and proposes a simple and widely applicable approach to set the coverage factor that defines an expanded uncertainty interval with a desired minimum coverage probability. Our hope is that the clarifications and the viewpoints presented here will promote a more consistent use of the GUM and facilitate its application to situations not explicitly covered in the original document.

175.

STATISTICAL EXPERIMENTAL DESIGN CONCEPTS FOR UNCERTAINTY EVALUATION. *Mark S. Levenson, Statistical Engineering Division, National Institute of Standards and Technology, 100 Bureau Drive Stop 8980, Gaithersburg, MD 20899-8980, Fax: 301-990-4127, mlev@nist.gov*

The sequence and arrangement of steps in the measurement process are important considerations in the reduction and quantification of uncertainty in analytical measurements. Such considerations are studied in the area of statistics known as experimental design. Without regard to basic experimental design concepts, the quantification of uncertainty may not be realistic or possible. This talk will cover these basic concepts, such as randomization, blocking, and allocation, for the purpose of uncertainty evaluation in analytical measurements.

176.

STEPWISE APPROACH TO QUANTIFICATION OF UNCERTAINTY IN ANALYTICAL MEASUREMENTS. *Thomas Vetter, Analytical Chemistry Division, National Institute of Standards and Technology, 100 Bureau Drive, Mail Stop 8393, Gaithersburg, MD 20899-8393, Fax: 301-975-8392, thomas.vetter@nist.gov*

Uncertainty in an analytical measurement can be quantified by using a step-wise approach. This approach starts with designing the analytical measurement approach, then is followed by the measurement itself and is completed by combining all sources of uncertainty in the measurement equation to determine the expanded uncertainty of the measured value. After all sources of uncertainty are combined, the magnitude of major sources is reexamined. This approach is applicable to any chemical determination. Examples of models used to quantify uncertainty and the total uncertainty budget for certification of Standard Reference Materials by classical gravimetry will be presented.

177.

SOURCES OF UNCERTAINTY IN INSTRUMENTAL NEUTRON ACTIVATION ANALYSIS. *Robert R. Greenberg, Analytical Chemistry Division, National Institute of Standards and Technology, 100 Bureau Drive, Stop 8395, Gaithersburg, MD 20899-8395, Fax: 301-208-9279, robert.greenberg@nist.gov*

Instrumental neutron activation analysis is an analytical technique capable of a high degree of accuracy. However to achieve a high level of accuracy, care must be taken to minimize and evaluate all the significant sources of uncertainty in

the entire measurement process. Unfortunately, this is not a common practice for many of the laboratories routinely applying this technique, and many of them do not consider some of the easier-to-control uncertainty sources. In addition, optimization of the experimental design can be a very valuable approach in reducing the level of the individual uncertainty components, as well as in simplifying their evaluation. This presentation will describe the fundamentals of instrumental neutron activation analysis, provide a complete description of all sources of uncertainty, and provide examples of methods to evaluate the sources of uncertainty for a particular analysis.

178.

ERRORS IN BOTH VARIABLES FOR CALIBRATION LINES. *Franklin Guenther, Analytical Chemistry Division, National Institute of Standards and Technology, 100 Bureau Drive, Gaithersburg, MD 20899-8393, Fax: 301-977-8393, fguenther@nist.gov, and Stefan Leigh, Statistical Engineering Division, National Institute of Standards and Technology*

In constructing a calibration line for an instrument, the normal course of action is to analyze a series of analytical standards of known concentration, and plot the instrumental response versus the concentration. The calibration line is then derived by linear regression of the data using the concentration of the standard as the X variate, and the instrument response as the Y variate. This procedure is applicable only when the error associated with Y is significantly greater than that associated with X. In cases where the X error is approximately equal to the Y error, a different underlying statistical model is applicable, and hence a different form of regression must be applied. In this paper we will be discussing specific tests that can be applied to data to determine which form of the regression model is most applicable, and presenting results using test data.

179.

QUANTIFYING UNCERTAINTY IN AN EDTA TITRATION. *Johanna M. Smeller, Analytical Chemistry Division, Gas Metrology and Classical Methods, National Institute of Standards and Technology, 100 Bureau Drive Stop 8393, Gaithersburg, MD 20899-8393, Fax: 301-977-8392, JSmeller@nist.gov*

Determining the uncertainty of a value not only provides information regarding the accuracy and precision of the measurement, but also can be used to evaluate and improve the measurement process itself. Uncertainty analysis begins with an examination of the specific measurement process. The uncertainty associated specifically with an EDTA titration of a metal will be discussed and determined. Type A uncertainties include the measurement replication of both the metal and the standardization of the titrant. Type B uncertainties include such factors as the metal impurities and the EDTA titratable impurities. Other factors specific to the measurement will be discussed. The combined uncertainty is calculated using the CIPM (International Committee for Weights and Measures) approach.

180.

QUANTIFICATION OF MEASUREMENT UNCERTAINTY FOR ORGANIC ANALYTICAL MEASUREMENTS: CURRENT PRACTICE — CURRENT/FUTURE NEEDS. *Reenie M. Parris, Michael J. Welch, and Michele M. Schantz, Analytical Chemistry Division, National Institute of Standards and Technology, 100 Bureau Dr, Stop 8390, Gaithersburg, MD 20899, Fax: 301-926-8671, reenie.parris@nist.gov*

The perceived need for a measurement uncertainty estimate for organic analytical measurements and the approaches for its quantification and use vary widely in current practice. Benefits of the realistic estimation, reporting, and use of this uncertainty, including its critical role in establishing traceability of chemical measurements, will be discussed. Examples from specific application areas such as the determinations of organic analytes of clinical and environmental interest in natural matrix materials will be used to illustrate the process of estimating measurement uncertainty. These will include estimating the uncertainty attributable to the calibrant(s) typically required for organic analyses.

181.

QUANTIFICATION OF MEASUREMENT UNCERTAINTIES OF REFERENCE MATERIALS MANUFACTURED BY SPEX CERTIPREP. *Ralph H. Obenauf, Nimi Koehlerakota, and Vanaja Sivakumar, SPEX CertiPrep, 203 Norcross Ave, Metuchen, NJ 08840, Fax: 732-494-1747, robenauf@spexcorp.com*

Certified values are almost always accompanied by an uncertainty. However, it is often unclear if the uncertainty is simply the measurement uncertainty or truly takes into account all the other parameters that effect the uncertainty of the reported certified value. The presentation will cover the evaluation of total combined uncertainties of reference materials manufactured by SPEX CertiPrep. The combined standard uncertainty is calculated taking into consideration the uncertainties resulting from the following:

1. Reference Material preparation: ·Starting material purity, assay of major element ·Weighing of the material ·Dissolution of the material and dilution to volume II. Verifying concentration: 1. ICP Analysis ·Reference material used in the calibration and its uncertainty ·Dilution of the reference material ·Dilution of the SPEX reference material (sample) ·Instrument drifts 2. Wet Assay ·Dilution of the SPEX reference material (sample) ·Uncertainties resulting from volumetric and gravimetric procedures Calculation of expanded uncertainty.

182.

ASSIGNMENT OF CERTIFIED VALUE AND UNCERTAINTY FOR THE NIST SRM 3100 SERIES OF SINGLE-ELEMENT STANDARD SOLUTIONS. *Gregory C. Turk, Analytical Chemistry Division, National Institute of Standards and Technology, 100 Bureau Drive, Stop 8391, Gaithersburg, MD 20899-8391, turk@nist.gov*

NIST SRMs 3101a through 3169 are a series of single-element standard solutions for sixty-seven different elements. These SRMs are intended for use as primary standards used for the preparation of the working standards that calibrate instruments and procedures for quantitative elemental analysis. Many commercially produced elemental solution standards are traceable to the corresponding 3100 Series SRM. Consequently, the certified value and uncertainty of each of these SRMs has a direct effect on many thousands of individual analyses performed in laboratories around the world.

The certified value is determined from the average of the gravimetric preparation value and an independent value assignment done by ICP Optical Emission Spectrometry (ICPOES). The latter is a comparative method, which relies on calibration by a set of independently prepared NIST primary standards. Sources of uncertainty associated with gravimetric preparation and the ICPOES measurement determine the uncertainty of the certified value. A detailed description of the uncertainty budget from several recent certifications will be presented.

183.

UNCERTAINTY BUDGETING IN THE CERTIFICATION OF REFERENCE MATERIALS BY ICP-MS. *Lee L. Yu, Analytical Chemistry Division, Spectrochemical Methods Group, National Institute of Standards and Technology, 100 Bureau Drive, Stop 8391, Gaithersburg, MD 20899-8391, Fax: 301-869-0413, lee.yu@nist.gov*

Certification of reference materials by ICP-MS or ICP-OES typically involves the dissolution of the sample, the preparation of standards, and the transfer of the calibration from the standards to the sample by means of instrumentation. An uncertainty is induced in each step of the calibration transfer process. A procedure is developed to evaluate the uncertainty of an analysis. All sources of uncertainties are identified after studying the flow chart of an analysis. These uncertainties are entered into a "cause and effect" diagram that shows both the sources of all uncertainties and the relation of one uncertainty to another. Uncertainties resulting from repeated observations (Type A) and those evaluated by scientific judgement (Type B) are combined to derive the uncertainty of the analysis, according to "The Guide to the Expression of Uncertainty in Measurement" published by the International Organization for Standardization. An example will be given to demonstrate how the uncertainty budgeting principles are employed in the certification of Standard Reference Materials by ICP-MS.