FACSS XIX

FINAL PROGRAM

Nineteenth Annual Meeting of the Federation of Analytical Chemistry and Spectroscopy Societies

September 20-25, 1992

Adams Mark Hotel
Philadelphia, Pennsylvania

Final Program

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September 20-25, 1992
Adams Mark Hotel, Philadelphia PA

Nineteenth Annual Conference of the Federation of Analytical Chemistry and Spectroscopy Societies

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* Advances in Plasma Spectrophotometry
* Solid and Slurry Sampling with GFAAS
* New Plasma Atomic Emission Instrumentation
* Peter Keliher Memorial Symposium
* Chemometrics in Signal Processing
* Industrial Applications of Raman Spectroscopy
* Recent Developments in Forensic Drug Analytical Chemistry
* Chromatography in the Delaware Valley - Past, Present, and Future
* Fourier Transform and Ion Trap Mass Spectrometry
* Separation Scientists of the 21st Century

Monday PM

* Chemometrics in Calibration
* Solid and Slurry Sampling with GFAAS
* Plasma Diagnostics
* Sampling of Solids with High Current Pulsed Discharges
* Industrial Applications of Raman Spectroscopy
* Recent Advances in the Analysis and Characterization of Explosives
* Chromatography in the Delaware Valley - Past, Present, and Future
* Fourier Transform and Ion Trap Mass Spectrometry
* Investigations of Chromatographic Stationary Phases
* LIMS: General

Tuesday AM

* Developments in Information Generation and Management in Plasma Spectrometric Labs
* Sample Introduction for Atomic Spectroscopy: What Does the Future Hold?
* Colonial Chemistry: The Age of Gases
* Electrothermal Atomizers in AAS: Fundamentals and Applications
* State of the Art Raman Spectroscopy
* Electrochemical Detection of the Future: Is There a Future After Catecholamines?
* Chemometrics in Chromatography
* Advances in Capillary Electrophoretic and Micellar Electrokinetic Separations
* Size Exclusion Chromatography
* High Molecular Weight Mass Spectrometry

Tuesday PM

* Developments in Information Generation and Management in Plasma Spectrometric Labs
* Molecular Analysis with Laser Techniques
* The Science of Ben Franklin: Then and Now
* Sample Introduction Strategies for ICP-AES
* Electrothermal Atomizers in AAS: Fundamentals and Applications
* State of the Art Raman Spectroscopy
* Analytical Laboratories on Chips: Genome Project for Analytical Chemistry?
* LIMS Discussion Session
* Advances in Capillary Electrophoresis and Micellar Electrokinetic Separations
* Size Exclusion Chromatography
* High Molecular Weight Mass Spectrometry
* Chemometrics in the Analysis of 3 Mode Data Arrays
* POSTER SESSION: Atomic Spectroscopy

Wednesday AM

- * STUDENT AWARD SYMPOSIUM ON CHROMATOGRAPHY
- * Dynamic Vibrational Spectroscopy
- * New Directions in Chiroptical Spectroscopy
- * Application of ICP-MS
- * Advances in Glow Discharge Sources for Atomic Spectroscopy
- * Electrothermal Atomizers in AAS: Fundamentals and Applications
- * Chemometrics in Process Analysis
- * New Ways of Looking at Surfaces: New Methods for New Materials
- * Secondary Ion Mass Spectrometry
- * Mass Spectrometry of Polymers
- * Advances in Biomolecule Separations

Wednesday PM

- * HIRSCHFELD AWARD SYMPOSIUM
- * ANACHEM AWARD SYMPOSIUM
  awardee: Milos Novotny
- * New Directions in Chiroptical Spectroscopy
- * Application of ICP-MS
- * Advances in Glow Discharge Sources for Atomic Spectroscopy
- * Element Selective Detectors
- * Acoustic Sensors for Process Analysis
- * Capillary Chromatography
- * New Ways of Looking at Surfaces: New Methods for New Materials
- * Secondary Ion Mass Spectrometry
- * POSTER SESSION: Chromatography

Thursday AM

- * Spectroscopic Process Analysis
- * Application of ICP-MS
- * Fluorescence Spectroscopy
- * LC/MS of Drugs, Biomolecules and Metabolites
- * Elemental Mass Spectrometry
- * Atomic Analysis with Laser Techniques
- * Chemometric Applications of Artificial Neural Networks
- * Surface Science
- * Advances in Preparative Chromatography
- * Flow Injection Techniques in Atomic Spectroscopy

Thursday PM

- * Spectroscopic Process Analysis
- * Application of ICP-MS
- * Fluorescence Spectroscopy
- * Pharmaceutical Applications of Mass Spectrometry
- * Sample Introduction and Pretreatment Methods in Atomic Spectroscopy
- * Chemistry of Helium Discharges
- * IR Microscopy
- * Mechanism and Application of Solid Phase Extraction in Analytical Chemistry
- * Detection Techniques for Capillary Electrophoresis and Liquid Chromatogrpahy
- * Laser Plasmas in Atomic Spectroscopy
- * POSTER SESSION: General

Friday AM

- * Atomic Spectroscopy: Instrumentation and Application
- * Molecular Spectroscopy
- * IR Applications
- * Flow Injection Analysis
- * Mass Spectrometry

Friday AM (cont'd)

- * Atomic Absorption Spectroscopy Applications
- * Infrared Spectroscopy
- * SCFE and Chromatography in the Delaware Valley
- * Liquid Chromatography
- * General Session

Colleagues and Spouses:

Welcome to FACSS XIX in Philadelphia. Thank you for helping to make this meeting a success. It is the goal of FACSS to provide a forum for the presentation and discussion of research ideas and results in the various fields of analytical chemistry and spectroscopy. Our annual FACSS meetings have perennially met this goal because of the catalytic number of attendees, the mixture of their expertise, and the comfortable atmosphere. Your attendance is evidence that this year is no exception.

The continuing success of FACSS meetings would not be possible, however, without the effort expended by many dedicated volunteers working to develop the program, implement improvements in the organization, ensure that the facilities are chosen and used efficiently, and organize and coordinate the many simultaneous events occurring before, during, and after FACSS week. These volunteers give up a lot of their time to help bring FACSS about. Please take a moment to look through the lists of volunteers and acknowledge their efforts when possible. For those interested in volunteering for next year, please make yourselves known to one of the FACSS officers and you will be directed where to go to sign up.

I hope you have a productive and fun week. Feel free to stop me in the hall and offer your suggestions (anyone with more than one gets automatically "volunteered" for next year). Cheers!

Matthew S. Klee
FACSS XIX General Chairman

After an absence of seven years, 1992 marks the return of FACSS to Philadelphia where many successful meetings were held in the late seventies and early eighties. It is fitting and proper that we again meet in the city where this organization began to mature as one of the premier international analytical chemistry meetings. We are sure that you'll find the city exciting to visit and the atmosphere at the Conference stimulating.

Many individuals and committees have been hard at work over the past year to make the 1992 meeting one of the best in a long line of excellent meetings. Program Chairman Barry Lavine, has assembled what looks to be another stimulating technical program. Under the able leadership of Matthew Klee, the Conference has been organized in such a way that everyone should have an enjoyable week while interacting with fellow conferees. The exhibits organized by Ed Brame will provide us with a chance to see some of the latest innovations in the areas of instrumentation and aides to analytical chemistry. We are sure that you will learn much from the technical sessions, that many new ideas will be exchanged among those in attendance, and that the after hours social events will provide an opportunity for all to relax and get to know each other better. To this end, we are glad you are here and wish you an enjoyable and profitable meeting.

O. Karmie Galle
FACSS XIX Governing Board Chairperson

Barry K. Lavine
FACSS Program Chair

Professor Lavine received his Bachelor's Degree at Temple University (1977), his M.S. at Ohio State University (1982), and his Ph.D. at Pennsylvania State University (1986). After graduating Penn State, he became a member of the faculty of the Chemistry Department at Clarkson University and was recently granted tenure. Professor Lavine has also been a guest scientist at NIST working with Stephen Wise and Lane Sanders.

Professor Lavine has served on the editorial advisory board of several journals, including *Chemometrics and Intelligent Laboratory Instrumentation*, and *Journal of Chemical Information and Computer Science*. He is a member of the Chemometrics Society, the American Chemical Society, and the Society for Applied Spectroscopy, and has been active in FACSS over the past six years.

Professor Lavine's research interests include liquid chromatography and chemometrics. Much of his current work focuses on retention mechanisms in micelle mediated separations. Solid state NMR and fluorescence spectroscopy are being utilized to better understand the role of the stationary phase in the retention process in micellar liquid chromatography. Molecular dynamics calculations and factor analytic based methods are also being employed in these studies. Other areas of current research include pattern recognition, multivariate calibration, neural networks, and structure-property and structure-activity relationship studies.

O. Karmie Galle
FACSS Governing Board Chair

Karmie Galle is a Senior Scientist in the Analytical Services Section of the Kansas Geological Survey. He received his B.S. degree from Bethel College in North Newton, Kansas in 1957. That same year he began work as an analytical chemist in the Geochemistry Section of the Kansas Geological Survey. In 1965 he was put in charge of the atomic absorption analysis for the Survey with primary emphasis on methods development. His research interests continue to be in this area with particular emphasis on methods for the graphite furnace and hydride generation technique.

Karmie has been involved with FACSS since its beginning. He was a member of the program committee from 1987 through 1992. This past year he has completed the Operations Manual for FACSS.

He has also been active in the Society for Applied Spectroscopy (SAS), chairing numerous committees and serving as the President in 1984. He was the parliamentarian to the Governing Board of SAS from 1985 through 1987 and currently is a member of the Editorial Board and Managing Editor of Applied Spectroscopy. In 1990 he received the SAS Distinguished Service Award.

Matthew S. Klee
FACSS General Chair

What is FACSS?

FACSS is the Federation of Analytical Chemistry and Spectroscopy Societies. FACSS is governed by a board with representatives from seven member organizations including: American Chemical Society Analytical Division, Analysis Division of the Instrument Society of America, Association of Analytical Chemists, Society for Applied Spectroscopy, Chromatography Forum of the Delaware Valley, Coblentz Society, and the Royal Society of Chemistry. FACSS is a cooperative of these nonprofit chemical and spectroscopic organizations. The intent of FACSS is to bring together scientists interested in analytical problem solving at an annual national conference.

The FACSS conference is a premier technical analytical meeting consisting of invited and contributed papers, workshops and short courses, and a technical instrumentation exhibit. A total of sixteen FACSS conferences have been held to date. Diverse analytical interests are represented in the technical program which typically includes papers in the areas of atomic spectroscopy, biotechnology and clinical chemistry, chemometrics, chromatography, electrochemistry, environmental analysis, infrared spectroscopy, lasers, mass spectrometry, nuclear magnetic resonance spectrometry, process analysis, raman spectroscopy, x-ray spectroscopy and surface analysis. Speakers include leaders in the field of these areas of research. Domestic and foreign speakers include scientists from academia, industry, and government. Workshops and short courses provide attendees with the opportunity to gain specialized technical skills in various areas of analytical chemistry. The exhibition allows conferees the opportunity to talk to the various vendors of analytical chemistry. Attendance at the annual meeting is approximately 2500. Approximately 1000 papers and posters are presented throughout the week in parallel sessions. FACSS is often referred to as being "just the right size meeting" because it is small enough that conferees run into the people they want to talk to, yet large enough to cover the full range of analytical sciences.

Who Should Attend? Individuals actively involved in analytical research often consider this to be the one meeting each year that they can't afford to miss. Any individual working in the field of analytical chemistry as a researcher, analyst, or technician will benefit from the exchange of information at FACSS.

Where is FACSS held? FACSS has been held in a variety of locations including: Philadelphia, St. Louis, Detroit, Cleveland, and Chicago. In 1993 it will be held in Detroit (October 17-22), in 1994 it will be held in St. Louis (October 2-7), and in 1995 it will be again held in Philadelphia (September 17-21).

How do you get more information? To get on the FACSS mailing list please sent a note to: FACSS, P.O. Box 278, Manhattan, KS 66502-0003. This will ensure that you receive a call for papers and a preliminary program containing registration materials for the next conference.

1992 FACSS

Federation of Analytical Chemistry and Spectroscopy Societies XIX

September 20-25, 1992
Philadelphia, Pennsylvania

Sponsoring Affiliates of FACSS

American Chemical Society, Analytical Division
Analysis Division of Instrument Society of America
Association of Analytical Chemists
Coblentz Society
Chromatography Forum of the Delaware Valley
Royal Society of Chemistry, Analytical Division
Society for Applied Spectroscopy

Chairpersons

O. Karmie Galle, FACSS Governing Board Chair
Kansas Geological Survey
University of Kansas

Barry Lavine, FACSS Program Chair
Clarkson University

Matthew S. Klee, General Chair
Hewlett-Packard Corp.

Ed Brame, Exhibits Chair
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Wilmington, DE 19804 (312) 994-8000

For more information, call the FACSS Office
301-846-4797

Committee Members

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Local Treasurer	Terry Grimm, Biorad
Local Publicity	Marshall Fishman, ERRC, USDA
National Publicity	Nancy Miller-Ihli, USDA
Printing	Felix Schneider and Dan Brown, U.S.F.D.A.
Audio/Visual	Jeffrey Brewster, ERRC, USDA
Arrangements Chairman	Leon Lakritz, ERRC, USDA
Arrangements	Joseph Unruh, ERRC, USDA
StudentAwards	Monte Evens, Conoco; Ivan Glaze, American Cast Iron Pipe Co.
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Employment Bureau Chairman	Marian McCurley, NIST
Registration Chairman	Robert B. Myers, Robert B. Myers Associates
Special Events Chairman	Ann Donnell
Assistant General Chairman	Jim Williamson, DuPont

Future FACSS Meetings

Detroit, MI • October 17-22, 1993

St. Louis, MO • October 2-7, 1994

Philadelphia, PA • September 17-21, 1995

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EDWARD. G. RENDELL
MAYOR

WELCOME TO PHILADELPHIA!

The City of Philadelphia is looking forward to welcoming the **FEDERATION OF ANALYTICAL CHEMISTRY AND SPECTROSCOPY SOCIETIES** to the Adam's Mark Hotel in September, 1992.

When you arrive in Philadelphia, you will see how its rich history augments its present. The City has also maintained its world-class standing with international acclaimed restaurants, first-class hotels, championship sports teams, the world's largest municipal park, fabled museums, superb shopping and a night life that doesn't quit. There is so much to admire and enjoy in our expanding city today, I can assure you will find your visit to Philadelphia a memorable experience.

Philadelphia has it all -- and we are eager to share it with you!

Sincerely,

Edward G Rendell

Edward G. Rendell
Mayor

GENERAL INFORMATION

We are proud to host FACSS once again in Philadelphia. In keeping with FACSS tradition, FACSS XIX combines a strong technical program, diverse workshops, and extensive exhibits with an ideal location. Come share in stimulating exchanges on the cutting edge of science and socialize with colleagues in the fields of analytical chemistry and spectroscopy.

Matthew S. Klee, General Chairman

FACSS has long been recognized as the premier scientific meeting for current research in the fields of analytical chemistry and spectroscopy. The scientific program will consist of a full week of symposia of invited and submitted papers and several focused poster sessions.

FACSS XIX returns to the city which helped build its reputation. From the mid 1970s to 1985 FACSS grew in Philadelphia into the quality analytical chemistry and spectroscopy meeting it is today. The Philadelphia area provides an ideal location for FACSS, being a hub of diverse industrial and academic research and a world renowned center of history and culture.

The FACSS program and exhibit will all be housed in the Adam's Mark Hotel on City Line Avenue (across the street from where FACSS meeting was last held in Philadelphia). The Adam's Mark hotel compliments excellent meeting facilities with a variety of dining, entertainment, and health facilities (racquetball, swimming, health club), helping to ensure that FACSS XIX will be a comfortable and productive meeting. The Holiday Inn, next door to the Adam's Mark, will house workshops, employment bureau, and committee meeting rooms, and provides accommodations at a slightly lower cost than the Adam's Mark Hotel.

Registration Hours

Day	Start	End
Sunday	3:00 p.m.	8:00 p.m.
Monday	7:30 a.m.	6:30 p.m.
Tuesday	7:30 a.m.	5:30 p.m.
Wednesday	7:30 a.m.	5:30 p.m.
Thursday	7:30 a.m.	5:30 p.m.
Friday	7:30 a.m.	9:30 a.m.

Registration Fees

Pre-Registration (to 8/16/92)	$125.00
On-Site Registration	$140.00
Single Day	$100.00
Student, Full-Time	$30.00
Exhibits Only	$20.00
Wednesday Evening Event (Time Out!)	$32.50

For additional information regarding registration prior to the conference, call 1-301-846-4797.

Instrument Exhibit

Day	Start	End	
Monday	5:30 p.m.	7:30 p.m.	(opening mixer)
Tuesday	10:00 a.m.	6:00 p.m.	
Wednesday	10:00 a.m.	6:00 p.m.	
Thursday	10:00 a.m.	2:00 p.m.	

The FACSS instrument exhibit supports and compliments the scientific program through the revenue it generates and by providing opportunities for attendees to get information on the latest analytical instrumentation, supplies, and publications. A partial list of exhibitors is included in this program.

Ground Transportation

Shuttle vans and rental cars are available for transportation from the Philadelphia International Airport to the meeting hotels (approximately 40 minutes transit time). Please refer to the enclosed map for local directions.

Parking

The Adam's Mark Hotel provides free parking for all guests and meeting attendees.

Message/Communications Cener

A message center will be open each day of the Conference. The number is 215-581-5000.

No-Smoking Policy

Smoking will be prohibited in the meeting and exhibit rooms the week of the conference. Designated smoking areas will be conveniently located nearby.

Employment Bureau

FACSS provides an employment bureau as a service to both employers and job seekers. Further information can be found elsewhere in this program. The employment bureau will be held during the following times.

Registration Hours

Day	Start	End
Sunday	3:00 p.m.	7:30 p.m.
Monday	8:30 a.m.	6:00 p.m.
Tuesday	8:30 a.m.	6:00 p.m.
Wednesday	8:30 a.m.	6:00 p.m.
Thursday	8:30 a.m.	6:00 p.m.

Special Events

A full special events and spouses program compliments the scientific program by providing attendees and spouses organized tours and social events. Details for these special events are provided elsewhere in this program.

Awards

The following awards and special symposia will be given at this year's FACSS Conference.

ANACHEM Award
SAS Meggers Award
SAS Lester Strock Award
SAS Student Award
SAS Distinguished Service
SAS Honorary Membership
FACSS Tomas Hirschfeld Scholar Award
FACSS Student Award

FACSS XIX Workshop Program

Twelve tutorial workshops presented by leading scientists from industry and academia have been arranged for FACSS XIX. Abstracts for each are included in the *FACSS XIX Workshop Program* section of this program. Their cost is minimal; $60 for half-day courses and $90 for full-day courses, except for the **Professional Analytical Chemists in Industry** workshop; it is *free*. Details for registration are on the enclosed conference registration forms.

Short Courses

Short courses will be sponsored by SAS and PACS. Registration and detailed information appears elsewhere in this program.

Society and Committee Meetings

Federation of Analytical Chemistry and Spectroscopy Societies

FACSS Exhibitors Breakfast	7:30 a.m.
Pierre's	Wednesday, September 23
1993 Planning Committee	10 a.m.
Delaware #3	Wednesday, September 23
Executive Committee - CLOSED	1:00-3:00 p.m.
Gettysburg #1	Thursday, September 24
Governing Board Dinner	6 p.m.
Gettysburg #1	Thursday, September 24
Governing Board Meeting	8 p.m.
Constitution A&B	Thursday, September 24

Society for Applied Spectroscopy

Executive Committee - CLOSED	1:00 p.m.
Executive Board Room-Adams Mark	Sunday, Sept 20
Executive Committee Dinner - CLOSED	6:00 p.m.
Franklin #2	Sunday, September 20

History of Spectroscopy Committee Meeting	4:00 p.m.
Gettysburg #1	Monday, September 21

Open to all interested persons

Awards Banquet	6:00 p.m.
Pierre's Dining Room	Tuesday, September 22
Governing Board Meeting	8:30 p.m.
Franklin #1	Tuesday, September 22

Coblentz

Governing Board Meeting	8 p.m.
Grand Ballroom A	Tuesday, September 22

ANACHEM

Award Luncheon	12 p.m.
Quincy's Bar	Wednesday, September 23

JCAMP

Governing Board Meeting-Lunch	12:00 - 1:00 p.m.
Delaware #4	Wednesday, September 23

ASTM E13 Molecular Spectroscopy

Raman TG 13.08.01	2-4 p.m.
Constitution A	Sunday, September 20
NIR Quant. TG 13.03.03	4-6 p.m.
Constitution A	Sunday, September 20
Executive Dinner Meeting	7-10 p.m.
Franklin #1	Sunday, September 20
Liaison 13.02	9-9:30 a.m.
Grand Ballroom E	Monday, September 21
Luminescence 13.06	9:30-11 a.m.
Grand Ballroom E	Monday, September 21
GC-IR TG Lunch 13.03.05	11-1 p.m.
Grand Ballroom E	Monday, September 21
NMR 13.07	2-3 p.m.
Grand Ballroom E	Monday, September 21
Fiber Optics 13.09	4-6 p.m.
Grand Ballroom E	Monday, September 21
NIR Main TG 13.03.03	7-9 p.m.
Grand Ballroom E	Monday, September 21
UV/VIS 13.01	9-11 a.m.
Delaware #3 & #4	Tuesday, September 22
IR TG Lunch 13.03	11-1 p.m.
Delaware #3 & #4	Tuesday, September 22
E-13 Main Committee	1:30-3:30 p.m.
Jefferson Room	Tuesday, September 22
Raman Symposium 13.08	4-5:30 p.m
Gettysburg #2, #3 & #4	Tuesday, September 22
Raman Reception for Speakers at Symposium and Committee Members	5:30-7 p.m.
Gettysburg #1	Tuesday, September 22
NIR-HC TG D02.04.0F	7-9 p.m.
Delaware #1 & #2	Tuesday, September 22
Continuation of Raman Symposium	
	Wednesday, September 23
Process Spectroscopy Symposium	
	Wednesday, September 23

Special Activities

Columbus sailed to America in the 1400*s*; William Penn arrived in the green country which he called Pennsylvania in the 1600*s*; Ben Franklin settled in the City of Brotherly Love in the 1700*s*. Philadelphia holds a year-long celebration in 1992 to mark the 500th anniversary of that first journey to this continent by Columbus and to honor all people who followed him and settled in a new home.

Philadelphia has many treasures and a great historic heritage. Explore the city and experience these for yourself. Tours have been arranged for you to see not only historic highlights but also some of the out of the way interesting nooks and cranies. Need help in selecting a special restaurant or in getting tickets for a sporting event or concert? If you want to see more, arrive a day earlier or stay a day later and let Guest Services at Adam's Mark arrange your day.

Monday, September 21

Coffee Break -- Monday through Thursday -- 9:30 a.m. to 10:30 a.m.
Start the day with coffee and conversation with fellow travellers. Special activities will be discussed and brochures for sightseeing in the area will be available. Admission by Guest Badge only.

Tour #1 -- Neighbors, Old and New -- 11:00 a.m. to 3:00 p.m.
Many of the newcomers from across the Atlantic settled along the shores of the Delaware River. They brought with them many of the customs and the cuisine from their homeland. Walk along the narrow cobblestone streets of Olde City and Society Hill with a knowledgeable guide and learn how the old coexists with the new. A midday intermission will provide time for a rest break and lunch.
Limit: 19 passengers. **Cost:** $22.50 (includes transportation)

Wine and Cheese -- 5:30 to 7:30 p.m.
The exhibition will open with a festive party for all. Enjoy the refreshments and find out what's new in analytical instrumentation. Admission by badge.

Tour #2 -- City Lights and Highlights -- 7:00 p.m. to 11:00 p.m.
Philadelphia takes on a new glamour when the lights are turned on. This tour in a Victorian-style trolley with a guide in Colonial dress will take you around town to see the sites of special interest: Boat House Row, Independence National Park, Penn's Landing, the Parkway and much more. The stop at Head House Square will be long enough to permit a late dinner in your choice of restaurants, a visit to a bistro, or just browsing in some of the many boutiques along South Street **Limit:** 25 passengers. **Cost:** $25.00 (does not include dinner)

Tuesday, September 22

Tour #3 -- Arts and Flowers -- 9 a.m. to 4 p.m.
A minibus with your personal guide will take you to Longwood Gardens, one of America's premier horticultural gardens started by Pierre du Pont in 1906. Over 11,000 different types of plants are displayed. Four acres under glass feature orchids, roses, palms and seasonal flowers. Enjoy a leisure lunch there and then continue to the Brandywine River Museum. Spend time with this outstanding collection of works by the Wyeth family as well as those by other contemporary artists. If time permits, there will be a stop at the Chadd's Ford Winery for a tour and tasting of their locally made vintage before returning to the hotel. **Limit:** 21 passengers. **Cost:** $42.50 with pre-registration only; $47.50 at meeting (includes transportation and admision fees; does not cover lunch).

Wednesday, September 23

Tour #4 – Art and Science on the Parkway – 10 a.m. to 4 p.m.
The Philadelphia Museum of Art, The Franklin Institute Science Museum, The Academy of Natural Sciences -- just to name several of an impressive collection of museums that are within walking distance of each other along the Benjamin Franklin Parkway. Reserve a seat on the day-long round trip, van service will drop you off and pick you up at any, or all, of these famous doors. Hourly departures leave the Adam's Mark, travel down the Parkway to City Hall and return. If you are interested in something really wild, there will be a stop along the way at the Philadelphia Zoo, the oldest in the country, with its newest exhibit, Carnivore Kingdom. **Limit:** 11 passengers per trip. **Cost:** $14.00 round trip (does not include admission fees)

Time Out! -- 6:00 p.m. to 10:00 p.m. ✪ FACSS Award Banquet ✪
After a busy day it is time to take time out. Make the short trip to the 12th floor of the nearby GSB building. Relax there with friends and enjoy a fun filled Social Hour with the atmosphere of the traditional Philly Block Party. Tap your feet to the rhythms of Mummers Music. You might even want to learn the *Mummers Strut!* Dinner follows at 7:30 and then the annual awardees will be recognized. Space is limited, so pre-registration is recommended. **Limit:** 200. **Cost:** $32.50 for Social Hour and Dinner (cash bar available)

Tour #5 -- Night Owls Only -- 9:30 p.m. to Midnight
How about some pub crawling to a few local "watering holes!" Discover the charm of the historic taverns from Manyunk to Fairmount and hear the fascinating stories about each. A van tour with guide for a favored few.
Limit: 14 passengers. **Cost:** $22.50 (refreshments not included)

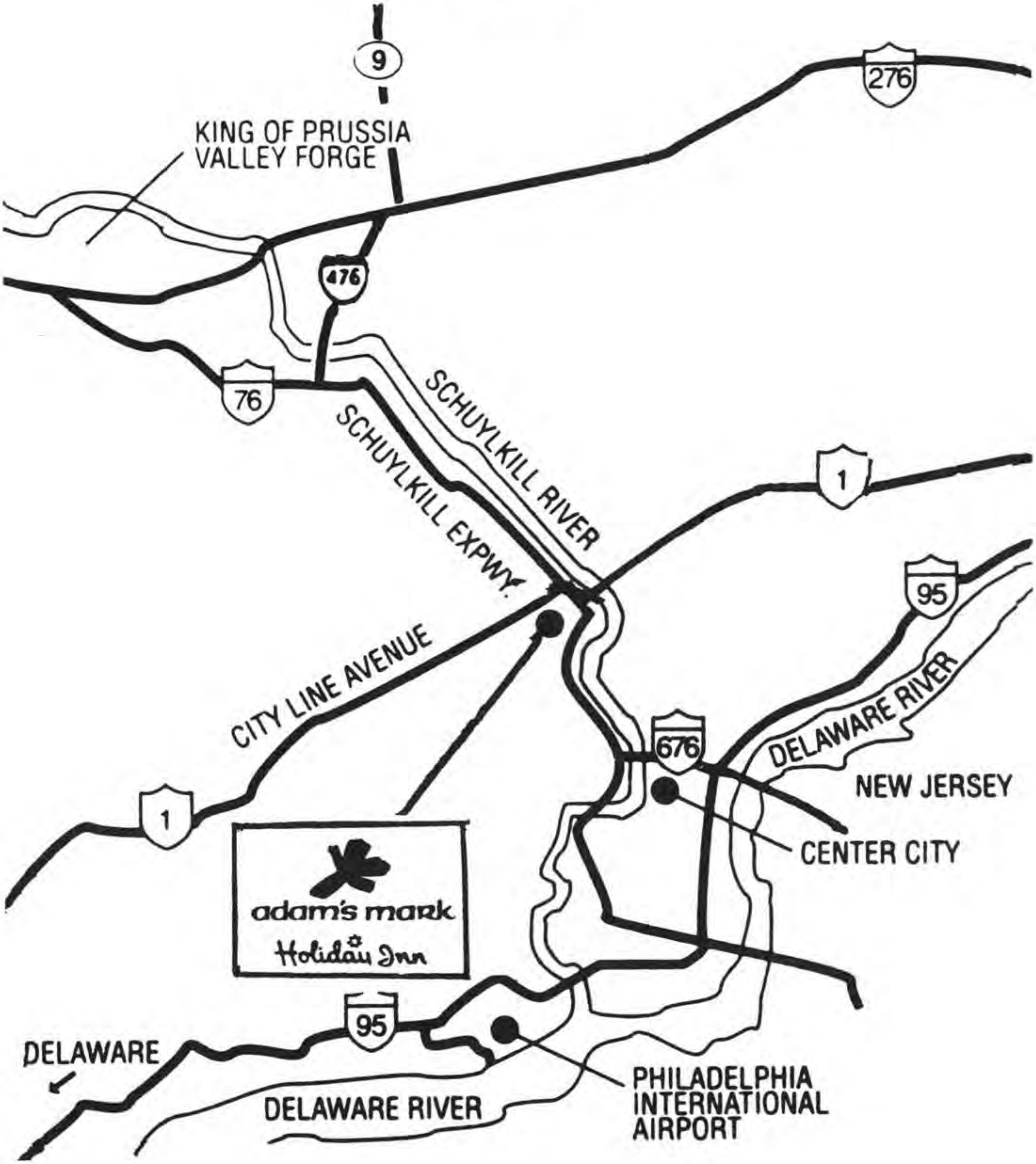
Thursday, September 24

Tour #6 -- City Highlights -- 10:30 a.m. to 12:30 a.m.
A renaissance has taken place in center city and modern skyscrapers now highlight the city skyline. After a look at these newcomers, spend time with the centerpiece of the city, City Hall. Your guide will explain the symbolism in some of Calder's many sculptures that embellish the building then take you on the tower tour. The view from under Billy Penn's hat is breathtaking!
Limit: 11 passengers. **Cost:** $20.00

Pre-Registration for Special Activities

Item		No.	Price	Total
Tour #1	Neighbors, Old and New		$22.50	
Tour #2	City Lights and Highlights		$25.00	
Tour #3	Arts and Flowers		$42.50	
Tour #4	Art and Science on the Parkway		$14.00	
Tour #5	Night Owls Only		$22.50	
Tour #6	City Highlights		$20.00	
Time Out, Awards Dinner			$32.50	

AREA MAP


9
276
KING OF PRUSSIA
VALLEY FORGE
476
76
SCHUYLKILL RIVER
SCHUYLKILL EXPWY.
1
CITY LINE AVENUE
95
DELAWARE RIVER
676
NEW JERSEY
CENTER CITY
1
adam's mark
Holiday Inn
95
DELAWARE
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INTERNATIONAL
AIRPORT

A Special Tribute to Edward G. Brame

At the conclusion of the 1992 FACSS Conference, Ed Brame will be stepping down from the position of Exhibits Director, a position he has held since 1986. Because his many years of service as Exhibits Director, as well as his extensive experience within the organization, it is appropriate that FACSS recognize Ed for his extraordinary efforts on behalf of the organization. What follows is a summary of the many things he has done to help FACSS become the success it is today.

In 1968, Ed Brame was among those on the Board Directors of the Eastern Analytical Symposium (EAS) who urged the formation of a coalition of analytical organizations. It was felt that the proliferation of small national and regional analytical chemistry meetings had become burdensome to chemists and exhibitors alike. Ed was given the task of chairing an EAS committee which was to explore the possibilities of organizing a coalition of analytical organizations for the purpose of holding one national meeting in the autumn of the year. This committee's work resulted in an initial meeting in November of 1970 of representatives of the Analytical Chemistry Division of the ACS, EAS, American Microchemical Society, Scientific Apparatus Makers Association, Mid-American Symposium on Spectroscopy, Anachem, Instrumental Society of America (ISA), Society for Applied Spectroscopy (SAS) and the Pittsburgh Conference to develop plans for the coalition. The result of this meeting and those that followed was that in March of 1971 the organization was formally born and baptized the *Federation of Analytical Chemistry and Spectroscopy Societies* or *FACSS* for short.

From the very beginning Ed was there when FACSS needed officers willing to serve. The following list is an indication of the many ways he has served the organization. A close look at this list of accomplishments reveals that the only office Ed has not held at one time or another is that of Program Chairman. This is a remarkable accomplishment and it must be noted that many of his efforts were a steadying influence during the early years of the organization.

1968-1974	Co-Founder of FACSS
1974	Governing Board Treasurer
1976	Governing Board Chairman
1976	Conference Chairman
1982, 1985, 1986	Governing Board Secretary
1986-1992	Exhibits Director

Ed will probably be best remembered for his work as the Exhibits Director. In 1986 he succeeded the late Peter Keliher in that position. The function of Exhibits Director required a willingness to take hundreds of phone calls day or night - regardless of office hours, a cheery upbeat nature in dealing with exhibitors, an astute sensitivity to their needs, and a readiness to tackle and solve problems brought about by different local situations and regulations while keeping a calm, unruffled demeanor. Ed Brame not only had all these qualities, but he displayed them unassumingly and naturally. Only modest recognition came his way for the good-will he spread to the exhibitors and for the untold funds he saved the organization as an unpaid volunteer.

On the occasion of Ed's leaving his post as FACSS Exhibits Director, we all thank him for his untiring efforts on behalf of FACSS. It is safe to say that he is the one individual who has had the most positive influence in making FACSS the success it is today. We wish him the very best and look forward to his continued association with the organization in the years to come.

Milos V. Novotny

Anachem Award

Milos V. Novotny earned B.S. and Ph.D. degrees in chemistry and biochemistry at the University of Brno, Czechoslovakia in 1962 and 1965, respectively. He then held research associateships at the Institute of Analytical Chemistry, Czechoslovak Academy of Sciences-Brno, the Royal Karolinska Institute - Stockholm, and the University of Houston - Houston, Texas before joining the faculty of Indiana University in 1971. He is currently the James H. Rudy Professor of Chemistry at Indiana University.

Professor Novotny has received many honors including the James B. Himes Merit Award (1983), the M. S. Tswett Award and Medal (1984), the ACS Award in Chromatography (1986) and Chemical Instrumentation (1988), the Eastern Analytical Symposium Award in Chromatography (1988), the Keene P. Dimick Award (1990), the Marcel J. E. Golay Award (1991), and most recently the ACS Award in Separation Science and Technology (1992). He has also been recognized for his teaching skills with the receipt of the Distinguished Faculty Research Lecture at Indiana University in 1988-89 and the ACS Exceptional Achievement Award for his Short Course on Capillary Gas Chromatography (1992).

Dr. Novotny has served on various NASA, NRC, and national laboratory committees and has been involved in the organization of the Gordon Research Conference and several international symposia on microcolumn separation methods, liquid chromatography, and capillary chromatography. He also serves or has served on the editorial boards of eleven journals.

Professor Novotny's research interests include separation science, analytical chromatography and capillary electrophoresis, physicochemical processes in critical fluids, chromatography/spectroscopy, mechanism of diabetic neuropathics, chemical communication in mammals, bioanalytical chemistry, and glycoproteins and carbohydrate metabolism. Dr. Novotny has authored more than 260 research articles, reviews, and book chapters.

SAS Distinguished Service Awards

Genevieve Bonini

In recognition of her outstanding contributions to the Society for Applied Spectroscopy, Genevieve Bonini has been named a recipient of the 1992 Distinguished Service Award.

Genevieve has made outstanding contributions to SAS, as well as FACSS and EAS, in a variety of capacities over a long career of energetic and enthusiastic work in support of science and in behalf of her colleagues. She was a founding member of the New England Section, where she is still a mainstay; she has put in countless hours at various committee and Governing Board meetings; and she has always served as our best good-will ambassador and promoter for SAS.

Society members feel particular gratitude to Genevieve for the time she served as the National Social Secretary in that period before the Society had paid staff to perform the duties that Genevieve carried out as a volunteer. Elected by a great margin and reelected to an unprecedented second term, Genevieve displayed remarkable skills as a manager, administrator, and diplomat. Her efforts not only facilitated the smooth running of the Society and the Journal but also contributed to the development of the office of Executive Secretary (later redesignated Executive Administrator). Her accomplishments during her six years as National Secretary, as well as her dedicated service as a local section leader, committee member, delegate to Governing Board meetings, and liaison with FACSS and EAS, recommend her as a worthy recipient of the SAS Distinguished Service Award.

James R. Lindsay

In recognition of his many contributions, at both the local and the national level, the Society for Applied Spectroscopy has named James Lindsay a recipient of the 1992 Distinguished Service Award.

Jim has worked on behalf of the Society for over twenty-five years, serving in many roles and capacities. He began his service at the local section level, contributing to the Baltimore-Washington section as Treasurer (1968-1970) and Secretary (1971), as well as serving as a local section delegate to the Governing Board. He went on to serve SAS at the national level in a number of important positions, including Treasurer (1975-1977), Chair of the Project Study and Advisory Committee (1978-1980), and Chair of the Executive Secretary Search Committee (1981). In addition, Jim and his wife Sharon edited the SAS Newsletter for a period of six years.

Jim has had a real influence on the overall development of the Society, the Journal, and, in particular, the establishment of the National Office; it is difficult to take full measure of all his efforts over the years, but he has certainly helped make the Society what it is today. He also established a record of active participation in EAS and FACSS, always serving the interests of the Society.

Along with his contributions to his field through membership in scientific societies, Jim has pursued his research interests in his work with the U. S. Geological Survey. He began his career in the Washington, D.C. area, where his initial focus was on x-ray spectroscopy; he later moved to Menlo Park, California, where he explored the use of a number of different analytical techniques (Auger, SIMS, ESCA, PES, and SEM), in research on the characterization of limestone as it is affected by acid rain. Jim is currently working with the J. S. Geological Survey field office in Spokane, Washington, and collaborating with colleagues at Eastern Washington University in order to remain actively involved in spectroscopic research.

Hirschfeld Awards

Vasilis Gregoriou

Vasilis Gregoriou is a graduate student in Physical/Analytical Chemistry at Duke University. A native of Greece, Vasilis received his B.S. in Chemistry from the National University of Greece at Patras in 1986. His undergraduate research focused on the effects of temperature on the radiochemistry of cobalt complexes. Vasilis came to the U. S. in 1987 to pursue an M.S. degree in Analytical Chemistry at East Carolina University under Dr. Paul J. Gemperline. During a project supported by Burroughs Wellcome Co., he developed multivariate calibration techniques to model nonlinearity associated with spectroscopic measurements of UV and NIR spectra used for quantitative analyses.

Vasilis has been at Duke University since 1989, working under the direction of Dr. Richard A. Palmer in applying time-resolved step-scan FT-IR spectroscopic techniques to liquid crystals and polymeric materials. He has used synchronous modulation and impulse-response time-resolved FT-IR to study the electric field induced reorientations of liquid crystals. The former technique can also be used in connection with two dimensional frequency correlation analysis (2D FT-IR) for polymer characterization using novel step-scan FT-IR rheo-optical methods. In addition, he is involved in the development of advanced step-scan FT-IR instrumentation. His research has produced six co-authored publications and eleven conference presentations. He enjoys sports, old Hollywood and contemporary European movies, but most of all, heated political discussions, so he is very happy in an election year.

Patrick A. Limbach

Patrick A. Limbach received his B.S. degree in Chemistry and Chemical Physics from Centre College of Kentucky in 1988. He is currently completing his Ph.D. in Analytical Chemistry at The Ohio State University under the direction of Dr. Alan G. Marshall. His research interests include coupling external ionization sources to a Fourier transform ion cyclotron resonance (FT/ICR) mass spectrometer, understanding the principles of high mass ion generation and detection in FT/ICR mass spectrometry, and performing quantitative analysis using an FT/ICR mass spectrometer. Pat has co-authored two publications and thirteen conference presentations. Pat expects to graduate this fall and will begin post-doctoral work with Dr. James McCloskey at the University of Utah, where he plans to enjoy skiing and mountain biking.

Jeff Mazzeo

Jeff Mazzeo is a graduate student in Analytical Chemistry working under the direction of Professor Ira S. Krull at Northeastern University in Boston, Massachusetts. Jeff was born in 1966 in Cambridge, Massachusetts, and received his B.S. in Chemistry, Cum Laude, from the University of Massachusetts-Lowell in 1988. Jeff attended the University of Massachusetts-Lowell on a Massachusetts State Honor Scholarship, given by the Massachusetts Board of Regents of Higher Education. His undergraduate research, directed by Professor Gene Barry, involved simplex optimization of an alternating current plasma detector for gas chromatography. As an undergraduate, Jeff received the Scattergood Award from University of Massachusetts-Lowell and worked part-time at Polymer Technology, a company which manufactures contact lenses. His graduate thesis work has involved the development of capillary isoelectric focusing in uncoated capillaries. Jeff has co-authored twelve publications and received numerous awards as a graduate student, including the Yitzhak Tapuhi Award, Douglas and Irene DeVivo Award, Outstanding Performance in Research Award from Northeastern University, Vern Berry International Graduate Student Prize, ACS Summer Fellowship in Analytical Chemistry, and the Philip L. Levins Memorial Prize. He is a member of the ACS, Sigma Xi, and Phi Lambda Upsilon. Jeff, who expects to receive his Ph.D. in December of 1992, is an avid outdoorsman and interested in American Indian culture.

Evelyn Guizhen Su

FACSS Student Award

Evelyn Guizhen Su is a graduate student at the University of Connecticut. She received her M.S. and B.S. under Professor Soulin Lin from the China University of Geosciences, Wuhan. Her B.S. thesis involved the atomization mechanism of lead in graphite furnace atomic absorption spectrometry (GFAAS) and the preparation and characterization of metal-coated graphite tubes. Her M.S. thesis focused on complete laser vaporization of powdered solid samples into an ICP.

In 1989 Evelyn joined the research group of Dr. Robert G. Michel. Her doctoral research has focused on the development of automatic background correction for laser-excited atomic and molecular fluorescence in flames and graphite furnaces. She has been involved with the development of ultra-sensitive analytical methods based on laser-excited atomic and molecular fluorescence in graphite furnaces, with focus on molecular fluorescence of diatomic molecules. Evelyn has also been involved with research on aspects of absolute analysis by GFAAS. She has co-authored nine conference presentations and seven journal publications with four more in preparation. Between 1990 and 1992 she received a research fellowship from Perkin-Elmer Corp-oration, Norwalk, CT. She was awarded the New York Section Society for Applied Spectroscopy 1992 Graduate Student Award. She also received the Gorden F. Kirkbright Bursary Award from the Association of British Spectroscopists, which allowed her to visit four British universities and to attend the Sixth Biennial National Atomic Spectroscopy Symposium, July 22-24, 1992, Plymouth, U. K. She is the recipient of a full-year ACS, Division of Analytical Chemistry, Fellowship, 1992-93. Her sponsor for this fellowship is Glaxo, Inc., Research Triangle Park, N. C. She also received the University of Connecticut's Charles E. Waring Award as the most outstanding first year chemistry graduate student, and the William T. Masterton Award for teaching excellence. She expects to receive her Ph.D. in 1993.

Cheryl A. Bye

SAS Student Award

Sponsored by Mattson Instruments

Cheryl A. Bye is a graduate student in the Analytical Chemistry program at the University of Illinois, Urbana-Champaign campus. She received her B.S. degree in Chemistry, Physics and pre-Engineering from Ball State University in 1987. In addition to graduating cum laude, Bye also graduated with honors in physics. She joined the research program of Dr. Alexander Scheeline in 1987. Her research focuses on the plasma and excitation dynamics of the analytical high voltage spark discharge using a variety of imaging and multidispersive techniques. Among her research interests are plasma spectroscopy, optical instrumentation, and environmental chemistry.

While at the University of Illinois, Bye has coauthored two publications and is currently working on four more. She has been the recipient of two University of Illinois graduate fellowships (1987 and 1990). In addition, she is co-winner of the 1992 William F. Meggers Award. She is also a member of Golden Key, Alpha Lambda Delta, Sigma Pi Sigma, Sigma Zeta, an Phi Lambda Upsilon (where she served as secretary in 1989-90). Besides chemistry, she enjoys the fine arts, playing the trombone, and tennis. She will receive her Ph.D. this fall.

Honor Symposium for Peter Keliher

With Peter Keliher's death on July 9, 1990, the analytical chemistry community lost one of its most popular and energetic members. As would be considered appropriate for a research spectroscopist, he was involved in a complete spectrum of activities. A full professor at Villanova, he was an established researcher in the area of analytical spectrometry and was well known for his contributions to the development of high resolution atomic spectrometry, the application of atomic fluorescence spectrometry, the determination of trace pollutants and the use of molecular absorption and luminescence spectrometry. As well as contributing to the analytical literature as an original researcher, he was equally well known for his stewardship of the growing body of literature as editor of the *Microchemical Journal* and for his insightful reviews of the literature relating to atomic emission spectrometry which delighted readers of the biennial *Analytical Chemistry* Fundamental Reviews between the years 1980 and 1990. He also contributed for many years to the production of the Royal Society of Chemistry's *Annual Reviews of Analytical Atomic Spectrometry* and was an active member of the editorial board of the *Atomic Spectrometry Updates* which now appear regularly in the *Journal of Analytical Atomic Spectrometry*.

Peter was extremely active within the FACSS organization having served on the Governing Board (including a term as chairman), as an assistant program chair and as the exhibits director. He also made significant contributions to the Eastern Analytical Symposium and was active within the Analytical Chemistry Division of the American Chemical Society, serving as its treasurer between 1978 and 1982.

Peter was one of the first to establish transatlantic links between the analytical communities in the UK and the USA, having obtained his graduate degree in the research group under T. S. West's direction at Imperial College, London University. He was almost as well known within the UK as he was in the US and actively encouraged contacts between the two communities.

The 19th annual FACSS meeting will celebrate Peter's many contributions with a symposium composed of representatives from the many facets of the profession of analytical chemistry, which benefitted from his generous and good-humored involvement.

FACSS XIX Workshop Program

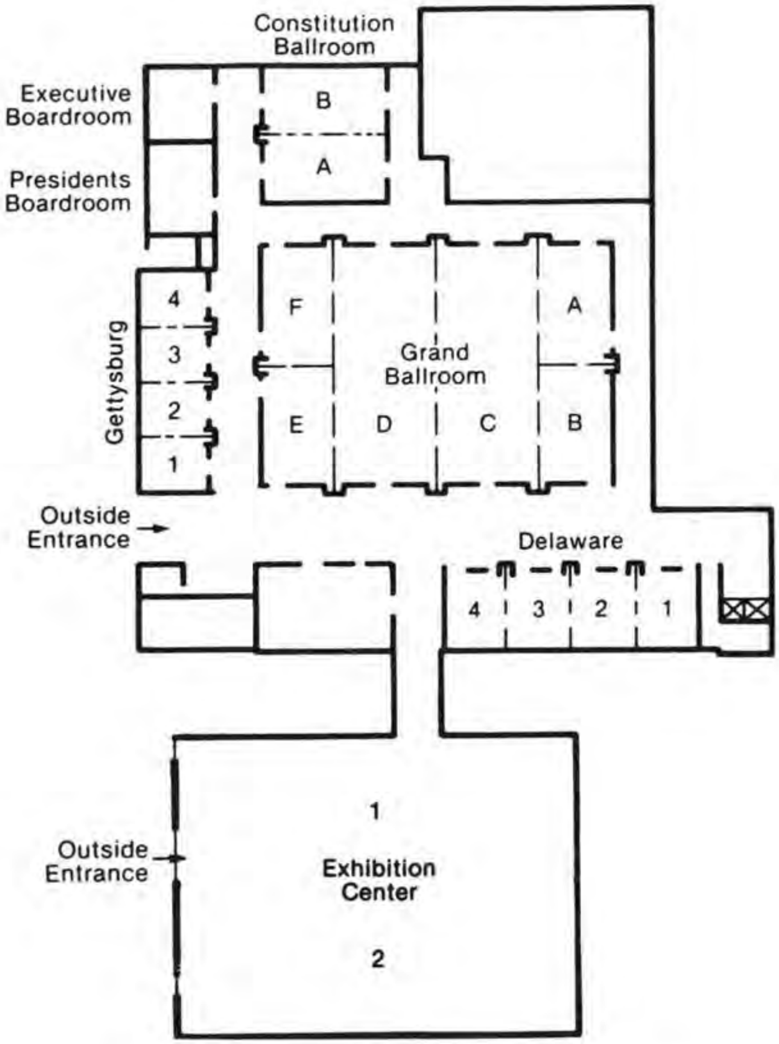
The Workshop Program presents the most cost-effective introductions available for a wide variety of important topics. All workshops will be held in the Holiday Inn adjacent to the Adam's Mark. The schedule and abstracts follow:

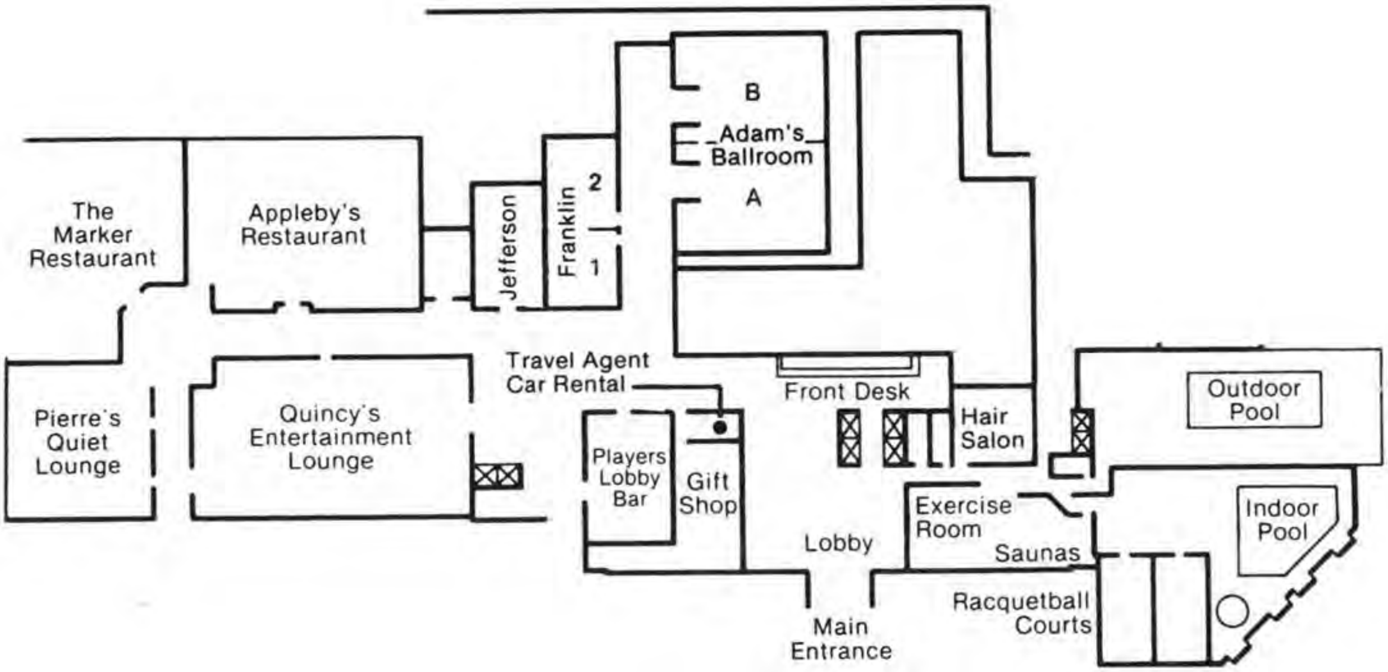
	MORNING 8:30-12:00	**AFTERNOON 1:00-4:30**
Monday September 21	A. **Sample Preparation** Theodore Rains	C. **Size Exclusion Chromatography** Barth and Yau
	B. **Basic Statistics** Workman and Mark	B. **Basic Statistics** Workman and Mark
Tuesday September 22	D. **Chemometrics** Brown and Lavine	D. **Chemometrics** Brown and Lavine
	E. **Lasers in Analysis** Parus, Morris and Liang	F. **Super Critical Chromatography** Susan Olesik
Wednesday September 23	G. **Professional Chemists** Thomas Thorpe	G. **Professional Chemists** Thomas Thorpe
	H. **ICP-MS** Samuel Houk	I. **Robotics** Jeffery Hurst
Thursday September 24	J. **Analytical GC** Walt Jennings	J. **Analytical GC** Walt Jennings
	K. **LC-MS** Marvin Vestal	L. **Optical Standards** Jeffery Hurst

Workshop registration information is contained on the conference registration form. Fur further information about the workshops contact:

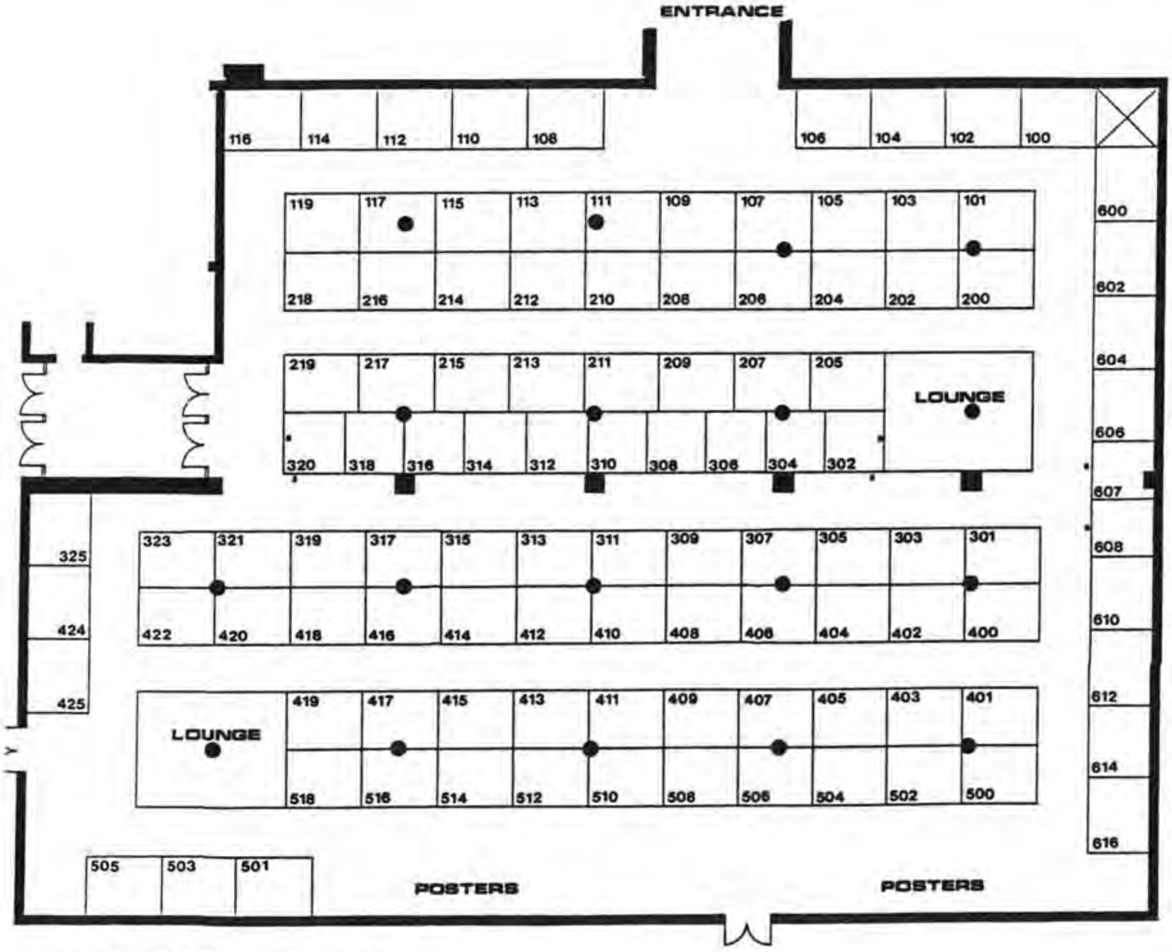
Ron Williams
Department of Chemistry
Clemson University
Clemson, SC 29634
(803) 656-5020

Meeting Floor Plan





Exhibitors Floor Plan



ALL BOOTHS 8'x10' UNLESS NOTED

Exhibitors

ACADEMIC PRESS

Booth(s) 106

1250 SIXTH AVENUE
SAN DIEGO, CA 92101

TELEPHONE: 619-231-0926
REPRESENTATIVE(S): Jane Ellis
EXHIBITING: Featuring an excellent assortment of new books and journals including: Grossman/Colburn's *Practical Capillary Electrophoresis*; Brittain's *Analytical Profiles of Drug Substances & Excipients*; Israelachvili's new edition of *Intermolecular and Surface Forces*; Zewail's *The Chemical Bond*; Bristol's *Annual Reports in Medicinal Chemistry*; Parriott's *Practical Guide to HPLC Detection;* Somani's *Chemical Warfare Agents*; and Rao/Weber's *Spectroscopy of the Earth's Atmosphere.*

AMERICAN LABORATORY

Booth(s) 424

30 CONTROLS DRIVE, POB 870
SHELTON, CT 06484

TELEPHONE: 203-926-9300
REPRESENTATIVE(S):
EXHIBITING: Copies of their journals, *American Laboratory, American Laboratory News, International Laboratory, International Laboratory News, Buyers' Guides and Postcard Decks.*

ANALECT FT-IR, see KVB/Analect

ANALTECH, INC.

Booth(s) 319

P.O. BOX 7558
NEWARK, DE 19714

TELEPHONE: 302-737-6960
REPRESENTATIVE(S):
EXHIBITING: Analtech will be exhibiting the UNISCAN Video Densitometer™ for thin layer chromatography and electrophoresis as well as TLC plates, supplies and equipment. Copies of the 1992 Analtech catalog will also be available.

AXIOM ANALYTICAL, INC.

Booth(s) 112

18103-C SKY PARK SOUTH
IRVINE, CA 92714

TELEPHONE: 714-757-9300
REPRESENTATIVE(S): Dr. Mike Doyle, Norman A. Jennings
EXHIBITING: A full line of FTIR sample interfacing equipment for both laboratory and process applications. Products include immersion probes, ATR tunnel flow cells, flowing gas cells, and surface sampling systems. Recent developments include the Dipper-210 universal immersion sampling system, the Diamond Tunnel Cell, and the SPR-520 sparging-IR wastewater analyzer.

BAIRD CORPORATION

Booth(s) 406

125 MIDDLESEX TURNPIKE
BEDFORD, MA 01730-1468

TELEPHONE: 617-276-6163
REPRESENTATIVE(S):
EXHIBITING: Baird will be exhibiting and distributing information on ICP emission spectrometers and accessories. The Baird environalysis package of hardware and software will be featured.

BALSTON, INC.

Booth(s) 410

501 SILVERSIDE ROAD
WILMINGTON, DE 19809

TELEPHONE: 301-791-9292
REPRESENTATIVE(S):
EXHIBITING: Air purification systems for analytical equipment.

BIO-RAD, DIGILAB DIVISION

Booth(s) 212, 214

237 PUTNAM AVENUE
CAMBRIDGE, MA 02139

TELEPHONE: 617-868-4330
REPRESENTATIVE(S): Daryl Deliman
EXHIBITING: New research-grade FT-IR with step-scan and kinetic-scan capabilities from the far-ir to the near-uv; new research-grade UMA 500 FT-IR microscope accessory; new dedicated FT-Raman spectrometer; and a variety of analytical-grade FT-IR systems and accessories.

BIO-RAD LABORATORIES, SADTLER DIVISION

Booth(s) 105

3316 SPRING GARDEN STREET
PHILADELPHIA, PA 19104

TELEPHONE: 215-382-7800
REPRESENTATIVE(S):
EXHIBITING: Sadtler digital libraries and search data bases for IBM PC and FT-IR data systems. Libraries of infrared, 13-C NMR, ultraviolet, Raman, fluorescene, capillary GC retention index library and search data base, molecular structure, molecular formula data base, chemical, physical properties, and chemical name search are offered for over 120,000 compounds.

BOMEM INC.

Booth(s) 202, 204

450 AVENUE ST-JEAN BAPTISTE
QUEBEC, QUE CANADA G2E 5S5

TELEPHONE: 418-877-2944, FAX: 418-877-2834
REPRESENTATIVE(S):
EXHIBITING: Bomem will display several MB series spectrometers. The MB series consists of a number of FT-IR implementations based on the patented "wishbone" interferometer design. Benchtop models are adapted for high performance research spectroscopy as well as for QA and quantitative analysis method development and implementation. A range of accessories are readily adapted to these systems including temperature controlled flowthrough cells, IR microscopes or fiber optic interfaces. Software for SQA, discriminant analysis, spectral search and P, K or PLS quant methods is also available. Industrial implementations of the MB series are designed for on line process monitoring and multicomponent continuous emissions monitoring. Portable systems are also implemented for environmental monitoring, for portable field analysis operations and for remote sensing.

BRIMROSE CORPORATION OF AMERICA

Booth(s) 400

5020 CAMPBELL BOULEVARD, SUITE E
BALTIMORE, MD 21236

TELEPHONE: 301-931-7200, FAX: 301-931-7206
EXHIBITING: The Brimrose Corporation, which has traditionally developed technology for the OEM photonics and spectroscopic communities, introduces its acousto-optic tunable filter (AOTF) series of UV/VIS/NIR miniature spectrometers. These spectrometers contain no moving parts, offer extremely fast scanning or random access wavelengths, and in combination with their embedded Process Control Language (PCL) are uniquely positioned to tackle analytical problems under the most demanding industrial conditions. Brimrose will also showcase other novel, AOTF based devices as well as their line of IR detectors and arrays.

BRUKER INSTRUMENTS, INC.

Booth(s) 209, 211

MANNING PARK
BILLERICA, MA 01821

TELEPHONE: 508-667-9580 E188
EXHIBITING: Analytical instruments such as NMR spectrometers, FTIR spectrometers (including Raman), mass spectrometers, data stations (including UNIX based systems), PC based data stations. Featured will be IRIS ICAP solid state spectrograph. The 0.38 meter purged Echelle spectrograph system has variable wave length coverage: 170-800 nm. The system is operated by Thermo SPEC CID software with Microsoft Windows 3.0. Also featured: the Smith-Hieftje 8000 automated AA/AE spectrophotometer with host computer and printer and 8 lamp configuration.

CAMAG SCIENTIFIC INC.

Booth(s) 116

1200 NORTH 23RD STREET
WILMINGTON, NC 28405

TELEPHONE: 919-343-1830, FAX: 919-343-1834
REPRESENTATIVE(S):
EXHIBITING: Complete TLC system which features the automatic TLC sampler for sample application, the automatic developing chamber for plate development and the CAMAG Scanner II for the most versatile densitometric evaluation available including variable calibration routine, spectra recording and multi wavelength scanning.

CETAC TECHNOLOGIES, INC.

Booth(s) 404

5600 SOUTH 42ND STREET
OMAHA NE 68107

TELEPHONE: 402-733-2829
REPRESENTATIVES:
EXHIBITING: Sample introduction systems for ICP including the U-5000AT ultrasonic nebulizer, the MICRONEB 2000 direct injection nebulizer, and the VERSATORCH family.

CHEM SERVICE, INC.

Booth(s) 208

660 TOWER LANE, P.O. BOX 3108
WESTCHESTER, PA 19381-9941

TELEPHONE: 215-692-3026
REPRESENTATIVES:
EXHIBITING: Chemicals in small quantities. Analytical and reference standards, environmental standards., pesticide and metabolite standards, and inorganic solution standards.

CHEMICAL CONCEPTS

Booth(s) 323, 422

BOSCHSTRASSE 12
D-6940 WEINHEIM, GERMANY

TELEPHONE: +49 6201 606-187, FAX: 606-430
REPRESENTATIVES: Jeremy Potter
EXHIBITING: SpecInfo, advanced spectroscopic interpretation software is now available in a new version based on a relational database system, which offers the user data integrity and security. Data entry is now much easier with JCAMP-DX, NMR peaklists and Molfile formats. SpecInfo offers a range of tools is available to help in the elucidation of unknown structures, including searching for similar and identical structures, similarity searching of NMR and IR spectra, sub-structure analysis and calculation of NMR spectra. SpecData is also the largest commercially available collection of spectra and associated structures. This unique collection consists of 66,000 C-NMR, 14,700 hetero-NMR, 19,300 IR and 160,000 mass spectra, all of which have been quality-checked by independent organizations and come with associated, assigned structures. Buying spectra in pre-sorted

packages is nothing new, but SpecData offers the unique opportunity of choosing your own special collection - one tailored to your needs. MassLib is a powerful structure-oriented software package for mass spectral interpretation, documentation and archiving. In addition to spectral similarity searches using SISCOM, the user can also carry out structural similarity and fragment code searches. Also available is neutral loss similarity searching, a powerful tool for structure elucidation. MassLib is able to automatically process a series of spectra, for instance from a GC-MS run, and suggest structures for each component.

CHEM SERVICE, INC.

Booth(s) 208

660 TOWER LANE, P.O. BOX 3108
WESTCHESTER, PA 19381-9941

TELEPHONE: 215-692-3026
REPRESENTATIVES:
EXHIBITING: Chemicals in small quantities. Analytical and reference standards, environmental standards., pesticide and metabolite standards, and inorganic solution standards.

CHROMATOGRAPHY FORUM DV

Booth(s) 417

SUPELCO, INC.
SUPELCO PARK
BELLEFONTE, PA 16823

TELEPHONE: 814-359-5428
REPRESENTATIVES:
EXHIBITING:

CRC PRESS, INC.

Booth(s) 301

2000 CORPORATE BOULEVARD N.W.
BOCA RATON, FL 33431

TELEPHONE: 407-994-0555
REPRESENTATIVE(S): Christina Martin
EXHIBITING: CRC Press presents its latest and best selling titles including the greatly revised 73rd edition of the *Handbook of Chemistry and Physics*, and *Concepts and Calculations in Analytical Chemistry.*

CVI LASER CORPORATION

Booth(s) 414

2505 DORADO PLACE S.E.
ALBUQUERQUE, NM 87123

TELEPHONE: 505-296-9541
REPRESENTATIVES:
EXHIBITING: CVI is displaying both instrumentation and optics. Monochromators, light sources, filters, fiber optics, detectors, and laser optics will be shown. Three new products will be featured; an RS232-controlled compact monochromator, a low-cost universal sample compartment, and a high-brightness infra-red source. A selection of laser optics will also be displayed.

EAS, INC.

Booth(s) 219

322 SOUTH MIDDLETOWN ROAD
NANUET, NY 10954

TELEPHONE: 914-623-3019
EXHIBITING:

ELEMENT ANALYSIS CORPORATION

Booth(s) 104

1696 CAPITAL CIRCLE, S.W.
TALLAHASSEE, FL 32310

TELEPHONE: 904-576-5115
REPRESENTATIVE(S): Linda Nolan, Hal Johnson
EXHIBITING: Element Analysis is currently the only commercial laboratory offering PIXE analysis. Using Proton Induced X-ray Emission (PIXE), EAC offers non-destructive, simultaneous analysis of solid, liquid and filter samples for the elements from Na through U, providing a valuable tool for applications ranging from R&D to routine quality control.

ELSEVIER SCIENCE PUBLISHING CO.

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655 AVENUE OF THE AMERICAS
NEW YORK, NY 10010

TELEPHONE: 212-989-5800
EXHIBITING: Scientific books and journals.

EM SCIENCE

Booth(s) 420

480 DEMOCRAT ROAD
GIBBSTOWN, NJ 08027

TELEPHONE: 1-800-222-0342
REPRESENTATIVES: James DeSandro, David Boyd, Kathy Priest-Esser
EXHIBITING: Chemical information software program, lab safety products--spills kits, chromatography supplies--TLC plates, high purity solvents for HPLC and biotech applications. Karl Fischer instruments and KF reagents, reagent grade chemicals, and analytical standards.

ENVIRONMENTAL TESTING & ANALYSIS

Booth(s) 607

1907 WEST BURBANK BOULEVARD, 2ND FLOOR
BURBANK, CA 91506

TELEPHONE: 1-818-842-4777
REPRESENTATIVES: Bobby Meeker
EXHIBITING: An industry publication serving the interests of professionals involved in environmental testing and analysis in the lab and onsite. Forms for free subscriptions and free copies will be distributed.

FACSS

Booth(s) 401

ATTENTION: DAVE COLEMAN
WAYNE STATE UNIVERSITY, CHEMISTRY 175
DETROIT, MI 48202

TELEPHONE: 313-577-2586
EXHIBITING: The 1993 FACSS meeting will be held at Cobo Convention Center in Detroit, Michigan, during the week of October 17.

FISONS INSTRUMENTS (APP RES LABS/VG INST)

Booth(s) 215, 217

32 COMMERCE CENTER CHERRY HILL DRIVE
DANVERS, MA 01923-9896

TELEPHONE: 508-777-8034
EXHIBITING: Fisons Instruments will exhibit a comprehensive range of ICP--mass spectrometry products including the Eclipse, the first compact ICP-MS, the PlasmaQuad--high resolution ICP-MS. Scientists from Fisons will present several technical papers covering topics such as helium plasma ion sources for mass spectrometry, high efficiency nebulizers for ICP-MS, and the use of mixed gas plasmas in ICP-MS.

GALACTIC INDUSTRIES CORPORATION

Booth(s) 109

395 MAIN STREET
SALEM, NH 03079

TELEPHONE: 603-898-7600
REPRESENTATIVE(S):
EXHIBITING: Galactic will be exhibiting their new Windows®-based product, GRAMS/ 386™, a processor and database for spectroscopic and chromatographic data. The software provides a complete library of data processing routines including curvefit, subtraction, peak picking and integration. A relational hierarchical database provides the complete solution to laboratory data management. Lab Calc™ and Spectra Calc™ will also be exhibited.

GALILEO ELECTRO-OPTICS CORPORATION

Booth(s) 205, 207

GALILEO PARK, P.O. BOX 550
STURBRIDGE, MA 01566

TELEPHONE: 508-347-9191
REPRESENTATIVE(S):
EXHIBITING: Galileo Electro-Optics Corporation will be exhibiting a full line of infrared fiber-based remote spectroscopy products. Liquid, gas and web monitoring systems for the near IR, mid-IR, and standard fiber cables and assemblies will be demonstrated. Visit Galileo's booth to find out how to move light...not samples.

GBC SCIENTIFIC EQUIPMENT, INC.

Booth(s) 320

3930 VENTURA
ARLINGTON HEIGHTS, IL 60004

TELEPHONE: 708-506-1900
REPRESENTATIVE(S): Robert Pelle, Dennis Guralnick, John Watkins
EXHIBITING: Flame and furnace atomic absorption spectrophotometers and a comprehensive range of accessories include the HG3000, a continuous flow hydride generator for the analysis of As, Se and other hydride forming elements as well as Hg by the cold vapor method. The HSA 3000 which is designed to do analysis solutions of up to 30% dissolved solids or for process monitoring. The automatic burner rotation accessory extends the effective dynamic range of AAS by a factor of 50. It does away with the need for diluting over-range samples.

GILSON COMPANY, INC.

Booth(s) 415

PO BOX 677
WORTHINGTON, OH 43085-0677

TELEPHONE: 614-548-7298
REPRESENTATIVE(S): Charles Ward, Director R&D, Steve Antalics, Chris Antalics
EXHIBITING: Laboratory instruments for particle size analysis, featuring the GilSonic AutoSiever for dry sieving of fine powders to 5 microns, vibratory sieve shakers for wet/dry sieving, and analyzers for sub-sieve measurements. Sample preparation equipment such as precision mini-splitters, spinning rifflers, and pulverizing/grinding mills including the Planetary Micro-Mill from Fritsch.

GROTON TECHNOLOGY, INC.. GT1/SPECTROVISION

Booth(s) 325

45 WINTHROP STREET
CONCORD, MA 01742

TELEPHONE: 1-800-486-4786
REPRESENTATIVE(S):
EXHIBITING: Diode array and fluorescence HPLC detectors. CZE systems. Featuring the SoloNet series of intelligent, high resolution diode array HPLC detectors. All feature high resolution and sensitivity, comprehensive software, standard data systems, and modular construction. The diode array detectors cover the UV to NIR spectral ranges with choices of sample cells.

HARRICK SCIENTIFIC

Booth(s) 206

88 BROADWAY, P.O. BOX 1288
OSSINING, NY 10562

TELEPHONE: 914-762-0020, FAX: 914-762-0914
REPRESENTATIVE(S): Joseph Lucania, Susan Berets
EXHIBITING: Complete line of IR-UV-VIS spectrometer accessories and a complete selection of crystals for optical spectroscopy. Featuring accessories with PermaPurge. For ATR studies: Horizon, a horizontal ATR. The Split Pea-ATR for small samples. The Seagull-a variable angle attachment used for ATR, diffuse reflection, and bi-directional external spectroscopy. Plus One-an enhanced version of the single reflection prism cell. Also on display: diffuse reflection attachment, beam condensers, gas cells, publications.

HIGH PRESSURE DIAMOND OPTICS, INC.

Booth(s) 216

7400 NORTH ORACLE ROAD, SUITE 372
TUCSON, AZ 85704

TELEPHONE: 602-544-9338
REPRESENTATIVE(S): Eric Van Valkenburg
EXHIBITING: Diamond anvil optical cells for analytical and high pressure investigations. These sample holders are designed to work with FTIR, UV spectrometers and IR microscopes and provide sharp, clear spectra of microgram size samples such as fibers, polymers, paint chips, liquids, and inorganic material. No sample preparation is necessary.

HIGH PURITY STANDARDS INC.

Booth(s) 405

P.O. BOX 30188
CHARLESTON, SC 29417

TELEPHONE: 803-556-3411, FAX: 803-766-1178
REPRESENTATIVE(S): Dr. Theodore C. Rains
EXHIBITING: High-purity inorganic spectrometric standard solutions for calibrating, interference check, QC, CLP and TCLP for AAS, ICP, ICP/MS and IC prepared in high-purity subboiling acids. Custom made mixtures for AAS, ICP and ICP/MS; single and multielement metallo-organic standards; simulated rainwater standards; certified reference standards for waters, air particulates and soils; matrix modifiers for GFAAS; consultation/training.

ICON SERVICES, INC.

Booth(s) 608

19 OX ROW LANE
SUMMIT, NJ 07901

TELEPHONE: 908-273-0449
REPRESENTATIVE(S):
EXHIBITING: Exhibiting a comprehensive range of stable isotope compounds used in chemical research. A new catalog with labeled compounds of deuterium, carbon-12, carbon-13, nitrogen-14, nitrogen-15, oxygen-16, oxygen-17, oxygen-18, sulfur-34, sulfur-36, chlorine-35, chlorine-37, bromine-81, noble gas isotopes and multiply labeled compounds available. Technical staff will be available for consultation on products, new compounds and custom synthesis work.

INFOMETRIX, INC.

Booth(s) 303

2200 SIXTH AVENUE, SUITE 833
SEATTLE, WA 98121

TELEPHONE: 206-441-4696, FAX: 206-441-0841
REPRESENTATIVE(S): Paul J. Bailey, Tom Wanne, L Scott Ramos
EXHIBITING: Infometrix will be exhibiting Pirouette® v 1.1 and EinSight® v 3.0, the latest versions of their chemometrics software packages employing pattern recognition, modeling, prediction, calibration, classification and exploratory data based techniques in a windowing, graphical interface. Curve deconvolution for HPLC will also be displayed using the factor analysis approach of QuickRes™. The BioCount™ new microbial detection system will also be featured.

INSTRUMENTS SA, INC./J-Y EMISSION DIVISION

Booth(s) 101

6 OLSEN AVENUE
EDISON, NJ 08820

TELEPHONE: 908-494-8660 or 1-800-533-5946
EXHIBITING: J-Y Emission Division of ISA will be exhibiting its new JY 36 and JY 74 ICP spectrometers. J-Y is a manufacturer of emission spectrometers for ICPs and glow discharge systems. ICP systems include simultaneous-sequential and combination and are designed for those routine systems from environmental analysis to sophisticated research and development systems.

INTERNATIONAL CRYSTAL LABS, INC.

Booth(s) 200

11 ERIE STREET
GARFIELD, NJ 07026

TELEPHONE: 201-478-8944
REPRESENTATIVE(S): Theresa M. Herpst
EXHIBITING: Optical crystals, cells, and accessories for FTIR, IR, UV-VIS spectro-scopy. Ask for their 20-page New Product Supplement featuring ATR systems, presses, variable temperature cells and much more.

JANDEL SCIENTIFIC

Booth(s) 317

2591 KERNER BOULEVARD
SAN RAFAEL, CA 94901

TELEPHONE: 415-453-6700
REPRESENTATIVE(S):
EXHIBITING: Jandel Scientific manufactures and markets microcomputer software products for scientific research. The products include SigmaPlot for the PC and Macintosh, creates publication quality charts and graphs; SigmaScan, scientific measurement and analysis software; JAVA, video measurement and analysis software; Peakfit, quantitative peak analysis software; TableCurve, automated curve fitting software.

JASCO

Booth(s) 407

8649 COMMERCE DRIVE
EASTON, MD 21601

TELEPHONE: 410-822-1220
EXHIBITING: JASCO will be exhibiting a full line of spectroscopic instrumentation. The J-700 series, circular dichroism/chiro-optical spectrometer system; the LC-900 series, the smallest full featured HPLC system ever offered; and the newly introduced Model Micro FTIR spectrometer with ATOS aperturing system.

KAISER OPTICAL SYSTEMS, INC.

Booth(s) 102

371 PARKLAND PLAZA, PO BOX 983
ANN ARBOR, MI 48106

TELEPHONE: 313-665-8083, FAX: 313-665-8199
REPRESENTATIVE(S): Harry Owen, Manager Holographic Products
EXHIBITING: State of the art holographic optical components including Holographic Notch and SuperNotch™ filters, holographic beam-splitters, holographic bandpass filters, and holographic transmission gratings in the 350nm to 1064nm wavelength range for laser applications including raman spectroscopy, fluorescence, and confocal microscopy.

KEYSTONE SCIENTIFIC, INC.

Booth(s) 411

PENN EAGLE INDUSTRIAL PARK
320 ROLLING RIDGE DRIVE
BELLEFONTE, PA 16823

TELEPHONE: 814-353-2300
REPRESENTATIVE(S):
EXHIBITING: HPLC columns, HPLC fittings and accessories, SFC columns, SFC fittings, SFE extraction vessels, Shandon Hypersil® packings and columns, Hypercarb® porous graphitized carbon columns. Featuring DELTABOND® columns for HPLC and SFC.

KRATOS ANALYTICAL, INC.

Booth(s) 503

535 EAST CRESCENT AVENUE
RAMSEY, NJ 07446

TELEPHONE: 201-825-7500
REPRESENTATIVE(S): Michael Peat
EXHIBITING: New from Kratos Analytical UK, the KOMPACT MALDI range of matrix assisted laser desorption, time of flight mass spectrometers in bench mounted format. Systems include COMPACT MALDI II with linear facilities as well as COMPACT MALDI III which has additional reflectron facilities. Both systems have easy to use, fully automated sample introduction techniques offering high sample throughput with no cross contamination and an unusually high level of flexibility. A sample drying unit ensure fast, even specimen preparation. The on-line SUN Microsystems SPARCstation IPC has full control of all system facilities and integral data processing routines include a spectrum processor, peptide calculator, reference editor, and data archiver.

KVB/ANALECT

(Formerly Laser Precision Analytical/Analect FT-IR)

Booth(s) 312, 314

17819 Gillette Avenue
IRVINE, CA 92714

TELEPHONE: 1-800-326-2328, 714-660-8801
FAX: 714-660-9269
REPRESENTATIVE(S):
EXHIBITING: Also known as Analect FT-IR, the Analect industrial laboratory and process FT-IR product line includes the new Analect Sparg-IR Wastewater Analyzer providing real-time monitoring for exit plant streams. Also included is the compact Analect Diamond-20 with integrated Windows software, the Analect Advanced Process Development System (APDS), the Analect EVM-6400 ambient air monitor and the Analect PCM-4000 process monitor.

LAB CONNECTIONS, INC.

Booth(s) 412

5 MOUNT ROYAL AVENUE
MARLBOROUGH, MA 01752

TELEPHONE: 508-480-9777, FAX: 508-481-9764
REPRESENTATIVE(S):
EXHIBITING: LC-TRANSFORM™ and LC-TRANSFORM POLYMER SYSTEMS™, providing an interface between HPLC/GPC and FTIR. The LC-TRANSFORM™ removes all solvents, including water and TCB, and collects the solutes for FTIR examination. Both units are off-line and can be used with most HPLC/GPC and FTIR units. Also displayed will be an adjustable flow divider used with multiple detectors in HPLC and GPC applications.

LECO CORPORATION

Booth(s) 321

3000 LAKEVIEW AVENUE
ST. JOSEPH, MI 49085

TELEPHONE: 609-231-0500
REPRESENTATIVE(S):
EXHIBITING: Leco Corporation will demonstrate the new ICP3000 diode array spectrometer. The ICP3000 allows both sequential and simultaneous (with cost effective programmable wavelength sets) operation. A fully solid-state RF source is employed to provide 2 kw of power at software selectable 27 or 40 mhz. High resolution eschelle optics and photodiode detection are also featured. Also featured on the Leco Mobile Laboratory, which will be located just outside the exhibit hall, are the CHNS932 elemental analyzer, the Leco 2005 image analysis system, and the GDS400A glow discharge spectrometer.

LEEDS & NORTHRUP/MICROTRAC DIVISION

Booth(s) 409

351 SUMNEYTOWN PIKE
NORTH WALES, PA 19454

TELEPHONE: 215-699-2000
EXHIBITING: Leeds & Northrup will demonstrate new features of the MICROTRAC 9200-Series particle analyzers which now measure from 0.003 to 700 microns in one forward light scattering, laser-based system with new enhanced data resolution. L&N will also display an automated, self-calibrating, self-zeroing surface area analyzer.

LEEMAN LABS, INC.

Booth(s) 113

55 TECHNOLOGY DRIVE
LOWELL, MA 01851

TELEPHONE: 508-454-4442
REPRESENTATIVE(S):
EXHIBITING: A complete line of ICP/eschelle spectrometers for multi-element determinations. Featuring the unique Super Sequential with the throughput of simultaneous and the flexibility of sequential systems. The totally automated preparation and analysis system for ultra-trace mercury measurement. An automated cyanide preparation and analysis system with improved sensitivity and productivity.

KURT J. LESKER COMPANY

Booth(s) 315

1515 WORTHINGTON AVENUE
CLAIRTON, PA 15025

TELEPHONE: 412-233-4200
REPRESENTATIVE(S): Michele Migliuolo
EXHIBITING: Featuring the Turner Spectrometry TS-"SOLA" ICP-MS unit. This system, which offers constant response across the mass range, advanced ion optics without photon stops, limits of detection in the ppt range, may be used for both solid and liquid analysis. A glow discharge module option allows the user to configure the SOLA ICP-200 from ICP to GD mode in about 30 minutes. Other options include laser ablation, ETV, hydride generators, ultrasonic nebulizers for limits of detection in the sub-ppt range, and more.

L T INDUSTRIES, INC.

Booth(s) 218

6110 EXECUTIVE BOULEVARD
ROCKVILLE, MD 20852

TELEPHONE: 301-468-6777, FAX: 301-468-2230
REPRESENTATIVE(S):
EXHIBITING: L T Industries Inc. will exhibit their high resolution VIS/NIR analyzers to include the **Quantum 1200 PLUS** (lab analyzer) a rapid scanning, monochromator with enhancements in signal-to-noise and wavelength stability. Complimenting their analyzers are Spectra-Metrix 1.9 software (MLR), **LighTcal PLUS** which features PLS and PCR methods and **TRANSPARENCY** software package designed for calibration integrity and downloading to field installations. Additionally, LTI will exhibit their full line of **FiberLine** fiber optic accessories including probes, cables, and cells.

MATTSON INSTRUMENTS, INC.

Booth(s) 305

1001 FOURIER COURT
MADISON, WI 53717

TELEPHONE: 608-831-5515
REPRESENTATIVE(S):
EXHIBITING:

McCARTHY SCIENTIFIC

Booth(s) 213

P.O. BOX 5332
FULLERTON, CA 92635
TELEPHONE: 714-526-2742
REPRESENTATIVE(S): Donald McCarthy, Evelina McCarthy
EXHIBITING: Accessories for infrared and UV-Visible spectrophotometers.

MILLIPRE EXTREL™ MASS SPECTROMETRY

Booth(s) 413

575 EPSILON DRIVE
PITTSBURGH, PA 15238

TELEPHONE: 412-963-7530
REPRESENTATIVE(S): Joseph E. Campana, Gary Astle
EXHIBITING: Extrel™ Mass Spectrometry, now a part of MILLIPORE, will be featuring the benchmark™ LC/MS system and FT/MS® Laser Probe™ mass spectrometer. Benchmark's LC/MS technology is a fully integrated, dedicated bench-top detection system. The benchmark is designed for qualitative and quantitative analysis. Extrel's FT/MS Laser Probe mass spectrometer provides ultrahigh resolution and accurate mass measurements for molecular surface analysis, laser desorption, and many other research applications.

NICOLET INSTRUMENT CORPORATION

Booth(s) 115, 117, 119

5225 VERONA ROAD
MADISON, WI 53711-4495

TELEPHONE: 608-271-3333
REPRESENTATIVE(S): Julie Bellefeuille, Marketing Services Coordinator, Peggy Crook, Marketing Communications Manager, Joni Hansen, Marketing Communications Specialist
EXHIBITING: Nicolet's Raman 910 FT-Raman spectrometer is a dedicated, standalone instrument designed for the measurement of Raman spectra and is not connected to a separate FT-IR instrument. Several design features optimize the Raman 910's performance and capabilities, including gold-coated optics, a large sample compartment, and several laser options. Nicolet will introduce its new Magna-IR 550 and 750 series FT-IR spectrometers. These spectrometers feature many advantages, including OMNIC™ Windows-based software for quick and easy data manipulation, pinned-in-place optics for highly accurate results and unbeatable signal-to-noise ratio, upgradeable resolution, and advanced diagnostics for pass/fail checks.

PERGAMON PRESS, INC.

Booth(s) 606

MAXWELL HOUSE, FAIRVIEW PARK
ELMSFORD, NY 10523

TELEPHONE: 914-592-7700
EXHIBITING: Pergamon Press is a leading publisher of scientific and technical books and journals. Please stop by for free sample copies.

PERKIN-ELMER CO.

Booth(s) 610, 612, 614, 616

761 MAIN AVENUE
NORWALK, CT 06859-0012

TELEPHONE: 203-762-1000
REPRESENTATIVE(S):
EXHIBITING: FTIR spectrophotometers, PE Sciex Elan ICP-MS with laser ablation sampling, Zeeman and graphite furnace AA; UV/VIS fluorescence and luminescence spectrophotometers, GC, GC-MS and FTIR/GC; HPLC systems and diode array detectors. Also exhibiting thermal analyzers, environmental analysis equipment and methodology; chromatography and lab and desktop data systems and lab information management systems.

PHOTOMETRICS LTD.

Booth(s) 408

CHRISTIANA EXECUTIVE CAMPUS
220 CONTINENTAL DRIVE
NEWARK, DE 19713

TELEPHONE: 302-453-8848
REPRESENTATIVE(S): Jim Malone, Jack Mills, Larry Phillips
EXHIBITING: New spectroscopic imaging detector systems based on CCD technology. Detectors available from 0.19-1.05 microns and either TE or LN_2 cooled. Compatible with most existing spectrometers and spectrographs, these new 2D detectors also include imaging capability and up to 16 simultaneous measurements when used with an imaging spectrograph.

POTOMAC PHOTONICS, INC.

Booth(s) 103

4720-E BOSTON WAY
LAMHAM, MD 20706

TELEPHONE: 301-459-3031, FAX: 301-459-3034
REPRESENTATIVE(S): Sara Cohn
EXHIBITING: Ultraviolet waveguide lasers are the smallest, most economical lasers at 308, 248 and 193 nm. Air-cooled and operating from a 110 volt line, these novel lasers find application in such diverse areas as photoablation, micromachining, micro-surgery, fluorescence spectroscopy, capillary electrophoresis, dye laser pumping, and surface analysis.

PRINCETON INSTRUMENTS, INC.

Booth(s) 308

3660 QUAKERBRIDGE ROAD
TRENTON, NJ 08619

TELEPHONE: 609-587-9797, FAX: 609-587-1970
EXHIBITING: Spectroscopic and imaging CCD detection systems featuring a 25mm LN cooled, thinned back-illuminated CCD; ideal for Raman and luminescence with 80% peak QE and 18% QE at one micron. See Princeton Instruments for the largest selection in scientific CCDs, intensified CCDs, diode arrays, intensified diode arrays, and NIR multichannel detectors.

PROCHROM INC.

Booth(s) 210

5622 WEST 73RD STREET
INDIANAPOLIS, IN 46278

TELEPHONE: 317-297-1667
REPRESENTATIVE(S):
EXHIBITING: Exhibiting the complete preparative HPLC series LC50 system featuring the 5 cm dynamic axial compression column (DAC), portable control systems with advanced automation, ternary gradient capability, automatic sample injection, fraction collection, etc. The DAC column is user packed for maximum flexibility, stability, and efficiency.

QUESTRON CORPORATION

Booth(s) 518

P. O. BOX 2387
PRINCETON, NJ 08543

TELEPHONE: 609-587-6898
REPRESENTATIVE(S): Pat Grillo
EXHIBITING: Microwave digestion system; mercury analyser.

ROYAL SOCIETY OF CHEMISTRY

Booth(s) 302

THOMAS GRAHAM HOUSE
SCIENCE PARK, MILTON ROAD
CAMBRIDGE, CB4 4WF UNITED KINGDOM

TELEPHONE: +44 (0)223-420066
REPRESENTATIVE(S):
EXHIBITING: Literature and RSC publications (journals, books, databases, information services) with emphasis on topical publications covering analytical chemistry and spectroscopy; sample journals (free); also see the CRC Press stand nearby for a display of RSC books. CRC Press acts as a RSC agent for books in the US and can take orders.

SANDA CORP.

Booth(s) 501

4005 GYPSY LANE
PHILADELPHIA, PA 19144

TELEPHONE: 1-800-999-2993, 215-849-8100
FAX: 215-849-8102
REPRESENTATIVE(S): Traude Sadtler, Philip Sadtler, Mike Brown
EXHIBITING: Sanda designs and manufactures computerized titration equipment:: the manual QC Model Thermo-Titrator, the internationally acclaimed FACTS™ fully automated computerized titration system,; for the first time, Sanda will be exhibiting their pioneering On-Line Analysis using Sanda copyrighted software.

SHIMADZU SCIENTIFIC INSTRUMENTS, INC.

Booth(s) 416, 418

7102 RIVERWOOD DRIVE
COLUMBIA, MD 21046

TELEPHONE: 1-800-477-1227

REPRESENTATIVE(S): Bob Clifford, Joe Greenbeck, Len Poirier, John Monti
EXHIBITING: Thermal analysis systems to include differential scanning calorimetry, thermogravimetry and thermomechanical analysis for complete quantitative analysis of materials such as: polymers, advanced composites, pharmaceuticals etc. New meaning for AA: Absolute Automation...automatically achieve increased productivity with repeatable programmed analyses, automated standard and sample dilution, auto matrix modification, auto positioning from flame to furnace mode, auto calibration, and optimization of gas flow and atomizer alignment.

SILK SCIENTIFIC, INC.

Booth(s) 108

P.O. BOX 533
OREM, UT 84059

TELEPHONE: 801-377-6978
REPRESENTATIVE(S): Jeff Silk
EXHIBITING: The Un-Plot-It automated digitizing system is designed for scientists. It uses a PC, an HP plotter, and Silk Scientific's optical pen to automatically read graphical data from paper into the computer in ASCII format. The user can then find peak areas, smooth data, take derivatives, re-scale the graph, or read the data into other software packages. IBM and Macintosh versions.

SOCIETY FOR APPLIED SPECTROSCOPY

Booth(s) 403

198 THOMAS JEFFERSON DRIVE, SUITE S-2
FREDERICK, MD 21701

TELEPHONE: 301-694-8122
REPRESENTATIVE(S): Jo Ann Brown, Barbara Stull, Sandy O'Neil, Karen Breen
EXHIBITING: The Society for Applied Spectroscopy is an association for scientific and professional people organized to advance and disseminate knowledge and information concerning spectroscopy and other allied sciences. Membership includes ten issues of *Applied Spectroscopy*, local section activities, videotape program, Bulletin Board, Tour Speakers program, educational courses and SAS newsletter.

SOLUTIONS PLUS, INC.

Booth(s) 111

2275 CASSENS DRIVE, SUITE 147
FENTON, MO 63026
TELEPHONE: 314-349-4922
REPRESENTATIVE(S): Nancy M. Brinner
EXHIBITING: Catalog has extensive listing which includes various standard solutions such as pH buffers, volumetrics, indicators, titrants, water-testing reagents, atomic absorption and plasma emission spectroscopy standards, metallo-organic standards, contract lab program blends, etc., which are routinely required by analytical chemists. In addition, custom-manufacturing and private labeling inquiries are welcome. We also offer resin-impregnated graphite furnace tubes.

SPECTRA HARDWARE INC

Booth(s) 500

1150 FIRST STREET
WESTMORELAND CITY, PA 15692

TELEPHONE: 412-863-7527
REPRESENTATIVE(S):
EXHIBITING: Dual-source ICP & DCP simultaneous and sequential spectrometers for elemental analysis, automatic samplers, data acquisition and control systems, pump and sample delivery systems and lab consumables.

SPECTRA-TECH, INC.

Booth(s) 402

652 GLENBROOK ROAD
STAMFORD, CT 06906

TELEPHONE: 203-357-7055, FAX 203-357-1713
REPRESENTATIVE(S):
EXHIBITING: A full line of FT-IR sampling accessories and supplies for the analysis of liquids, solids, microsamples and gases. New sampling technology for the IR-Plan® microscope: grazing angle microscopy and ATR microscopy. Also on display, easy-to-use sampling accessories for the QC, analytical, and research laboratory.

SPECTRAL SYSTEMS

Booth(s) 110

50 SOUTH BUCKHOUT STREET
IRVINGTON, NY 10533

TELEPHONE: 914-591-5055, FAX: 914-591-5099
REPRESENTATIVE(S): L. Boutis, F. Wesley, B. Darnell, C. Guajardo
EXHIBITING: High quality crystalline optical components for spectroscopy, detectors and interferometers. Items include windows, ATR plates, prisms, hemispheres and mirrors. Materials include zinc selenide, potassium bromide, sodium chloride, KRS-5, germanium, cadmium teluride, cesium iodide, zinc sulfide, silicon, sapphire, calcium fluoride, and barium fluoride.

SPECTROSCOPY

Booth(s) 425

195 MAIN STREET
METUCHEN, NJ 08840

TELEPHONE: 908-549-3000
REPRESENTATIVE(S): Basil Scaperdas
EXHIBITING: *Spectroscopy* is the only publication exclusively dedicated to covering the diverse field of spectroscopic analysis. Articles span the complete range of modern spectroscopic methods, including: UV/VIS, infrared, ICP/DCP, AA, X-ray, FT-IR, mass spectrometry, laser, fluorescence, surface analysis, hybrid techniques, and NMR.

SPEX INDUSTRIES, INC.

Booth(s) 107

3880 PARK AVENUE
EDISON, NJ 08820

TELEPHONE: 908-549-7144
REPRESENTATIVE(S):
EXHIBITING: For inorganic spectroscopy, SPEX offers a full line of certified aqueous and organometallic standards for ICP, DCP, AA, XRF, and OES analysis as well as EPA-certified quality control samples. Also offered are grinders, mills, and automated fusion equipment for sample preparation as well as our NEW microwave digestion system. The SPEX instrument department can assist you with your needs in Raman, fluorescence, and optical spectroscopy.

SUPELCO, INC.

Booth(s) 419

SUPELCO PARK
BELLEFONTE, PA 16823-0048

TELEPHONE: 814-359-3441
REPRESENTATIVE(S):
EXHIBITING: Separations technology and products for the petroleum/chemicals, life sciences, environmental, and food and beverage markets. Packings, capillary, electrophoreses and HPLC columns, guard columns, inlet liners, ferrules for chromatography. Air monitoring, sample preparation products and chemical standards for your needs. We provide selections of accessories and custom products.

THERMO JARRELL ASH CORPORATION

Booth(s) 602, 604

8E FORGE PARKWAY
FRANKLIN, MA 02038

TELEPHONE: 508-520-1880 E170
REPRESENTATIVE(S):
EXHIBITING: The Enviro I has been designed specifically for trace level determination of elemental pollutants in environmental samples. This instrument is capable of routinely meeting the demanding analytical and sample throughput requirements of the EPA contract laboratory program. It incorporates purge polychromator optics and 22 analytical channels to cover the EPA's list of priority elemental pollutants plus an additional 15 optional channels to fulfill elemental requirements of an environmental testing laboratory. This instrument is fully automatic with the peristaltic pump speed, gas flows, and R. F. power all under microprocessor control. The self-tuning, crystal controlled R. F. generator makes it possible to perform analysis on both aqueous or organic samples.

UNICAM ANALYTICAL SYSTEMS

Booth(s) 306

1001 FOURIER COURT
MADISON, WI 53717

TELEPHONE: 608-831-6609, FAX: 608-831-5156
REPRESENTATIVE(S):
EXHIBITING: Introducing the new family of modular SOLAAR™ AA spectrometers featuring WINDOWS™ 3 software, stockdale double beam optics, quad lamp turret, gas furnace, autosampler, and flow injector. Also the full line of UV/VIS/NIR spectrometers from fixed wavelength to research grade products will be shown.

VARIAN ANALYTICAL INSTRUMENTS

Booth(s) 307, 309, 311, 313

220 HUMBOLDT COURT
SUNNYVALE, CA 94089

TELEPHONE: 800-926-3000, FAX: 415-858-0480
REPRESENTATIVE(S): Patricia Grant
EXHIBITING: Chromatography systems including the Saturn II GC/MS, autosamplers, and PC-based workstations; and optical spectroscopy systems including new generation Cary UV-Vis-NIR spectrometers, atomic absorption spectrometers, and the Liberty ICP.

JOHN WILEY & SONS

Booth(s) 100

605 THIRD AVENUE
NEW YORK, NY 10158

TELEPHONE: 212-850-6000
REPRESENTATIVE(S):
EXHIBITING: A fine selection of professional reference books and journals of interest to those in fields of analytical chemistry, chromatography, and applied spectroscopy.

YMC, INC.

Booth(s) 114

51 GIBRALTAR DRIVE
MORRIS PLAINS, NJ 07950

TELEPHONE: 201-285-1776
REPRESENTATIVE(S):
EXHIBITING: YMC offers a wide range of silica- and polymer-based stationary phases and accessories for liquid chromatography. An expanded range of HPLC columns for analysis/purification of numerous chemical compounds will be presented. New products include Protein RP for protein and peptide analysis and Polymer C18 for high pH separations.

1992 FACSS PROGRAM

MONDAY MORNING

New Plasma Atomic Emission Instrumentation

Grand Ballroom A and B

C. Boss; North Carolina State University, Presider

8:20—1. A 22-mm Torch for Atomic Emission and Mass Spectrometry. J.A. Horner*, G.M. Hieftje; Indiana University

8:40—2. Design Features of a Graphite Furnace Capacitively Coupled Plasma Source for Atomic Spectroscopy. D.C. Liang*, H. Yang, K. Leung, W. Gauley, P. Banks; Aurora Instruments Ltd

9:00—3. Temporal Evolution of the Emission Signal from a Microcavity Hollow Cathode. P.D. Mixon, S.T. Griffin, J.C. Williams*; Memphis State University

9:20—4. Plasma Parameter Effects on Crater Shapes in RF Glow Discharge Sputtering. C.S. Lazik*, C.N. Hammond, R.K. Marcus; Clemson University

9:40—5. Effect of Aging the Hollow Cathode by Sputtering on the Analytical Precision of the Hollow Cathode Discharge Emission Source. J.C. Williams*, J.L. Tseng, J.Y. Kung, S.T. Griffin; Memphis State University

10:00 BREAK

10:40—6. Sputtering Characteristics of Glasses and Ceramics Via RF Glow Discharge Atomization. C.J. Lazik*, R.K. Marcus; Clemson University

11:00—7. Characterization of a Graphite Furnace Capacitively Coupled Plasma Source for Atomic Spectroscopy. P. Banks*, D. Huang, D.C. Liang; Aurora Instruments Ltd

11:20—8. Characterization of the Charge Injection Device as a Detector for ICP Spectroscopy. R.W. Foster*, A.E. Pellowe; Thermo Jarrell Ash Corp

11:40—9. A Mechanically Stable Photometer Design for the Analysis of Microsamples Using a Hollow Cathode Emission Source. S.T. Griffin, J.C. Williams*; Memphis State University

Sampling of Solids and Slurries with the Graphite Furnace

D. Bradshaw; Perkin Elmer Corporation, Organizer

Grand Ballroom D

D. Bradshaw; Perkin Elmer Corporation, Presider

8:40—10. A Systematic Approach to Ultrasonic Slurry GFAAS for Environmental Monitoring. N.J. Miller-Ihli; USDA,ARS,BHNRC,NCL

9:20—11. The Determination of Elements of Various Volatilities in Coal, Coke, Ash and Sludge Samples Using Slurry Sampling Graphite Furnace AAS. G. Schlemmer*, W. Erler; Perkin-Elmer GmbH

9:40—12. Taking the Slurry Sampling Method to the Limit ... Determining Ultratrace Constituents in High-Purity Materials. M. Epstein; NIST

10:00 BREAK

10:40—13. Solid Sampling with ETV-ICP/AES – A Contribution to the Methodology. U. Kurfurst, P. Verrept, R. Dams; University of Fulda

11:00—14. Determination of Trace Elements in Food and Agricultural Samples by Graphite Furnace Atomic Absorption Spectrometry with Solid and Slurry Sampling. D.J. Butcher*, E.D. Byrd; Western Carolina University

11:20—15. Solid Sampling of Metal Alloys for the Determination of Antimony, Phosphorus, Tellurium and Tin by the use of Laser-Excited Atomic Fluorescence with an Electrothermal Atomizer. R.G. Michel, R.F. Lonardo*, Z. Liang; University of Connecticut

Professor Peter Keliher Memorial Symposium

J. Tyson; University of Massachusetts, Organizer

Grand Ballroom F

J. Tyson; University of Massachusetts, Presider

8:00—16. Compensation of Physical and EIE Effects Due to High Concentrations of Ca, Mg, Na and Li for Ultrasonic Nebulization. I.B. Brenner*, S. Erlich; Geological Survey of Israel

8:20—17. Studies on an Excimer Laser Ablated Plasma. J. Sneddon*, Y. Lee, T. Thiem, Y.Y. Teng; University of Massachusetts

8:40—18. The Concept and Use of Hollow Cathode Lamp Excited Atomic Fluorescence Spectrometry in an Inductively Coupled Plasma. S.F. Franz*; Spectro Incorporated

9:00—19. Analytical Chemistry of Chromium: Simultaneous Detection of Cr(III) and Cr(VI). S.I. Shupack; Villanova University

9:20—20. An Investigation of the Chromium(III)-2,6 Pyridine- Dicarboxylic Acid Complexation Reaction Using the Method of Continuous Variation and Coupled ICP-ICPAES. D.J. Gerth*, T. Howell, S.I. Shupack; Lancaster Labs

9:40—21. Atomic Spectroscopy and Neural Networks: Application to Florida Orange Juice. S. Nikdel; Florida Department of Citrus

10:00 BREAK

10:40—22. Current Economic Influences on Analytical Instrument Development. A.T. Zander; Varian Associates Inc

11:00—23. How to Write Your Own CLP Software. C.C. Wohlers; Energy & Environmental Engineering

11:20—24. The Fundamental Review in Atomic Emission Spectrometry. L. Voress; American Chemical Society

11:40—25. ARAAS and ASU. J. Egan; Royal Society of Chemistry

12:00—26. The American Microchemical Society, Microchemical Journal, Peter Keliher and Me. L.C. Klein; FMC Corp

Advances in Plasma Spectrometry

A. Montaser; The George Washington University, Organizer

Grand Ballroom C

A. Montaser; The George Washington University, Presider

8:40—27. 1492–1992: Plasma Mass Spectrometry and the Age of Discovery. R.S. Houk; Iowa State University

9:20—28. The Effect of Aerosol Droplets and Particles on Inductively Coupled Plasma Mass Spectrometry Signals: Time Gated Measurements by Laser-Induced Fluorescence Spectroscopy and Mass Spectrometer. S.E. Hobbs, J.W. Olesik*; Ohio State University

9:40—29. New Concepts for Thermospray Sample Introduction to Atomic Spectrometry. T.S. Conver*, J.A. Koropchak; Southern Illinois University

10:00 BREAK

10:40—30. The Glow Discharge as a Reactive Analytical Cell. W.W. Harrison*, S.K. Ohorodnik, P.H. Ratliff; University of Florida

11:20—31. Elemental Analysis Using Ion-Trap Mass Spectrometry. C. Gill*, M.W. Blades; University of British Columbia

11:40—32. Optical Imaging Studies of Argon and Helium Inductively Coupled Plasmas by a CID-Based Spectrometer. C. Hsiech, A. Montaser*; George Washington University

Chemometrics in Signal Processing

S. Rutan; Virginia Commonwealth University, Organizer

Delaware Rooms 1 and 2

S. Rutan; Virginia Commonwealth University, Presider

8:20—33. Digital Filters: They're Not Just for Smoothing Anymore. P.D. Wentzell*, S.J. Vanslyke, S.G. Hughes; Dalhousie University

9:00—34. Application of Digital Filtering Techniques to Problems in Quantitative FT-IR Spectroscopy. G.W. Small; Ohio University

9:40—35. Resolution of Component Spectra Using Successive Average Orthogonalization and Iterative Target Transformation. X. Liang, J.E. Andrews, J.A. de Haseth*; University of Georgia

10:00 BREAK

10:40—36. Adaptive Kalman Filtering. S.D. Brown; University of Delaware

11:20—37. Adaptive Filters and Information. Y. Hayashi, S.C. Rutan*; Virginia Commonwealth University

12:00—38. Self-Modelling Curve-Resolution Applied to the Simultaneous Study of Different Spectroscopic Titrations of Multiequilibria Systems. R. Tauler*; University of Washington

Separation Scientists of the 21st Century
J. Dorsey; University of Cincinnati, Organizer
Franklin Rooms 1 and 2
J. Dorsey; University of Cincinnati, Presider

8:30—39. Probing Selective Binding Interactions of Proteins Using Capillary Zone Electrophoresis. J.F. Wheeler*, A.C. Cater; Furman University

9:00—40. Angle-Resolved Photoacoustic Spectroscopy: A New Probe for Molecular Orientation. K.L. Rowlen*; University of Colorado

9:30—41. New Directions in Chiral Separations. A.M. Stalcup; University of Hawaii

10:00 BREAK

10:40—42. Analysis of Biological Microsamples by Capillary Separation Techniques. R.T. Kennedy*, N. Shultz, L. Cole, L. Huang; University of Florida

11:10—43. Nuclear Magnetic Resonance Spectroscopy: A Versatile Tool for Studying Molecular Interactions in Liquid Chromatography. K.B. Sentell*, D.M. Bliesner, S.T. Shearer; University of Vermont

Chromatography in the Delaware Valley: Past, Present and Future Symposium Honoring Joseph C. Touchstone, Univ. of Pennsylvania
J.M. DiBussolo; Perkin-Elmer Corporation, Organizer
Adam's Ballroom A
J.M. DiBussolo; Perkin-Elmer Corporation, Presider

8:20—44. The Chromatography Forum of Delaware Valley – 25 Years of Bringing Together Separation Scientists. J.M. Di Bussolo; Perkin Elmer Corporation

8:40—45. Gas Chromatography – Advances Made in Delaware Valley (1965–1992). R.L. Grob; Villanova University

9:20—46. The Center of Column Development, Centre County Pennsylvania. W.R. Supina; Consultant

10:00 BREAK

10:40—47. Gas Chromatography in Environmental Analysis—The Last 25 Years. M.A. Kaiser*, R.L. Grob; DuPont Engineering

11:00—48. The Invention of the Fused-Silica Capillary Column: An Industrial Perspective. E. Zerenner, R.D. Dandeneau*; Hewlett Packard

11:20—49. Negative Peaks in Chromatography. A. Satinder; Ciba-Geigy

11:40—50. Bright Lights and Small Peaks: Hewlett-Packard's 25-Year Effort in GC-AED. J.J. Sullivan*, B.D. Quimby; Hewlett-Packard

Fourier Transform and Ion Trap Mass Spectrometry
J. Amster; University of Georgia, Organizer
Constitution Rooms A and B
J. Brodbelt; University of Texas, Presider

8:20—51. Matrix Assisted Laser Desorption in a Fourier Transform Mass Spectrometer. C.L. Wilkins*, C. Koster, J.A. Castoro; University of California

8:40—52. Matrix-Assisted Laser Desorption for the Investigation of X-Ray Induced Damage to Nucleic Acid Constituents. B. Hettich*, H. Yoshida; Oak Ridge National Lab

9:00—53. Bioscience Applications of FTMS. R. Hein, B. Becker, Z. Liang, J. Campana*; Extrel FTMS

9:20—54. New Developments in Trapping, Excitation, and Detection in FT/ICR Mass Spectrometry. S. Guan*, A.G. Marshall, M.V. Gorshkov, P.B. Grosshans, C.W. Ross III, L. Schweikhard, T.L. Ricca; Ohio State University

9:40—55. High Resolution Tandem Mass Spectrometry of Large Molecules. D. Suckau*, F.W. McLafferty, S.C. Beu, Y. Shi, M.W. Senko, J.P. Quinn, F.M. Wampler III; Cornell University

10:00 BREAK

10:40—56. High Magnetic Field Electrospray FTICR. D.A. Laude Jr.*, Z. Guan, V.L. Campbell; University of Texas – Austin

11:00—57. Glow Discharge-FTICR Mass Spectrometry: High Resolution Elemental Analysis. J.R. Eyler*, C.M. Barshick, C.H. Watson; University of Florida

11:20—58. Surface Analysis by Laser-Induced Thermal Desorption/FTMS and FT Reflection-Absorption IR: Organic Thin Films on TI and Oxidized TI Metal Foils. D.P. Land*, N.A. Thornburg, I. Abdelrehim; University of California

11:40—59. A Gas-Phase Study of Fe(phenyl)$^+$ with Alkanes. Y. Li*, E. Garcia, Y. Huang, B.S. Freiser; Purdue University

Industrial Applications of Raman Spectroscopy I
M. Carrabba; EIC Laboratories, Organizer
Gettysburgh Rooms 2, 3, and 4
M. Carraba; EIC Laboratories, Presider

8:20—60. In Situ Monitoring of Emulsion Polymerization Using Fiber-Optic Raman Spectroscopy. C.K. Mann*, C. Wang, J.B. Schlenoff, T.J. Vickers; Florida State University

8:40—61. Investigation of Wall Deposits in Tungsten Halogen Lamps by Raman Spectroscopy. P.J. Codella*, L. Bigio; General Electric

9:00—62. Detection of Hydrogen Gas Leaks with Raman Spectroscopy. K.M. Spencer*, M.M. Carrabba, R.B. Edmonds, M.D. Arnett; EIC Labs Inc

9:20—63. Applications of Raman Spectroscopy to Industrial Processes. S. Farquharson; Dow

9:40—64. Applications of Fiber Optic Raman Spectroscopy to Environmental Monitoring. M.M. Carrabba*, K.M. Spencer, R.B. Edmonds, J. Haas III; EIC Laboratories Inc

10:00 BREAK

10:40—65. Industrial Applications Using FT-Raman Spectroscopy. J.A. Graham; Hercules Incorporated

11:00—66. FT-Raman Spectroscopy – A Technique in Flux. D.A.C. Compton, P.J. Stout; Bio-Rad, Digilab Division

11:20—67. Recent Developments in Fourier Transform Raman Microanalysis; Instrumentation and Applications. A.J. Sommer*, J.E. Katon; Miami University

11:40—68. Surface-Enhanced Raman Spectroscopy of Serotonin and Melatonin. W.K. Kowalchyk, K.L. Davis, E.A. Todd, M.D. Morris*; University of Michigan

Recent Developments in Forensic Analytical Chemistry
I. Lurie; USDEA Special Testing, Organizer
Adam's Ballroom B
I. Lurie; USDEA Special Testing, Presider

8:20—69. Drug Determinations – Medical Legal Toxicology. D.T. Stafford; University of Tennessee

8:40—70. Serial Capillary GC/IR/MS: Quantitation and Identification of Amphetamine, Methamphetamine, and Amphetamine Analogs in Human Urine. G.E. Platoff*, D.W. Hill, T.R. Koch, Y.H. Caplan; US Army

9:00—71. Combination of Microcrystals & FTIR Microscope to Solve Challenging Drug Analysis Problems. H.A. Harris*, T. Kane, T. Rodwell; Monroe Co Pub Safety Lab

9:20—72. Canadian Designer Drugs. M. LeBelle; Bureau of Drug Research

9:40—73. Micellar Electrokinetic Capillary Chromatography (MECC) of Drugs and Related Compounds of Forensic Interest. I.S. Lurie; DEA

10:00 BREAK

10:40—74. GC/FT-IR Methods for Drug Analysis. K.S. Kalasinsky*, J. Magluilo, Jr., T. Schaefer; Armed Forces Institute

11:00—75. Identification of Blood and Semen Stains on Clothing Using Near-Infrared Spectroscopy. E.W. Ciurczak*, F.A. DeThomas, J.E. Carroll; NIRSystems Inc

11:20—76. Electric Birefringence Imaging of Nucleic Acid Electrophoresis. D.W. Grossman, M. Lanan, M.D. Morris*; University of Michigan

MONDAY AFTERNOON

Laboratory Information Management Systems: General
Delaware Rooms 1 and 2
T. Gills; NIST, Presider

1:40—77. Considerations in Selecting a LIMS: Flexibility, Turn-Key Operation, Vendor Support. R.D. Beaty; Telecation, Inc

2:00—78. Strategies for Spectral Identification: Deducing Information about Structural Composition from Spectral Searches. W.M. Grim III*, B.A. Woods, M. Boruta; Bio-Rad, Sadtler Division

2:20—79. Electronic Notebook Using Microsoft Windows. N.J. Shah*, R.J. Obremski, J.W. Slizel; Beckman Instruments Inc

2:40—80. ASTM E49 Committees on Chemical Data Standardization – Standards For Chemical Data. R. Lysakowski*; Digital Equipment Corp

3:00 BREAK

3:20—81. NIST Gas Standard Reference Materials; Status and Philosophy. T.E. Gills; NIST

3:40—82. Creating Industry-Wide Analytical Data Interchange and Storage Standards (ADISS) for Analytical Chemistry. R. Lysakowski*; Digital Equipment Corp

4:00—83. Analytical Data Systems Based on Client Server Technology – A Case Study. J.M. Read; DuPont Merck Pharmaceutical Co

Plasma Diagnostics

Grand Ballroom A and B

P. Farnsworth; Brigham Young University, Presider

1:40—84. Charge Transfer in the ICP: A Survey of the Transition Metals. C. Ogilvie, P.B. Farnsworth*, C; Hemming; Brigham Young University

2:00—85. Data Acquisition and Evaluation by a Computer-Controlled Langmuir Probe System. J.M. Weston*, C.S. Shick, R.K. Marcus, H. L. Hunter; Clemson University

2:20—86. Effects of EIEs and non-EIEs on the Fundamental Parameters of the Inductively Coupled Plasma. N.N. Sesi*, D.S. Hanselman, M. Huang, G.M. Hieftje; Indiana University

2:40—87. Aerosol Desolvation and Particle Vaporization in ICPs. J.W. Olesik*, S.E. Hobbs; Ohio State University

3:00 BREAK

3:20—88. Effect of Desolvation on the Easily Ionized Element Interference in ICP Spectrometry. M. Wu*, G.M. Hieftje; Indiana University

3:40—89. Excitation Temperature Measurements Without the Boltzman Equation. G.D. Rayson*, M. Duarte; New Mexico State University

4:00—90. Number Density Distributions of Cr(I) Sampled by the Unidirectional Waveform Spark. L.M. Lograsso*, D.M. Coleman; Wayne State University

4:20—91. Hydrocarbon Dissociation Equilibria in Nitrogen and Argon Microwave-Induced Plasmas. M.P. Dziewatkoski, C.B. Boss*; North Carolina State University

4:40—92. Radio Frequency-Powered Glow Discharge Mass Spectrometry at 40 MHz. H. Zhang, A. Montaser*; George Washington University

5:00—93. Preliminary Studies of the Precision and Accuracy of Determination of Spectral Line Positions in High Resolution Inductively Coupled Plasma Fourier Transform Spectrometer. J.C. Travis*, M.L. Salit, M.R. Winchester; NIST

Sampling of Solids with High Current Pulsed Discharges

A. Scheeline; University of Illinois, Organizer

Grand Ballroom F

A. Scheeline; University of Illinois, Presider

1:40—94. Ablation of Graphite Plasma Facing Components in Tokamaks. M. Ulrickson; Princeton Plasma Physics

2:20—95. Aspects of Quantitation with a Theta Pinch Emission Source. D.L. Miller*, A. Scheeline; University of Illinois

2:40—96. Planar Magnetron Sampling with Knock-on and Reactive Ion Sputtering. R.D. Sacks*, S. Brewer, Z. Shi, T. Woodrum, K. Dehghan; University of Michigan

3:00 BREAK

3:20—97. Re-excitation of Plasma Gun Vapor Using Pulsed and Steady-State Microwave Plasmas. J.M. Goldberg, L.A. Lanning*; University of Vermont

3:40—98. Strategies for RF Re-excitation of Vapor Produced by a Plasma Gun Atom Source. J.M. Goldberg, G.J. McGowan*; University of Vermont

4:00—99. Chemical Synthesis Through Condensed-Phase Plasmas. V. Majidi*, M. Meier; University of Kentucky

4:20—100. Analytical Implications of Plasma Dynamics in the High Voltage Spark Discharge. C. Bye*, A. Scheeline; University of Illinois

Sampling of Solids and Slurries with the Graphite Furnace

D. Bradshaw; Perkin Elmer Corporation, Organizer

Grand Ballroom D

D. Bradshaw; Perkin Elmer Corporation, Presider

1:40—101. Influence of Sample Heterogeneity to Graphite Furnace Solid Sampling Data. U. Kurfurst; University of Fulda

2:20—102. The Role of Extraction in Slurry Analysis Using Graphite Furnace AAS. M.T.C. Vollebregt*, P. Van Oosten; Delft University of Technology

2:40—103. Analysis of Carbon Slurries by ETAAS after Trace Metal Preconcentration. K.W. Jackson*, T.M. Mahmood; University of Albany/SUNY

3:00 BREAK

3:20—104. The Analysis of Paint Chips Using Slurry Sample Introduction for Graphite Furnace AAS. D.K. Bradshaw; Perkin-Elmer Corp

3:40—105. Comparison of Direct Analysis of Solid Polymers by Graphite Furnace AAS with Microwave Digestion and Conventional Ashing. D.A. Anderson, E.M. Skelly Frame*; GE Corporate Research

Chemometrics in Calibration

D. Haaland; Sandia National Laboratories, Organizer

Grand Ballroom C

D. Haaland; Sandia National Laboratories, Presider

1:40—106. Multivariate Calibration: Overview, Challenges, and Pitfalls. D.M. Haaland; Sandia National Lab

2:20—107. The Role of Diagnostic Tools in Multivariate Calibration. R. Spragg*, R. Aries, D. Lidiard; Perkin-Elmer Ltd

3:00 BREAK

3:20—108. Comparison of Algorithms for Transferring Multivariate Calibrations Between Spectrometers. K. Beebe*, S. Ramos; Dow Chemical Company

4:00—109. Some Comparative Investigations of Neural Networks in Calibration. T.B. Blank, S.D. Brown*; University of Delaware

4:20—110. NIR Analysis of Combined Aromatic-Aliphatic Hydrocarbon Mixtures. E.W. Stark*, K. Luchter; KES Analysis

Investigations of Chromatographic Stationary Phases

M.J. Wirth; University of Delaware, Organizer

Franklin Rooms 1 and 2

M.J. Wirth; University of Delaware, Presider

1:40—111. Molecular Transport and Kinetics at Silica/Solution Interfaces. J.M. Harris*, W.B. Lacy, S.W. Waite, H. Wang; University of Utah

2:20—112. NMR Studies of Silica Surfaces. G.E. Maciel*, I.S. Chuang, D. Kinney; Colorado State University

3:00 BREAK

3:20—113. Selectivity Control in Reversed-Phase Liquid Chromatography. J.G. Dorsey*, S.R. Cole; University of Cincinnati

4:00—114. Orientational Dynamics of Molecules Interacting with Chromatographic Surfaces. M.J. Wirth*, M.E. Montgomery, J. Durbage; University of Delaware

Chromatography in the Delaware Valley: Past, Present and Future

J.M. Di Bussolo; Perkin-Elmer Corporation, Organizer

Adam's Ballroom A

J.M. Di Bussolo; Perkin-Elmer Corporation, Presider

1:40—115. Selecting Mobile Phases and Columns for Superior Reversed-Phase HPLC Separations. J.J. Kirkland; Rockland Technologies Inc

2:20—116. Fascinating Experiences in Preparative Chromatography. R. Sitrin; Merck Sharp and Dohme

3:00 BREAK

3:20—117. Design and Characterization of a Novel Hydrolytically Stable C_{18} Stationary Phase. H.O. Fatunmbi*, M.J. Wirth; University of Delaware

3:40—118. High-Performance Bonded Phases for Chromatography – 12 Years of Research, Development, and Commercialization for J.T. Baker, Inc. M.P. Henry; J.T. Baker Inc

4:00—119. Chromatographic and Electrophoretic Analysis Strategies for Biotechnology. J. Adamovics*, C. Heacock, D. Farb, C. Silverman; Cytogen Corp

4:20—120. Copolymeric Bonded-Phase Extraction of Compounds from Biological Matrices. D.J. Fox*, E.T. Heebner, M.J. Telepchak; Worldwide Monitoring

4:40—121. Supercritical Fluid Technology in the Materials and Environmental Sciences. S.A. Liebman*, E.J. Levy; CCS Instrument Systems

5:00—122. Chiral Separations in Support of New Drug Discovery. K.M. Kirkland*, K.L. Neilson, D.A. McCombs; ICI Pharmaceuticals Group

Fourier Transform and Ion Trap Mass Spectrometry

J. Amster; University of Georgia, Organizer
Constitution Rooms A and B
J. Amster; University of Georgia, Presider

1:40—123. Experiment and Simulation of Ion Behavior in a Quadrupole Ion Trap. R. Julian*, R.G. Cooks; Purdue University
2:00—124. Laser Photodissociation Probe of Ion Motion in the Ion Trap. P.M. Hemberger*, M.L. Alexander, M.E. Cisper, N.S. Nogar, J.D. Williams, R.G. Cooks, J.E.P. Syka; Los Alamos National Lab
2:20—125. Particle Beam LC/MS on the Quadrupole Ion Trap. R.A. Yost, B.L. Kleintop*, D.M. Eades, T.D. Behymer, W.L. Budde; University of Florida
2:40—126. Laser Desorption and Selective Ion-Molecule Reactions in a Quadrupole Ion Trap Mass Spectrometer. J.S. Brodbelt*, A. McIntosh, T. Donovan, C.C. Liou; University of Texas
3:00 BREAK
3:20—127. Rapid Analysis Using Direct Sampling Ion Trap Mass Spectrometry. M.V. Buchanan*, S.A. Rossi, M.B. Wise, C. Thompson, R. Merriweather; Oak Ridge National Lab
3:40—128. Recent Advances in Biomolecule Analysis Using an Ion Trap Mass Spectrometer. G. Van Berkel, S. McLuckey*, G. Glish; Oak Ridge National Lab
4:00—129. An Ion Trap Storage/Time-of-Flight Mass Spectrometer. S.M. Michael*, M. Chien, D.M. Lubman; University of Michigan
4:20—130. Atmospheric Pressure Ionization of Biological Compounds Using an Ion Trap Storage/Time-of-Flight Mass Spectrometer. M. Chien*, S.M. Michael, D.M. Lubman; University of Michigan
4:40—131. Photodissociation of $Ag(benzene)^+$ and $Ag(toluene)^+$ in a Fourier Transform Mass Spectrometer. S. Afzaal*, Y. Huang, B.S. Freiser; Purdue University

Industrial Applications of Raman Spectroscopy II

M. Carrabba; EIC Laboratories, Organizer
Gettysburg Rooms 2, 3, and 4
P. Codella; GE Research & Development Center, Presider

1:40—132. Compact Raman Sensor Using Holographic Optical Components. H. Owen; Kaiser Optical Systems
2:00—133. Recent Developments with the Portable Raman Fiber-Optic Spectrometer. A. Leugers*, R. McLachlan, D. Lafevor, L. Wright; Dow Chemical Co
2:20—134. Sensitive, Compact Raman Spectrometers Based on Diode Lasers, CCD's and Imaging Spectrographs. R.L. McCreery*, C. Frank, M. Fryling; Ohio State University
2:40—135. Turn-Key Raman Systems for the Chemical Analyst. F. Adar*, F. Purcell, R. Grayzel; Instruments SA Inc
3:00 BREAK
3:20—136. Compact Line-of-Sight Remote Raman Spectrometer for Intermediate-Range Chemical Detection and Mapping. T.J. Kulp*, S.M. Angel, T. Vess; Lawrence Livermore Lab
3:40—137. Micro Raman Spectroscopy: C.L.R. – Confocal Laser Raman Near IR Excitation. B. Lenain*, J. Barbillat, E. Dasilva, M. Delhaye; EG&G/PAR – Dilor
4:00—138. Critical Factors in Raman and FT-Raman Microspectroscopy. A.J. Sommer*, J.E. Katon; Miami University
4:20—139. FT-Raman Spectroscopy as an Analytical Tool for Inorganic and Organometallic Complexes. N.T. Kawai, T.J. Johnson*; Bruker Instruments
4:40—140. Micron and Submicron Electrodes for Use in Surface Enhanced Raman Spectroscopy. E. Todd, W. Kowalchyk, K.L. Davis, M.D. Morris*; University of Michigan
5:00—141. Raman Microprobe with Holographic Optical Elements. D.M. Pallister, K-L Liu, A. Govil, M.D. Morris*; University of Michigan

Recent Advances in the Analysis and Characterization of Explosives

B. McCord; FBI Academy, FSRTC, Organizer
Adam's Ballroom B
B. McCord; FBI Academy, Presider

1:40—142. Detection of Trace Explosive Evidence by Ion Mobility Spectrometry. D.D. Fetterolf; FBI Academy
2:00—143. Infrared Analysis of Explosives. E.G. Bartick*, R.A. Merrill; FBI Academy
2:20—144. Detection of the Organic Constituents of Explosive and Gunshot Residues Using Micellar Electrokinetic Capillary Electrophoresis (MECE). D.M. Northrop*, W.A. McCrehan; WFP Crime Lab
2:40—145. Capillary Electrophoresis of Low Explosive Residues. K.A. Hargadon*, B.R. McCord; FBI
3:00 BREAK
3:20—146. The Analysis of Alkyl Amine Nitrates in Emulsion and Water Gel Explosives. E.G. Bender; Bureau of Alcohol, Tobacco, and Firearms
3:40—147. Smokeless Powder Characterization – An Investigative Tool in Pipe Bombings. C.L. Wallace*, E.G. Bender; Bureau of Alcohol, Tobacco, and Firearms
4:00—148. Trace Analysis of Nitrate Esters in Industrial Wastewater Streams. B.P. Thomas; NSWC/IHD
4:20—149. Recent Advances in Propellant Stabilizer Analysis. G.Y. Stine; NSWC/IHD

TUESDAY MORNING

Developments in Laboratory Information Generation and Management in Plasma Spectrometric Laboratories

I.B. Brenner; Geological Survey of Israel, Organizer
Grand Ballroom C
I.B. Brenner; Geological Survey of Israel, Presider

8:20—150. A New Generation of Combined Optical Emission ICP Mass Spectrometric Instrumentation. M.B. Denton; University of Arizona
9:00—151. The Hidden Information in ICP-OES Multichannel Data. A. Lorber; Nuclear Research Center
9:20—152. Scientific Visualization for ICP Spectrometry: Interpretation of Multidimensional Plasma Images. M. Glick, G. Hieftje*; Indiana University
9:40—153. Multivariate Methods Applied to Simultaneous Emission Spectra from the Inductively Coupled Plasma. J.C. Ivaldi*, T. Barnard, D. Tracy, W. Slavin; Perkin-Elmer Corp
10:00 BREAK
10:40—154. The Challenge of Digital Filtering Techniques in Multielement ICP-AES. M.T.C. Vollebregt*, E.H. van Voon; Delft University
11:00—155. Fundamental Atomic Reference Data—Where Have We Come in 5 Years?. A. Scheeline; University of Illinois
11:20—156. Electronic Publishing in Spectroscopy: Current Status and Future Perspectives of Spectrochimica Acta Electronica (SAE). P.W.J.M. Boumans; Philips Research Labs
11:40—157. Multielement Line Selection in Inductively Coupled Plasma Atomic Emission Spectrometry (ICP-AES). P.W.J.M. Boumans; Philips Research Labs

Sample Introduction for Atomic Spectrometry: What Does the Future Hold?

E. Salin; McGill University, Organizer
Grand Ballroom D
E. Salin; McGill University, Presider

8:40—158. New Approaches to the Analysis of Small Samples. M.W. Blades*, T. Hettipathirana, C. Gill, C. Le Blanc; University of British Columbia
9:00—159. A Critical Look at the Thermodynamic and Kinetic Features of Atom Formation for Analytical Spectrometry. J. Tyson; University of Massachusetts
9:40—160. On the Realization of Expert Systems for Atomic Spectrochemical Analysis. M.B. Denton; University of Arizona
10:00 BREAK
10:40—161. The Search for a Solid Solution. E. Salin*, J.M. Ren, L. Blain, G. Legere; McGill University
11:20—162. Direct Analysis of Solid Sample in Inductively Coupled Plasma Spectrochemistry. J.M. Mermet; University Claude Bernard – Lyon I
11:40—163. Use of Near Infrared Radiation to Enhance Desolvation and Sample Introduction for Plasmas: Where have all the atoms gone?. A.R. Eastgate*, L. Banlaky, R. Dahlquist; Fisons Instruments, ARL

Electrothermal Atomizers in Atomic Absorption Spectrometry: Fundamentals and Applications

G. Rayson; New Mexico State University, Organizer
Grand Ballroom F
V. Majidi; University of Kentucky, Presider

8:20—164. Mechanism of Aluminum Atomization in Graphite Furnace Atomic Absorption Spectrometry. C.L. Chakrabarti*, A.K. Gilmutdinov, D.C. Gregoire, J.C. Hutton, M.M. Lamoureux; Carleton
8:40—165. Atomization of Al, Ga, In, Tl in ETA-AAS. D.A. Katskov*, A.M. Stephan; State Institute of Applied Chemistry, Russia
9:20—166. Mass Spectrometric Elucidation of Mechanisms that Control the Electrothermal Atomization of Tin. G.N. Brown*, D.L. Styris; Battelle
9:40—167. Digital Imaging and Computer Simulation of Atom Formation and Dissipation in a Graphite Furnace for Analytical Atomic Spectrometry. J.C. Hutton*, C.L. Chakrabarti, A.K. Gilmutdinov, R. Mrasov; Carleton University
10:00 BREAK
10:40—168. Surface Studies Using Tube-in-Tube Electrothermal Atomizers. R.W. Fonseca*, J.A. Holcombe; University of Texas
11:00—169. Temporally and Spatially Resolved Gas Phase Temperature Measurements in Electrothermal Atomizers. B. Welz*, M. Sperling, J. Hertzberg, G. Marowsky; Perkin-Elmer GmbH
11:20—170. Metal-Surface Reactions at Elevated Temperatures on Various Surfaces. J.G. Jackson*, J.A. Holcombe; University of Texas
11:40—171. Evaluation of the Performance of the Transversely Heated, Longitudinally Zeeman-Corrected Furnace AAS. G.R. Carnrick*, W. Slavin; Perkin-Elmer Corp
12:00—172. Solid Sample Speciation Using Pressure-Regulated Electrothermal Atomizer Atomic Absorption. P. Wang, J.A. Holcombe*; University of Texas

Chemometrics in Chromatography

S. Ramos; Infometrix, Organizer
Franklin Rooms 1 and 2
S. Ramos; Infometrix, Presider

8:40—173. Computer Modeling in Liquid Chromatography Method Development. J.D. Dolan, T. Jupille, M. Watkins*; LC Resources
9:00—174. Multivariate Approaches to Peak Purity Determinations in HPLC. B.G. Archer; Beckman Instruments
9:20—175. Investigation of Window Factor Analysis and Matrix Regression Analysis in in Chromatography. K. Schostack, E.R. Malinowski*; Stevens Institute of Technology
9:40—176. Pattern Recognition of Chromatographic Profiles for Product Monitoring. D.R. Burgard; The Procter & Gamble Co
10:00 BREAK
10:40—177. Pattern Recognition Methods Applied to Chromatographic Data for Fish Speciation. B.J. Tenge, L.S. Ramos*, S.J. Kwolek, N.L. Dang, J.A. Nolan, J.D. Barnett, M.M. Wekell; U.S. Food and Drug Administration
11:00—178. Prediction of Chromatographic Retention of Organic Compounds from Molecular Structure. P.C. Jurs*, T.P. Woloszyn; Pennsylvania State University
11:20—179. Exploring the Solution Space via Constrained Nonlinear Optimization. S. Neal; University of California
11:40—180. A New Approach to Chromatography Pattern Recognition Using Three-Dimensional Multivariate Plots. F.O. Geiser*, C. Golt, L. Kung, Jr., J.D. Justice, L. Fluckiger; Geiser Scientific Inc

Advances in Capillary Electrophoresis and Micellar Electrokinetic Separations

J. Foley; Villanova University, Organizer
Adam's Ballroom B
J. Foley; Villanova University, Presider

8:30—181. Dispersion in Electrokinetic Separations. S.L. Delinger, J.M. Davis*; Southern Illinois University
9:00—182. Capillary Zone Electrophoresis of Biopolymers with Coupled Fused-Silica Capillaries. Z. El Rassi*, W. Nashabeh; Oklahoma State University
9:30—183. Optimization of Selectivity in Capillary Electrophoresis. M.R. Hadjmohammadi, B. Ye, M.G. Khaledi*; North Carolina State University
10:00 BREAK
10:40—184. Optimization of Experimental Parameters in Capillary Zone Electrophoresis. H.J. Issaq*, K.C. Chan, G.M. Janini, G.M. Muschik; Program Resources Inc
11:20—185. Random Walk Treatment of Band-Broadening Processes in Micellar Electrokinetic Chromatography. K. Nielsen, J.P. Foley*; Villanova University

Advances in Size Exclusion Chromatography

P. Dubin; Indiana/Purdue University, Organizer
Adam's Ballroom A
P. Dubin; Indiana University/Purdue University, Presider

8:30—186. Recent Advances in Molecular-Weight-Sensitive Detectors for Size Exclusion Chromatography. H.G. Barth*, W.W. Yau, C. Jackson; E.I. du Pont de Nemours
9:00—187. The "Size" of Molecules and Instrumental Broadening. P.J. Wyatt; Wyatt Technology
9:30—188. Characterization of Semi-flexible Polymers by Size Exclusion Chromatography with Multi-angle Light Scattering. P.M. Cotts; IBM Research Division
10:00 BREAK
10:40—189. System Requirements for Multiple Detector Characterization of Polymer Systems. J. Lesec, R. Nielson, T. Havard*; Waters-Millipore
11:20—190. Characterization of High-Molecular-Weight Polyethylenes Using GPC, GPC-LALLS and GPC-DV. A.W. de Groot*, W.U. Hamre, H. Perkins; Dow Chemical Company

Electrochemical Detection of the Future: Is There a Future After Catecholamines?

R.P. Baldwin; University of Louisville, Organizer
Delaware Rooms 1 and 2
R.P. Baldwin; University of Louisville, Presider

8:30—191. Measuring Pharmacological Events In Vivo with LCEC: New Challenges and Opportunities. C. Duda, J. Gitzen, R.E. Shoup*, P. Kissinger; Bioanalytical Systems Inc
9:00—192. Identification and Quantitation of Peptides and Proteins by Liquid Chromatography − Electrochemical Detection with Post-Column, Photolytic Derivatizations (HPLC-hν-EC). I.S. Krull*, L. Dou, L. Chen, J.R. Mazzeo; Northeastern University
9:30—193. New Electrode Materials and Structures for Chemical Analysis. R.P. Baldwin*, P. Luo, X. Qi, J. Ye; University of Louisville
10:00 BREAK
10:840—194. Scanning Electrochemical Detection in Narrow-Bore Capillary Electrophoresis. S.E. Sloss*, A.G. Ewing; Penn State University
11:20—195. Ultramicro Amperometric Biosensors. A.M. Yacynch*, E.R. Reynolds; Rutgers University

Colonial Chemistry: The Age of Gases

E.G. Brame; The Cecon Group Inc, Organizer
Grand Ballroom A and B
E.G. Brame; The Cecon Group Inc, Presider

8:20—196. Colonial Chemistry: The Age of Gases. A. Bober; State of Maryland
8:40—197. Limelights to Semiconductors − Industrial Gases from a Historical Perspective. A.J. Ellgren; BOC Group Inc
9:20—198. Linde's Contributions to the U.S. Industrial Gas Industry. T.F. Fisher; Union Carbide
10:00 BREAK
10:40—199. Discovering the Halogens. F. Schweighardt, A.J. Woytek; Air Products & Chemicals

High-Molecular-Weight Mass Spectrometry

R. Beavis; Memorial University, Organizer
Constitution Rooms A and B
R. Beavis; Memorial University of Newfoundland, Presider

8:30—200. Experimental Parameters in LDMS Ion Sources. R.C. Beavis; The Memorial University

9:00—201. Velocity and Time Spreads in Matrix-Assisted Laser Desorption. W. Ens*, K. Standing; University of Manitoba

9:30—202. Mass Spectrometric Investigation of Proteins Separated by Two-Dimensional Gell Electrophoresis. W. Zhang*, B.T. Chait; Rockefeller University

10:00 BREAK

10:40—203. Matrix-Assisted Laser Desorption of Proteins: Current Status. P. Williams; Arizona State University

11:20—204. Use of Capillary Electrophoresis – Electrospray Ionization Mass Spectrometry to Characterize Biomolecules. D.R. Goodlett*, J.H. Wahl, H.R. Udseth, R.D. Smith*; Battelle

11:40—205. Nanosecond vs. Picosecond Matrix-Assisted Laser Desorption/Ionization. T. King, S. Colby, J.P. Reilly, R. King, R. Goldschmidt, K. Owens*; Drexel University

State of the Art Raman Spectroscopy I

M. Carrabba; EIC Laboratories, Organizer

Gettysburg Rooms 2, 3, and 4

M. Carrabba; EIC Laboratories, Presider

8:40—206. Multichannel Raman Spectroscopy: Making the Most of Many Channels. M.J. Pelletier; Procter & Gamble Co

9:20—207. Current Status of Raman Spectroscopy at 1 Micron and Beyond. B. Chase; E.I. DuPont

10:00 BREAK

10:40—208. Advances in Remote Raman Spectroscopy. S.M. Angel*, T. Vess, T.J. Kulp, M.M. Carrabba; Lawrence Livermore

11:20—209. Waveguide Raman Spectroscopy of Polymer Laminates. C.G. Zimba*, F.P. Chen; Polaroid Corporation

TUESDAY AFTERNOON

Sample Introduction Strategies for ICP-AES

Grand Ballroom F

J. Koropchak; Southern Illinois University, Presider

1:40—210. Direct Powder Introduction – Inductively Coupled Plasma Emission Spectrometry with a Photodiode Array Spectrometer. N. De Silva*, R. Guevremont; Geological Survey of Canada

2:00—211. Special Considerations in the Selection of Internal Standard for the Analysis of Slurry Samples by ICP-AES. A. Merrick*, D. Schatzlein; Spectro Analytical Instruments

2:20—212. Characterization of a Plasma Gun Direct Solid Sampling Source for ICP-AES. J.L. McKinstry*, J.M. Goldberg; University of Vermont

2:40—213. Spectrochemical Analysis of Difficult Samples by ICP-AES Using a New High Efficiency High Solids Nebulizer. G.A. Meyer*, D. Arniaud, L.C. Goldstone; Battelle

3:00 BREAK

3:20—214. Analysis of Low-Volume Nebulized Samples by Inductively Coupled Plasma Atomic Emission Spectrometry. L. Thompson, C.B. Boss*; North Carolina State University

3:40—215. Analysis of Small-Volume Hydrofluoric Acid Samples by Direct Injection Nebulization ICP Spectrometry. D.R. Wiederin*, T.L. Pinkston; Cetac Technologies

4:00—216. Flow Injection Donnan Dialysis Preconcentration for Trace Metals Analysis by ICP-AES. J.A. Koropchak, K. Narasimhan*; Southern Illinois University

4:20—217. Recent Investigations of Meinhard Concentric Nebulizers. H. Tan*, B.A. Meinhard, J.E. Meinhard; J E Meinhard Assoc Inc

4:40—218. Monodisperse Dried Microparticulate Injection. B. Etkin, J.B. French, R. Jong*; University of Toronto

The Science of Ben Franklin: Then and Now

N. Heindel; Lehigh University, Organizer

Grand Ballrooms A and B

N. Heindel; Lehigh University, Presider

1:40—219. Promoting Useful Knowledge: Benjamin Franklin and the American Philosophical Society. R.E. Goodman; American Philosophical Society

2:20—220. Benjamin Franklin's Electrical Connection: Scientific Correspondence between Petter Collinson and Franklin. A. Armstrong; Core States/PNB

3:00 BREAK

3:20—221. Electricians and Electrical Engineers: Changes Since the Time of Franklin. J.M. Gibson; Rutgers University

4:00—222. The Ben Franklin Partnership: Ben's Spirit Survives in Pennsylvania's Technology Development Program. M.S. Lang; Ben Franklin Partnership

4:20—223. A Day in the Life of Ben Franklin. R. Archbold;

Developments in Laboratory Information Generation and Management in Plasma Spectrometric Laboratories

I.B. Brenner; Geological Survey of Israel, Organizer

Grand Ballroom C

I.B. Brenner; Geological Survey of Israel, Presider

1:40—224. Challenges of Data Collection and Diffusion in Toxicology. S. Caroli; Istituto Superiore

2:20—225. Application of Laboratory Data Management Systems for Inorganic Environmental Analysis. A.F. Ward; Ward Associates

2:40—226. An Intelligent Data Management System for Water Quality Studies. H.E. Taylor, D.B. Peart*; US Geological Survey

3:00 BREAK

3:20—227. Interpretation of Multielement Analytical Data Using Principal Components Analysis. D.A. Yates*, R. Aries; Perkin-Elmer Corporation

3:40—228. Use of ICP-AES and ICP/MS for Multielement Determination in Geochemical Prospecting. M. Borsier*, I.B. Brenner; BRGM

4:00—229. Quality-Control Procedures for Inductively Coupled Plasma – Optical Emission Spectrometry at the U.S. Geological Survey National Water Quality Laboratory. E.J. Zayhowski*, T.J. Bushly, C.A. Gable; U.S. Geological Survey

Electrothermal Atomizers in Atomic Absorption Spectrometry: Fundamentals and Applications

G. Rayson; New Mexico State University, Organizer

Grand Ballroom E

G. Rayson; New Mexico State University, Presider

1:20—230. Chemical Modification in Graphite Furnace Atomic Absorption Spectrometry Investigated by Inductively Coupled Plasma Mass Spectrometry. C.L. Chakrabarti*, D.C. Gregoire, M.M. Lamoureux, T. Ly; Carleton University

2:00—231. Mechanism of Palladium Modification for the Removal of Chloride Interference in ETAAS. K.W. Jackson*, H. Qiao; SUNY of Albany

2:20—232. A Study of Matrix Modifiers on Heated Graphite Surfaces. N. Xu, C. Eloi*, J.D. Robertson, V. Majidi; University of Kentucky

2:40—233. Bulk Diffusion-Induced Analyte Loss in Graphite Atomizers. D.L. Styris*, J.A. Harris, D.A. Redfield; Battelle

3:00 BREAK

3:20—234. Pretreatment Time as a Parameter for the Evaluation of Matrix Modifiers in ETA-AAS. G.D. Rayson*, M.R. Fresquez, K. Hall; New Mexico State University

3:40—235. Mechanism of Interferences of Hydride-Forming Elements on the Determination of Selenium. B. Welz*, P. Stauss; Perkin-Elmer GmbH

4:00—236. Real World Applications of a Multielement GFAAS. G.R. Dulude*, M.J. Dauzvardis, S. Karpova; Thermo Jarrell Ash Corp

4:20—237. Development of a Microanalytical Method for the Determination of Selenium in Bovine Heart Tissue Using Zeeman Graphite Furnace Atomic Absorption Spectrometry. C.M. Tummalapalli, J.C. Williams*; Memphis State University

4:40—238. Electrothermal Atomization of Solid Samples for Element Concentration Determinations in Individual Hairs. R.D. Koons*, C.A. Peters, B. Donnelly; FBI Lab

Chemometrics in the Analysis of Three-Mode Data Arrays

Y. Wang; University of Washington, Organizer

Franklin Rooms 1 and 2

Y. Wang; University of Washington, Presider

1:20—239. Overview of Three-Way Data Analysis in Chemistry and Psychology. P. Gelndi; University of Umea

2:00—240. Moving Beyond Three-Way Data Arrays. H.S. Eskensen; Center for Industrial Research

2:20—241. An Empirical Investigation of Noise Effects on the Resolution of Trilinear Arrays. D.S. Burdick*, B.C. Mitchell; Duke University

3:00 BREAK

3:20—242. Three-Way Data Analysis on Differences Between Stationary Phases. A.K. Smilde*, B.R. Kowalski, D.A. Doornbos; University Center for Pharmacy

4:00—243. Effects of Random Errors on the Generalized Rank Annihilation Method. K. Booksh, B.R. Kowalski*; University of Washington

4:20—244. Similarity Transformations for the Generalized Rank Annihilation Method. S. Li*, P.J. Gemperline; East Carolina University

4:40—245. A Study on Alternating Least Squares Used in Three-Way Data Analysis. P. Gemperline; East Carolina University

5:00—246. Some Theoretical Aspects in Second Order Calibration. Y. Wang, B. Kowalski; University of Washington

Advances in Capillary Electrophoresis and Micellar Electrokinetic Separations

J. Foley; Villanova University, Organizer

Adam's Ballroom B

J. Foley; Villanova University, Presider

1:40—247. The Assay of Peptides Using Multichannel Detection in Capillary Electrophoresis. J.V. Sweedler*, A.T. Timperman, S.E. Tracht, R.R. Fuller; University of Illinois

2:00—248. Direct Control of Electro-osmosis and Retention Window in Micellar Electrokinetic Capillary Chromatography. B. Patel, P. Tsai, C.S. Lee*; University of Maryland

2:30—249. Ultramicro Enzyme Assays in a Capillary Electrophoretic System. J. Bao, F.E. Regnier*; Purdue University

3:00 BREAK

3:20—250. Separations of Polyaromatic Hydrocarbons Using Micellar Electrokinetic Capillary Chromatography. M.J. Sepaniak*, T.D. Staller, C. Copper; University of Tennessee

3:50—251. Structured Method Development in CE/MECC: Analogies and Differences with HPLC. J.K. Strasters*, M.G. Khaledi; Sterling Winthrop

4:20—252. Looking at Particulates with Capillary Electrophoresis. B. Van Orman, G.L. McIntire*; Sterling Winthrop Inc

Advances in Size Exclusion Chromatography

P. Dubin; Indiana/Purdue University, Organizer

Adam's Ballroom A

P. Dubin; Indiana University – Purdue University, Presider

1:30—253. Contrasting the Mechanisms of Size Exclusion Chromatography and Gel Electrophoresis. D.A. Hoagland*, E. Arvanitidou; University of Massachusetts

2:00—254. On the Mechanism of Size Exclusion Chromatography. M. Potschka; Vienna

2:30—255. Carboxylated Starburst Dendrimers as Calibration Standards for Aqueous Size Exclusion Chromatography. P.L. Dubin*, S.L. Edwards, J.I. Kaplan, M.S. Mehta, D. Tomalia, J. Xia; Indiana University/Purdue University

3:00 BREAK

3:20—256. Investigations of Poly(Vinyl Alcohol) Using Dual Detector SEC. L.Z. Vilenchik*, G.C. Kingston; Monsanto Chemical Co

4:00—257. Size Exclusion Chromatography in an Analytical Perspective. L. Hagel; Pharmacia LKB Biotech

Analytical Laboratories on Chips: Genome Project for Analytical Chemistry?

B.R. Shaw; University of Connecticut, Organizer

Delaware Rooms 1 and 2

B.R. Shaw; University of Connecticut, Presider

1:40—258. Monitoring Dynamic Chemical Events at Individual Biological Cells. R.M. Wightman*, J. Jankowski, T. Schroeder; University of North Carolina

2:20—259. Microanalytical Laboratories on a Chip: Prospects and Pitfalls for a Fantastic Voyage. J.L. Anderson*; University of Georgia

3:00 BREAK

3:20—260. Chemistry for the Microscopic Mapping of Synaptic Gluramate. L. Li*, M. Arnold, J. Dordick; University of Iowa

3:40—261. Wonders of Micromachining: Chemical Analysis and Electrophoresis on a Chip. K. Seiler*, D.J. Harrison, A. Manz; University of Alberta

4:20—262. Stabilized Surfactant Films – Coatings for Multiplex Sensors. J.F. Rusling; University of Connecticut

High-Molecular-Weight Mass Spectrometry

R. Beavis; Memorial University, Organizer

Constitution Rooms A and B

R. Beavis; Memorial University of Newfoundland, Presider

1:40—263. Applications of MALDI-TOF to Biological Problems. R.W. Nelson*, M.A. McLean, T.W. Hutchens, M.L. Vestal; Vestec Inc

2:20—264. Simultaneous High Resolution – High Sensitivity Reflectron Matrix-Assisted Laser Desorption of Proteins. F. Laukein*, K. Norbash, J. Wronka; Bruker Instruments Inc

3:00 BREAK

3:20—265. Models for Laser-Pulse Desorption. R.E. Johnson; University of Virginia

4:00—266. Development of High-Performance Time-of-Flight Instrumentation for Analysis of Biological Molecules. T. Cornish*, R. Cotter; Johns Hopkins

Molecular Analysis with Laser Techniques

E. Voightman; University of Massachusetts, Organizer

Grand Ballroom D

E. Voightman; University of Massachusetts, Presider

1:40—267. Determination of Intracellular Species at the Level of a Single Erythrocyte Via Capillary Electrophoresis with Direct and Indirect Fluorescence Detection. E.S. Yeung, B.L. Hogan, T. Lee*; Iowa State University

2:20—268. Multiwavelength Thermal Lens Spectrophotometer Based on Acousto-optic Tunable Filter. C.D. Tran*, M. Bartelt, V. Simianu; Marquette University

2:40—269. A Laser-Based Optical Polarimeter: Computer Simulation and Experimental Evaluation. M.E. Johnson*, E. Voigtman; University of Massachusetts

3:00 BREAK

3:20—270. Probing Solvation Dynamics in Supercritical Fluids by Picosecond Laser Spectroscopy. F.V. Bright*; SUNY at Buffalo

3:40—271. Trace Detection of Vapors Using Laser Photogragmentation and Ionization Spectroscopy with Mass Spectrometric Detection. J.B. Simeonsson*, G.W. Lemire, R.C. Sausa, A.W. Miziolek; U.S. Army Ballistics

4:00—272. Advances in Sensors Based on Raman and Luminescence Detection. T. Vo-Dinh*, J.P. Alarie, K. Houck, D.L. Stokes; Oak Ridge National Lab

4:20—273. An Approach to Single-Molecule Detection by Laser-Induced Fluorescence of a Flowing Dye in a Capillary. S.J. Lehotay*, Y.H. Lee, B.W. Smith, J.D. Winefordner; USDA

4:40—274. Wavelength-Dependant Metastable Decay of Dipeptides in a Reflectron Time-of-Flight Mass Spectrometer Using Multiphoton Ionization. S.T. Fountain*, D.M. Lubman; University of Michigan

5:00—275. Three Dimensional Characterization of Molecular Anisotropy in Freestanding Polymer Films by a New Wave Guide Coupling Technique. R.J. Samuels*, S. Hardaker, S. Moghazy; Georgia Institute of Tech

State of the Art Raman Spectroscopy II

J. Haas III; Oak Ridge National Labs, Organizer

Gettysburg Rooms 2, 3, and 4

J. Haas III; Oak Ridge National Laboratories, Presider

1:40—276. Resonance Raman Spectroscopy – A Selective Tool for Making Complex Problems Simple and Simple Problems Complex. S.A. Asher; University of Pittsburgh

2:20—277. Raman Microspectroscopy and Imaging. Advances in Two and Three-Dimensions. M.D. Morris; University of Michigan

3:00 BREAK

3:20—278. Advances in Analytical Applications of Surface-Enhanced Raman Spectroscopy. R.L. Garrell; UCLA

Atomic Spectroscopy Poster Session
Exhibition Hall
3:30–5:30

279. USP Heavy Metals Testing – Can Atomic Spectroscopy Offer Significant Advantages?. A.W. Steele*, R.L. Petty; Glaxo Inc
280. Comparison of Sn and Au Concentrations in Films on Silicon Substrates by ICP and Flame AA Spectrometry. D.A. Anderson, W.E. Balz, E.M. Skelly Frame*; GE Corporate Research
281. Inductively Coupled Plasma Atomic Emission Determination of the Amount of an Iron Oxide-Based Ink Transferred to a Pharmaceutical Tablet During the Manufacturing Process. K.D. Dunn*, A. Steele, T. Garcia, J. Kristof, R. Hilborn; Glaxo Inc
282. Determination of Trace Metals in Environmental Samples Using Fast Graphite Furnace AAS Techniques. G.D. Taylor, Jr.*; Bionomics Laboratory Inc
283. Sensitivity Enhancement of Electric Field Measurements of Surface Wave Plasmas for Gas Chromatography Detection. G.H. Webster, C.B. Boss*; North Carolina State University
284. Sample Matrix Influences on Atomization and Ionization in Glow Discharge Mass Spectrometry. J. Tend*, F.L. King; West Virginia University
285. Trace Element Analysis Using Modulated Glow Discharges. C. Pan, F.L. King*; West Virginia University
286. Correlation Between Plasma Observables and Polyatomic Ions in Glow Discharge Mass Spectrometry. G. Chen*, F.L. King; West Virginia University
287. Tandem Mass Spectrometry for the Characterization of Glow Discharges. L.R. Meadows*, F. Fotia, F.L. King; West Virginia University
288. Low Level Determination of Copper and Zinc in Water and Wastewater by Graphite Furnace Atomic Absorption and Inductively Coupled Plasma Atomic Emission Spectroscopy. B.M. Patel*, A.H. Ali, D.D. Johnson, C.T. Mansfield; Texaco Inc
289. Instrumentation for Current Control in a Pulsed Hollow Cathode Discharge. J.A. Moore, P.D. Mixon, C.W. Bray, S.T. Griffin, J.C. Williams*; Memphis State University
290. Low PPB Measurements Using a Sequential ICP-AES with an Ultrasonic Nebulizer. J. Shkolnik*, T. Nham, G. Tyler; Varian Associates Inc
291. Hydride Trapping on Palladium and Subsequent Determination by Electrothermal Vaporization Inductively Coupled Plasma Mass Spectrometry (ETV-ICP-MS). J.A. Caruso, I. Marawi*, J. Wang; University of Cincinnati
292. Trace Metal Analysis of Coal Fly Ash by RF Glow Discharge Mass Spectrometry (RF GD/MS) and Inductively Coupled Plasma Mass Spectrometry (ICP/MS). J.J. Giglio, J. Wang, J.A. Caruso*; University of Cincinnati
293. Determination of Selenium in Human Red Blood Cells by Graphite Furnace Atomic Absorption Spectrometry. S. Yadav*, J.P. Day; University of Manchester
294. Atomic Absorption Spectroscopy with a Flame Emission Source. C.P. Calloway, Jr.*, B.T. Jones; Wake Forest University
295. Material Verification of 90/10 Platinum/Iridium Parts by Zn Fusion-ICP/AES. K.D. Soderquist; Medtronic Inc
296. Determination of Siloxanes in Spent Sulfuric Acid. V.J. Abraham, J.D. Hatheway, D.A. Anderson, E.M. Skelly Frame*; GE Corporate Research
297. Implementation of a Direct Injection Nebulizer (DIN) for Analysis of Volatile Hydrocarbon Samples and Analytes. M.A. Shepherd*, A.R. Forster, G.J. Kamla; Shell Development Co
298. Two-Step Laser-Enhanced Atomic Fluorescence of Mercury. W. Resto*, R. Badini, J.D. Winefordner; University of Florida
299. Linearization of Electrothermal Atomic Absorption Calibration Curves. C.B. Boss*, J. Bray, C. Hamilton; North Carolina State University
300. Use of PC/Absorb to Collect Atomic Absorption Data for Stray Light Linearization Computations. J.C. Hamilton; Hamilton and Associates
301. PC Databases from NIST. J. Gallagher; NIST
302. Implementation of a Direct Injection Nebulizer (DIN) for Analysis of Volatile Hydrocarbon Samples and Analytes. M.A. Shepherd*, A.R. Forster, G.J. Kamla; Shell Development Co
303. Determination of Rare Earth Elements (REEs) and Transition Metals in Natural Waters by Chelation Preconcentration-ICP-MS. J.E. Vaive*, G.E.M. Hall, J.C. Pelchat; Geological Survey of Canada
304. New Method for the Determination of Metalic Elements by Atomic Absorption Spectrophotometry in Crude Oils and Petroleum Products. O. Platteau, J. Medina*; INTEVEP, S.A.
305. The Nature of the C6H4X-Ions (X=F,Cl,Br,I) In the Gas Phase. J.M. Riveros*, H.V. Linnert; Universidade de Sao Paulo

WEDNESDAY MORNING

Tomas Hirschfeld Award Symposium – Part I
M. Evans; Conoco, Organizer
Franklin Rooms 1 and 2
M. Evans; Conoco, Presider

8:40—306. Photophysical Properties of Polycyclic Aromatic Compounds: Characterization and Probe Character. S.A. Tucker*, W.E. Acree Jr.; University of North Texas
9:00—307. Development, Characterization and Application of EOF-Driven Capillary Isoelectric Focusing. J. Mazzeo*, I. Krull; Northeastern University
9:20—308. Molecular Analyses of Frozen Aqueous Solutions Using Ion-Beam-Induced Desorption and Multiphoton Resonance Ionization. M.H. Ervin*, M.C. Wood, N. Winegrad; Pennsylvania State University
9:40—309. Comparison of a New Liquid Extraction Method to Traditional Methodology in the Recovery of Trace Level Organics from Aqueous Environmental Matrices. L.C. Schrier, K.P. Kelly*, T.S. Wood; ABC Laboratories Inc
10:00 BREAK
10:40—310. High Sensitivity Fluorescence Detectors and Their Applications in High Speed DNA Sequencing Analysis by Capillary Gel Electrophoresis. D.Y. Chen*, N.J. Dovichi; University of Alberta
11:00—311. Determination of Trace and Ultratrace Chlorine by Graphite Furnace Laser Excited Molecular Fluorescence Spectrometry of Indium Monochloride. E.G. Su*, R.G. Michel; University of Connecticut
11:20—312. Digital Imaging in Atomic Absorption Spectrometry. J.C. Hutton*, C.L. Chakrabarti, A.K. Gilmutdinov, R. Mrasov; Carleton University
11:40—313. Investigation of Sub-molecular Liquid Crystal Dynamics by use of Step-Scan and Stroboscopic Continuous-Scan FT-IR. V.G. Gregoriou*, H. Toriumi, J.L. Chao, R.A. Palmer; Duke University

Secondary Ion Mass Spectrometry
D. Leta; Exxon Research & Engineering, Organizer
Constitution Rooms A and B
D. Leta; Exxon Research & Engineering Co, Presider

8:20—314. Chemical Imaging in Biology and Medicine Using Ion Microscopy. G.H. Morrison; Cornell University
9:00—315. Compositional SIMS Quantitation Using the CsM+ Molecular Ion Method. H.E. Smith*, W.C. Harris; Digital Equipment Corp
9:20—316. Applications of SIMS in Modern Metallurgy. J.A. Jackman; CANMET
10:00 BREAK
10:40—317. Analysis of Trapped and Quenched Silicate Melt by SIMS: Application to Volcanic Eruptions. J. Webster; American Museum
11:00—318. High Resolution SIMS Imaging of FCC Catalysts. J.K. Lampert*, M. Deeba, G.S. Koermer, R. Levi-Setti, J. Chabala; Engelhard Corporation
11:40—319. Understanding Oxide Formation Across Liquid Surfaces: An Imaging SIMS Analysis. J.M. Chabala*, R. Levi-Setti; University of Chicago

Electrothermal Atomizers in Atomic Absorption Spectrometry: Fundamentals and Applications
G. Rayson; New Mexico State University, Organizer
Grand Ballroom D
G. Rayson; New Mexico State University, Presider

8:40—320. Effect of High-Intensity Source Pulsing on Detection Limits for Graphite Furnace AAS with a Continuum Source and Photodiode Array Detection. J.M. Harnly; USDA, ARS, BHNRCC
9:00—321. Simultaneous Determination of Cadmium and Calcium in Urine by Continuum Source Atomic Absorption Spectrometry. R. Fernando*, F.K. Ennever, B.T. Jones; Wake Forest University
9:20—322. Characteristic Masses and Detection Limits for Graphite Furnace AAS with A Continuum Source and Photodiode Array Detector. J.M. Harnly; USDA, ARS, BHNRC

9:40—323. Multielement Detection by Electrothermal Atomization Mass Spectrometry Using Second Surface Trapping. A.J. Scheie*, J.A. Holcombe; University of Texas

10:00 BREAK

10:40—324. Determination of Ultra-Trace Amounts of Copper, Cadmium, Lead and Cobalt in Seawater by Graphite Furnace Atomic Absorption and Laser-Excited Fluorescence with a Flow Injection On-line Preconcentration System. M. Wang*, A.I. Yuzefovsky, R.G. Michel; University of Connecticut

11:00—325. Use of Recirculating Loop Flow Injection Techniques for Sample Introduction in Graphite Furnace Atomic Absorption Spectrometry. R.M. LaRue*, J.F. Tyson; University of Massachusetts

11:20—326. On-Line Separation and Preconcentration for Electrothermal Atomic Absorption Spectrometry. L.C. Azeredo, R.E. Sturgeon*; NRC – Canada

11:40—327. Determination of As and B by Hollow Cathode – Furnace Atomization NonThermal Excitation Spectrometry. C. Smith*, P. Riby, J. Harnly; USDA, ARS, BHNRC

Advances in Glow Discharge Sources for Atomic Spectrometry

R.K. Marcus; Clemson University, Organizer
Grand Ballroom F
R.K. Marcus; Clemson University, Presider

8:20—328. FAPES: A Biased Approach. R.E. Sturgeon*, V.T. Luong, S.N. Willie; NRC of Canada

8:40—329. Characterization of a Helium Plasma in Hollow Anode – FANES. P.G. Riby*, J.M. Harnly; USDA

9:00—330. Effects of Water Vapor on Plasma Reactions in Glow Discharge Mass Spectrometry (GDMS). W.W. Harrison*, P.H. Ratcliff; University of Florida

9:20—331. Determination of Non-Metals in Vapors by Gas-Sampling Glow Discharge-Atomic Emission Spectrometry. R. Pereiro, T.K. Starn, G.M. Hieftje*; Indiana University

9:40—332. Thermabeam Aqueous Sample Introduction into a Hollow Cathode Discharge. J. You, R.K. Marcus*; Clemson University

10:00 BREAK

10:40—333. The Glow Discharge as an Analytical Emission Source for Fourier Transform Spectroscopy. M.R. Winchester*, J.C. Travis, M.L. Salit; NIST

11:00—334. Applicability of Low-Pressure Discharges to the Analysis of Nonconducting Materials. S. Caroli*, O. Senofonte, M.G. De, M. Tamba, I.B. Brenner; Istituto Superiore

11:20—335. The Application of a Microwave-Boosted Glow Discharge Lamp to the Analysis of Nonconducting Powders. F. Leis; Institut für Spektrochemie

11:40—336. Practical Applications of Quantitative Depth Profile Analysis by Glow Discharge Atomic Emission Spectrometry. J. Mitchell*, J. Shirley, V. Caldwell; LECO Corp

Applications of ICP-Mass Spectrometry

E. Pruszkowski; Perkin-Elmer Corporation, Organizer
Grand Ballroom A and B
E. Pruszkowski; Perkin-Elmer Corporation, Presider

8:20—337. An On-Line Method for the Analysis of Seawater by Inductively Coupled Plasma Mass Spectrometry. J.W. McLaren, J.W.H. Lam, S.S. Berman, M.A. Azeredo; NRC of Canada

9:00—338. The Measurement of Trace Elements in Large Rivers by ICP-MS. H.E. Taylor*, J.R. Garbarino; U.S. Geological Survey

9:20—339. Characterization of Trace Metals in Ground Water in Southern Nevada by ICP-MS. K. Zarrabi*, M. Amano, V. Hodge, K. Stetzenbach; University of Nevada, Las Vegas

9:40—340. Determination of Sources of Lead in Tap Water by ICP-MS. G.S. Hall*, E. Murphy; Rutgers University

10:00 BREAK

10:40—341. Source Identification of Lead and Other Metals at Mineral Processing Sites Using Inductively Coupled Plasma Mass Spectrometry. M. Ketterer; U.S. EPA

11:00—342. Comparison of ICP-MS with Zeeman GFAAS for the Assessment of Thallium Exposure. D.E. Nixon*, M.M. Kershisnik, T.P. Moyer, K.O. Ash; Mayo Clinic

11:20—343. Analysis of Mercury in Vacuum Pump Oil (U). M.E. Chisum*, A.A. Duncan; Mason&Hanger-Silas Mason

11:40—344. Multielemental Analysis of Tree Rings by ICP-MS. X. Wu*, G.S. Hall, E.T. Williams; Rutgers University

12:00—345. Determination of Radium 226 in Drinking Water by ICP-MS. V.F. Hodge, G.A. Laing*; Lockheed

Student Award Symposium in Chromatography

L. Lakritz; USDA, Organizer
Grand Ballroom E
L. Lakritz; USDA, Presider

8:20—346. Separation and Identification of the Metabolites of Para-Aminophenol. Z. Yan*, J.G. Nikelly; Philadelphia College

8:40—347. Analysis of Lipase Catalyzed Interesterification of Triglycerides by High-Performance Liquid and Gas Liquid Chromatography. K.A. Petruso*, T.A. Foglia; Chestnut Hill College

9:00—348. HPLC Separation of Biogenic Polyamines Using 2-(1-Pyrenylethyl) Chloroformate as a New Fluorophoric Derivatizing Reagent. M.A. Cichy, D.L. Stegmeier, H. Veening*, H.D. Becker; Bucknell University

9:20—349. Gradient HPLC Separation of Platinum-Labeled Adducts of Cytochrome. A.M. Bonser*, O.A. Moe; Lebanon Valley College

9:40—350. The Principal Component of Human Body Odor. The Synthesis and Chromatographic Separation of (E)- and (Z)-3-Methyl-2-Hexenioc Acid. G. Preti, X.N. Zeng, N.H. Nemeroff*, S. Meyerschoff; Philadelphia College

10:00 BREAK

10:40—351. Chromatographic and FT-IR Spectroscopic Studies of a Series of Monosubstituted Ferrocenes. D.M. Byler, J.F. Troy*, J.M. Axten, N.H. Nemeroff; Philadelphia College

11:00—352. The Synthesis and Chromatographic Separation of 4-(Ferrocenyl)3-Substituted Pyrrole Derivatives. N.H. Nemeroff, J.M. Axten*; Philadelphia College

11:20—353. Liquid-Liquid Equilibria of Polymer Solutions. D.J. Gevekc*, R.P. Danner; Pennsylvania State University

11:40—354. Effect of Chain Length of *n*-Alcohol Modifiers on the Internal Viscosity of Sodium Dodecyl Sulfate Micelles. D.A. Piasecki*, M.J. Wirth; University of Delaware

Advances in Biomolecule Separations

R.A. Barford; USDA, Organizer
Adam's Ballroom B
R.A. Barford; USDA, Presider

8:20—355. Preparative HPLC of Oligosaccharides. A.T. Hotchkiss, Jr*, K.B. Hicks; USDA, ARS ERRC

8:40—356. Characterization of Starches by HPSEC with Viscosity/Refractive Index Detection. M.L. Fishman*, L. Rodriguez, P.D. Hoagland; U.S. Dept of Agriculture

9:00—357. Applications of Salt-Polymer Two-Phase Extraction Systems to Purify Proteins and Nucleic Acids. K.D. Cole; NIST

9:20—358. Recent Biomedical Applications of Field-Flow Fractoination. K.D. Caldwell*, H. Li, J. Li, Y.S. Gao, B. Langwost; University of Utah

9:40—359. Analytical Uses of Affinity Chromatography: Probing Macromolecular Recognition and Assembly Using Immobilized Ligands. I. Chaiken*, D. Myszka, D. May, J. Culp; SmithKline Beecham

10:00 BREAK

10:40—360. High-Resolution Separation Methods for DNA Polymerase Chain Reaction Products. D.J. Reeder*, M. Kline, K. Srinivasan; NIST

11:00—361. Analysis and Characterization of Recombinant Proteins by High Performance-Capillary Electrophoresis (HPCE). K. Tsuji; The Upjohn Company

11:20—362. Coupled Microcolumn Separations and Time-of-Flight Mass Spectrometry for the Characterization of Biomolecules. M.L. Lee*, E.D. Lee; Brigham Young University

11:40—363. Sulfonamide/Cyclodextrin Complexes: Conformations and Association Energies from Molecular Modeling Studies. G. King*, R.A. Barford; USDA, ARS

12:00—364. Electro- embrane Sample Preparation for HPLC Analysis of Veterinary Pharmaceuticals in Biofluids. J.D. Brewster*, E.G. Piotrowski; U.S. Dept of Agriculture

New Ways of Looking at Surfaces: New Methods for New Materials

J.L. Anderson; University of Georgia, Organizer

Delaware Rooms 1 and 2

J.L. Anderson; University of Georgia, Presider

8:20—365. Scanning Tunnelling and Atomic Force Microscopic Studies of Organic Monolayer Films. M.D. Porter*, C.A. Alves, J. Zak, E.L. Smith; Iowa State University
9:00—366. Surface Chemistry of Compound Semiconductor Electrodes. J.L. Stickney; University of Georgia
9:40—367. Infrared Spectroscopy as a Probe of Ionic Interactions at the Electrode/Solution Interface: Elimination of Bulk Interferences. C. Korzeniewski*; V.B. Paulissen; University of Michigan
10:00 BREAK
10:40—368. In Situ Structural Studies of UPD Layers Using X-Ray Diffraction. O.R. Melroy; IBM Almaden Research Center
11:20—369. Fluorescence Imaging of Localized Processes at the Electrode/Solution Interface. R.C. Engstrom*, Q. Hongwei, D.L. Fritza; University of South Dakota

Mass Spectrometry of Polymers

P. Danis; Rohm and Haas, Organizer

Adams A

P. Danis; Rohm and Haas, Presider

8:30—370. Tandem Mass Spectrometry (MS/MS) of Poly(Ethylene Glycol) Proton- and Deuteron-Attachment Ions. R.P. Lattimer; BF Goodrich
9:00—371. Secondary Ion Mass Spectrometry of Polymers. D.M. Hercules; University of Pittsburgh
9:30—372. Characterization of Architectured Polymers by K$^+$IDS Mass Spectrometry. W.J. Simonsick Jr.; E.I. duPont de Nemours Co
10:00 BREAK
10:40—373. Polymer Analysis by Laser and Field Desorption Mass Spectrometry. C.E. Costello, P. Juhasz*; MIT
11:10—374. Mass Spectrometric Methods for the Characterization of Oligomeric and Polymeric Species. K. Rollins; ICI
11:40—375. The Characterization of Water Soluble Polymers by Field and Laser Desorption Mass Spectrometry. P.O. Danis*, D.E. Karr, F. Mayer, A. Holle; Rohm and Haas Company

New Directions in Chiro-optical Spectroscopy

L. McGown; Duke University, Organizer

Grand Ballroom C

D. Bobbit; University of Arkansas, Presider

8:20—376. Magneto-optical Rotation and Kerr Effect Detection in Liquid Chromatography. E.S. Yeung*, X. Xi, T. Lee; Iowa State University
8:40—377. New Polarization Modulation Techniques in Raman Optical Activity. L.A. Nafie; Syracuse University
9:20—378. Ultrafast Circular Dichroism Spectroscopy. J.D. Simon; University of California
10:00 BREAK
10:40—379. Studies of Induced Chirality Using Lifetime-Resolved Fluorescence-Detected Circular Dichroism. L.B. McGown*, K. Wu, L. Geng, M.A. Jarrell; Duke University
11:00—380. Thermal Lens Detection of Circular Dichroism. C.D. Tran; Marquette University

Chemometrics in Process Analysis

D. Ihlman; University of Washington, Organizer

Gettysburg Rooms 2, 3, and 4

D. Ihlman; University of Washington, Presider

8:20—381. Biased Regression for Identification of Dynamic and Statistical Process Control Models. B.M. Wise, D.J. Veltkamp*; Battelle Labs
8:40—382. Ultrasonic Investigations of Polymerization Reactions. R.S. Bear, Jr., S.D. Brown*; University of Delaware
9:00—383. Process Chemometrics Applications from Norwegian Metallurgical and Mineral Extraction Industries. K.H. Esbensen; Center for Industrial Research
9:20—384. In Situ Analysis of High-Level Radiation Waste Tanks Using Chemometrics. P. O'Rourke; Westinghouse
9:40—385. Automatic Updating of Process Models. D.J. Veltkamp; University of Washington
10:00 BREAK
10:40—386. Constrained Principal Spectra Analysis (CPSA). J.M. Brown; Exxon Research & Engineering Company
11:00—387. An Advanced Process Composition Monitoring Environment. J. McGuire*, B. McIntosh, E. Barnes, J.M. Brown, B.N. Perry; KVB Analect
11:20—388. Chemometric Estimate of Gasoline Properties: Global or Local Models. J.S. Gethner; Adaptive Analyzer Technology
11:40—389. Model Selection and Validation for On-Line Processes. D.A. Russell; DuPont Engineering

WEDNESDAY AFTERNOON

Capillary Chromatography

Adam's Ballroom A

S. Olesik; Ohio State University, Presider

1:40—390. High-Purity Supercritical Fluids – Standards and Modifiers. S.B. Miller*, R.G. Heckert; Scott Specialty Gases
2:00—391. A Comparison of Supercritical Fluids and Fluidity-Enhanced Liquid for Extraction Chemistry. S.V. Olesik*, Y. Cui; Ohio State University
2:20—392. The Separation and Identification of Picogram Levels of PCBs by GC/Cryogenic Trapping FT-IR. D.J. Johnson*, B. Smith, W. McCarthy; Bio-Rad Analytical Instruments
2:40—393. Capillary Column Gas Chromatography Formercury Speciation. C. Bi; University of Cincinnati
3:00 BREAK
3:20—394. The Maximum Injection Volume onto a Capillary Column with a Retention Gap. R.E. Murphy; Rohm and Haas Company
3:40—395. Capillary GC Columns for the Resolution of Co-Planar PCB Isomers. D. Rood*, M. Hastings; J&W Scientific
4:00—396. Capillary Chromatography Using Porous Glassy Carbon. S.V. Olesik*, T.M. Engel, L.D. Giddings; Ohio State University
4:20—397. New Applications of Metal Capillary Columns for High-Temperature GC. J. Buyten, J. De Zeeuw, N. Vonk, J. Sparks*; Chrompack Inc

Anachem Award Symposium

M.L. Lee; Brigham Young University, Organizer

Adam's Ballroom B

M.L. Lee; Brigham Young University, Presider

1:40—398. Microcolumn Separation Systems: Past, Present, and Future. M.V. Novotny; Indiana University
2:20—399. Two-Dimensional Separations by LC-CE. J.W. Jorgenson*, J.P. Larmann, A.W. Moore, A.V. Lemmo; University of North Carolina
2:40—400. Impact of Separation Science on the Quality of Pharmaceuticals Under Development. J. Vessman*, O. Gyllenhaal, K.E. Karlsson, S.O. Jansson, J. Snopek; Astra Hassle AB
3:00 BREAK
3:20—401. Analytical Applications of Microelectrodes. R.M. Wightman; University of North Carolina
3:40—402. Fluorescence Quenching as a Detection Method for Liquid Chromatography. V.L. McGuffin*, S.H. Chen, F.K. Ogasawara, Y. Wang; Michigan State University
4:00—403. Separation of Chiral Pharmaceuticals by Capillary Electromigration Techniques. H. Soini*, M.V. Novotny; Indiana University
4:20—404. High-Speed Chromatography Mass Spectrometry. M.L. Lee*, Z. Liu, E.D. Lee; Brigham Young University

Chromatography Poster Session

Exhibition Hall

3:30–5:30

405. Unbreakable Metal Capillary Columns With Chemically Bonded Phases for Process GC. J. Buyten, N. Vonk, J. De Zeeuw, J. Sparks*; Chrompack Inc

406. The Triple Detector Concept for SEC. D.T. Gillespie, W.W. Yau*, M.A. Haney; Viscotek Corp

407. Identification of Pharmaceutical and Food Contaminant Using FT-IR/Microscopy. S.C. Yasui*; U.S. Food & Drug Administration

408. Determination of Protein Secondary Structure via FTIR Spectroscopy and Infrared Microscopy. M.H. Huang*, N. Asgari; Bristol-Myers Squibb

409. Mercury Catalyzed Dissolution of Aluminum. R.P. Paradkar*, R.R. Williams; Clemson University

410. Organic Acid Analysis by Ion Chromatography/Particle Beam Mass Spectrometry. J.N. Alexander IV*, C.J. Quinn; Rohm and Haas Co

411. Characterization of Chain Orientation in Roll-Drawn Polypropylene by Polarized Raman and Birefringence. P.M. Killough*, D.W. Mead, C.K. Harris; Shell Development Co

412. Application of Laser Spectroscopy to Decontaminate Metals. Y.M. Hamrick*, R.J. Lipert, M.C. Edelson; Iowa State University

413. Raman Versus Infrared Spectral Libraries and Library Matching Algorithms. M.P. Fuller*, T.R. Peterson; Nicolet Instrument Corp

414. Evaluation of Remote ATR Methods for Nondestructive FT-IR Analysis. F.J. Wessner*, T. May; Nicolet Instrument Corp

415. Characterization of Coated Interfaces Using Fourier Transform Infrared Microspectroscopy. T. Nishioka*, N. Kitagawa, N. Teramae, Y. Gohshi; Idemitsu Petrochemical Co

416. NMR Study of GnRH Antagonist Analog Peptides in Solution. M.I. Liff*; Philadelphia College

417. HPLC Determination of Diastereomeric Purity in Lometrexol Sodium Using Beta-Cyclodextrin as a Movile Phase Additive. L.M. Osborne*, G.M. Wilson; Eli Lilly & Company

418. The Interaction of Aluminum and Osteocalcin Using Aluminium-26 Tracer and Chromatographic Studies. L.J.A. Evans*, J.P. Day; University of Manchester

419. Determination of Radiostrontium in Environmental and Biological Samples Using a Strontium-Specific Ion Chromatography Column. T.L. Brand*, J.P. Day; University of Manchester

420. High-Pressure Liquid Chromaotgraphic Method for the Determination of SCH 39304 in Plasma. H. Kim*, C. Lin; Schering Corporation

421. Carbon-13 NMR Sequence Analysis of Ethylene-α Methylstyrene Copolymers. T. Kanezaki*, M. Kijima, T. Asakura, K. Kume; Idemitsu Petrochemical Co

422. Enhancement in Large Ion Detection Efficiency for a Dual Microchannel Plate Time-of-Flight Mass Spectrometer. R.C. King, K.G. Owens*; Drexel University

423. Characterization of Properties of Phenolic Triazine Resin. M.A. Kimble; Allied-Signal Aerospace

424. Separation of Mn(II)DPDP and Possible In Vivo Metabolites in Plasma by HPLC. J.J. Lai*, G. Jamieson, C.A. Chang; Salutar Imaging

425. Various Co-immobilization Parameters of Enzyme, Mediator, and Poly-Electrolyte During the Anodic Electropolymerization of Pyrrole for Use in Glucose Biosensor. P. Caglar*, G.E. Wnek; Hacettepe University

426. UV Lidar Detection of Biological Aerosols. M.S. DeSha, A. Wong, S.D. Christesen*, J. Butler, C.N. Merrow, M. Wilson; U.S. Army Chemical Department

427. FT-IR Analyses of Plant Germplasm Viability. S. Sowa; USDA/ARS

428. Multiple Matrix Deposition Speeds for GC-Matrix Isolation FT-IR/MS. C. Klawun*, N. Ragunathan, C.L. Wilkins; University of California

429. Determination of Ester Composition of Sucrose Fatty Acid Polyesters in Chocolate by Liquid Adsorption Chromatography. S. Takahashi*, S. Ohsone, M. Suzuki; Mitsubishi Kasei Corp

Tomas Hirschfeld Award Symposium – Part II
M. Evans; Conoco, Organizer
Franklin Rooms 1 and 2
M. Evans; Conoco, Presider

1:40—430. Trapping Efficiencies of Capillary Cold Traps for C_2-C_{10} Hydrocarbons. X.L. Cao; Lancaster University

2:00—431. Determination of Trace Metals in Solid Samples Via On-Line Digestion Flame Atomic Absorption Spectrometry. T.J. Gluodenis, Jr*, J.F. Tyson; University of Massachusetts

2:20—432. A Quantitative Method to Detect Explosives and Selected Contaminants in Soil Samples by Fourier Transform Infrared Spectroscopy. M. Clapper-Gowdy*, J. Demirgian, K. Lang, G. Robaittaille; Argonne National Lab

2:40—433. Surface Enhanced Raman (SER) Optical Fiber Probes. K.I. Mullen*, K. Carron; University of Wyoming

3:00 BREAK

3:20—434. New Analytical Capabilities for Fourier Transform Ion Cyclotron Resonance Mass Spectrometry (FT/ICR/MS). P.A. Limbach*, A.G. Marshall; Ohio State University

Student Award Symposium on Chromatography II
L. Lakritz; USDA, Organizer
Grand Ballroom E
L. Lakritz; USDA, Presider

1:40—435. Random Walk Treatment of Band Broadening for Charged Solutes in Micellar Electrokinetic Capillary Chromatography. K.R. Nielsen*, J.P. Foley; Villanova University

2:00—436. Electroosmotic Flow Control via an Applied Radial Voltage for Capillary Electrophoresis. M.A. Hayes*, A.G. Ewing; Penn State University

2:20—437. Retention Index for Micellar Electrokinetic Capillary Chromatography (MECC). E.S. Ahuja*, J.P. Foley; Villanova University

Element Specific Detection in Chromatography Using Plasmas
G. Long; Virginia Polytechnic Institute, Organizer
Grand Ballroom D
G. Long; Virginia Polytechnic Institute, Presider

1:20—438. The Responses of the Microwave-Induced Plasma Reflected Power Detector to Permanent Gases, Alkanes and Alcohols. C.B. Boss*, R.M. Alvarez Bolainez; North Carolina State University

1:40—439. Performance of an Echelle-Based He-MIP-AES Detector for SFC. G.L. Long, G. Ducatte*; Virginia Tech

2:00—440. Improved Analyte Transport Efficiency with a Moving Band Interface for LC/MIP. P.B. Mason*, J.W. Carnahan; Northern Illinois University

2:20—441. Diagnostics and Chemical Reactions in an Atomic Emission Detector for GC. J.J. Sullivan*, B.D. Quimby; Hewlett-Packard Company

2:40—442. Exploring the Periodic Table with GC-AED. P.C. Uden*, J. Seeley, J. Slowick, Y. Zeng; University of Massachusetts

3:00 BREAK

3:20—443. Atomic Emission Detection in Gas Chromatography. B.D. Quimby*, J.J. Sullivan; Hewlett-Packard Company

3:40—444. Application of GC-AED in the Petroleum Industry. J.J. Kosman*, R.G. Lukco; BP Research

Advances in Glow Discharge Sources for Atomic Spectroscopy
R.K. Marcus; Clemson University, Organizer
Grand Ballroom F
R.K. Marcus; Clemson University, Presider

1:20—445. Parametric Evaluation of Sputtering in an RF Atomizer for Atomic Absorption Spectrometry. C.L. Chakrabarti*, G. Absalan, J.C. Hutton, M.H. Back, C. Lazik, R.K. Marcus; Carleton University

1:40—446. Analytical Figures of Merit for RF Glow Discharge Atomic Emission Spectrometry. T. Harville*, R.K. Marcus; Clemson University

2:00—447. Analysis of Nonconductive Coatings Used in Various Industrial Applications. P. Hunault*, T. Nelis, J.L. Baudoin, M. Chevrier, R. Passetemps; Jobin Yvon

⊡2:20—448. Comparison of Several Magnetically Enhanced RF Glow Discharge Source Configurations. M.J. Heintz*, G.M. Hieftje; Indiana University

2:40—449. Investigations of Plasma Excitation/Ionization Mechanisms in Low-Pressure Glow Discharge Devices. J. Drozdick, A.D. Augstadt, J. Vizzoni, R. Steiner, K.R. Hess*; Franklin & Marshall College

3:00 BREAK

3:20—450. The Effects of Alternative Discharge Gases on Ion Signal Profiles in Pulsed Glow Discharge Mass Spectrometry. S.K. Ohorondnik*, W.W. Harrison; University of Florida

3:40—451. Evaluation of Alternative Plasma Gases for RF Glow Discharge. J. Giglio, J.A. Caruso*; University of Cincinnati

4:00—452. Sampling Radio-Frequency Powered Glow Discharges with a Quadrupole Ion Trap. S.A. McLuckey, G.L. Glish, D.C. Duckworth*; Oak Ridge National Lab

4:20—453. Elemental Analysis by RF-GDMS: Instrumentation and Analytical Capabilities. J.A. Olivares*, A.K. Huff, E.M. Garcia, N.C. Schroeder; Los Alamos National Lab

4:40—454. Characteristics of a New RF-GDMS System. C. Shick*, R.K. Marcus; Clemson University

Application of ICP-Mass Spectrometry
E. Pruszkowski; Perkin Elmer Corporation, Organizer
Grand Ballrooms A and B
E. Pruszkowski; Perkin Elmer Corporation, Presider

1:40—455. Recent Developments in Flow Injection ICP-Mass Spectrometry. E.R. Denoyer*, Q. Lu, A. Stroh; Perkin-Elmer Corporation

2:00—456. Multielemental Analysis of Soils by Flow Injection with Slurry Nebulization and ICP-MS. D. Beauchemin*, M.J. Payer, H.E. Jamieson, G.W. Van Loon; Queen's University

2:20—457. Investigations into the Use of Methane Addition to ICP-MS to Reduce Polyatomic Interferences. M. Ford, S. Hill, R.C. Hutton*; VG Elemental

2:40—458. Enhancement of Some Analyte Signals by Carbon Compounds in ICP-MS. G.F. Wallace*; Perkin-Elmer Corporation

3:00 BREAK

3:20—459. Recent Studies on Helium Inductively Coupled Plasma Mass Spectrometry. S.H. Nam*, H. Zhang, C. Hsiech, A. Montaser, W. Masamba; George Washington University

3:40—460. Evaluation of a High-Efficiency Nebulization System Coupled to a High-Resolution ICP-MS Instrument. N.M. Reed, R.C. Hutton*, A. Kingston, G. Gibson; VG Elemental

4:00—461. Performance Evaluation of ICP-MS with Sample Introduction by Ultrasonic Nebulization. U. Voellkopf*, W. Barger, A. Blum; Perkin-Elmer GmbH

4:20—462. Experimental Studies of Ion Kinetic Energies in ICP-MS. S.D. Tanner; SCIEX

New Ways of Looking at Surfaces: New Methods for New Materials
J.L. Anderson; University of Georgia, Organizer
Delaware Rooms 1 and 2
J.L. Anderson; University of Georgia, Presider

1:40—463. Spectroscopic and Electrochemical Characterization of Chemically Modified Electrodes. T. Cotton; Iowa State University

2:20—464. Electrochemical Investigations of Environmental Redox Components. J.L. Anderson*, C.E. Todd, M.C. Delgado, N.L. Wolfe; University of Georgia

3:00 BREAK

3:20—465. Electrodeposition Copper on Polypyrrole Films. M. Hepel*, S. Perkins, T. Hepel; SUNY at Potsdam

3:40—466. Potentiometric Solid-State Ion/Biosensors Based on Asymmetric Polyurethane Membranes. D. Liu*, H.D. Goldberg, R.B. Brown, M.E. Meyerhoff; University of Michigan

4:00—467. Simulation Methods and Extended Kalman Filtering for Kinetic Determinations in Step Voltammetry. R.S. Bear, Jr., S.D. Brown*; University of Delaware

4:20—468. Electrochemically Generated Ru(bpy)$_3^{3+}$ for the Direct Chemiluminescent Detection of Amino Acids. D.R. Bobbitt*, W.A. Jackson; University of Arkansas

4:40—469. Dual Potential – Pulsed Amperometric Detection at a Single Electrode Following High Performance Liquid Chromatography. W.R. LaCourse; University of Maryland

Secondary Ion MS
D. Leta; Exxon Research & Engrr Company, Organizer
Consitution Rooms A and B
D. Leta; Exxon Research & Engrr Company, Presider

1:40—470. Recent Advances in Time-of-Flight SIMS of Organic Surface Characterization. R.W. Linton; University of North Carolina

2:00—471. Surface Chemistry of Langmuir-Blodgett and Self-Assembled Molecular and Macromolecular Layers. J.A. Gardella Jr., P.C. Schamberger*; SUNY at Buffalo

2:20—472. Quantitative Surface Analysis of Miscible and Immiscicle Polymer Blends by Static-SIMS and XPS. P. Thompson; Eastman Kodak Company

2:40—473. Applications of an Imaging SIMS-MS/MS Microprobe to Complex Organic Systems. P.J. Todd*, R.T. Short; Oakridge National Lab

3:00 BREAK

3:20—474. Trace Analysis of Molecular Surfaces Using Resonant Laser Ionization Detection. M.J. Pellin; Argonne National Labs

3:40—475. SIMS-SALI of Plasma-Treated Polymer Surfaces. S. Mackay; Perkin Elmer Corp

4:00—476. Static SIMS Determination of the Surface Composition of Polyolefin Blends. P. Brant*, A. Karim, F. Bates; Exxon Chemical Co

4:20—477. Multiphoton Post-Ionization SIMS for Quantitative Analysis. S.R. Bryan*, M. Nicholas, G.J. Havrilla; BP Research

4:40—478. Investigations into Depth Profling Using Glow Discharge Mass Spectrometry. A. Raith, R.C. Hutton*; VG Elemental

New Directions in Chirooptical Spectroscopy II
L. McGown; Duke University, Organizer
Grand Ballroom C
L. McGown; Duke University, Presider

1:40—479. Chiro-optical Luminescence Studies of Intermolecular Chiral Discriminatory Interactions. D.H. Metcalf, F.S. Richardson*; University of Virginia

2:20—480. Extending Linear Dichroism Measurements into the Vacuum Ultraviolet for Improved Information Content. L. Zhong, W.C. Johnson, Jr.*; Oregon State University

3:00 BREAK

3:20—481. Protein Secondary Structure Determination Using Amide I and II Vibrational Circular Dichroism Bands. T.A. Keiderling*, P. Pancoska; University of Illinois

4:00—482. Polarization Selective Spectroscopy: New Techniques for Studying Complex Biomolecular Structure. D.R. Bobbitt*, K. Ng; University of Arkansas

4:20—483. Vibrational Circular Dichroism Studies of Azide Ligand Binding in Heme Proteins: A Novel Approach for Studying Noncovalent Ligand Protein Interactions. S.A. Asher*, R. Bormett, L. Nafie, T. Freedman; University of Pittsburgh

Acoustic Sensors for Process Analysis
G. Frye; Sandia National Laboratories, Organizer
Gettysburg Rooms 2, 3, and 4
G. Frye; Sandia National Laboratories, Presider

1:40—484. A Temperature-Controlled Multi-SAW Resonator System. W.D. Bowers*, R.L. Chuan, J.W. Grate; Femtometrics

2:00—485. Application of a Temperature Controlled SAW Array Detector. E.B. Overton*, K. Carney, X. Yan; Louisiana State University

2:20—486. Models of Polymer-Coated SAW Sensor Responses to Organic Vapors. S.J. Patrash*, E.T. Zellers, M. Han; University of Michigan

2:40—487. Theory and Application of Acoustic Plate Mode Devices for Sensing in a Fluid Media. J.F. Vetelino*, J.C. Andle, F. Josse, Z. Shana; University of Maine

3:00 BREAK

3:20—488. Piezoelectric and Optical Analysis of Polymeric Films. E.M. Bowman, L.W. Burgess*, S.W. Wenzel, R.M. White; University of Washington

3:40—489. Acoustic Wave Sensors for Real-Time Monitoring of Volatile Organics. G.C. Frye*, R.W. Cernosek, S.J. Martin; Sandia National Labs

4:00—490. PC-Based Digital Signal Processing: Fast Fourier Transform on the Millisecond Timescale. L.E. Bowman, A.P. Wade*; University of British Columbia

THURSDAY MORNING

Surface Science
Delaware Rooms 1 and 2
R. Dluhy; University of Georgia, Presider

8:20—491. The Influence of Temperature on the Orientation and Order in Molecular Monolayers. C.E. Evans*, P.W. Bohn; University of Illinois

8:40—492. Langmuir-Blodgett Monolayer Films Studied by IR Spectroscopy: Substrate-Mediated Structural Reorganization. F.R. Rana, S. Widayati, R.A. Dluhy*; University of Georgia

9:00—493. Combined IR Spectroscopy and Scanning Tunneling Microscopy of Langmuir-Blodgett and Self-Assembled Monomolecular Films. B. Gregory, R.A. Dluhy*; University of Georgia

9:20—494. Hydrocarbon Chain Conformations of Surfactants Adsorbed at Mineral Oxide Surfaces. W.M. Cross, J.D. Miller*; University of Utah

9:40—495. Use of External Reflection Infrared Spectroscopy to Study the Surface Structure and Orientation of Polymer Films. D.J. Walls; Du Pont Company

10:00 BREAK

10:40—496. FT-IR as a Probe for Structural Gradients at Polymer Surfaces. G. Chen*, L.J. Fina; Rutgers University

11:00—497. The Infrared Spectroscopic Evaluation of Slip Additive Migration in Polypropylene Film. D.E. Pivonka*; Hercules Inc

11:20—498. Application of a Single Bounce ATR-IR Geometry to the Study of Orientation and Conformation in Polyester and Polyimide Films. D.J. Walls*, R.S. Peacock; DuPont Co

11:40—499. Langmuir-Blodgett Films of Phospholipid Binary Mixtures: IR Studies of Monolayer Film Composition. F.R. Rana, R.A. Dluhy*; University of Georgia

12:00—500. Phase Transition Behavior of Surfactants at Surfaces. Y.S. Tung*, L.J. Fina; Rutgers University

Elemental Mass Spectrometry

Grand Ballroom F

P. Farnsworth; Brigham Young University, Presider

8:20—501. Time-of-Flight Mass Spectrometry with Atmospheric-Pressure Plasma Ion Sources. P.B. Farnsworth*, M. Wu, M. L. Lee, E. Lee, J. Prince; Brigham Young University

8:40—502. Preliminary Characteristics of a Plasma-Source Time-of-Flight Mass Spectrometer. D.P. Myers*, G.M. Hieftje; Indiana University

9:00—503. Fundamental Studies of ETV-ICP-MS. C.M. Sparks*, T.L. Pinkston, J.A. Holcombe; University of Texas

9:20—504. Helium MIP Quadrupole MS – Some Fundamentals. P. Brown, D. Gregson*, M. Liezers, F. Godwin; VG Elemental

9:40—505. The Application of Spark Sampling ICP-MS to the Quantitative Analysis of Solids. K.A. Ivanovic, D.M. Coleman*, F.W. Kunz, D. Schuetzle; Wayne State University

10:00 BREAK

10:40—506. Trace Detection of Organic Species Using an Atmospheric Pressure RF Glow Discharge Ionization Source. J. Zaho, D.M. Lubman*; University of Michigan

11:00—507. Solution Residue Analysis Using Glow Discharge Mass Spectrometry. C.M. Barshick*, D.C. Duckworth, D.H. Smith; Martin Marietta

11:20—508. Platinum Impurity Analysis by GDMS. D. Fang*, R. Madan, T. Altasas, R. Mathews; Materials Research Corp

11:40—509. Evaluation of Sample Preparation Methods for W/Ti Sputtering Target Materials in the Determination of Alkali Elements by GDMS. D. Fang*, P. Seegopaul; Materials Research Corp

Fluorescence Spectroscopy I

Adam's Ballroom B

F. Bright; SUNY at Buffalo, Presider

8:20—510. A Simple Instrument for Use in Excitation-Emission Fluorescence Polarization Measurements. K.A. Destrampe*, G.M. Hieftje; Indiana University

8:40—511. Correction of Fluorescence Emission and Excitation Spectra. J.W. Hofstraat*, M.J. Lathuhihin; Akzo-ARLA

9:00—512. A Comparison of Stroboscopic and Step-Scan Time-Resolved Spectroscopy. B. Lerner*, M. Daun; Nicolet Instrument Corp

9:20—513. Fluorescence Analysis of Biological Samples in the Near Infrared: Nature of Background Signals and Limitations on Sensitivity. J.W. Silzel*, R.J. Obremski; Beckman Instruments Inc

9:40—514. Comparison Between Covalent Attachment and Physisorption of Fluorescent Probe-Protein Adducts and Complexes. R. Wang*, F.V. Bright; SUNY at Buffalo

10:00 BREAK

10:40—515. Comparison of Inter- and Intramolecular Cyclodextrin Complexes. R.A. Dunbar*, F.V. Bright; SUNY at Buffalo

11:00—516. Ultrafast Evolution of Emission from a Polycyclic Aromatic Hydrocarbon. G.J. Blanchard; Michigan State University

11:20—517. Role of Barium as a Matrix Modifier in the Formation of Magnesium Monofluoride as Determined by Laser Excited Molecular Fluorescence Spectrometry in a Graphite Tube Furnace. A.I. Yuzefovsky*, R.G. Michel; University of Connecticut

11:40—518. $UO^{2+}{}_2$ Luminescence as a Probe of Nonradiative Energy Transfer in Solid $UO^{2+}{}_2$ – *Datura*. G. D. Rayson*, H.Y.D. Ke; New Mexico State University

12:00—519. Solid-State Luminescence Studies of Metal Binding to *Datura Innoxia*. H.Y.D. Ke, G.D. Rayson*, P.J. Jackson; New Mexico State University

Flow Injection Techniques in Atomic Spectroscopy

S. McIntosh; Perkin Elmer Corporation, Organizer

Constitution Rooms 1 and 2

S. McIntosh; Perkin Elmer Corporation, Presider

8:20—520. Enhancement of Atomic Spectroscopies by Flow Injection Analysis. J. Ruzicka; University of Washington

8:40—521. Overcoming Kinetic Limitations of the Flow Injection Atomic Spectrometry Combination. J.F. Tyson; University of Massachusetts

9:00—522. Flow Injection Analysis Extraction as Pretreatment to Atomic Spectroscopy. G.E. Pacey*, P. Spinx, B. Karlberg; Miami University

9:20—523. On-Line Preconcentration of Trace Elements in Biological Materials for Determination by Atomic Absorption Spectrometry. B. Welz*, M. Sperling, X. Sun; Perkin-Elmer GmbH

9:40—524. Evaluation of On-Line Preconcentration Techniques for ICP-MS. D. Beauchemin*, E. Denoyer, Z. Li; Queen's University

10:00 BREAK

10:40—525. Determination of Barium in Water by Flow Injection Sample-to-Standard Addition Method and Inductively Coupled Plasma-Mass Spectrometry. R.M. Barnes*, C.J. Amarasiriwarden, S.F. Durrant, E.G. Bakowska, Y. Israel; University of Massachusetts

11:00—526. Improving Detection Limits by an Order of Magnitude by Coupling Hydride Generation Flow Injection Techniques with Electrothermal Atomization. G. Schlemmer*, M. Feuerstein; Perkin-Elmer GmbH

11:20—527. Dispersion of Discrete Samples in Aerosol Form: Fundamental Studies. J.A. Koropchak*, L.B. Allen, J.M. Davis; Southern Illnois University

11:40—528. Closed-Loop Recirculating Manifold for Matrix Isolation in Flow Injection Flame Atomic Absorption Spectrometry. E. Debrah, M.W. Hinds, J.F. Tyson*; University of Massachusetts

Applications of ICP-Mass Spectrometry

E. Pruszkowski; Perkin-Elmer Corporation, Organizer

Grand Ballrooms A and B

E. Pruszkowski; Perkin-Elmer Corporation, Presider

8:40—529. Elemental Speciation by Inductively Coupled Plasma Mass Spectrometry with Direct Injection Nebulization. S.C.K. Shum, H.M. Pang, R.S. Houk*; Iowa State University

9:00—530. Fast Transient ICP-MS: How Many Ions Are Enough? E.R. Denoyer*, S. Beres; Perkin-Elmer Corporation

9:20—531. Speciation of Arsenic Compounds by Supercritical Fluid Chromatography with Inductively Coupled Plasma Mass Spectrometric Detection. U.T. Kumar*, N.P. Vela, J.G. Dorsey, J.A. Caruso; University of Cincinnati

9:40—532. Low-Pressure Inductively Coupled Plasma Mass Spectrometry as a Detector for Gas Chromatography. T.M. Castillano*, E.H. Evans, J.J. Giglio, J.A. Caruso; University of Cincinnati

10:00 BREAK

10:40—533. Cation Exchange Patterns for 50 Elements in Hydrochloric Acid Media by ICP-MS. V. Hodge*, M. Amano, K. Zarrabi, K. Stetzenbach; University of Nevada, Las Vegas

11:00—534. Inductively Coupled Plasma Mass Spectrometric Detection of Chromium Containing Compounds Using High-Performance Liquid Chromatography. F.A. Byrdy*, U.T. Kumar, J.A. Caruso; University of Cincinnati

11:20—535. Supercritical Fluid Extraction Followed by Inductively Coupled Plasma Mass Spectrometry for the Analysis of Organometallics. N.P. Vela*, J.A. Caruso; University of Cincinnati

11:40—536. Nickel and Vanadium Separation Via Liquid Chromatography with ICP-MS Detection. M.J. Tomlinson*, U.T. Kumar, J.A. Caruso; University of Cincinnati

Atomic Analysis with Laser Techniques

B. Smith; University of Florida, Organizer

Grand Ballroom E

B. Smith; University of Florida, Presider

8:20—537. Laser-Excited Fluorescence in Graphite Furnaces for Metals and Non-Metals. R.G. Michel; University of Connecticut

9:00—538. Resonance Detection of Photons. G.A. Petrucci*, R.G. Badini, B.W. Smith, J.D. Winefordner; University of Florida

9:20—539. Collisional Coupling Rates of Copper and Silver in an ICP and an Air Acetylene Flame Using Fluorescence Dip Spectroscopy. D.J. Robie*, J. Simeonsson, B.W. Smith, J.D. Winefordner; University of Florida

9:40—540. Resonance Line Lasers as Excitation Sources for Atomic Spectrometry. N.L. Ayala*, T.E. Barber, J.D. Winefordner; University of Florida

10:00 BREAK

10:40—541. High-Resolution Spectroscopy of Atomic Vapors Using Diode Lasers. R.J. Lipert*, S.C. Lee, M.C. Edelson; Iowa State University

11:00—542. First Observation of Actinide Elements by Optogalvanic Spectroscopy Using a Diode Laser Source. S.C. Lee*, R.J. Lipert, M.C. Edelson; Iowa State University

11:20—543. Ultratrace Determination of Uranium by Time-Resolved Laser-Induced Fluorescence. C. Moulin*, P. Decambox, P. Mauchien; CEA/DCC/DPE/SPEA/SPS

11:40—544. LEAFS Development for Direct Analysis of Environmental Samples. V. Cheam*, J. Lechner, I. Sekerka, R. Desrosiers; National Water Research Institute

Chemometric Applications of Artificial Neural Networks

P. Gemperline; East Carolina University, Organizer

Gettysburg Rooms 2, 3 and 4

P. Gemperline; East Carolina University, Presider

8:40—545. Minimal Neural Networks Temperature – Jump Training. P. Harrington; Ohio University

9:20—546. Identification of Organic Functional Groups Using Vapor Phase Infrared Spectra and Artificial Neural Networks. B.J. Wythoff*, S.E. Stein; NIST

10:00 BREAK

10:40—547. Spectroscopic Calibration with Artificial Neural Networks: Some Comments on Optimal Configurations. P.J. Gemperline*, S. Li; East Carolina University

11:00—548. The Use of Artificial Neural Networks for Functional Group Analysis in Vapor-Phase Spectra. R.M. McMillan*, P.J. Gemperline, R.C. Morrison, D. Lunney; East Carolina University

11:20—549. Pitfalls of Applying Neural Networks for Multivariate Calibration. A. Lorber; Nuclear Research Centre

11:40—550. Sorting of Waste Plastics Using Near-Infrared Spectroscopy and Neural Networks. M.K. Alam*, S.L. Stanton; Sandia National Labs

Advances in Preparative Chromatography

H.G. Barth; E.I. duPont deNemours & Co, Organizer

Adam's Ballroom A

H.G. Barth; E.I. duPont deNemours & Co, Presider

8:30—551. Optimization of Preparative Chromatography Without Equations. G. Guiochon*, A. Felinger, S. Golshan-Shirazi, S. Jacobson; University of Tennessee

9:00—552. Bulk Chiral Separations for Pharmaceutical Studies. A.J. Mical; DuPont Merck Pharmaceutical Co

9:30—553. Selection and Optimisation of Preparative Liquid Chromatographic Methodologies. G.B. Cox; Prochrom Inc

10:00 BREAK

10:40—554. Strategies for Successful Preparative LC. B.A. Bidlingmeyer; AC Enterprises

11:00—555. Perfusion Chromatography with 50 μm Media. F.E. Regnier*, N. Afeyan; Purdue University

11:40—556. Preparative Chiral Separations Using the Sample Self-Displacement Technique. J. Newburger*, S. Taylor, G. Guiochon; Bristol-Myers Squibb

Dynamic Vibrational Spectroscopy

R.A. Palmer; Duke University, Organizer

Grand Ballroom C

R.A. Palmer; Duke University, Presider

8:20—557. Recent Advances in Dynamic 2D IR Spectroscopy. C. Marcott*, A.E. Dowrey, I. Noda; Procter & Gamble

8:40—558. FT-IR Time Resolved Spectroscopy Using a Dynamically-Aligned Step-Scan FT-IR Spectrometer. R.A. Crocombe*, S.V. Compton, J.D. Leonardi; Bio-Rad Digilab Division

9:00—559. Investigation of Sub-molecular Liquid Crystal Dynamics by Use of Step-Scan and Stroboscopic Continuous-Scan FT-IR. V.G. Gregoriou, H. Toriumi, J.L. Chao, R.A. Palmer*; Duke University

9:20—560. Spectroscopy and Kinectics of Transient Molecules by Time-Resolved Fourier Transform Emission Spectroscopy with 50 ns and 0.25 cm^{-1} Resolution. G.V. Hartland, D. Qin, H.L. Dai*; University of Pennsylvania

9:40—561. Using Stroboscopic FTIR Spectroscopy to Track Ions as they are Transported Across Biomembranes. M.S. Braiman*, A.L. Klinger, R.E. Jonas, T.J. Walter; University of Virginia

10:00 BREAK

10:40—562. Raman Saturation Spectroscopy is a New Technique to Measure Excited State Relaxation Rates. S.A. Asher; University of Pittsburgh

11:00—563. Pulsed Flow Time-Resolved Surface Enhanced Raman Spectroscopy. R.P. Van Duyne*, L. Sun; Northwestern University

11:20—564. Ultrafast Infrared Spectroscopy of Molecular and Protein Dynamics. R.M. Hochstrasser; University of Pennsylvania

11:40—565. Time-Resolved Vibrational Studies of Heme Proteins. R.B. Dyer*, P.O. Stoutland, K.A. Peterson, T. Causgrove, K.A. Bagley, M.W. Schauer, S.E. Plunkett, V.G. Gregoriou, J. L. Chao, R. A. Palmer; Los Alamos National Labs

LC/MS of Drugs, Biomolecules, and Metabolites

W.A. Korfmacher; National Center for Toxicological Research, Organizer

Franklin Rooms 1 and 2

W.A. Korfmacher; National Center for Toxicological Research Presider

8:40—566. Liquid Chromatography/Time-of-Flight Mass Spectrometry with a Pulsed Sample Introduction Interface. A.P.L. Wang, L. Li*; University of Alberta

9:00—567. Determination of Peptide Sequence and Disulfide Bonds by LC/MS and LC/MS/MS. M.S. Bolgar*, G.C. DiDonato; Bristol-Myers Squibb

9:20—568. Analysis of Platelet-Activating Factor and Related Compounds by LC/MS and LC/MS/MS. B.M. Warrack; Bristol-Myers Squibb

9:40—569. The Utility of HPLC/MS Using the Particle Beam Interface. P.A. Lehman*, J. Bloom, A. Radominska; University of Arkansas Medical Sciences

10:00 BREAK

10:40—570. Pharmaceutical, Biotechnology and Environmental Applications of LC/MS and LC/MS/MS Using Atmospheric Pressure Ionization Techniques. M.H. Allen*, B. Shushan, T. Convey, R. Bonner, T. Sakuma, G. Scott; PE-SCIEX

11:00—571. Utility of HPLC/MS/MS for the Analysis of Various Drug Metabolites. K.J. Ng*, E.C. Huang; Schering-Plough Research

11:20—572. Quantitative Analysis of Low-Molecular-Weight Pharmaceutical Compounds by HPLC Combined with Atmospheric Pressure Ionization Mass Spectrometry. D. Wang-Iverson; Bristol-Myers Squibb

11:40—573. The Rapid and Systematic Identification of Drug Metabolites Using LC/MS and LC/MS/MS Techniques. M.S. Lee*, E.H. Kerns, K.J. Volk, J. Liu; Bristol-Myers Squibb Co

Spectroscopic Process Analysis I

P.K. Aldridge; Pfizer Inc, Organizer

Grand Ballroom D

P.K. Aldridge; Pfizer Inc, Presider

8:40—574. On-Line NIR Determination of Water and Methanol in Multiple Streams of an Organic Synthesis Process. P.K. Aldridge*, D.M. Pfisterer, C.L. Evans, M.M. Andino; Pfizer Inc

9:00—575. Semiconductor Lasers and Detectors in Analytical Spectroscopy. G. Patonay*, G. Casay, D. Shealy; Georgia State University
9:20—576. Characterization of Immunochemical-Based Fiber-Optic Sensors. M.J. Sepaniak*, J.R. Bowyer, T. Vo-Dinh, M.M. Armstrong; University of Tennessee
9:40—577. Near Infrared (NIR) Spectroscopy as a Process Analytical Technique for Monitoring the Resolution of Enantiomers via the Formation of a Diastereomeric Salt. P.A. Hailey; Pfizer Central Research
10:00 BREAK
10:40—578. Progress in On-Line Application of Raman Spectrometry for Distillation Process Control. A.A. Garrison*, C.F. Moore, P.D. Hall, M.J. Roberts; University of Tennessee
11:00—579. A Compact Solid-State Spectrophotometer System for Control Applications. D.M. Mayes*, A.G. Cavinato, D.S. Koza; D^2 Development
11:20—580. Customized Electronic Wavelength Switching and Acquisition for Transient Monitoring with Acousto-Optic TFS. D.L. Wetzel*, A.J. Eilert; Kansas State University
11:40—581. High-Speed Sorting and Quality Control with a Solid-State NIR Analyzer. D. Honigs*, S. Knepper, D. Lynch; Katrina Inc
12:00—582. An All-Solid-State NIR Spectrometer for Remote, On-Line Applications. X. Wang*, J. Soos, J. Crystal, J. Havlik; Brimrose Corp of America
12:20—583. Near Infrared Determination of Benzene in Gasoline. S.J. Foulk*, B.E. DeSimas, R.L. Muegge; Guided Wave, Inc

THURSDAY AFTERNOON

IR Microscopy

Delaware Rooms 1 and 2

D. Wetzel; Kansas State University, Presider

1:40—584. Detection Limits in FT-Infrared and FT-Raman Microspectroscopy: How Low Can You Go?. R.T. Carl, C.J. Petty*, J.M. Casper, J.A. Reffner; Nicolet Instrument Corp
2:00—585. A Unit Magnification FT-IR Microscope: Performance Advantages for both Optical and Infrared Microscopy. R.G. Messerschmidt*, D.E. Roberts; Connecticut Instruments
2:20—586. Surface Characterization by FT-IR Microscopy. W.T. Wihlborg; Spectra-Tech Inc
2:40—587. Reflectance Mapping of Mineral Surfaces with an Infrared Microscope. P.J. Stout*, S.L. Hill, K. Kirshnan; Bio-Rad Digilab Division
3:00 BREAK
3:20—588. Study of Potential Intrusion from Packaging of Food Products with FT-IR Microspectroscopy. D.L. Wetzel*, R.L. Wehling; Kansas State University
3:40—589. In Situ Analysis of Brain White Matter in Twitcher and Normal Mice by FT-IR Microspectroscopy. D.L. Wetzel*, S.M. LeVine; Kansas State University
4:00—590. Scanning Infrared Microprobe Analysis of Biological Tissues. J.A. Reffner*, P.A. Martoglio; Spectra-Tech Inc
4:20—591. Quantitative Analysis of Polymers with the Infrared Microprobe. J.A. Reffner*, K.J. Ward; Spectra-Tech Inc
4:40—592. Automated FT-IR Grazing Angle Microscopy for Micro Spatial Chemical Mapping. F.P. Eng*, C.D. Shebib; IBM
5:00—593. Forensic Analysis of Acrylic Fibers by Infrared Microscopy. M.W. Tungol*, E.G. Bartick, A. Montaser; FBI Laboratory

Fluorescence Spectroscopy II

Franklin Rooms 1 and 2

L. McGown; Duke University, Presider

1:40—594. A New Approach to Studies of Size and Size Distribution of Small Molecular Aggregates Using Fluorescence Anisotropy Decay. G. Li*, L.B. McGown; Duke University
2:00—595. A Multidistributional Approach to Fluorescence Probe Studies of Microheterogeneous Systems. L. Geng*, L.B. McGown; Duke University
2:20—596. Effects of Antilipidemic Pharmaceuticals on the Fluorescence Characteristics of Human Serum. R.D. Stevens*, L.B. McGown; Duke University
2:40—597. Improved Characterization of Complex Coal Liquid Samples Using Phase-Resolved-Fluorescence Spectroscopy. J.M. Shaver*, L.B. McGown; Duke University
3:00 BREAK
3:20—598. Characterization of Humic Substances in Aquatic Samples by Phase-Resolved Fluorescence Spectroscopy. S.L. Hemmingsen*, L.B. McGown; Duke University
3:40—599. Studies of Nucleic Acid Binding Using Lifetime-Resolved Fluorescence-Detected Circular Dichroism. M.A. Jarrell*, L.B. McGown, K. Wu; Duke University
4:00—600. Enzyme Behavior in Microaqueous Environments Under Supercritical Conditions. J. Zagrobelny*, F.V. Bright; SUNY at Buffalo
4:20—601. Pressure-Dependent Solvent Relaxation within Reverse Micelles Formed in Supercritical Fluids. J. Zhang*, F.V. Bright; SUNY at Buffalo
4:40—602. Probing the Local Solute Environment in Supercritical Fluids. J.K. Rice, T.A. Betts, F.V. Bright*; SUNY at Buffalo

Sample Introduction and Pretreatment Methods in Atomic Spectroscopy

Grand Ballroom F

G. Turk; NIST, Presider

1:40—603. Food Analysis by Inductively Coupled Plasma – Atomic Emission Spectrometry with a Low-Cost Ultrasonic Nebulizer. A. Montaser, H. Liu*; George Washington University
2:00—604. Determination of Total Iodine in Foods by On-Line Volatilization ICP-AES. S.P. Dolan*, A.K. Montaser; U.S. Food and Drug Administration
2:20—605. Determination of Total Mercury in Environmental, Clinical and Waste Effluent Samples by Flow Injection Cold Vapor Atomic Absorption Spectrometry. C.P. Hanna*, J.F. Tyson, S. McIntosh; University of Massachusetts
2:40—606. Use of Yeast Metallothionein in Trace Metal Analysis. B.R. Anderson*, J.A. Holcombe; University of Texas
3:00 BREAK
3:20—607. Determination of Trace Metals by Plasma Spectrometric Detection with Supercritical Fluid Extraction. S.L. Cleland*, N.P. Vela, J.A. Caruso; University of Cincinnati
3:40—608. Trace Metal Analysis of Mixed Phase (Water-Sediment) Samples. S. Wells-Sendler*, R.D. Foust, Jr.; Northern Arizona University
4:00—609. An Improved Method for the Determination of Mercury Speciation by Aqueous Phase Ethylation, and Carbotrap Preconcentration, followed by Isothermal Gas Chromatography with Cold Vapor Atomic Fluorescence Spectrometric (CVAFS) Detection. L. Liang*, M. Horvat, N. Bloom; Brooks Rand, Ltd
4:20—610. Sample Pretreatment and Microwave Digestion of Biological Samples for Analysis by Inductively Coupled Plasma Spectrometry. B.S. Barnes*, L.A. Kaine, B.S. Sheppard, M.P. Votel, K.A. Wolnik; U.S. Food and Drug Administration
4:40—611. Optimization of Microwave Acid Digestion Procedures for Organic Sample Matrices Using a Dual Pressure and Microwave Immune Fiber-Optic Temperature Control System. W.G. Engelhart; CEM Corp

Detection Techniques for Capillary Electrophoresis and Liquid Chromatography

Adam's Ballroom A

J. Koropchak; Southern Illinois University, Presider

1:40—612. An Interface for Acridinium Chemiluminescence Detection with Capillary Electrophoresis. M.A. Ruberto*, M.L. Grayeski; Seton Hall University
2:00—613. A Novel Interface for Capillary Zone Electrophoresis and a Reflection Time-of-Flight Mass Spectrometer. A.P. D'Silva*, S.J. Bajic; Iowa State University
2:20—614. A Preliminary Investigation of Capillary Electrophoresis with ICP-MS for Trace Element Determinations. J. Wang*, L.K. Olson, J.A. Caruso; University of Cincinnati
2:40—615. Structure and Dynamics of Gels in Electrophoresis Capillary Columns Studied by Raman Microprobe Spectroscopy. T.L. Rapp, K.L. Davis, K.L. Liu, W.K. Kowalchyk, E.A. Todd, M.D. Morris*; University of Michigan
3:00 BREAK

3:20—616. Capillary Array Electrophoresis Using Confocal Fluorescence Detection: An Approach to High-Speed, High-Throughput DNA Sequencing. X.C. Huang*, M.A. Quesada, R.A. Mathies; University of California

3:40—617. A Laser-Excited Fluorescence EEM Detector for HPLC. T.A. Taylor, S. Mathew, J.E. Kenny*; Tufts University

4:00—618. Capillary Zone Electrophoresis with Indirect Fluorometric Detection of Inorganic Anions. M. Gunshefski*, A.M. Pless, J.D. Winefordner; University of Florida

4:20—619. Enhanced Evaporative Light Scattering Detection for Liquid Chromatography. L.B. Allen*, J.A. Koropchak; Southern Illinois University

Poster Session – General
Delaware Rooms 3 and 4
3:30–5:30

620. Networking for Improved Productivity and Electronic Archival of Mass Spectrometric Data. M.J. Hayward*, P.V. Robandt, J.T. Meek, D.H. Chidester, R.S. Wayne, M.L. Thomson; American Cyanamid Company

621. Nickel Oxide Electrode Amperometry and Potentiometry. Y. Arikawa, B. Hui, C. Strommen, C.O. Huber*; University of Wisconsin

622. A Solid Inorganic Gel Membrane Sensor for Mercury. S.K. Srivastava*, V. Sahgal, H. Vardhan; University of Roorkee

623. Electro-oxidation Behavior of Sulfaphenazole at a Pyrolytic Graphite Electrode. A. Mittal*, R.N. Goyal; University of Roorkee

624. The Determination of Emulsion Ionic Strength by AC Impendance. C.J. Barbour*, R.S. Beckley; Rohm & Haas Co

625. The Application of Multivariate Instrument Standardization in Gamma Ray Spectrometry. C.X. Xu*, R.R. Williams; Clemson University

626. Correction of Cotton Strength Measurements for Moisture Changes Using Genetic Algorithms. E.W. Setzer*, R.R. Williams, R.A. Taylor; Clemson University

627. Submicron Optical Fiber Chemical and Biological Sensors. W. Tan*, Z.Y. Shi, R. Kopelman; University of Michigan

628. A Computer Program for Processing Laser-Excited Fluorescence EEMs. S. Mathew*, T.A. Taylor, J.E. Taylor; Tufts University

629. Application of an Automatic Standard Preparation Unit in the Contemporary Analytical Lab. P. Grandsard*, R. Megargle, M. Markelow; Cleveland State University

630. Analytical Methods for Cyanide: A Comparative Study for Groundwaters. K.M. Cirillo-Penn*, S.K. Deiseroth; Aluminum Co of America

631. Investigation of the Effect of pH, Ionic Strength, and Solvent Polarity on the Chemiluminescent Reaction of Aldehydic Pheromones with Reduced FMN. D.R. Bobbitt*, S.N. Brune, D.B. Frazier, J.R. Phillips; University of Arkansas

632. Bringing Research Reflectance FT-IR Spectrometry into the Quality Control Laboratory. C. Baulsir*, J. D'Agostino; Spectra-Tech Inc

633. Gastrointestinal Uptake in Humans Using Aluminium-26 Mass Spectrometry. J. Templar*, J.P. Day; University of Manchester

634. A Spectroscopic Imaging Database Management System. K.N. Davis; Spectral Intelligence

635. Some Fundamental Problems in the Hydrogen-Ion Concept. C.E. Moore*, B. Jaselskis, A. von Smolinski; Loyola University

636. Bone Lead Analysis: Development of Sampling and Analytical Methodology for Milligram Samples. K.S. Subramanian*, M.J. Inskip, J.W. Connor; Environmental Health

637. Determination of Nitrogen in Titanium Alloys: A Rapid, Quantitative Dissolution Procedure. N.A. Marotta, E.M. Skelly Frame*; GE Corporate Research

638. A Precise, Computer-Controlled Microtitrator. D.A. Lee*, C.C. Hanzelka, W.W. Johnson; Martin Marietta

639. Development of Recognition Coatings for Chemical Sensors. E.J. Poziomek*, J. Li, H. Wohltjen, J.R. Lint, N.L. Jarvis; University of Nevada, Las Vegas

640. The Net Weight Dispenser: A Device for Rapid and Very Precise Sample and Standard Preparation. J.O. Beyer*, Q.G. von Nehring; Dow Chemical

641. Generic JCAMP-DX/BDX. R.S. McDonald*, C.R. Anderson; JCAMP

642. Thermosonimetry of Polymers. K.A. Soulsbury, A.P. Wade*; University of British Columbia

643. Industrial Applications of An HPLC-FTIR Interface. J.L. Dwyer*, J.N. Willis; LAB Connections Inc

644. Quantitative Bromate Analysis via Reduction with Sodium Nitrite. R.C. Duty*, J.S. Ward; Baylor University

LC/MS
R.D. Voyksner; Research Triangle Institute, Organizer
Grand Ballroom E
R.D. Voyksner; Research Triangle Institute, Presider

1:20—645. The Investigation of "Zinc Fingers" by Electrospray Mass Spectrometry. M.H. Allen*, C.M. Li, T.T. Yip, T.W. Hutchens; PE-SCIEX

1:40—646. Use of Capillary Electrophoresis-Electrospray Ionization Mass Spectrometry to Characterize Biomolecules. D.R. Goodlett, J.H. Wahl, H.R. Udseth, R.D. Smith*; Battelle PNL

2:00—647. Fundamentals of Electrospray Ionization for Liquid Chromatography/Mass Spectrometry Applications. C.M. Whitehouse*, S. Shen, F. Banks; Analytica of Branford Inc

2:20—648. Continuous-Flow FAB as a LC-MS Interface Past!!! Present... Future ??? J.E. Coutant*, B.L. Ackerman, B.T. Regg, T.M. Chen; Marion Merrell Dow

2:40—649. Development of an HPLC/MS Method for the Quantitative Determination of a Biologic. P.E. Farrow*, J.N. Kyranos, A.D. Little; Arthur D. Little Inc

3:00 BREAK

3:20—650. Thermospray LC/MS for the Measurement of Endogenous Production Rates of Cortisol and 25-OH Vitamin D. A.L. Yergey*, D. Vicchio, K. O'Brien, N.V. Esteban, D.J. Liberato; National Institutes of Health

3:40—651. Utility of Thermospray HPLC/MS for the Analysis of Pharmaceuticals and Metabolites. W.A. Korfmacher*, J. Abian, J. Bloom, M.I. Churchwell, C.C. Lin; Schering-Plough Institute

4:00—652. Analysis of Triasulfuron, A Sulfonylurea Herbicide, and Its Major Metabolites in Water by HPLC/MS. J.N. Kyranos*, P.E. Farrow; Arthur D. Little Inc

4:20—653. Combined High Performance Liquid Chromatography/Mass Spectrometry: An Integral Component in Pharmaceutical Development. D.L. Norwood*, B.P. Downey; Glaxo Research Institute

4:40—654. Problem Solving with Particle Beam LC/MS. R.C. Willoughby*, E. Sheehan; Extrel Corp/Millipore

Chemistry of Helium Discharges
J. Carnahan; Northern Illinois University, Organizer
Gettysburg Rooms 2, 3, and 4
J. Carnahan; Northern Illinois University, Presider

1:20—655. Surface Wave-Induced Plasmas as Reactors for Helium Plasma Chemistry. J. Hubert; Universite de Montreal

1:40—656. Modeling and Simulation of Helium ICPs: Torch Design. M. Cai*, A. Montaser, J. Mostaghimi; George Washington University

2:00—657. Molecular Decomposition Processes in Microwave Plasmas. M.P. Dziewatkoski, C.B. Boss*; North Carolina State University

2:20—658. Mechanistic and Analytical Examinations of MIP's in the 100 to 200 nm Spectral Region. J.W. Carnahan, J.S. Alvarado*, P.G. Brandl; Northern Illinois University

2:40—659. Characteristics of Radio-Frequency Capacitive Discharges in Helium. M.W. Blades*, T. Hettipathirana, C. LeBlanc, D. Huang; University of British Columbia

3:00 BREAK

3:20—660. Spatial Characterization of an Atmospheric Pressure Helium Microwave Plasma. Y.N. Pak, S.R. Koirtyohann*; University of Missouri

3:40—661. Plasma Mass Spectrometry with Helium MIP Sources. J.A. Caruso; University of Cincinnati

4:00—662. Influence of Water on a Helium MIP. G.L. Long*, K.A. McCleary; Virginia Polytechnic

4:20—663. Development and Characterization of an Annular Microwave-Induced Plasma. S.R. Goode*, J. Emity; University of South Carolina

4:40—664. Emission Characteristics of Laser-Induced Plasmas in Helium. V. Majidi, M. Joseph*; University of Kentucky

Laser Plasmas in Atomic Spectroscopy
V. Majidi; University of Kentucky, Organizer
Constitution Rooms A and B
V. Majidi; University of Kentucky, Presider

1:20—665. Fluorescence Imaging of Gas Phase Molecules Produced by Matrix-Assisted Laser Desorption. E.S. Yeung, T.W. Heise*; Iowa State University

1:40—666. Rapid, Field-Based Detection of Lead in Paint Using the Laser Spark. D. Cremers*, K.Y. Kane; Los Alamos National Lab

2:00—667. Laser Plasma Sampling for Elemental Mass Spectrometry. M. Owens*, V. Majidi; University of Kentucky

2:20—668. Hydrodynamic Modeling of Laser-Solid Interaction: What Can We Learn From It? A. Vertes; George Washington University

2:40—669. Theta Pinch Re-excitation of a Laser Plasma. F. Dorman, E. O'Brien, J. Goldberg*; University of Vermont

3:00 BREAK

3:20—670. Investigation of a Carbon Rod Atomization System for Laser Breakdown Spectroscopy. J.R. Ridge*, S.R. Crouch; Michigan State University

3:40—671. Laser Plasma Excitation of Electrothermally Atomized Species. M. Joseph, V. Majidi; University of Kentucky

4:00—672. Gas Breakdown Behavior in an Excimer Laser-Ablated Plasma. Y.I. Lee*, S. Kamtekar, K.H. Kim, Y.Y. Teng, J. Sneddon; University of Massachusetts

4:20—673. Rapid Analysis of Metal Particles on Filters by Laser Ablation-Inductively Coupled Plasma Spectroscopy. A. Koskelo*, D. Cremers; Los Alamos National Lab

4:40—674. Solid Sample Analysis by Optical Emission Spectroscopy in Laser Produced Plasma. P. Mauchien, A. Briand, N. Andre, A. Semerok; DPE/SPEA/SPS

Applications of ICP-Mass Spectrometry

E. Pruszkowski; Perkin-Elmer Corporation, Organizer

Grand Ballroom A and B

E. Pruszkowski; Perkin-Elmer Corporation, Presider

1:40—675. The Challenge of the Successful ETV-ICP-MS Analysis. R.E. Ediger; Perkin-Elmer Corporation

2:20—676. Multielement Determination of Trace Contaminants in Tetramethylammonium Hydroxide by Inductively Coupled Plasma Mass Spectrometry. T.L. Pinkston, C. Sparks*; Sematech

2:40—677. Applications of Slurry Sampling – Electrothermal Vaporization of ICP-Mass Spectrometry. S.A. Beres*, R.D. Ediger; Perkin-Elmer Corp

3:00 BREAK

3:20—678. Determination of Alkaline Earth and Rare Earth Elements in Marine Ferromanganese Deposits. E.H. De Carlo*, E. Pruszkowski; University of Hawaii

3:40—679. Determination of Pt, Pd, Rh, and Ir in Geological Materials by Direct Solid Sampling of Fire Assay Beads Using Spark Ablation ICPMS. R.L. Van Hoven*, M.W. Doughten, S.H. Nam, A.F. Dorrzaph, A. Montaser; George Washington University

4:00—680. Use of Principal Components Analysis with Laser Sampling ICP-MS. K.J. Fredeen*, D.A. Yates; Perkin-Elmer Corp

Pharmaceutical Applications of Mass Spectrometry

S. Unger; Glaxo Inc., Organizer

Grand Ballroom C

S. Unger; Glaxo Inc, Presider

1:30—681. Characterization and Structural Elucidation of Pharmaceuticals and Natural Products with Mass Spectrometry. M.M. Siegel; American Cyanamid Company

2:00—682. Applications of FAB and ESI Techniques to Molecules of Pharmaceutical Interest. L. Baczynskyj; The Upjohn Company

2:30—683. Application of Mass Spectrometry to the Structural Characterization of Antibiotics and Non Covalent Protein Complexes. B.N. Pramanik*, P. Bartner, A.K. Ganguly; Schering-Plough Research Institute

3:00 BREAK

3:20—684. Quantitative and Structural Elucidation Aspects of Capillary-HPLC/Electrospray/Mass Spectrometry. D.A. Garteiz*, K.T. McManus, R.A. Newman; TEXms Analytical Sciences

3:50—685. The Impact of Mass Spectrometry in Pre-clinical ADME Studies. S.E. Unger*, M.A. Moseley, K.A. Halm; Glaxo Inc

4:20—686. Capillary Electrophoresis – Electrospray Ionization Mass Spectrometry. D.R. Goodlett*, J.H. Wahl, H.R. Udseth, R.D. Smith; Battelle PNL

Mechanism and Application of Solid-Phase Extraction in Analytical Chemistry

J. Stewart; University of Georgia, Organizer

Adam's Ballroom B

J. Stewart; University of Georgia, Presider

1:20—687. Overview of the Mechanisms in Solid-Phase Extractions. N. Simpson; Varian Associates

1:40—688. Comparison of Glass vs Plastic SPE Solumns. P. Sadek; Burdick & Jackson

2:00—689. Use of Dual Mechanisms in SPE. P. Burke; University of Arizona

2:20—690. The SPEC Microcolumn Approach to Solid Phase Extraction. C.M. O'Donnell; Toxi-Lab, Inc.

2:40—691. Environmental Analysis Using Solid Phase Extraction Disks. C. Markell; 3M Center

3:00 BREAK

3:20—692. Therapeutic Drug Monitoring Using Empore Solid-Phase Extraction Membrane. G.L. Lensmeyer; University of Wisconsin Hospital

3:40—693. Utilization of SPE in Additive Analysis in Polymers. N. Mady; Ciba-Geigy

4:00—694. Determination of Oil and Grease in Wastewater by Solid-Phase Extraction. M.J.M. Wells; Tennessee Tech University

4:20—695. Solid Phase Extraction for Estrogens. S.U. Sheikh, J.C. Touchstone*; University of Pennsylvania

Spectroscopic Process Analysis II

P.K. Aldridge; Pfizer Inc, Organizer

Grand Ballroom D

P.K. Aldridge; Pfizer Inc, Presider

1:40—696. Absolute Instrument Standardization for Near-Infrared Spectrometry. T. Davidson, A. Ganz, R. Hoult, D. Tracy*; Perkin-Elmer Corp

2:00—697. Use of Near-Infrared Spectroscopy to Identify Pharmaceutical Dosage Forms. E.W. Ciurczak*, F.A. DeThomas, S. Monfre; NIRSystems Inc

2:20—698. On-Line Analysis of Solids and Analysis of Flowing Materials by Transient Infrared Spectroscopy. R.W. Jones*, J.F. McClelland; Iowa State University

2:40—699. Simultaneous Determination of Dopant Concentrations, Sample Thickness, and Sample Temperature Using Infrared Emission Spectroscopy. T.M. Niemczyk*, B. Wangmaneerat, C. Chen, J.E. Franke, D.M. Haaland; University of New Mexico

3:00 BREAK

3:20—700. In Situ Monitoring of Thin Film Dielectrics Using FT-IR Reflection Spectroscopy and Multivariate Calibration Techniques. J.E. Franke*, L. Zhang,, T.M. Niemczyk, D.M. Haaland; University of New Mexico

3:40—701. Application of Fourier Transform Infrared Spectroscopy to the Real-Time Analysis of Automotive Exhaust Emissions. A.Q. McArver; ManTech Environmental

4:00—702. Monitoring for Chlorine in Process and Stack Applications Using Ion Mobility Spectroscopy. A.T. Bacon, Jr.; Environmental Technology

4:20—703. Optical High Acidity Process Sensors – An Update. H.L. Nekimken*, B. Jorgensen; Los Alamos National Lab

4:40—704. Potential of NMR on Flowing Streams. M.L. Snoddy; Amoco Corp

FRIDAY MORNING

Supercritical Fluid Extraction and Chromatography in the Delaware Valley

J. Foley; Villanova University, Organizer

Gettysburg Rooms 2 & 3

J. Foley; Villanova University, Presider

8:40—705. Paper Chemical Applications of Supercritical Fluid Chromatography. W.E. Barber*, S.F. Nitchman; Hercules Inc

9:00—706. Supercritical Fluid Extraction of Thermally Labile Compounds from Aqueous Matrices. L.R. Betz*, M.E. McNally; Widener University

9:20—707. Systematic Optimization Strategies in Supercritical Fluid Chromatography. J.P. Foley; Villanova University

9:40—708. Packed Column Selectivity in Supercritical Fluid Chromatography. M.S. Klee*, T.A. Berger, W.H. Wilson; Hewlett-Packard Corp

10:00 BREAK

10:40—709. Trace Level Isolation of Veterinary Antibiotics from Biological Matrices Using Supercritical Fluid Extraction. R.J. Maxwell*, J.W. Hampson, O. Parks, E.G. Piotrowski; ERRC/USDA

11:00—710. SFC Applications in Pharmaceutical Excipient Analysis. J.B. Nair*, R.M. Graham, A.J. Chetram; Bristol-Myers Squibb

11:20—711. SFE/GC-MS Determinations of PAHs in Soil. L.A. Dolata*, J.M. Levy, A.C. Rosselli, R.M. Ravey; Suprex Corporation

Flow Injection Analysis

Adam's Ballroom B

J. Tyson; University of Massachusetts, Presider

8:20—712. Laguerre-Domain Representation of Flow Injection Peak Shapes. O. Lee*, A.P. Wade, P. Tournier, G.A. Dumont; University of British Columbia

8:40—713. Comparison of Optimized Manifold Configurations for Increased Sensitivity in Flow Injection Analysis. S.J. Chalk*, J.F. Tyson; University of Massachusetts

9:00—714. A Flow Injection Method for the Determination of Hg(II) Based on Perturbation of the Belousov-Zhabotinskii Oscillating Chemical Reaction. R.T. Echols*, J.F. Tyson; University of Massachusetts

9:20—715. Solid-State Detectors for Time-Based Measurements in Flow Injection Analysis. M.K. Carroll*, J.F. Tyson; University of Massachusetts

9:40—716. Flow Injection Analysis (FIA) Method for the Determination of Active Peroxides in Chloroprene Monomer. P. Karges*, J. Englert, Jr.; Eppendorf North America

10:00 BREAK

10:40—717. Colorimetric Flow Injection Method for Determination of Residual Chlorine Dioxide. M.J. Wintjes, M.D. Kester, A.P. Wade*; University of British Columbia

11:00—718. FIA Monitoring of the Degradation of Organic Pollutants. A.H. Que*, L.E. Bowman, A.P. Wade; University of British Columbia

11:20—719. A Versatile, Interactive, Graphical User Interface for Sequential Injection Analysis and Flow Injection Analysis. M.D. Kester, A.P. Wade*, I.H. Brock; University of British Columbia

Liquid Chromatography – General

Adam's Ballroom A

K. Sentell; University of Vermont, Presider

8:00—720. Improved Chromatographic Selectivity of Structurally Similar Steroids via Low-Temperature Reversed-Phase Liquid Chromatography. K.B. Sentell*, S.T. Shearer; University of Vermont

8:20—721. Determination of Polynucleo Aromatic Hydrocarbons in Motor Vehicle Oil and Grease, and Environmental Matrices by Reversed Phase Chromatography with UV Absorption Photometry and Particle Beam Mass Spectrometer. I.S. Kim*, F.I. Sasinos, R. Roehl, R.D. Stephens; Hazardous Materials Lab

8:40—722. Improved Separations of Heterocyclic Nitrogeneous Compounds Utilizing Surfactant-Based RPLC and CE Methods. M.T. Swartz*, M.C. Danielski, K.B. Sentell; University of Vermont

9:00—723. GPC Cleanup of Oily Samples: Removal of Aliphatic Interferants During Semivolatile Organics Analysis. N.S. Henegar, E.E. Conrad, K.P. Kelly*, O.U. Ukoha; ABC Laboratories

9:20—724. Determination of Cocaine and Benzoylecgonine in Human Serum Using Capillary Electrophoresis. H. Chen, Y. Xu*, M.P.C. Ip; Cleveland State University

9:40—725. Enantiomeric Quantitation Without Separation of Tramadol Intermediates via Laser-Based Polarimetry. T.J. Edkins*, M. Fronheiser, D.R. Bobbitt, J.E. Mills, T. Rossi; RW Johnson Pharmaceutical Research Institute

10:00 BREAK

10:40—726. Improved HPLC/Post-Column Techniques for Rugged Carbamate and Glyphosate Analysis. M.W. Dong*, J. DiBussolo; Perkin-Elmer Corp

11:00—727. Photodiode Array Detection for Quality Control in Petrochemical Analysis. K.M. Gorski*, G.E. Barringer, T.J. Stanton; Groton Technology

11:20—728. Determination of Copper Speciation in a Hydrocarbon Matrix by HPLC. D.B. Taylor*, R.E. Synovec; University of Washington

11:40—729. Fundamental and Practical Aspects of HPLC Methods Validation. M.W. Dong*, J. DiBussolo; Perkin-Elmer

Atomic Spectrometric Instrumentation and Applications

Grand Ballroom C

J. Sneedon; University of Massachusetts, Presider

8:40—730. The Development of a Universal Spray Chamber Design for Flame Atomic Absorption Spectrometry (FAAS). D.E. Shrader*, C. Flajnik, J. Moffett, H. Howarth; Varian Associates Inc

9:00—731. Multielement Atomic Absorption Spectrometry. J. Sneddon*, K.S. Farah, P.R. Pascucci; University of Massachusetts

9:20—732. Multielement Determinations by Continuous Flow Hydride Generation. G.R. Dulude*, S. Karpova, D.L. Pfeil; Thermo Jarrell Ash Corp

9:40—733. A Study of the Chemistry of Natural Surface Water on the Hopi Indian Reservation. M.T. Bell, Jr.*, R.D. Foust, Jr.; Northern Arizona University

10:00 BREAK

10:40—734. Real-Time Internal Standardization for Trace and Major Elemental Determination in Lubricating Oil by ICP-AES. S.F. Franz*, D.P. Anderson, M.X. Lukas; Spectro Incorporated

11:00—735. Spectral Interference Correction Factor Instabilities in ICP-OES. E.F. Paski; Bondar-Clegg & Co Ltd

11:20—736. An Intelligent System for Automation of Quality Assurance and Control Procedures in Graphite Furnace Atomic Absorption Spectrometry (AAS). F. Delles*, M. Knowles; Varian Associates Inc

IR Applications

Gettysburg Room 1

E.G. Brame; The Cecon Group, Presider

8:00—737. Examining Complex Thermal Decomposition Products Using TG-GC-IR. S.C. Pattacini, B.J. McGrattan*, G.L. McClure; Perkin-Elmer Corp

8:20—738. Measurement of Ferrocyanides and Oxyanions in Waste Sludges by Fourier Transform Infrared Reflection Methods. T.V. Rebagay*, D.A. Dodd, D.W. Jeppson; Westinghouse Hanford Co

8:40—739. Analysis of Outgasing in High-Temperature Composite and Ceramic Materials by TGA/FT-IR. D.E. Roberts; Mattson Instruments Inc

9:00—740. Air-borne Asbestos Analysis Using Diffuse Reflection Infrared Spectroscopy. P.L. Lang*, V.V. Chu, D.W. Schiering; Ball State Universityersity

9:20—741. Application of FT-IR for Certification of High-Accuracy Calibration Gases. K.C.C. Wong, S.B. Miller, L.A. Burgess*; Scott Specialty Gases

9:40—742. The Use of TGA/FT-IR Techniques as a Development Tool in Evaluations of Curing of Phenolic Resins. J.C. Bowman*, F.J. Weesner; Nicolet Instrument Corp

10:00 BREAK

10:40—743. Infrared Investigation of Materials for Eye Implants. N.I. Afanasieva, E.G. Brame*, A.R. Koriodsky, O.V. Arinushkina, V.V. Kireev; The Cecon Group Inc

11:00—744. Spectroscopy of Reactions in Supercritical Water. T.B. Brill*, M. Kieke, J. Schoppelrei; University of Delaware

11:20—745. Estimation of Globular Protein Secondary Structure by Solvent-Elimination MAGIC/FT-IR Spectrometry. V.E. Turula, Jr.*, J.A. de Haseth, R.F. Browner; University of Georgia

11:40—746. Effect of Surfactant in Polyurethane Foams Monitored by Mid-Infrared Fiber Fourier Transform Spectrometry. J.A. Caughran, W.M. McClarin, M.C. Berry, J.A. de Haseth, K. Braden; University of Georgia

General Session

Delaware Room 1

M. Hayward; American Cyanamid Co, Presider

8:20—747. A Study of Solute Influence on the Binding of Metals to *Stichococcus Bacillaris* ^{113}Cd NMR. W. Zhang, V. Majidi*; University of Kentucky

8:40—748. Automated Analysis of Potential Agriculture Chemicals Using Flow Injection Thermospray Mass Spectrometry. M.J. Hayward*, J.T. Snodgrass, M.L. Thomson; American Cyanamid Co

9:00—749. Ion Mobility Detector for Chromatography. F.E. Bales*; Pylon Electronics Inc

9:20—750. Resonance Raman Excited (200–257 nm) Spectra of Bacteria. S. Chadha, R. Manoharan, P. Moenne-Loccoz, W.H. Nelson*, W.L. Peticolas, J.F. Sperry; University of Rhode Island

9:40—751. Analytical Spectroscopy and Structure of Small Biomolecules Using an Ab Initio Computational Method. Y. Choi, D.M. Lubman*; University of Michigan

10:00 BREAK

10:40—752. Ab Initio Approach to Uncover Tryptamine Conformers Observed in ^{1}C-R$_2$PI Spectrum. T. Barstis*, L. Grace, T.M. Dunn, D.M. Lubman; University of Michigan

11:00—753. Electrochemical Determination of Total Dissolved Aluminum in Hemodialysis Water after Microwave Decomposition. J.E. Tahan, R.A. Romero*; Universidad del Zulia

11:20—754. Anodic Stripping Voltammetry of Blood Plasma Copper. J.E. Tahan, R.A. Romero*; Universidad del Zulia

Atomic Absorption Spectroscopy Applications
Gettysburg Room 4
K. Carney; Argonne National Labs-West, Presider

8:20—755. Analysis of Electric Arc Furnace Dust Using Spectrasol Reagents. K.W. Gieg II, M.E. Tatro*; Spectra Inc

8:40—756. Forensic Comparison of Household Aluminum Foils Using ICP-AES. R.D. Koons*, R.A. Merrill, C.A. Peters; FBI Laboratory

9:00—757. Analyte Isoformation Affecting the Vanadium Spectroscopic Response in the Graphite Tube. R.A. Romero*, J.A. Navarro, V.A. Granadillo; Universidad del Zulia

9:20—758. Spectrometric Determination of Trace Metals in Uremia. V.A. Granadillo*, R.A. Romero, J.A. Navarro; Universidad del Zulia

9:40—759. Mineralization of Biological Materials to Permit Total Mercury Evaluation by the Cold Vapor Technique. R.A. Romero*, J.M. Sanchez, H.S. Cubillan, V.A. Granadillo, J.E. Tahan; Universidad del Zulia

10:00 BREAK

10:40—760. Assessing Water Metal Quality for Drinking Purposes by Atomic Spectrometry. J.A. Navarro*, H.S. Cubillan, J.M. Sanchez, J.E. Tahan, R.A. Romero; Universidad del Zulia

Infrared Spectroscopy
Delaware Room 2
N. Lewis; National Institute of Health, Presider

8:20—761. Near-Infrared Acousto-optic Imaging Microscopy: Principles and Applications. P.J. Treado, I.W. Levin, E.N. Lewis*; NIH

8:40—762. FT-IR Step-Scan Photoacoustic Spectroscopy with Variable Sampling Depth. J.F. McClelland*, R.W. Jones; Iowa State University

9:00—763. Photoacoustic Spectroscopy Using a Dynamically Aligned Step-Scan FT-IR Spectrometer. D.J. Johnson*, R.A. Crocombe, W.J. McCarthy; Bio-Rad Digilab Division

9:20—764. Strategies for Step-Scan FT-IR Photoacoustic Depth Profiling. R.M. Dittmar, J.L. Chao, R.A. Palmer*; Duke University

9:40—765. Quantitative DRIFTS Using an Optimized Integrating Sphere Accessory. F.J. Wessner*, M.P. Fuller; Nicolet Instrument Corp

10:00 BREAK

10:40—766. Three Independently Purged FT-IR Attachments for QC Analysis. J. Lucania*, S.L. Berets, N.J. Harrick, M. Milosevic; Harrick Scientific Corp

11:00—767. The New 3M Disposable IR Card for Qualitative Mid-Infrared Analysis. J.E. Gagnon*, N. Povey, Jr.; 3M Corp

11:20—768. Analysis of FT-IR Spectroscopic Data. J.T. Reilly*, J.M. Walsh, M.L. Greenfield, M.C. Donohue; Johns Hopkins University

11:40—769. The Use of a Plume Dispersion Model with Concentration Data from the EPA Region VII FT-IR Intercomparison Study. R.H. Kagann*, O.A. Simpson, R.L. Scotto, B.C. Sanders; MDA Scientific Inc

Mass Spectrometry – General
Delaware Rooms 3 and 4
K. Owens; Drexel University, Presider

8:00—770. Theoretical Analysis of the Lensing Effect of Wire Mesh Grids on Ion Transmission in Time-of-Flight Mass Spectrometry. R.C. King*, K.G. Owens; Drexel University

8:20—771. Design of a Reflection Time-of-Flight Mass Spectrometer Using Simplex Optimization. R.C. King, K.G. Owens*; Drexel University

8:40—772. A Laser Ablation-Time of Flight Mass Spectroscopy System for the Analysis of Environmental Samples. D. Baldwin*, S. Bajic, A.P. D'Silva; Iowa State University

9:00—773. Separation and Detection of the Fragments of a Laser Ablated Polymer Using Reflection Time-of-Flight Mass Spectrometer and Capillary Column GC. Y. Choi, S. Fountain, D.M. Lubman*; University of Michigan

9:20—774. MS/MS Peptide Sequencing by Laser Time-of-Flight Mass Spectrometry. R.C. King*, K.G. Owens; Drexel University

9:40—775. Characteristics of Ions and Neutrals Ejected During Matrix-Assisted Laser Desorption. C.D. Mowry, M.V. Johnston*; University of Delaware

10:00 BREAK

10:40—776. Photodissociation – Photoionization Mass Spectrometry. P.L. Ross, S.E. Van Bramer, M.V. Johnston*; University of Delaware

11:00—777. Gas-Phase Chemistry of Alkyl Halides with Phenyl Iron. E. Garcia*, Y. Li, Y. Huang, B.S. Freiser; Purdue University

11:20—778. Collision-Induced and Infrared Multiphoton Dissociation Studies on M(acetone)$_2^+$ (M = Al, Fe, Co, ScO) in the Gas Phase. I. Surjasamita*, B.S. Freiser; Purdue University

Molecular Spectroscopy: General
Grand Ballroom A
D. Bobbit; University of Arkansas, Presider

8:20—779. Wavelength Calibration Methods for Diode-Array Spectrometers. J.T. Brownrigg; American Holographic Inc

8:40—780. Tuning the Diode Lasers by Mode Hopping. R.L. Chien; Varian Associates Inc

9:00—781. Light Scattering Measurements of Particles: Visible vs. NIR Light Sources. M.L. Cheng*, N.J. Shah, R.J. Obremski, M. Ordpour; Beckman Instruments Inc

9:20—782. Characterization of "Noise" and Software Filters of Light Scattering Measurements. N.J. Shah*, M.L. Cheng, R.J. Obremski; Beckman Instruments Inc

9:40—783. General Method for the Production of Biospecific Optical Fiber Sensors Based on a Dynamically Associated Surface Interaction. D.R. Bobbitt*, Y. Wang, K.P. Titus, F.K. Ogasawara; University of Arkansas

10:00 BREAK

10:40—784. Optical Sensor Based on Polymer Swelling Coupled to a Change in Fluorescence. M.F. McCurley; NIST

11:00—785. A Novel Substrate for Surface-Enhanced Raman Scattering (SERS) Determination of Sulfonamides. S.T. Pagano*, J.D. Winefordner; University of Florida

Spectroscopic Process Analysis III
Grand Ballroom B
A. Cavinato; D2 Development, Presider

8:40—786. A Comparison Between Scanning Grating NIR Analyzers and Fixed-Filter Photometers in Industry. R.C. Moessner; E.I. du Pont de Nemours Co

9:00—787. Difficult Applications of NIR Spectroscopy: Viscous Fluids and Moving Films. J.M. Pope; LT Industries, Inc

9:20—788. Near Line Process Monitoring of Toothpaste Using FTIR. J.W. Rydzak; Colgate-Palmolive

9:40—789. Process Monitoring of Emulsion Polymerization of Styrene by SW-NIR. C. Wu*, J.D.S. Danielson, J.B. Callis; University of Washington

10:00 BREAK

10:40—790. Monte Carlo Rationization for Optimal Sensor Design. Z. Ge*, J.B. Callis, A. Li; University of Washington

11:00—791. Reduced Noise of Quantitation in NIR Through FT-Spectroscopy. M. Trygstad; Bomem/Hartmann & Braun

ABSTRACTS

1 A 22-MM TORCH FOR ATOMIC EMISSION AND MASS SPECTROMETRY.

J. A. Horner and G. M. Hieftje, Department of Chemistry, Indiana University, Bloomington, IN 47405.

Entrainment of atmospheric gases into an inductively coupled plasma (ICP) has posed difficulties in both optical emission spectroscopy due to spectral interferences and in mass spectrometric analysis due to oxide and nitride ion formation. In an effort to reduce the amount of atmospheric gases reaching the central channel and to increase the stability of the ICP, a larger diameter torch has been designed. This 22-mm torch has been characterized using both optical emission spectrometry and mass spectrometry. The magnesium ion to atom line intensity ratio has been optimized using a modified simplex algorithm. Optimum values of Mg(II)/Mg(I) approach those predicted by LTE models. Optimum operating conditions were used for all subsequent studies. Molecular nitrogen ion spatial emission profiles have been measured and will be compared to those for a conventional torch. Short- and long-term stabilities of selected emission signals have been evaluated and will be discussed. In addition, differences in sodium oxide and nitride ion levels for each torch obtained by ICP atomic mass spectrometry will be discussed.

1. J. M. Mermet, *Anal. Chim. Acta*, **250**, 85 (1991).

2 DESIGN FEATURES OF A GRAPHITE FURNACE CAPACITIVELY COUPLED PLASMA SOURCE FOR ATOMIC SPECTROSCOPY.

Dong C. Liang, Huacheng Yang, Kenneth Leung, Wayne Gauley and Peter Banks, Aurora Instruments Ltd. 3031 Main Street, Vancouver, British Columbia, Canada V5T 3G6.

A new source combining the analytical merits of both GF-AAS and ICP-AES has been developed by generating an atmospheric pressure capacitively coupled plasma inside a graphite furnace. High atomization efficiency coupled with plasma excitation yields a technique capable of sub-PPB detection limits with high sample throughput. Some of the latest advances made in GFAAS technology have been incorporated into the device including rapid heating rates approaching 2500 °C/sec and transverse furnace heating. The radio-frequency plasma sustained inside the furnace is generated by a free running oscillator circuit which possesses some unique advantages relative to the more common crystal frequency control. The complete design of the source is compact and versatile allowing for a simple interface to many existing spectrometers.

3 TEMPORAL EVOLUTION OF THE EMISSION SIGNAL FROM A MICROCAVITY HOLLOW CATHODE.

P. D. Mixon, S. T. Griffin, and J. C. Williams, Departments of Electrical Engineering and Chemistry, Memphis State University, Memphis, TN 38152.

Temporal profiles of the emission signal for a range of pulse widths from 15 to 500 microseconds for Al, Ti, Mo, Nb, C, and stainless steel microcavity hollow cathodes will be presented. The temporal variation of the electrical characteristics of a pulsed discharge will be described. The most recent results from efforts towards the application of pulse techniques to the quantitative analysis of microsamples will be discussed. Instrumentation for control of a pulsed hollow cathode discharge will be described.

4 PLASMA PARAMETER EFFECTS ON CRATER SHAPES IN RF GLOW DISCHARGE SPUTTERING.

Cory Nathan Hammond, Chris Lazik, and R. Kenneth Marcus; Howard L. Hunter Chemistry Laboratories, Clemson University, Clemson, SC 29634-1905.

Glow Discharge (GD) devices have emerged as prominent analytical sources for the direct analysis of solid materials. This is especially true in the area of depth resolved analysis of thin film systems, where the number of GD applications has increased rapidly in recent years. In this laboratory, an external sample mount radio frequency (rf) powered GD source has been developed for the direct assay of both electrically conducting and nonconducting solid materials. Because of their ability to directly atomize nonconducting samples, rf-GD devices can be employed in the analysis of a much broader range of sample materials than DC powered systems. In the case of thin film systems, both nonconducting films and/or substrates can be analysed directly without any prior matrix modification. In this report, the potential for the rf-GD source to be employed in depth resolved analyses of solids is investigated. In particular, profilograms of the sputter crater surfaces are examined to determine the optimal discharge conditions that promote 'layer by layer' sample ablation. These discharge conditions of output power, pressure, and cathode surface area that produce uniform sample erosion profiles are determined and will be presented.

5 EFFECT OF AGING THE HOLLOW CATHODE BY SPUTTERING ON THE ANALYTICAL PRECISION OF THE HOLLOW CATHODE DISCHARGE EMISSION SOURCE.

J. C. Williams, Jih-Lie Tseng, Jan-Yurn Kung, and Steven T. Griffin, Departments of Chemistry and Electrical Engineering, Memphis State University, Memphis, TN 38152.

Sputtering changes the analytical performance of the hollow cathode as an emission source. Proper conditioning (aging) of the hollow with sputtering greatly improves precision. Conditioning decreases the blank emission signal and changes the shape of the hollow. Micrographs which show the evolution of the bottom of the hollow into a stable bulb shape are presented. The blank emission signal decreases with aging of the hollow and approaches a constant value when the hollow is properly conditioned. A short-term stability ($n = 5$) of approximately 1.8% RSD has been observed frequently. An average long-term stability over several days ($n = 45$) of 4.5% for Li and 3.5% for Na in the emission signal from microsamples (<50 nL) deposited in the hollow cathode discharge source is reported here. Instrumentation, operation, and sample preparation procedures are described.

6 SPUTTERING CHARACTERISTICS OF GLASSES AND CERAMICS VIA RF GLOW DISCHARGE ATOMIZATION;

Chris Lazik and R. Kenneth Marcus; Howard L. Hunter Chemistry Laboratories, Clemson, SC 29634-1905.

A radio frequency powered Glow Discharge Atomic Emission (rf-GD-AES) source has been developed in this laboratory for the direct elemental assay of solid materials. The rf-GD-AES system has proven to be an effective atomization/excitation source for the direct analysis of conducting sample materials and has recently provided some exceptional analytical figures of merit for a variety of conducting sample matrices. More recently, this system has been applied in the direct assay of nonconducting glass and ceramic sample materials. In this report, the sputtering and emission characteristics of the rf-GD-AES system for nonconductors under various discharge conditions of power and pressure are described. Sample loss rates, emission intensity profiles, and temporal stability measurements are compared to those obtained with conducting sample materials. Finally, the potential for this rf-GD-AES system to be employed in applications involving the analysis of nonconductors is discussed.

7 CHARACTERIZATION OF A GRAPHITE FURNACE CAPACITIVELY COUPLED PLASMA SOURCE FOR ATOMIC SPECTROSCOPY.

Peter Banks, Degui Huang and Dong C. Liang, Aurora Instruments Ltd., 3031 Main Street, Vancouver, British Columbia, Canada V5T 3G6.

The need for a faster furnace technique which provides the typical sensitivity of GFAAS, but with an improved sample turn-around time has been addressed. The graphite furnace capacitively coupled plasma source (GF-CCP) relies on atomic emission detection through plasma excitation inside the furnace volume to provide simultaneous, multi-element analysis which can substantially improve sample throughput. Some analytical figures of merit will be presented with an emphasis on detection limits for both metals and non-metals and how they compare to other, established methods (i.e. GFAAS and ICP-AES). For example, the absolute detection limit for P is 29 pg which is more than three orders of magnitude smaller than that available using GFAAS. In addition, a signal reproducibility of 2% RSD was found for 20 μL injections of 20 PPB Tl. A number of pertinent applications, where the GF-CCP has the potential to provide uncomparable performance, will be investigated. These areas include the environmental analysis of the elements As, Pb, Sb, Se and Tl and blood and serum analysis for a number of elements.

8 CHARACTERIZATION OF THE CHARGE INJECTION DEVICE AS A DETECTOR FOR ICP SPECTROSCOPY.

R. W. Foster, A. E. Pellowe, Thermo Jarrell Ash Corporation, 8E Forge Parkway, Franklin, MA 02038.

The CID or charge injection device offers some distinct advantages over the conventional photomultiplier tube (PMT) as a detector for ICP spectroscopy. In addition to supplying the same detection limits, sensitivities and linear ranges, it provides continuous wavelength coverage, simultaneous background coverage and a permanent elemental "fingerprint" which can be stored away on disk for future analysis. This paper focuses on the analytical performance of the CID in a commercial ICP instrument, the Iris CID spectrograph. A variety of matrices have been analyzed and the results presented which highlights the unique features offered by this solid state detector.

9 A MECHANICALLY STABLE PHOTOMETER DESIGN FOR THE ANALYSIS OF MICROSAMPLES USING A HOLLOW CATHODE EMISSION SOURCE.

S. T. Griffin and J. C. Williams, Departments of Electrical Engineering and Chemistry, Memphis State University, Memphis, TN 38152.

Microanalysis using the hollow cathode emission source has been investigated in this laboratory for several years. The hollow cathode discharge source has been shown to have adequate detection limits for the microanalysis of several samples. For example, it appears that several components in nanoliter sized samples of renal fluid can be simultaneously determined using this emission source. However, the lack of consistent performance of the source over extended time periods has reduced its utility. A significant cause of imprecision of the emission source is attributed to the lack of mechanical stability of the optical system and to the lack of reliable positioning of the hollow cathode itself. Thus, the multichannel spectrometer used for several years has been completely redesigned. Detailed instrument parameters and a complete optical analysis of the new instrument will be presented.

10 A SYSTEMATIC APPROACH TO ULTRASONIC SLURRY GFAAS FOR ENVIRONMENTAL MONITORING.

N. J. Miller-Ihli, U.S. Department of Agriculture, ARS, BHNRC, Nutrient Composition Laboratory, Beltsville, MD 20705.

Ultrasonic Slurry graphite furnace atomic absorption spectrometry has proven to be a useful technique for the direct determination of solid samples and is well suited for environmental studies. A systematic approach to the establishment of optimum graphite furnace conditions will be reviewed and means for optimizing slurry preparations will be discussed. The influence of particle size and density as well as the distribution of analyte in the slurry will be considered. The benefits and limitations of analyte extraction into the liquid phase of the slurry will be highlighted and the influence of sample size used for slurry preparations will be discussed. Benefits of reduced particle size will be demonstrated and a simplified cryogenic grinding technique will be outlined. A method will be presented for the determination of lead in dust, soil, paint, and water samples. Average accuracies are ±5–10% based on the analysis of certified reference materials. Benefits and limitations of this analytical technique will be reviewed focusing on sample heterogeneity and minimum sample mass requirements. The suitability of this technique for environmental monitoring will be discussed.

11 THE DETERMINATION OF ELEMENTS OF VARIOUS VOLATILITIES IN COAL, COKE, ASH AND SLUDGE SAMPLES USING SLURRY SAMPLING GRAPHITE FURNACE AAS.

Gerhard Schlemmer and Wolfgang Erler, Bodenseewerk Perkin-Elmer GmbH, P.O. Box 101164, D-7770 Uberlingen, Germany.

Solid sampling graphite furnace AAS has proven to be an attractive alternative for the determination of elements in matrices which are hard to decompose. This is especially true for the analysis of coal, fly ashes, glass, etc., where decompositions are generally analytically demanding and time consuming. When powdered solids are suspended into a solution, slurries are formed which can be handled similar to solutions from decompositions or digestions in conventional graphite furnace AAS. This holds true for the automation of sample introduction as well as for atomization characteristics, chemical modification, standard addition and graphite furnace time/temperature programs. Volatile, medium volatile and refractory elements have been determined in slurries from coal, coke, ashes and sludges. The slurries have been prepared by ultrasonic homogenization of the powdered material in a solution containing 5% nitric acid and 0.1% Triton X-100. Standard graphite furnace programs and modifiers have been used for most of the determinations. The results were generally in good agreement with results obtained from decomposed samples analyzed by conventional graphite furnace AAS. The precision between slurries containing different masses of sample were typically better than 10% and as good, if not better than the precision found between various decompositions. Various particle size distributions in one of the samples had only a minor influence on the absolute value and on the standard deviation of the results obtained.

12 TAKING THE SLURRY SAMPLING METHOD TO THE LIMIT . . . DETERMINING ULTRATRACE CONSTITUENTS IN HIGH PURITY MATERIALS.

Michael Epstein, Chemical Science and Technology Laboratory, National Institute of Standards and Technology, Gaithersburg, MD 20899.

The determination of ultra-trace transition metal concentrations in high-purity chemicals is perhaps the most challenging problem that can be encountered by an analytical chemist. The combination of low analyte concentration, high matrix concentration, and the ubiquitous nature of transition metals leads to problems with detection, interferences and contamination for most instrumental methods. Graphite furnace atomic absorption spectrometry (GFAAS) is certainly no exception to this rule when applied in the normal configuration of liquid sample introduction after external sample preparation. However, the use of the slurry sample introduction method, in which a suspension of the untreated sample is directly introduced into the furnace, can overcome many of the problems encountered in the conventional use of GFAAS for difficult analyses. One specific analytical problem was the determination of iron, nickel, copper and cobalt at the ng/g level in high-purity aluminum fluoride, a precursor in the manufacture of glass for fiber optic use. Aluminum fluoride is difficult to dissolve and iron contamination is impossible to avoid when any sample preparation is involved. Our approach to this problem was to investigate the conditions under which the sampling system could quantitatively handle very high percent (i.e. 50%) suspended solids. This provided an effective dilution factor of 2x, rather than the typical 20x to 100x dilution used for conventional sample preparation or slurry analysis. Detection limits were less than 10 ng/g for all four elements and nickel, iron and copper were quantitatively determined in several different samples of aluminum fluoride.

13 SOLID SAMPLING WITH ETV-ICP/AES—A CONTRIBUTION TO INSTRUMENTATION AND METHODOLOGY.

P. Verrept and R. Dams, Lab. of Analytical Chemistry, Institute of Nuclear Sciences, University of Ghent, B-9000 Ghent, Belgium. U. Kurfürst, University of Fulda (Fachhochschule), D-6400 Fulda, Marquardstr. 35, Germany.

The interest and urge for direct introduction of solid samples into an ICP/AES is rapidly increased during the last years. An existing graphite furnace which was optimised for solid samples introduction was modified in order to transport the analyte to the plasma and to keep the plasma in stable working conditions. Observation height and carrier gas flow were optimised for different elements and materials. The transport efficiencies for liquid and solid samples and for solid sampling ETV and pneumatic nebulisation were studied. Some analytical and methodical features will be presented for Cd, Pb an Cu and first results of testing the developed system by means of the analysis of standard reference materials.

14 DETERMINATION OF TRACE ELEMENTS IN FOOD AND AGRICULTURAL SAMPLES BY GRAPHITE FURNACE ATOMIC ABSORPTION SPECTROMETRY WITH SOLID AND SLURRY SAMPLING.

David J. Butcher and Eric D. Byrd, Department of Chemistry and Physics, Western Carolina University, Cullowhee, NC 28723.

Graphite furnace atomic absorption spectrometry (GFAAS) is a sensitive method for the determination of trace elements in samples. Conventional methods of sample preparation involve dissolution, which is frequently an inconvenient procedure that requires more time than the analysis. Alternative methods of sample introduction include solid and slurry sampling which were investigated for copper, iron, lead, manganese, silver, and zinc in National Institute of Standards and Technology food and agricultural standard reference materials. Optimized char and atomization temperatures were obtained for each of the elements. Goals of the research included a comparison of the accuracy and precision of solid and slurry sampling to dissolution methods, a comparison of the magnitude of the background signals for each of these sampling techniques, and an evaluation of the effectiveness of deuterium arc background correction to account for these background signals. Slurry sampling was shown to be give results that were statistically the same as the certified values, but the solid sampling results gave poor agreement. Slurry sampling was also compared to a conventional dissolution method for the determination of the metals in biological samples.

15 SOLID SAMPLING OF METAL ALLOYS FOR THE DETERMINATION OF ANTIMONY, PHOSPHOROUS, TELLURIUM, AND TIN BY THE USE OF LASER-EXCITED ATOMIC FLUORESCENCE WITH AN ELECTROTHERMAL ATOMIZER.

Robert F. Lonardo, Zhongwen Liang, and Robert G. Michel, Department of Chemistry, University of Connecticut, Box U-60, Storrs, CT 06269.

Solid sampling of nickel based alloys for the determination of antimony, phosphorus, tellurium, and tin through the use of laser-excited atomic fluorescence with an electrothermal atomizer (ETA-LEAFS) was investigated. ETA-LEAFS was shown to possess linear dynamic ranges between five and seven orders of magnitude and detection limits between one and four orders of magnitude superior to atomic absorption. Since solid sampling required no sample preparation, possible advantages included greater analytical sensitivity and a reduced risk of contamination. Experimental results obtained for the determination of tellurium in nickel based alloys were in agreement with certified values. Quantitative results obtained for antimony, phosphorous, and tin were lower than the certified values due to an inability to completely vaporize these elements away from the sample matrices.

16 COMPENSATION OF PHYSICAL AND EIE EFFECTS DUE HIGH CONCENTRATIONS OF Ca, Mg, Na AND Li FOR ULTRASONIC NEBULIZATION.

I. B. Brenner, and S. Erlich.

The effects of high concentrations of salt and major cations constrain the application of ultrasonic nebulization (usn) for the analysis of environmental, geological and related materials. As a result of these interferences, the well-documented enhanced limits of detection are not obtained. Furthermore, interferences due to eie's result in inaccurate analytical results due to transport effects in the nebulizer and ionization processes in the plasma. In this presentation results obtained with an air-cooled usn are discussed. The efficacy of internal references using ion-atomic sc line pairs, and the mgii/mgi ratio as an eie interference index in the plasma is evaluated. The accuracy of the methodology is established by analysing standard reference waters and waters containing a wide range of salt concentrations.

17 STUDIES ON AN EXCIMER LASER ABLATED PLASMA.

J. Sneddon, Y. I. Lee, T. L. Thiem, and Y. Y. Teng, Department of Chemistry (J. S. and Y. L.) and Physics (Y. T.), University of Massachusetts, Lowell, Massachusetts 01854, Phillips Laboratory (T. T.), Hanscom AFB, Bedford, MA 01731.

Laser ablation and the subsequent development of a high temperature plasma is receiving increased interest as an alternative to conventional plasma sources (i.e., inductively coupled plasma, direct current plasma, glow discharge plasma, etc.,) for the spectrochemical analysis of solid materials. Recent developments in this laboratory[1,2] describe fundamental studies on the ablation process of the excimer laser-ablated plasma as well as the spectrochemical analysis by atomic emission spectrometry. This paper will describe a study of the atomic emission spectra produced by the plasma as a function of axial position from the surface of various ablated metal targets. The characteristics of the plasma and instrumentation used to characterize and evaluate the plasma will also be described in detail. The emission spectra were characterized by varying the pressure of the ablation chamber over the range of 1–760 torr, and the composition of the atmosphere (air, argon, and helium) to optimize the line-to-background (L/B) ratio. Studies on the analytical application of this plasma are currently in progress. The analytical performance characteristics of detection limit for selected elements, precision, and linear dynamic range of the laser ablated plasma will be presented and compared to more traditional plasma sources.

1. Y. I. Lee, S. P. Sawan, T. L. Thiem, Y. Y. Teng, and J. Sneddon, *Applied Spectroscopy*, 1992, **46**, 436.
2. Y. I. Lee, T. L. Thiem, G. H. Kim, Y. Y. Teng, and J. Sneddon, *Applied Spectroscopy*, 1992, submitted.

18 THE CONCEPT AND USE OF HOLLOW CATHODE LAMP EXCITED ATOMIC FLUORESCENCE SPECTROMETRY IN AN INDUCTIVELY COUPLED PLASMA.

Sue F. Franz (In memorial of Professor Peter N. Keliher) Spectro Incorporated, 160 Ayer Road, Littleton, MA 01460.

Atomic fluorescence spectrometry, in comparison of atomic absorption spectrophotometry and atomic emission spectrometry exhibits many advantages in terms of low detection limits, less spectral and chemical interferences, unmatched long term baseline stability and selectable multielemental determination capability. Inductively Coupled Plasma—Atomic Fluorescence Spectrometry, using an ICP as excitation source, combines the advantages of ICP-AES and flame AAS in theory. In this paper, experimental results from a commercial ICP-AFS will be presented. Advantages and disadvantages of the instrument will be discussed. Analytical performances for aqueous and organic samples were compared. In some cases, an oxygen or propane doped plasma was used to improve analytical signal to background ratios of some elements. The use of surfactant and a model for explaining the effects of surfactant on atomic fluorescence signals will also be presented. Comparison of ICP-AFS and ICP-AES will be discussed briefly.

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Abstract not received at time of printing.

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Abstract not received at time of printing.

21 ATOMIC SPECTROSCOPY AND NEURAL NETWORKS: APPLICATION TO FLORIDA ORGANGE JUICE.

Seifollah Nikdel, Florida Department of Citrus, 700 Experiment Station Road, Lake Alfred, FL 33850.

In today's modern analytical laboratory, the analyst has choice of selecting among the diverse emission, absorption, and fluorescence spectrochemical techniques to solve the problem of current interest. Atomic emission spectroscopy (AES) is the oldest multielement method and with the introduction of plasma as atomization and excitation source, has regained its popularity. Pattern recognition systems, such as "Arthur," have been used to identify the country of origin of juices. However, in contrast to "Arthur," a newly developed system, newly, artificial neural network (ANN) has a learning capability. "ANN" mimics the brain's own problem solving process. Just as humans apply knowledge gained from past experience to new problems or situations, an artificial neural network takes previously solved examples to build a system of "neurons" that makes new decisions, classifications, and forecasts. The problems which best applicable to an artificial neural networks solution are those which do not have precise computational answers but which require "pattern recognition" or "fuzzy logic." An extensive analytical project has been underway for several years by the Florida Department of Citrus to answer the following questions: Where is your orange juice from?; and Is your orange juice pure and unadulterated?. In this presentation, I will explore the use of ICP-AES and ANN to find an answer to the above questions via combination of atomic emission spectroscopy and artificial neural networks.

22 CURRENT ECONOMIC INFLUENCES ON ANALYTICAL INSTRUMENT DEVELOPMENT.

Andrew T. Zander, Varian Associates, Inc., E. L. Ginzton Research Center, Palo Alto, CA., 94304-1025.

It is well-established that there are a number of factors which drive new instrument development. The "market pull" of user's requirements and the "technology push" of advanced performance improvements are continual topics of discussion. These are coupled with economic influences which are often difficult to identify well enough to provide complete confidence in R&D planning. A number of current economic issues influencing R&D planning, particularly for instrumentation development, will be discussed. Among these will be the effects of changes in government support; the impact of mergers and acquisitions of corporations on R&D; market developments outside North America; and environmental, regulatory, and quality certification issues.

23 HOW TO WRITE YOUR OWN CLP SOFTWARE.

Charles C. Wohlers, Energy & Environmenmtal Engineering, P.O. Box 215, E. Cambridge, MA 02333.

Much activity in environmental labs today is oriented towards CLP analyses and data reporting. CLP is a series of analytical methods, QC, and data reporting requirements developed by the EPA to produce legally defensible analytical data. The requirements, although complex, are very well defined. This combination makes it almost imperative that computer software be used to generate the 14-plus different forms required in a CLP package. Although several commercial products are available, it is often practical (at least for Inorganics) to produce your own software in-house. The major benefits include the ability to tailor the system to your own needs and control software changes so that the system may be easily adapted to different clients and to future changes in CLP protocols and interpretations. This paper describes a CLP package written at E3I in dBase IV which has evolved over the past five years into a complete Inorganics CLP reporting system. dBase was chosen as it is a database program and this is clearly a database application, dBase is fairly easy to program in, and the language is quite rich. Some other applications which might be used to produce CLP software will also be discussed. These include FoxPro, Lotus 1-2-3, Q&A, and Object Vision.

24 THE FUNDAMENTAL REVIEW IN ATOMIC EMISSION SPECTROMETRY.

Louise Voress, Analytical Chemistry, American Chemical Society, 1155 16th St., N.W., Washington, DC 20036.

Analytical Chemistry's Fundamental Reviews issue is published in even years, and includes technique-oriented critical reviews of significant advances in the field. Topics covered include all areas of spectroscopy, chromatography, electroanalytical chemistry, and mass spectrometry as well as microscopy, kinetics, thermal analysis, radiochemical analysis, chemical sensors, and chemometrics. The origins of the reviews issues, how topics are chosen, how the reviews have grown and changed over the years, and how authors go about preparing a review will be discussed. Particular emphasis will be given to Peter Keliher's contributions to the understanding of atomic emission spectroscopy through his preparation of authoritative, comprehensive, and highly readable review articles.

25 ARAAS AND ASU.

Judith Egan, Journal of Analytical Atomic Spectrometry, Royal Society of Chemistry, Thomas Graham House, Science Park, Milton Road, Cambridge, CB4 4WF, UK.

Annual Reports on Atomic Spectroscopy (ARAAS) were first published in 1971, as a book by the then Society for Analytical Chemistry, as a direct consequence of the biennial International Conferences on AA and AF held in Sheffield, UK. These meetings brought together workers with a wide variety of interests from all parts of the world and facilitated setting up the Editorial Board of ARAAS, the members of which furnished up-to-date information and wrote the reports. Peter Keliher became a member of the rapidly expanding Editorial Board in 1983. In 1971 the reports covering fundamental, instrumentation and methodological aspects, were based on about 1000 papers appearing in that year. Changing circumstances led to a new format for the reports in 1986, to that of Atomic Spectrometry Updates (ASU), appearing in the six regular issues of JAAS, published by the now RSC. The active participation of overseas Board Members such as Peter Keliher is vital to the production of these reviews—in 1991 over 4000 published papers and conference abstracts were included. The success of the ASUs has led to more increases in Board Membership to provide comprehensive coverage. The current format is flexible, enabling coverage to be changed as current interests change, e.g., establishment of Updates devoted to ICP-MS and XRF. The latest development is the forthcoming introduction of JAASbase—a PC product containing all the table entries and references.

26 THE AMERICAN MICROCHEMICAL SOCIETY. MICROCHEMICAL JOURNAL PETER KELIHER AND ME.

Leonard C. Klein, FMC Corporation, Box 8, Princeton, NJ 08543.

The society was originally called the New York-New Jersey Microchemical Society when it was formed in 1935. Its' purpose is to promote the teaching and practice of microanalysis. In 1938, the name was changed to The Metropolitan Microchemical Society and in 1967, the American Microchemical Society. Although essentially a local organization, the society has members from all over the world. In 1959, along with other groups, the society became a sponsor of Eastern Analytical Symposium and in 1974 became a sponsor of the FACSS. The Microchemical Journal was started in 1957 with Dr. Cheronis as its' first editor. Dr. Steyermark became editor in 1962. In 1973, when Leonard Klein became secretary of the society, a search for a new editor began because it was rumored that Dr. Steyermark might retire. It was in 1973 or 1974 that Peter Keliher gave a talk at a meeting of the American Microchemical Society. After the meeting he applied for membership. Leonard Klein asked Peter to represent the society on the FACSS program committee. Peter went on to hold additional offices with FACSS. Leonard Klein also discussed the journal editorship with Peter. He indicated he would be interested if and when Dr. Steyermark left the position. Upon the death of Dr. Steyermark in 1984, Leonard Klein nominated and was greatly instrumental in the appointment of Peter as editor of the Microchemical Journal. He also served as organizer of the Benedetti-Pichler Award Symposia in connection with both EAS and FACSS and represented the society on the program committee of EAS. Upon Peters' death, academic press appointed Dr. Joseph Sneddon editor of the journal.

27 1492–1992: PLASMA MASS SPECTROMETRY AND THE AGE OF DISCOVERY.

R. S. Houk, Iowa State University, Ames Lab USDOE, Ames, IA 50011.

The early days of ICP-MS are remarkably similar to the voyages of Christopher Columbus, the Admiral of the Ocean Sea. These parallels will be described for the personages and events of both areas of discovery. Recent exploratory efforts, such as cryogenic desolvation, improvements in ion optics, and application of new types of mass analyzers to elemental analysis, will be surveyed. The threat posed by electrospray to established methods of elemental analysis will also be discussed.

28 THE EFFECT OF AEROSOL DROPLETS ON INDUCTIVELY COUPLED PLASMA MASS SPECTROMETRY SIGNALS: TIME GATED MEASUREMENTS BY LASER INDUCED FLUORESCENCE SPECTROSCOPY AND MASS SPECTROMETRY.

Steven E. Hobbs and John W. Olesik, Laboratory for Plasma Spectrochemistry, Laser Spectroscopy and Mass Spectrometry, Department of Geological Sciences, The Ohio State University, 1090 Carmack Road, Columbus, OH 43210.

Incompletely desolvated droplets and vaporizing particles cause large fluctuations in inductively coupled plasma atom and ion emission intensities and mass spectrometry signals. The magnitude of analyte ICP-MS signals depend on analyte ion density in the plasma as well as the ion transmission efficiency through the sampling interface, ion optics and mass spectrometer. Analyte ICP-MS signals increase near vaporizing particles. Laser induced fluorescence measurements show that the increase in the ICP-MS signal is due to a large local analyte ion concentration in the plasma near a particle. Near incompletely desolvated droplets, analyte ICP-MS signals are depressed by up to 100%. However, laser induced fluorescence data show that the analyte ion density is not depressed near an incompletely desolvated droplet. This would suggest that the transmission efficiency of ions from the plasma to the MS detector is reduced near a droplet. Laser induced ion to atom fluorescence intensity ratios have been used together with the Burton-Blades model to estimate electron number densities and temperatures. When a droplet entered the observation zone, the calculated temperature decreased from about 8500 to 6200 K, while the calculated electron number density fell from about 3×10^{15} to 5×10^{13} cm^{-3}. The effect of a vaporizing particle was similar to that of a droplet (the temperature dropped from about 8000 to 6300 K).

29 NEW CONCEPTS FOR THERMOSPRAY SAMPLE INTRODUCTION TO ATOMIC SPECTROMETRY.

Timothy S. Conver and J. A. Koropchak, Department of Chemistry and Biochemistry, Southern Illinois University, Carbondale, IL 62901.

Thermospray has recently been shown to be an advantageous alternative to conventional pneumatic sample introduction for atomic spectrometry (1). Substantially improved analyte transport, signal-to-noise ratios, and limits-of-detection have been reported, even for complex sample matrices containing high concentrations of dissolved solids using thermospray systems constructed from stainless steel. More recently, we have developed thermospray systems based on relatively large internal diameter fused silica capillaries (150 μm i.d.) to the exit of which short lengths of smaller internal diameter (25–50 μm) fused silica apertures have been laser fused (2,3). These thermospray systems provide the additional features of high chemical stability, low background contamination, and relatively low pressure operation at moderately high liquid sample flow rates (1–2 mL/min). In this report, we will describe the application of this fused-silica aperture thermospray sample introduction system to ICP-AES, with specific emphasis on the characterization and minimization of matrix effects. Of particular emphasis will be matrices resulting from the EPA's Toxicity Characteristic Leaching Procedures (TCLP). In addition, we will introduce a new concept in aerosol generation, called thermojetspray, and it's application to ICP spectrometries. General principles, design considerations, and unique capabilities of this sample introduction system will be described.

1. J. A. Koropchak and H. Aryamanya-Mugisha, *Anal. Chem.* **60,** 1838 (1988).
2. J. A. Koropchak, M. Veber, and J. Herries, *Spectrochim. Acta,* **Part B,** in press.
3. J. A. Koropchak, M. Veber, J. Herries, and T. S. Conver, *Appl. Spectrosc.,* in press.

30 THE GLOW DISCSHARGE AS A REACTIVE ANALYTICAL CELL.

W. W. Harrison, S. K. Ohorodnik, and P. H. Ratliff, Department of Chemistry, University of Florida, Gainesville, FL 32611.

The glow discharge (GD) can produce a stable discharge with a variety of gases, ranging from inert to reactive. In the normal analytical mode, argon is frequently used as the discharge gas, but it should not be assumed to be truly inert. Metal argides are relatively common at low concentrations and may create spectral interferences. More troublesome are the reactive contaminants such as air and water vapor that are always present to some extent. The aim of most analytical methods involving the GD is to minimize these chemical interactions. On the other hand, the GD offers a unique opportunity to examine certain types of reactions. The ability of the GD to generate a steady-state population of metal atoms for atomic reactions is quite useful. In addition to the intrinsic sputter formation of analytical species, the investigator may add reagents by gaseous sample introduction through a bleed valve or by periodic injection of gaseous reagent through a fast pulse valve. The discharge itself may be run in the steady state or in a pulsed mode, as may be useful in following time dependent processes. This talk will focus on some of the GD reactions that are exemplary of the plasma processes under a variety of conditions. Time resolution studies are utilized to show the importance of both gas phase and surface reactions that occur in analytical applications. The substitution of metal samples by geological materials introduces yet a greater complication as evidenced in the sputtering of atomic and molecular species. Many opportunities are seen for the exploration of glow discharges as a reactive environment.

31 ELEMENTAL ANALYSIS USING LASER ABLATION ION-TRAP MASS SPECTROMETRY.

Chris Gill and M. W. Blades, University of British Columbia, Department of Chemistry, Vancouver, British Columbia, Canada V6T 1Z1.

Plasma source mass spectrometry has had a profound effect on the field of inorganic analysis through the popular techniques of Inductively Coupled Plasma Mass Spectrometry (ICPMS), Laser Micro Mass Analyzer (LAMMA) methods, Glow Discharge Mass Spectrometry (GDMS), and Spark Source Mass Spectrometry (SSMS). An area which is being been explored in our laboratory for obtaining mass and optical spectra of small samples is ion generation inside an radio frequency quadrupole ion-trap using a laser to both atomize and ionize solid samples or liquid samples which have been deposited on a sampling probe. Since the sample is directly ablated in the trapping volume, transport loses can be kept small. Ionization of the sampled material can take place either in the laser produced plasma plume or a second ionization source, such as a laser of electron gun can be used. The qualitative and quantitative aspects of laser ablation ion trap mass spectrometry, focusing on the effects of laser power and wavelength (532 and 266 nm), sample characteristics, and mode of quadrupole operation will be discussed.

32 OPTICAL IMAGING STUDIES OF ARGON AND HELIUM INDUCTIVELY COUPLED PLASMAS BY A CID-BASED SPECTROMETER.

Chunming Hsiech and Akbar Montaser, Department of Chemistry, The George Washington University, Washington, DC 20052.

A novel optical system is constructed for the acquisition of spatially resolved information from an inductively coupled plasma (ICP) operated with either Ar or He. The system uses a 35-cm focal length Czerny-Turner monochrometer with a 2-mm entrance slit to provide spectral resolution of 4 nm. A solid state charge-injection device (CID), having 388 by 488 sensor elements, is used to provide quantitative image maps of the plasmas. Because of the solid-state stability and anti-blooming capability of CID, high quality images and high spatial resolution are obtained. For example, with a 17% image magnification, the entire image of plasma can be monitor simultaneously with a spatial resolution of 0.13 mm. In addition, by using the Abel inversion, the lateral distribution of plasma emission intensities is converted to a radial distribution format. The image maps of argon and helium plasmas will be presented at various forward powers, gas flow rates, and sample uptake rates to illustrate unique features of He ICP as compared to the commonly used Ar ICP.

33 DIGITAL FILTERS; THEY'RE NOT JUST FOR SMOOTHING ANYMORE.

Peter D. Wentzell, Stephen J. Vanslyke and Stephen G. Hughes, Trace Analysis Research Centre, Department of Chemistry, Dalhousie University, Halifax, Nova Scotia, Canada B3H 4J3.

Digital filters have long been perceived by chemists mainly as a tool for smoothing noisy data or computing derivatives. While these are certainly the most widespread applications of digital filtering methods, much more powerful signal processing techniques exist. For example, digital filters have been employed for parameter extraction, model testing, response surface mapping, and multivariate calibration. The strengths of digital filters are their versatility, simplicity, speed and recursive nature, which allow them to be applied to data in real-time. This presentation will focus on non-traditional ways of using digital filters to extract information from multivariate data sets. In particular, it will be shown that the Kalman filter can be used to detect and resolve components present in mixtures such as those found in chromatography and equilibrium studies. Furthermore, for certain types of measurements, the Kalman filter approach can be more effective than traditional methods of analyzing data, such as factor analysis. The Kalman filter is a recursive algorithm which is used to fit model parameters to measurements. For multivariate data sets, several models based on the assumption of one, two, or more chemical components can be employed. The validity of these models can be continuously assessed, allowing the number of components present to be determined. The Kalman filter approach can be superior to batch methods of rank analysis for two reasons. First, it is truly evolutionary; that is, it evaluates the validity of the models after each measurement is acquired, thereby exploiting the progressive evolution of the rank. Second, the innovations sequence, which is used to reflect model error, provides a meaningful reference point for evaluation of the number of components. These principles will be illustrated with examples from a number of sources and the general utility of this approach will be examined.

34 APPLICATION OF DIGITAL FILTERING TECHNIQUES TO PROBLEMS IN QUANTITATIVE FTIR SPECTROSCOPY.

Gary W. Small, Center for Intelligent Chemical Instrumentation, Department of Chemistry, Clippinger Laboratories, Ohio University, Athens, OH 45701-2979.

Fourier transform infrared (FTIR) spectroscopy is used in a variety of quantitative analysis applications in chemistry. Current state-of-the-art procedures for implementing an FTIR-based quantitative analysis focus on the use of multivariate calibration models based on spectral variables obtained by applying principal components analysis (PCA) or partial least-squares (PLS) analysis to a set of calibration spectra. Multiple linear regression analysis is used to correlate known concentrations to the spectral variables. The PCA and PLS procedures are useful largely because they allow spectral information pertaining to the analyte to be extracted from that due to interferences or spectral noise. In analyses in which analyte concentrations must be determined near the limit of detection, however, the PCA and PLS methods are not as efficient at suppressing noise as are traditional signal processing methods such as digital filtering. In the work presented here, digital filtering techniques are coupled with PCA and PLS methods to improve the precision of FTIR-based quantitative analyses. Automated techniques are demonstrated for designing optimized digital filters that can be applied to spectra before the PCA or PLS calculations are performed. It will be shown that multivariate calibration models based on the combination of digital filtering and PCA/PLS analysis outperform models based on PCA/PLS alone.

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35 RESOLUTION OF COMPONENT SPECTRA USING SUCCESSIVE AVERAGE ORTHOGONALIZATION AND ITERATIVE TARGET TRANSFORMATION.

XiHui Liang, Jennifer E. Andrews, and James A. de Haseth, Department of Chemistry, University of Georgia, Athens, GA 30602-2556.

In the investigation of reaction kinetics through time-resolved spectroscopic data, one must consider the contribution of intermediates that might be unknown or are difficult to isolate for study. A possible solution to this problem involves the use of Successive Average Orthogonalization (SAO) followed by Iterative Target Transformation Factor Analysis (ITTFA). In this method, SAO is applied to decomposition of a data set in the spectral space to produce eigenvectors that are related to spectral variations, including contribution from different components as well as noise. The primary eigenvectors are then subjected to ITTFA, which returns the pure component spectra. SAO is advantageous in the investigation of large data sets, as it treats data successively without the need of a large computer memory. In fact, SAO allows the treatment of potentially an unlimited number of spectra. In ITTFA, tests are made, without a priori knowledlge of the real components, to find out the peak positions of the real components and then these are transformed to component spectra. The constraint set in the transformation was that no negative adsorption was allowed. The effectiveness of SAO was studied on various synthesized spectral data sets. The major features obtained by SAO were compared to those obtained by some other methods such as Sinigular Value Decomposition (SVD) and Non-linear Iterative Partial Least-Squares (NIPALS). Synthesized spectra with different extent of overlapping bands were analyzed to resolve component spectra. The results demonstrate that this technique can resolve highly overlapped mixture spectra, producing spectra comparable to the original components, except for cases where the maxima of major peaks were exactly overlapped. The technique was also applied to the analysis of simulated time-resolved spectra as well as multiple spectral files collected during the formation of polyurethane foams to demonstrate the potential of its use as a tool in the investigation of kinetics in complex processes.

36 ADAPTIVE KALMAN FILTERING. Steven D. Brown, Department of Chemistry and Biochemistry, University of Delaware, Newark, DE 19716.

When calibration and prediction are done on the same chemical system, any of a number of multi-component calibration methods work well. When, however, the nature of the samples changes between the calibration and prediction steps, multicomponent analysis is seldom successful. Sequential regression methods such as the Kalman filter can be used when the uncalibrated analyte variation can be localized to a few elements of the response vector. Simple modifications to the sequential regression permit the calibration model to adapt to the regions of the data where the calibration model is valid. This talk discusses several adaptive Kalman filters for use in multicomponent analysis. Second-order adaptive Kalman filters can be used to estimate noise processes, even in the presence of an incomplete or incorrect calibration model. First-order adaptive Kalman filters can be used to estimate well-modeled components and compensate for unmodeled components. Examples of othe application of adaptive Kalman filters to chemical analysis will be given.

37 ADAPTIVE FILTERS AND INFORMATION. Yuzuru Hayashi and Sarah C. Rutan, Department of Chemistry, Virginia Commonwealth University, Richmond, VA 23284-2006.

For many problems in analytical chemistry, a desired signal may be overlapped with a unknown interferant signal. One means of quantifying the target signal with good accuracy and precision, in the presence of an interferant, is adaptive filtering. Here, an adaptive filter based on the recalculation of the measurement variance using the observed fit residuals has been used, and its performance has been characterized for a wide range of peak ratios and peak overlaps. Accurate and precise estimates for the target peak amplitude can be obtained for systems where the target peak is severely overlapped with an unknown interferant peak. It has been found that information theory can be used to provide a reliable estimate for the precision of the analysis of the target peak, as well as for the area under the peak corresponding to the interferant signal. The implications of this relationship between the adaptive filter results and the information will be discussed.

38 SELF MODELLING CURVE RESOLUTION APPLIED TO THE SIMULTANEOUS STUDY OF DIFFERENT SPECTROSCOPIC TITRATIONS OF MULTIEQUILIBRIA SYSTEMS. Roma Tauler, Department of Chemistry, University of Washington, BG-10, Seattle, WA 98195.

Self modelling curve resolution of individual spectroscopic titrations of multiequilibria systems based on evolving factor analysis does not provide a unique solution even when the constraints of non-negativity, closure and unimodality are applied. The rotational and intensity ambiguities still present can only be resolved when a selectivity region is present for every species and several titrations at different starting conditions are analyzed simultaneously.

39 PROBING SELECTIVE BINDING INTERACTIONS OF PROTEINS USING CAPILLARY ZONE ELECTROPHORESIS. John F. Wheeler and Amy C. Cater, Department of Chemistry, Furman University, Greenville, SC 29613.

Although high performance capillary electrophoresis has undergone remarkable fundamental development in recent years, the application of this technique in areas outside of analytical research has been rather limited. One of the most promising areas for HPCE in biomedical or clinical applications is in the separation of macromolecules, particularly if capillaries can be modified in such a manner to eliminate wall interactions. This investigation focuses on the use of HPCE for probing macromolecule/ligand interactions for protein systems using binding analysis. Such analyses are well suited to HPCE, since typically limited amounts of sample are available, the HPCE conditions employed are compatible with retaining protein structure, and the separation permits individual quantitation of both free and bound species in a single analysis. Further, the high efficiency and resolution associated with free zone HPCE and isoelectric focusing permit an *in situ* characterization of the specific proteins or protein fractions undergoing binding. Examples of selected model systems including hemoglobin, histones, and previously characterized associated ligands will be discussed.

40 ANGLE-RESOLVED PHOTOACOUSTIC SPECTROSCOPY: A NEW PROBE FOR MOLECULAR ORIENTATION. Kathy L. Rowlen, Department of Chemistry, University of Colorado, Boulder, CO 80309.

Photoacoustic spectroscopy (PAS) is a nearly univeral detection method that offers the sensitivity of fluorescence with the simplicity of absorbance. PAS can be used to probe the orientation of transition dipoles on a flat surface by varying the angle between a plane polarized excitation beam and the surface. Preliminary studies have focused on the development of a sensitive "surface coupled" cell and new waveform processing techniques. Submonolayer detection limits have been achieved with an extremely simple to use cell design. Conversion of the entire time-domain waveform to the frequency domain has provided unique insight into the dynamics of photo-induced processes. A first-order model to describe the PAS signal as a function of angle has been developed and will be discussed in terms of experimental calibration data. The long term goal is to apply this technique to systems in which molecular orientation is an important and poorly understood parameter, such as retention in chromatography.

41 Abstract not received at time of printing.

42 ANALYSIS OF BIOLOGICAL MICROSAMPLES BY CAPILLARY SEPARATION TECHNIQUES. R. T. Kennedy, N. Schultz, L. Cole, L. Huang, Department of Chemistry, University of Florida, Gainesville, FL 32611.

The time-resolved, in vivo measurement of bioactive substances is an important research tool in the characterization of biochemical systems. A number of approaches have proven useful in such studies including sensors, nmr, and microdialysis. In microdialysis, a probe consisting of a hollow fiber, semi-permeable membrane is inserted into the tissue of interest. The interior of the probe is perfuse with a buffer which approximates the extracellular matrix. Analytes diffuse across the membrane and are then washed out with the buffer which is collected in fractions. The fractions are then analyzed by HPLC or other appropriate technique. Many of the limitations of current microdialysis methodology result from the relatively low mass sensitivity of the analytical technique that is coupled with the probe. We are exploring the possibility of coupling microdialysis to capillary separation techniques such as capillary liquid chromatography and capillary electrophoresis. The high mass sensitivity and high resolving power of the capillary separation techniques should greatly improve the time resolution, quantitation, and spatial resolution of microdialysis measurements. Successful coupling of microdialysis to microcolumn separations will require innovations in sample introduction, detection, sample derivatization, and separation speed. This combination of techniques will be explored for its potential as a general approach to make sensor-like measurements using dialysis probes and rapid separation techniques.

43 NUCLEAR MAGNETIC RESONANCE SPECTROSCOPY: A VERSATILE TOOL FOR STUDYING MOLECULAR INTERACTIONS IN LIQUID CHROMATOGRAPHY. David M. Bliesner, Scott T. Shearer and Karen B. Sentell, Department of Chemistry, University of Vermont, Burlington, VT 05405-0125.

A better understanding of molecular interactions between the stationary and mobile phases is essential for improved prediction of retention and optimization of resolution in reversed phase liquid chromatography (RPLC). Solute retention, efficiency and selectivity measurements are useful in studying these systems, but chromatographic experiments alone can only provide indirect information about stationary and mobile phase structure and interactions at the molecular level. Nuclear Magnetic Resonance (NMR) spectroscopy is a complimentary analytical technique which can often provide a more direct probe of these environments than can be ascertained from chromatographic measurements alone. NMR is a versatile method for these studies because it can provide distinct information about the environments experienced by solute, stationary and mobile phase components in RPLC systems, often from a single experiment. To illustrate the utility of NMR for fundamental chromatographic studies, we will discuss NMR experiments in progress in our laboratory which are providing additional information on the role of stationary and mobile phase structure and interaction in RPLC retention and selectivity.

44 THE CHROMATOGRAPHY FORUM OF DELAWARE VALLEY—25 YEARS OF BRINGING TOGETHER SEPARATION SCIENTISTS. J. M. Di Bussolo, Perkin Elmer Corp., 860 Springdale Drive, Exton, PA 19341.

The Delaware Valley, which joins Pennsylvania, Delaware and New Jersey, is one of the richest areas in the world for chromatography. Here you will find a remarkably high concentration of chromatographers and chromatographic technology. For over twenty five years the Chromatography Forum of Delaware Valley has fostered this regional legacy by bringing together people interested in separation science with local, national and international experts. This symposium, commemorating the Forum's 25 years of service to the scientific community, highlights the many advances in chromatography that have taken place and continue to originate in the Delaware Valley. This symposium is dedicated to the Forum's first president and untiring mainstay Dr. Joseph C. Touchstone of the University of Pennsylvania.

45 GAS CHROMATOGRAPHY-ADVANCES MADE IN THE DELAWARE VALLEY (1965–1992). Robert L. Grob, Villanova University, Villanova, PA 19085.

The Chromatography Forum of the Delaware Valley (CFDV) was initially a center for much activity and advances in this area of gas chromatography (GC) and later in chromatography in general. The CFDV was founded in 1965 and originally named The Gas Chromatography Forum; its purpose to have a forum where chromatographers could gather and discuss their work in this growing area of separation science. The function of the CFDV soon became an organization to educate, inform and bring together separation scientists on a regular basis. This was achieved by monthly meetings, offering training courses in chromatography (GC, LC & TLC), sponsoring symposia and funding of awards. An historical overview of GC will be presented with emphasis on the people, companies and events which have contributed to the success of this technique in the Delaware Valley. The presentation will not be an all-inclusive coverage of each and every fact-but the highlights of this important era in the Delaware Valley.

46 THE CENTER OF COLUMN DEVELOPMENT, CENTRE COUNTY PENNSYLVANIA. Dr. Walter R. Supina (Retired Co-Founder of Supelco), 525 Ridge Ave., State College, PA 16803.

Many of the pioneers in chromatography had their roots at Penn State University in Centre County Pennsylvania . . . Arthur Rose, Professor of Chemical Engineering founded Applied Science Labs, which was responsible for the development of many important packed column materials used in the 1960's and 1970's such as Gas Chrom Q, JXR, and EGSS-X. Applied Science became the spawning ground for Superlco, and for Analabs (which was founded in Connecticut). Supelco then provided the training ground for the founders of Restek. Alltech Associates acquired the remainder of Applied Science Labs. George Fleming of the Chemistry Department at Penn State founded Scientific Systems and in the 1960's it was involved primarily in manufacture of stainless steel fittings for high pressure instrumentation. This led to contacts with Perkin Elmer and other instrument companies and Scientific Systems eventually became a manufacturer of HPLC instrumentation and columns. The founder of Keystone Scientific used experience at both Scientific Systems and Applied Science Labs to develop a company specializing in HPLC. In a non-commercial area, Dr. Stuart Patton of the Dairy Science Department at Penn State pioneered the use of GC in studies of milk products.

47 GAS CHROMATOGRAPHY IN ENVIRONMENTAL ANALYSIS—THE LAST 25 YEARS. Mary A. Kaiser, Du Pont Company, PO Box 6094, Newark, DE 19714-6094 and Robert L. Grob, Department of Chemistry, Villanova University, Villanova, PA 19085.

Some of the major contributions to the interface between gas chromatography and environmental analysis originated from scientists in the Delaware Valley. This paper first gives a status report on environmental analysis 25 years ago and the role that gas chromatography played at that time. Then the paper samples the contributions of many members of the Chromatography Forum and other contributors from the Delaware Valley in the development of instrumentation, instrumentation enhancements, and new methodology for environmental analysis using gas chromatography. In 1969 the National Environmental Policy Act (NEPA) became our National Charter for protection of the environment. NEPA required that an environmental impact statement be a part of every recommendation or report on proposals for legislation and other major federal actions significantly affecting the quality of the human environment. NEPA opened the door for the 1970 "Clean Air Act," the "Clean Water Act," RCRA, Superfund/CERCLA . . . meanwhile Delaware Valley scientists were developing a cryogenic, programmable gas chromatograph for air pollutant analysis; a method for improving the measurement of COS in H2S; building a commercial portable gas chromatograph for environmental analysis; developing guidelines for the screening of organic pollutants in water suplies, running environmental impact studies for proposed new road construction; developing computer programs to enhance trace analysis; improving our understanding of selective detectors for environmental analysis, and working with governmental agencies to improve the precision, accuracy, and detection limitations of official methods.

48 THE INVENTION OF THE FUSED-SILICA CAPILLARY COLUMN: AN INDUSTRIAL PERSPECTIVE. R. D. Dandeneau & E. H. Zerenner, Hewlett-Packard Company, P.O. Box 900, Avondale, PA 19311.

Fused silica as a material for columns and transfer lines has greatly changed the way the world does high resolution gas chromatography. The author was privileged to be a part of the original team that invented and developed fused silica capillary columns, and will give an account of the development. The time period covered will be from the very exciting discovery period in 1978–79 up to the introduction of Megabore columns in 1983. The talk will include our initial observations on the surface chemistries of different glasses and their impact on chemical inertness, and our quest to make stronger tubing, which ended in the commercialization of Megabore columns as an alternative to packed columns.

49 Abstract not received at time of printing.

50 BRIGHT LIGHTS AND SMALL PEAKS: HEWLETT-PACKARD'S 25-YEAR EFFORT IN GC-AED. James J. Sullivan & Bruce D. Quimby, Hewlett-Packard Co., Box 900, Avondale, PA 19311.

It is not well known that Hewlett-Packard has been investigating atomic spectroscopy since the late 60's, but the atomic emission detector for GC was not announced until 1988. This paper describes the false starts, interesting but impractical plasmas, and the frustrating wait for new technology. In 1967, a compact, multi-channel atomic absorption instrument was being developed. Hopes that this would lead to a GC detector for nonmetals were never realized. In 1969, studies of an atomic emission detector had several good ideas—the plasma had to be in helium, at atmospheric pressure, and be relatively energetic for good quantitation and empirical formulas. A bad ideas was the nearly spark-like pulsed DC plasma. Computers were not ready yet—the proposal included a teletype! In the 70's, both low-pressure microwave discharges and DC discharges with platinum electrodes were developed. Both used the vacuum ultraviolet spectral region. In the late 70's, there were three critical developments: Beenakker's atmospheric pressure MIP, Hewlett-Packard's photodiode array, and HP's 200 series computer, capable of running a mass spectrometer or an AED. In the 80's, the commercial AED was developed. There were surprises: water-cooling inside the microwave cavity, discharge tubes made from GC capillary columns freedom from microwave tuning, and software that doesn't require knowledge of wavelengths.

51 MATRIX ASSISTED LASER DESORPTION IN A FOURIER TRANSFORM MASS SPECTROMETER. Claus Köster, John A. Castoro, and Charles L. Wilkins, Department of Chemistry, University of California, Riverside, Riverside, CA 92521.

A subject of great interest during the past few years was research intended to adapt the matrix-assisted laser desorption/ionization (MALDI) methodology to Fourier transform mass analyzers. For a variety of reasons, this was a more difficult task than anticipated, with the primary difficulty apparently arising from the relatively high kinetic energies of the desorbed analyte ions. However, earlier this year we reported a procedure[1], involving the use of an appropriate retarding potential during the desorption event, that allowed low resolution FTMS detection of protein ions with masses up to 34,000 daltons. However, the mass resolution obtained for these examples was very poor, ranging from around 50 to about 300 (worse than typical time-of-flight measurements). It appears that this resulted from a choice of experimental conditions that produced ions sufficiently excited to undergo efficient metastable decay. Accordingly, changes in desorption matrix were investigated, in an attempt to produce cooler ions susceptible to observation for the length of time required to obtain high mass resolution. By using a comatrix of sugar with 2,5-dihydroxybenzoic acid, mass resolution in excess of 10,000 can be obtained for a variety of small proteins. These recent results will be discussed.

1. J. A. Castoro, C. Köster, and C. Wilkins, *Rapid Comm. in Mass Spectrom.*, **6**, 239 (1992).

52 MATRIX-ASSISTED LASER DESORPTION FTMS FOR THE INVESTIGATION OF X-RAY INDUCED DAMAGE TO NUCLEIC ACID CONSTITUENTS*, Robert Hettich and Hiroko Yoshida, Oak Ridge National Laboratory, Oak Ridge, TN 37831-6120.

Ionizing radiation damages DNA by causing strand breaks as well as base and sugar modifications, which may lead to mutations and ultimately cell death. Matrix-assisted laser desorption (MALD) FTMS provides a useful method for the direct examination of products generated by irradiation (^{60}Co gamma rays) of aqueous solutions of nucleotides and oligonucleotides. This technique enables simultaneous detection and identification of products ranging from free nucleic bases to small oligonucleotides, and eliminates the need to hydrolyze and derivatize the sample prior to mass spectral examination. The ion manipulation and accurate mass measurement capabilities of FTMS provide detailed structural information for picomole quantities of these biological products. MALD-FTMS revealed that the major radiation damage was simple bond cleavages, although some hydroxylated products, such as thymine glycol and hydroxydihydrothymine, were also observed. In some cases, reverse phase liquid chromatography was used to purify fractions for subsequent identification by FTMS. Current research is focussed on extension of the MALD-FTMS technique for larger oligonucleotides as well as further development of HPLC for quantitation of the dose dependence of the products.

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53 Abstract not received at time of printing.

54 NEW DEVELOPMENTS IN TRAPPING, EXCITATION, AND DETECTION IN FT/ICR MASS SPECTROMETRY. Shenheng Guan, Alan G. Marshallo,† Michael V. Gorshkov, Peter B. Grosshans, Charles W. Ross, III, Lutz Schweikhard,§ and Tom L. Ricca.‡ Department of Chemistry (†Department of Biochemistry, ‡Campus Chemical Instrument Center, §Institute of Physics, U. Mainz, Germany), The Ohio State University, 120 West 18th Avenue, Columbus, OH 43210.

A magnetic rf ion tap makes possible simultaneous detection of both positive and negative ions:[1] the ultrahigh mass resolving power of FT/ICr/MS resolves $^{35}Cl^{+}$ and $^{35}Cl^{-}$, separated by just twice the electron mass (~0.001 u). We also demonstrate two-dimensional FT/ICR/MS produced by a series of stored-waveform excitation waveforms: the usual mass spectrum appears as peaks on the diagonal of a 2D-display, whereas forward (or reverse) ion-molecule reactions show up as peaks on one (or the other) side of the diagonal.[2] Finally, quadrupolar excitation is shown to axialize initially off-axis ions[3] for cooling of externally injected and/or translationally and internally excited ions. Work supported by N.S.F. (CHE-9021058), N.I.H. (GM-31683), and The Ohio State University.

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2. Ross, C. W., III; Gaun, S.; Grosshans, P. B.; Ricca, T. L.; Marshall, A. G. *Proc. 40th ASMS Conf.*, Washington, D.C., June, 1992, ThP 125.
3. Guan, S.; Schweikhard, L.; Marshall, A. G., *ibid.* TP 91.

55 HIGH RESOLUTION TANDEM MASS SPECTROMETRY OF LARGE MOLECULES. Detlev Suckau, Steven C. Beu, Yueer Shi, Michael W. Senko, John P. Quinn, Francis M. Wampler, III, and Fred W. McLafferty. Baker Chemistry Laboratory, Cornell University, Ithaca, NY 14853-1301.

In recent reports (1) it was demonstrated that a 2.8 Tesla fourier-transform mass spectrometer (FTMS) with electrospray ionization (ESI) can give 70,000 resolving power and <0.1 Da mass errors for molecules as large as myoglobin (17 kDa). Resolved isotopic peaks provide charge state assignment based on the unit mass separation of the isotopes, avoiding errors due to impurities or adducts included in measured peak envelopes. The unique MS/MS features of FTMS were utilized to obtain sequence information from molecules as large as ubiquitin (8.6 kDa). In a new 6.2 T instrument similar in overall design, unit resolution for 150 kDa molecules should be possible. For hydrogen/deuterium exchange of protein ions with D_2O in the gas phase, pseudo-first-order kinetics was generally observed. Cytochrome C as well as S-derivatized ribonuclease exhibit two different exchange reactions, corresponding to the co-existence of conformers having substantially different numbers of reactive hydrogens (113, 74 and 135, 61, respectively). These values are consistent with conformer compactness in solution; ions of native ribonuclease (four cross-linking S-S bonds) exchange only 32 H atoms.

1. Loo et al. (1992) *Proc. Natl. Acad. Sci. USA 89*, 286.

56 HIGH MAGNETIC FIELD ELECTROSPRAY FTICR. Z. Guan, V. L. Campbell, and D. A. Laude, Jr., Department of Chemistry and Biochemistry, The University of Texas at Austin, Austin, TX 78712.

A generalized interface was constructed to facilitate high pressure electrospray ionization within the bore of a superconducting magnet to be used for FTICR detection. This was accomplished by combining a series of differentially pumped concentric tubes to permit ion formation in a 3.0 T field at atmospheric pressure with detection occurring only a few cm away at 10^{-8} torr. The advantage of this type of source compared to more conventional external high pressure sources is that the strong radial-confining nature of the magnetic field precludes the need for elaborate focusing of externally generated ions and increased ion current delivered to the cell. Coupled with the use of a supersonic expansion to carefully control axial kinetic energy, efficient trapping schemes become possible. New results to be presented include an evaluation of relaxation mechanisms responsible for rapid homogeneous cooling of cyclotron motion. With relaxation times on the hundred millisecond timescale, nondestructive remeasurement of the same ion packet is achieved with 100% efficiency. For example, 250 remeasurements of bovine albumin dimer ions permit detection limits to be pushed to the sub-femtomole level.

57 GLOW DISCHARGE—FTICR MASS SPECTROMETRY: HIGH RESOLUTION ELEMENTAL ANALYSIS. J. R. Eyler, Department of Chemistry, University of Florida, Gainesville, FL 32611-2046; C. M. Barshick, Analytical Chemistry Division, Oak Ridge National Laboratory, Oak Ridge, TN 37831-6375, and C. H. Watson, Bruker Instruments, Inc., 19 Fortune Drive, Billerica, MA 01821.

A number of advantages can be realized in the coupling of glow discharge (GD) sources to fourier transform ion cyclotron resonance (FTICR) mass spectrometers [C. M. Barshick and J. R. Eyler, J. Am. Soc. Mass Spectrom. 1992, 3, 122]. Foremost of these is mass resolving power in the range of 1 part in 200,000 to 500,000. A considerable improvement over all currently-available commercial instrumentation. The ability to trap GD-generate ions in the FTICR analyzer cell and subject them to ion/molecule reactions or laser irradiation also adds to the power of this technique. This talk will present examples of several different GD-FTICR coupling approaches, and will illustrate the power of the technique in resolving potential isobaric interferences at both low (M/Z 50–60) and high (M/Z 190–240) masses.

58 SURFACE ANALYSIS BY LASER-INDUCED THERMAL DESORPTION/FTMS AND FT REFLECTION ABSORPTION IR: ORGANIC THIN FILMS ON TI AND OXIDIZED TI METAL FOILS. Donald P. Land, Nick A. Thornburg, and Ihab Abdelrehim, Department of Chemistry, University of California, Davis, CA 95616.

The surface composition of Ti biomedical implants is thought to play a major role in infectious rejection of implants. Molecular identification of species on Ti and TiO surfaces has proven difficult, however. In this study, numerous organic species are adsorbed on Ti and oxidized Ti foils and surface analysis is performed by Auger electron spectroscopy (AES), laser-induced thermal desorption with post-ionization and Fourier transform mass spectrometry (LITD/FTMS), and Fourier transform reflection absorption infrared spectroscopy (FTRAIRS). This is accomplished using a new instrument designed and constructed at UCD combining these three technologies for the first time on a single instrument. Efficacies and sensitivities for the three techniques are compared for the two types of surface for species containing varying functional groups.

59 A GAS-PHASE STUDY OF Fe(PHENYL)$^+$ WITH ALKANES: Y. Li, E. Garcia, Y. Huang, B. S. Freiser, Department of Chemistry, Purdue University, West Lafayette, IN 47907.

The gas-phase reactivities of Fe(phenyl)$^+$ with small alkanes (C_nH_{2n+2}, $n = 1 - 6$) were studied by laser desorption-Fourier transform mass spectrometry (FTMS). Fe(phenyl)$^+$ was formed from the reaction of Fe$^+$ with iodobenzene by loss of I$^\cdot$. Collision-induced dissociation of Fe(phenyl)$^+$ yields loss of phenyl ligand, exclusively, over the energy range of 3 eV to 54 eV. Fe(phenyl)$^+$ reacts with linear alkanes larger than ethane via several pathways including: alkene elimination to form $FeC_6H_7^+$, dehydrogenation involving ligand coupling, and condensation to form Fe(phenyl)(alkane)$^+$. The first two processes involve C-H insertion almost exclusively. In contrast to the linear alkanes, when Fe(phenyl)$^+$ reacts with branched alkanes, such as 2-methylpropane and 2,3-dimethylbutane, no condensation reactions are observed due to the active secondary hydrogen. Mostly condensation and no dehydrogenation was observed with neopentane as expected since there are no β-hydrogens. A C-C insertion product was also observed in minor amounts for the branched alkanes. The reactions of Fe(phenyl)$^+$ are significantly different from that of bare Fe$^+$ with alkanes, with the latter reacting predominantly by oxidation addition of the metal into C-C bonds. These results indicate that the attachment of the phenyl ligand to the bare metal ion center has a significant effect on the reactivity of the metal center.

60 IN SITU MONITORING OF EMULSION POLYMERIZATION USING FIBER-OPTIC RAMAN SPECTROSCOPY, C. Wang, T. J. Vickers, J. B. Schlenoff, C. K. Mann, Department of Chemistry, Florida State University, Tallahassee, FL 32306-3006.

This is a study of the feasibility of using Raman spectroscopy to monitor the composition of micelles during emulsion polymerization. Laser excitation was introduced through a silica fiber enclosed in a glass sheath immersed in the reaction mixture. Scattered light collected by six fibers arranged concentrically about the excitation fiber was taken to a dispersive spectrometer fitted with an intensified diode array detector. Measurements were made using an estimated 100 mW excitation at the sample with 180-second integration times. After spectra were corrected for detector element variations, quantitation was performed by least-squares fitting. The test reaction was polymerization of syrene. Disappearance of styrene was followed by monitoring the C = C peak at about 1600 cm^{-1}. A nearby ring vibration band was used as an internal standard. The limit of detection for styrene in a suspension of polystyrene was determined to be about 0.3%. To validate the Raman analysis, a parallel set of measurements was carried out by repeatedly sampling the reaction mixture. The samples were diluted with cold water to stop the reaction. They were analyzed by extracting the styrene into CH_2Cl_2 and measuring UV absorbance. That extraction procedure gave recoveries of about 95%. Allowing for that, essentially the same results were obtained by both methods.

61 INVESTIGATION OF WALL DEPOSITS IN TUNGSTEN HALOGEN LAMPS BY RAMAN SPECTROSCOPY. Peter J. Codella and Laurence Bigio, General Electric Corporate R&D Center, P.O. Box 8, Building K1-2A52, Schenectady, NY 12301.

Previous efforts in our laboratory focused on the quantification of gaseous species within the envelope of tungsten halogen lamps. The work was done non-destructively using FT-IR. In some cases, burning lamps produce a deposit on the inside of the envelope. These deposits can be pure metal or a compound formed with gaseous components. This talk will present the results of our efforts to identify and study these deposits using Raman Spectroscopy. Again the investigations are designed to be non-destructive allowing the continuation of lifetime testing. In a few cases, samples were sacrificed and the deposits examined by X-ray photoelectron spectroscopy. Elemental data provided by these experiments, coupled with a review of the literature on Raman lines of likely compounds, assisted in the assignment of some of the Raman peaks. Reference spectra were also obtained from powdered samples of WO_3 and MoO_3. For example, one lamp with yellow deposit, yielded 7 Raman lines, 81, 93, 119, 231, 270*, 737, & 810* wavenumbers. Peaks, due to WO_3 are starred.

62 DETECTION OF HYDROGEN GAS LEAKS WITH RAMAN SPECTROSCOPY. Kevin M. Spencer, Michael M. Carrabba, Robert B. Edmonds, Michael D. Arnett, Martin W. Rupich, and R. David Rauh, EIC Laboratories, Inc., 111 Downey Street, Norwood, MA 02062.

Most Raman applications require the need for complex spectrographic systems for complete data analysis. However, there are certain processes where the monitoring of one spectral band of interest is necessary. In this situation, it is feasible to replace the spectrometer with a filter and monitor changes in signal intensity on a single channel detector. In this manner, we have monitored changes in hydrogen gas concentration on a silicon photodiode detection unit. Preliminary results, including detection of 1% hydrogen and collection of hydrogen data utilizing a laser diode will be discussed. In addition, current improvements which are being made to the detector will be discussed which should allow ppm H_2 detection.

63 APPLICATIONS OF RAMAN SPECTROSCOPY TO INDUSTRIAL PROCESSES. Stuart Farquharson, Dow, U.S.A., Bldg. A-915, Freeport, TX 77541.

The role of on-line chemical analyzers is vital to process monitoring, control and product quality. Although traditional optical filter methods; UV, VIS, NIR, and IR has enjoyed considerable success when applied on-line, they often require complex sampling schemes. These inconveniences can be largely eliminated by fiber optic probes as evidenced by their growing popularity. Fiber optics also allow remote location of full spectrum analyzers which in turn allow multicomponent analysis. Recently we have developed a portable mini Raman spectrograph, composed of a HeNe or Diode laser source, a small spectrometer, and a CCD detector. We are most successful with this system when it is applied to processes as a short term investigative technique. Examples of contaminant identification, reaction rates, and process optimization will be given.

64 APPLICATIONS OF FIBER OPTIC RAMAN SPECTROSCOPY TO ENVIRONMENTAL MONITORING. Michael M. Carrabba, Kevin M. Spencer and Robert B. Edmonds, EIC Laboratories, Inc., 111 Downey Street, Norwood, MA 02062. John Haas III, Oak Ridge National Laboratory, P.O. Box 2008, Oak Ridge, TN 37831.

The importance of techniques to sense and monitor the environment are becoming increasingly more important with the intensifying presence of groundwater, soil and air contaminants. Our research and development effort is aimed at producing a commercial, field portable instrument for the field screening/*in situ* monitoring of contaminants based on Raman spectroscopy techniques with fiber optic probes. Some of the advantages of this technique for monitoring contamination sites are cost, small size of sampling probe, real-time analysis, the capability of sensing in adverse environments, and the ability of using a central detection facility. The technique has an advantage over current integrating fiber optic chemical sensing methods in that it provides direct chemical analysis in "real-time." We will discuss the methodologies, instrumentation, and field deployment results of the fiber optic Raman system for environmental monitoring.

65 INDUSTRIAL APPLICATIONS USING FT-RAMAN SPECTROSCOPY. J. A. Graham, Hercules Incorporated, Research Center, c/o 1313 N. Market St., Wilmington, DE 19894-0001.

FT-Raman spectroscopy has proven useful in a variety of applications and has become accepted as a technique that is complementary to IR and conventional Raman spectroscopies. Aside from the obvious benefits resulting from reduced fluorescsence, the ability to computerize the data and use one spectrometer for both Raman and infrared analyses is quite useful. There appears to be a select number of applications that are well suited for FT-Raman spectroscopy. Some of these applications include, mechanistic studies of polymer reactions, characterization of synthetic materials, and studies of polymer stability. This presentation will discuss a number of these applications. Emphasis will be directed towards the experimental and data processing parameters necessary to effectively carry out these applications.

66 FT-RAMAN SPECTROSCOPY—A TECHNIQUE IN FLUX. David A. C. Compton and Philip J. Stout, Bio-Rad, Digilab Division, 237 Putnam Avenue, Cambridge, MA 02139.

Each year, for the past four years or so, there has been a step-forward in FT-Raman technology. These steps have cumulatively moved the technique from being a research tool to a routine laboratory tool. The last two years have seen an improvement in signal-to-noise ratio due to the use of a Germanium detector, and now a move from FT-Raman accessories to the development of dedicated FT-Raman spectrometers. We will discuss the utility of a new design of stand-alone spectrometer in solving a range of laboratory problems, and demonstrate how such an instrument can be a powerful addition to the analytical capabilities of a modern laboratory. The principal novel features of this instrument include dynamic alignment of the interferometer, a choice of both refractive and reflective sampling optics, and interchangeable sampling holders.

67 RECENT DEVELOPMENTS IN FOURIER TRANSFORM RAMAN MICROANALYSIS; INSTRUMENTATION AND APPLICATIONS. A. J. Sommer and J. E. Katon, Molecular Microspectroscopy Laboratory, Department of Chemistry, Miami University, Oxford, OH 45056.

Recent improvements to a Fourier transform Raman microprobe have enabled the system to become an analytically viable technique for the study of materials possessing weak Raman scattering cross-sections. Although most enhancements have been made through improvements to the spectrometer, significant gains have been realized within the design of optical components contained in the microprobe. The design of these optical components will be discussed and highlighted with regard to spatial resolution, stray light rejection and employment of the microprobe for a wide variety of sample sizes. Several examples of the systems utility for the analysis of weakly scattering materials and industrial problem solving will be presented.

68 SURFACE-ENHANCED RAMAN SPECTROSCOPY OF SEROTONIN AND MELATONIN. Will K. Kowalchyk, Kevin L. Davis, Elizabeth A. Todd, Michael D. Morris, Department of Chemistry, University of Michigan, Ann Arbor, MI 48109-1055.

Surface-enhanced Raman Spectroscopy (SERS) is emerging as a technique for the analysis of various neurotransmitters in mammalian systems. The technique is sensitive and selective enough for use in neurochemical analyses. SERS does not require an electro-active molecule for detection, and does not suffer from interferences by ascorbate or uric acid. We have previously reported application to the catecholamines and histamine. We now report the SERS spectra of serotonin and melatonin at silver electrodes. Serotonin is found mostly in the hypothalamus and has been implicated in many neurological disorders. Melatonin is found in the pineal gland and is involved in the regulation of diurnal behavior. The SERS spectra of these molecules consists primarily of the aromatic ring breathing modes from the indole ring structure. Although the spectra of serotonin and melatonin are qualitatively similar, there are differences of 5–15 cm^{-1} in most bands and one or two bands unique to each molecule. The dependences of the spectra as a function of pH and electrode potential will be discussed, as will the trade-offs between sensitivity and selectivity. In order to assess the feasibility of using SERS as a probe of neurochemical samples, the optimization of SERS conditions will be detailed. The use of Nafion and cellulose acetate as electrode coatings for protein rejection and analyte preconcentration will be addressed. Such coatings will be necessary if protein-rich samples are to be analyzed using SERS.

69 DRUG DETERMINATIONS-MEDICAL LEGAL TOXICOLOGY. David T. Stafford, University of Tennessee Toxicology Laboratory, 3 N. Dunlap Street, Memphis, TN 38163.

The examination of blood, urine, and other tissues for the presence of drugs and poisons, and the interpretation of the analytical results in order to assist the medical examiner in determining cause and manner of death represents a special set of problems. The task frequently requires searching for, confirming, and quantitating low concentrations of a rather wide variety of compounds or combination of compounds which must be isolated from sometimes difficult matracies, with little or no information as to the substances which might be present. In addition, each of these cases has the potential for involvement in criminal and/or civil litigation. This presentation will address the use of modern techniques to isolate and identify and quantitate drugs and/or poisons in these cases, and the interpretation of the results. Several recently encountered situations will be used as examples to illustrate the approach to analysis. The preparation for court and courtroom appearance will also be addressed.

70 SERIAL CAPILLARY GC/IR/MS: QUANTITATION AND IDENTIFICATION OF AMPHETAMINE, METHAMPHETAMINE, AND AMPHETAMINE ANALOGS IN HUMAN URINE. Gennady E. Platoff, David W. Hill, Thomas R. Koch, and Yale H. Caplan, U.S. Army Forensic Toxicology Drug Testing Laboratory, Fort Meade, MD 20755.

Forensic urine drug test procedures emphasize the confirmation of presumptive positives using a specific and sensitive method. In most accredited laboratories, amphetamine (AMP), methamphetamine (MAMP), and amphetamine analogs are confirmed by GC/MS selected ion monitoring (SIM). This study describes the application of a sensitive and accurate single injection gas chromatography/fourier transform infrared spectrometry/mass spectrometry-electron ionization (GC/IR/MS) method for both qualitative and quantitative IR and quantitative MS-SIM determinations of AMP, MAMP, and amphetamine analogs in human urine.

71 COMBINATION OF MICROCRYSTALS & FT/IR MICROSCOPE TO SOLVE CHALLENGING DRUG ANALYSIS PROBLEMS Howard A. Harris, Ph.D., J.D., Thomas Kane, and Thomas Rodwell, B.S. M.S., Monroe County Public Safety Laboratory, Public Safety Building, Room 524, Rochester, NY 14614.

The identification of LSD has posed an analytical challenge for forensic laboratories. Where a few doses are seized, only microgram quantities are available, often in forms which make isolation difficult. The scheme describes combines preparative thin layer chromatography followed by wick evaporation and fourier transform infrared spectroscopy (FT/IR). The sample is purified by preparative thin layer chromatography (TLC) on 1″ × 3″ plates. The band of interest is scraped from the plate and wick evaporation is used to yield small crystals of pure LSD in a form well-suited for analysis using a microscope sampling device with a FT/IR spectrometer. These crystals produce excellent spectra from samples containing less than 50 micrograms of LSD. Distinguishing between LSD, isolsd and lysergic acid *n*-(methyl-propyl) amide (LAMPA) poses no problem with the spectra obtained. A number of other drugs can be conveniently analyzed using this scheme, which appears to be quite general. Most solids which crystalize and can be purified by preparative TLC can be isolated, using wick evaporation, as microcrystals suitable for micro-infrared or other analytical techniques.

72 CANADIAN DESIGNER DRUGS. Michael LeBelle, Health Protection Branch, Drug Identification Laboratory, Bureau of Drug Research, Ottawa, Ontario, K1A 0L2, CANADA.

Canada has a long history of the production of new illicit drug substances that are structurally related to recognized psychoactive substances. Often, clandestinely produced drugs are encountered in Canada before they appear elsewhere. For example, many years ago, 4-methoxyamphetamine was identified shortly before its appearance in the United States. Since that time, numerous other substances have been encountered particularly in the wake of the journalistic attention given to designer drugs. The identification and international implications of some of the designer substances related to the amphetamines, phencyclidine and meperidine recently identified in Canada will be discussed. The practicality of the prediction of future candidates will also be addressed.

73 MICELLAR ELECTROKINETIC CAPILLARY CHROMATOGRAPHY (MECC) OF DRUGS AND RELATED COMPOUNDS OF FORENSIC INTEREST. Ira S. Lurie, Drug Enforcement Administration, Special Testing and Research Laboratory, 7704 Old Springhouse Road, McLean, VA 22102-3494.

The application of micellar electrokinetic capillary chromatography (MECC) for the analysis of drugs and related compounds of forensic interest is presented. MECC is overall superior to high performance liquid chromatography (HPLC) in terms of resolution and speed for the analysis of these compounds. Drugs investigated include opium alkaloids, local anesthetics, barbiturates, benzodiazepines, amphetamines, fentanyls, hallucinogens, anabolic steroids and cannabinoids. Since all compounds elute at the same time or before the micelle, MECC is an excellent technique for drugs screening. The suitability of MECC for quantitative analysis of anabolic steroids is presented. In addition the applicability of MECC for analysis of optical isomers of phenethylamines is shown. The procedure involves separation of diastereoisomers formed by derivatization with 2, 3, 4, 6-tetra-o-acetyl-b-d-glucopyranosyl isothiocyanate (GITC). For the separation of these compounds the effects of organic modifier type, organic modifier concentration, voltage, temperature and SDs concentration are described.

74 GC/FT-IR METHODS FOR DRUG ANALYSIS. K.S. Kalasinsky, J. Magluilo, Jr. and T. Schaefer, Armed Forces Institute of Pathology, Division of Forensic Toxicology, Washington, D.C. 20306.

Studies for infrared method development for drugs of abuse are currently being pursued by several laboratories for routine drug testing. Vapor phase GC/FT-IR techniques have been successfully developed for absolute concentrations of low nanogram amounts which are equivalent to 200 ng/mL urine. Cryogenic deposition GC/FT-IR techniques are being developed which indicate low picogram amounts of material are detectable. Some preliminary work with amphetamines have shown that reference quality spectra can be obtained with as little amount of material as 600 picograms, and quantities below 150 pg can be obtained for identification purposes. The prime advantage of GC/FT-IR methods over GC/MS method is the absolute identification that is available from infrared of the drug, its isomers and metabolites. The sensitivities of the cryogenic deposition GC/FT-IR techniques are now comparable to that of GC/MS.

75 IDENTIFICATION OF BLOOD AND SEMEN STAINS ON CLOTHING USING NEAR-INFRARED SPECTROSCOPY.

E. W. Ciurczak, F. A. DeThomas, J. E. Carroll, NIRSystems, Inc., 12101 Tech Road, Silver Spring, MD 20904.

Modern biological testing methods are used to type blood and semen and the results are usable in court as evidence. The methods are costly and time-consuming. NIRS may be used as a screening technique to determine whether the stains are biological in origin or something mundane such as ketchup or paint. Spectra and an identification algorithm will be shown in this paper.

76 ELECTRIC BIREFRINGENCE IMAGING OF NUCLEIC ACID ELECTROPHORESIS,

Daniel W. Grossmann, Maureen Lanan, Michael D. Morris, Department of Chemistry, University of Michigan, Ann Arbor, MI 48109-1055.

We describe progress in electric birefringence imaging (EBI) for non-invasive, on-line monitoring of DNA electrophoresis in agarose slab gels. Our system is based on sodium D line (589 nm) illumination and slow-scan video, with high resolution digitization. Plastic film polarizing optics are used throughout. We use simple image processing to separate the observed birefringence signals to Kerr effect and hydrodynamic (gel distortion) components, which monitor the local DNA concentration and its gradient along the migration direction, respectively. For small fragment sizes, the gel distortion signal is larger than the Kerr effect signal. Above about 50 kilobase pairs, the Kerr effect signal becomes the major contributor to the image. In the low kilobase pair range, both components have similar magnitudes. Since the dominant signal is a function of fragment length, the image processing technique used is changed according to the size range under examination, allowing non-invasive imaging in the low nanogram range. We will describe optical design details of the current generation of imagers and discuss the electrooptic properties of several commercial agaroses. We will discuss recent analytical results obtained with the system, including on-line monitoring of DC and pulsed-field electrophoretic separations.

77 CONSIDERATIONS IN SELECTING A LIMS: FLEXIBILITY, TURNKEY OPERATION, VENDOR SUPPORT.

Richard D. Beaty, Ph.D., Telecation, Inc., 19423 N. Turkey Creek, Suite C, Morrison, CO 80465.

While many laboratories are currently exploring their options for implementing their first LIMS, a significant number of other laboratories are purchasing their second LIMS system. The need for a second LIMS is largely due to the deficiencies of past LIMS in adapting to growth and change. This paper will discuss the important issues involved in selecting a LIMS system, including turnkey operation, user modifiability, and propensity of a user modified system for continued vendor support.

78 STRATEGIES FOR SPECTRAL IDENTIFICATION: DEDUCING INFORMATION ABOUT STRUCTURAL COMPOSITION FROM SPECTRAL SEARCHES.

W. M. Grim, III, B. A. Woods and M. Boruta, Bio-Rad Laboratories, Sadtler Division, 3316 Spring Garden St, Philadelphia, PA 19104.

Databases of Infrared, NMR and Mass Spectra have been used for years to verify suspected or identify unknown chemicals. Collections of printed spectra have evolved into databases of digital spectra, which can be interrogated by standard similarity algorithms to extract concealed information as well as that which is readily apparent. The effectiveness of such databases and software may be compromised when the unknowns are mixtures of related or unrelated compounds, or are simply not in the database at all. Recent advances in software tools which enable correlation of functional groups can aid general identification, and databases of structures, which can be interrogated by substructure search techniques can also aid general classification. Improved spectroscopic database management techniques have enabled better correlation of spectroscopic data for confirmation of spectral search and implementation of spectral prefiltering. Revisiting the classic technique of peak searching also proves to be a valuable tool for general classification as well as a stand-alone search technique for inseparable mixtures.

79 ELECTRONIC NOTEBOOK USING MICROSOFT WINDOWS.

Nalin J. Shah, Robert J. Obremski, John W. Silzel, Beckman Instruments, Inc., 200 South Kraemer Blvd., Brea, CA 92621.

With the maturation of the personal computer technology and electronic notebook to replace a patent notebook may become the reality if the appropriate hardware and softwares are used. The software packages should allow a user to perform the functions usually accomplished with a laboratory notebook while at the same time employing newer electronics capabilities. The hardware must be compatible with a chemistry laboratory while the environment should also allow the user to authorize the notes by importing the authorized signature. In this paper, we will review the commercial softwares and hardware which may be used to achieve this goal and will comment on our experiences in the implementation. The environment discussed will be limited to microsoft windows.

80 "ASTM E49 Committees on Chemical Data Standardization—Standards for Chemical Data."

Rich Lysakowski, Chairman, ASTM Committee E49.52—Computerization of Analytical Sciences Data, Digital Equipment Corp., Four Results Way, MRO4-3/C9, Marlboro, MA 01752.

Scientific data standards are a major issue for most large scientific organizations today. Data are one of a research organization's most valuable assets. However, those assets are not being used as effectively as possible. Too much time is spent trying to use data because it is not standardized. Too much time is wasted creating custom interfaces to move data around. A formal mechanism has been needed to spur the creation of chemical data standards. In 1990, three new ASTM Committees formed to focus on this problem. The three Committees are:

1) ASTM E49.51—Chemical Structural Information
2) ASTM E49.52—Computerization of Analytical Sciences Data
3) ASTM E49.53—Data Exchange Formats for Physical and Chemical Quantities

Since 1990, these committees have started producing their first usable specifications. This talk will briefly introduce each committee's efforts and give status details for each one. A call to action will conclude the talk, because the Committees wish to speed up development of the standards.

81 NIST GAS REFERENCE MATERIALS: STATUS AND PHILOSOPHY.

Thomas E. Gills, National Institute of Standards & Technology, Bldg. 202, Rm. 215, Gaithersburg, MD 20899.

One important role of the National Institute of Standards and Technology (NIST) is to provide standards necessary to assure data quality in measurements related to atmospheric and industrial pollutants. The NIST Standard Reference Materials program serves as a source of primary gas Standard Reference Materials (SRMs) for agencies that regulate or monitor the emissions of atmospheric pollutants as well as industries that must control the levels of pollutants emitted by their processes. There are approximately 84 gas SRMs, comprising eighteen (18) different types, and four (4) permeation devices of two (2) types that are available from NIST. The gas SRMs are certified using well established protocols that consist of the following:

1) Tightly controlled NIST specifications
2) NIST primary standards
3) Analytical techniques/methods program
4) Long term stability testing and update
5) Measurement quality assurance program

This paper will address the current status of gas SRMs and present discussions on the philosophy of NIST gas SRM certification.

82 "Creating Industry-Wide Analytical Data Interchange And Storage Standards (ADISS) For Analytical Chemistry".

Dr. Rich Lysakowski, ADISS Project Director, Digital Equipment Corp., Four Results Way, MRO4-3/C9, Marlboro, MA 01752.

Monumental steps were taken in 1992 by the analytical instrument and software industries to create laboratory data standards. Scientists now have a standardized basis for sharing, storing, and retrieving analytical data. This frees them from proprietary constraints and allows them to use and re-use their data easily. Leading vendors and end users introduced both specifications and a public-domain implementation based on the Analytical Data Interchange and Storage Standards (ADISS). The ADISS solution specifies both an analytical information model and a public-domain implementation. The ADISS Project gives scientists a unified technical architecture and strategy for standardized analytical data sharing. Industry, government, end users, and standards organizations are cooperating at it. Thus far, ADISS has been applied to chromatography, mass spectrometry, and surface science. Currently, ADISS data dictionaries are being rapidly developed for NMR, IR, UV-VIS, ICP, AA, flow cytometry, and other analytical techniques. The ADISS Analytical Information Model covers the most common uses of analytical data—data communications, storage, and archival. The public-domain ADISS software, called the network Common Data Form (netCDF), gives users a standardized interface to their data. NetCDF's internal sophistication is hidden by its object-oriented design, to give an easy-to-use system that is platform-, architecture-, and vendor-independent. NetCDF is freely available over public computer networks and other distribution channels. The ADISS Architecture (data models, data dictionaries, data access interface, and tools) goes far beyond all previous technical solutions to the analytical laboratory data sharing problem, because the combined ADISS/netCDF approach is a complete software system with a high level of funding, international vendor supply, and a dedicated technical support group. It is rapidly becoming the industry standard for analytical data communications, storage, and archival. This talk will cover some details of the ADISS Architecture, data models, and software tools, with examples of their usage, plus some status information on the ADISS Project.

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ANALYTICAL DATA SYSTEMS BASED ON CLIENT-SERVER TECHNOLOGY—A CASE STUDY. John M. Read, DuPont Merck Pharmaceutical Company, The DuPont Experimental Station, Bldg 353, Box 80353, Wilmington, DE 19880-0353.

A large-scale analytical data system based on the client-server model has been implemented in the research laboratory. The system collects and coordinates data from a variety of sources and makes them available to researchers through workstations on their desks. The system also acts as a fast, transparent fileserver to PC, Macintosh and UNIX workstations, and provides smooth access to VAX/VMS machines. It has proven to be particulary valuable as a mechanism for sharing data among users of these platforms.

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CHARGE TRANSFER IN THE ICP: A SURVEY OF THE TRANSITION METALS. Christian Ogilvie, Charles Hemming and Paul B. Farnsworth, Department of Chemistry, Brigham Young University, Provo, UT 84602.

Measurements of correlations between intensity fluctuations in neutral atom resonance lines and ionic lines have been used to identify the mechanism by which the ionic lines are excited. Spikes in the atomic resonance line emission are caused by incompletely atomized droplets of analyte solution. They are associated with regions of elevated neutral atom density and depressed temperature. Ionic lines excited by charge transfer, which is only weakly temperature dependent, show a positive correlation with atomic resonance line emission. Ionic lines excited by electron impact, which is strongly temperature dependent, show a negative correlation. This difference in correlation behavior has been used to identify ionic levels in the third row transition metals that are excited by charge exchange. The results of a survey of charge exchange excitation in the third row transition metals by the correlation method will be presented in this paper.

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DATA ACQUISITION AND EVALUATION BY A COMPUTER CONTROLLED LANGMUIR PROBE SYSTEM. J. M. Weston, C. S. Shick, R. K. Marcus, Howard L. Hunter Chemical Laboratories, Clemson University, Clemson, SC 29634-1905.

As glow discharge devices are becoming of increased analytical interest, there has also been a renewed interest in the modelling and understanding of the plasma phenomena which are responsible for the observed spectroscopy. Because of the low pressure (about 1 torr) which the devices operate, particle densities are so low that assumptions based on the existence of local thermodynamic equilibrium (LTE) cannot be made. As such, commonly applied optical measurements based on Maxwell-Boltzmann equations are not relevant. One of the most common means of assessing charged particle properties in low pressure plasmas is the use of Langmuir (electrostatic) probes. These devices allow for the measurement of plasma potential, particle number densities, electron temperatures, electron energy distribution functions (EEDF), and average electron energies. While such data can be acquired manually, computer controlled acquisition is a practical necessity to insure that data are taken before the probe is fouled by sputtering deposition. More demanding, though, is the development of suitable mathematical expressions for processing the data through interrelated calculations. For these reasons, we have developed in this laboratory a data acquisition and processing system based on a Macintosh microcomputer, a National Instruments data acquisition board, and Labview 2 and HyperCard software.

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EFFECTS OF EIEs AND NON-EIEs ON THE FUNDAMENTAL PARAMETERS OF THE INDUCTIVELY COUPLED PLASMA. N. N. Sesi, D. S. Hanselman, M. Huang and G. M. Hieftje, Department of Chemistry, Indiana University, Bloomington, IN 47405.

Mechanisms involved in the excitation and ionization of analyte species in ICP-AES are not fully understood. Electrons are known to play a significant role in energy transfer, excitation, and ionization within the ICP so the measurement of electron temperatures (T_e), electron number densities (n_e) and gas temperatures (T_g) are a necessary step in an attempt to understand these processes. The use of laser-light Thomson and Rayleigh scattering are direct methods used in our laboratory to obtain T_e, n_e, and T_g on a spatially- and temporally-resolved basis without the need for either Abel-inversion or assumptions of local thermodynamic equilibrium (LTE). Postulated reasons for easily ionized element (EIE) and non-EIE effects include shifts in analyte ionization equilibrium, changes in plasma electrical and/or thermal conductivity, and increases in the ambipolar diffusion rate. These mechanisms can be examined in part by studying changes in the local electron number density and changes in the electron and gas temperatures. Isocontour maps of n_e, T_e, T_g, and Ar ionization temperatures with and without the addition of analyte species will be presented and discussed.

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AEROSOL DESOLVATION AND PARTICLE VAPORIZATION IN ICPS. John W. Olesik and Steven E. Hobbs, Laboratory for Plasma Spectrochemistry, Laser Spectroscopy and Mass Spectrometry, Department of Geological Sciences, The Ohio State University, 1090 Carmack Road, Columbus, OH 43210.

Aerosol desolvation and particle vaporization in inductively coupled plasmas has been difficult to study because droplets of different sizes complete the desolvation and vaporization processes at different points in the plasma. However, some liquid aerosol droplets produced by conventional nebulizer/spray chamber systems survive even in the analytical zone of the inductively coupled plasma. The droplets can be detected in the plasma via laser light scattering or by their effect on atom and ion emission intensities. By measuring time resolved emission, fluorescence or laser light scattering signals, aerosol desolvation and particle vaporization can be directly studied. While we have observed droplets that survive for long periods of time (ms) in the plasma, desolvated particles appear to be rapidly vaporized. Multichannel detection systems using a series of fiber optics coupled to individual photomultiplier tubes or a gateable charge coupled device detector allow us to monitor a single droplet or particle as it travels through the plasma. New insight into the factors controlling droplet desolvation and particle vaporization in the ICP will be discussed. Initial studies of the effect of plasma gas composition, sample solvent and concomitant species on droplet desolvation and particle vaporization will be described.

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EFFECT OF DESOLVATION ON THE EASILY IONIZED ELEMENT INTERFERENCE IN ICP SPECTROMETRY. Min Wu and Gary M. Hieftje, Department of Chemistry, Indiana University, Bloomington, IN 47405.

Desolvation has been shown to improve markedly the analytical performance of both ICP-AES and ICP-MS. However, it has never been clearly shown how the use of desolvation influences interference effects in the ICP. Early experiments carried out with dual nebulizers and desolvation units suggested that the interferences do not arise principally in the spray chamber but rather originate in the plasma [1]. Yet, it is still not clear how easily ionized element (EIE) effects are influenced when desolvation is used. In order to clarify the influence of desolvation on the easily ionized element effect, a thermostatted desolvation system was designed, in which the solvent loading can be monitored accurately. Two-dimensional CCD imaging spectrometry was employed to measure analyte emission intensity and excitation temperatures with and without a desolvation system and in the presence or absence of an EIE. Such spatially resolved measurements have demonstrated that the use of desolvation results in a reduction in interference effect. The influence of solvent loading and EIE effects on the plasma impedance was also studied. The outcome of these studies are used to clarify the influence of solvent vapor, aerosol droplets, and analyte particles on the EIE effect in inductively coupled plasma spectrometry.

1. P. W. J. Boumans and F. J. De Boer, *Spectrochimica Acta*, **31B**, 355(1976).

89 EXCITATION TEMPERATURE MEASUREMENTS WITHOUT THE BOLTZMAN EQUATION.

Gary D. Rayson and Michael W. Duarte, Chemistry Department, Box 30001, New Mexico State University, Las Cruces, NM 88003.

The measurement of excitation temperatures within the inductively coupled plasma (ICP) is a useful diagnostic tool for characterizing this ambient-pressure agron gas discharge. However, the ICP does not typically exhibit adherence to predicted behavior based on local thermodynamic equilibrium (LTE) conditions. Because the ICP is not at LTE, the application of LTE-based criteria for the characterization of the plasma is questionable at best. Often the justification for the use of the Boltzman equation to describe an "excitation temperature" has been the lack of alternate approachs to such diagnostic temperature measurements. Studies have been undertaken which involve the measurement of the apparent time constant associated with different radiative transitions occurring within the plasma. These measurements have been made by sinusoidally modulating the amplitude of the applied rf power waveform and monitoring the phase and magnitude of the resulting emission intensity for numerous transitions. Apparent time constants for argon atomic emission transitions have been observed to vary from 0.1 to 3 ms with a dependence upon the magnitude of the upper energy level of the transition. From these excitation "rate constants", excitation temperatures have been measured which are independent of an equilibrium assumption. The implications of these measurements for understanding the mechanisms of excitation within the ICP will be discussed.

90 NUMBER DENSITY DISTRIBUTIONS OF Cr(I) SAMPLED BY THE UNI-DIRECTIONAL WAVEFORM SPARK.

Laura Lograsso, David M. Coleman, Wayne State University, 171 Chemistry, Detroit, MI 48201.

The anomalous dispersion method (a.k.a. "hook spectroscopy") for measuring atomic number densities and oscillator strengths in gaseous media is well known. Instrumentation to perform time- and spatially-resolved hook spectroscopy has been developed in our laboratory to selectively determine number densities of species in transient analytical discharges. The present work demonstrates the efficacy of using this technique to profile number densities of Cr(I) sampled from the cathodic electrode of a unidirectional high voltage spark. The accuracy of this technique provides unique data which characterizes the spark's sampling and excitation capabilities in a manner which has never been attained.

91 HYDROCARBON DISSOCIATION EQUILIBRIA IN NITROGEN AND ARGON MICROWAVE INDUCED PLASMAS.

M. P. Dziewatkoski and C. B. Boss, Department of Chemistry, North Carolina State University, Raleigh, NC 27695-8204.

Microwave Induced Plasmas (MIP's) sustained in molecular gases possess very different analyte excitation and dissociation characteristics in comparison to their monoatomic counterparts. Plasmas sustained in N_2 gas have been shown to have a higher sample loading capacity and excite emission from refractory compounds better than plasmas in Ar gas. These characteristics have been attributed to molecular gas plasmas being more thermal than monoatomic gas plasmas. This presentation will focus on the dissociation of hydrocarbon samples, introduced into the plasma in the gas phase, and the resulting chemical reactions and equilibria that occur for MIP's sustained in N_2 and Ar gas. The dissociation equilibria differences between the two plasmas will be explained in terms of the high chemical reactivity of N_2 gas. Changes in excitation and dissociation temperature as a function of the power introduced to the plasma will be used to explain the relative emission intensities from atomic and molecular species in each plasma.

92 RADIO FREQUENCY-POWERED GLOW DISCHARGE MASS SPECTROMETRY AT 40 MHz.

Hao Zhang and Akbar Montaser, Department of Chemistry, The George Washington University, Washington, DC 20052.

A radio frequency-powered glow discharge source for mass spectrometry is explored for operation at 40 MHz. The source is used to sample solid nonconductors such as ceramics, glasses and zircons for atomic emission and mass spectrometry. Fundamental properties such as ion energy, ion energy distribution and ion number density of the source are examined as a function of gas pressure. RF power and sampling position. In addition, analytical properties of the plasmas formed at 27 and 40 MHz are compared.

93 PRELIMINARY STUDIES OF THE PRECISION AND ACCURACY OF DETERMINATION OF SPECTRAL LINE POSITIONS IN HIGH RESOLUTION INDUCTIVELY COUPLED PLASMA FOURIER TRANSFORM SPECTROMETRY.

J. C. Travis, M. L. Salit, and M. R. Winchester, National Institute of Standards and Technology, Gaithersburg, MD 20899.

The modern Fourier Transform Spectrometer (FTS) derives impressive wavelength accuracy from the use of a stabilized HeNe laser to track the position of the moving arm of the interferometer. This inherent accuracy may be further improved by single point calibration to correct for the small cosine error between the laser optical axis and that of the experiment. This study examines instrument drift and the effects of line width, resolution, and signal-to-noise ratio on the precision of centroid determination via least-squares fitting. Of somewhat more fundamental concern is the transfer of absolute accuracy from a low-pressure lamp—with narrow lines and positions characterized to better than one part in 10^7—to the atmospheric pressure ICP—with documented[1] pressure and/or Stark shifts on the order of 5 to 10 parts in 10^7. The goal of the present work is to establish a suite of wavelengths in the ICP which are known to sufficient accuracy to be used for periodic recalibration of the FTS, and for calibration transfer to dispersive ICP atomic emission spectrometers.[2]

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2. J. C. Travis, M. L. Salit, R. K. Winge, D. E. Eckels, and S. J. Weeks, Second Topical Meeting on High Resolution Fourier Transform Spectroscopy, Boulder, CO, August 27–29, 1992.

94 ABLATION OF GRAPHITE PLASMA FACING COMPONENTS IN TOKAMAKS,[1]

Michael Ulrickson, Plasma Physics Laboratory, Princeton University, P.O. Box 451, Princeton, NJ 08543.

Graphite is the preferred plasma-facing material in magnetically-confined fusion devices (tokamaks) because of its low atomic number and high temperature capabilities. The strength of graphite and the absence of melting are the most important high temperature properties for fusion applications. During normal operation the heat flux to the graphite is $<15\ \mathrm{MW/m^2}$. However, there are events called disruptions where the plasma current decays in about 10 msec. The plasma stored energy of about 10 MJ is lost to the plasma-facing components. The resulting heat flux is up to $500\ \mathrm{MW/m^2}$. Peak surface temperatures of up to 3000° C have been observed. The sublimation of carbon leads to the formation of craters in the surface of the component. Depths of up to 2 mm over hundreds of square centimeters have been found. Much of the evaporated carbon is redeposited near the hot spot because of the presence of the plasma and the magnetic fields in the machine. These redeposited areas can be removed by subsequent plasma operation. We have also observed spallation of graphic due to the high heat flux. We have recently started using carbon-fiber composite to reduce the spallation. In addition to normal sublimation at high temperatures, we have also observed enhanced ablation at temperatures above 1600° C due to plasma-ion-induced damage to the graphite. This enhanced erosion effects even non-disruptive plasmas. This effect limits the maximum operating temperature to $\sim$1700° C.

[1] Work supported by USDoE Contract No. DE-AC02-76-CHO-3073.

95 ASPECTS OF QUANTITATION WITH A THETA PINCH EMISSION SOURCE.

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Theta pinch discharges are capables of sampling and exciting a wide variety of materials for emission spectrochemical analysis. Response, even of elements which readily display self-absorption (such as Mg II) is linear. Sampling is poor from bulk solids, and irreproducible from sub-micron-diameter particulates, but acceptable from μm to mm-sized particles. We report experiments using mixed oxide powders cast in epoxy. As any material sampled from the epoxy will be atomized, and decomposition temperature for the epoxy is, at least approximately, independent of particle composition, these experiments demonstrate the extent to which plasma/sample interaction controls overall signal reproducibility. Both internal and external standard methods are discussed.

96 Abstract not received at time of printing.

97 RE-EXCITATION OF PLASMA GUN VAPOR USING PULSED AND STEADY-STATE MICROWAVE PLASMAS.

Lisa A. Lanning and J. M. Goldberg, University of Vermont, Department of Chemistry, Burlington, VT 05405-0125.

The plasma gun source developed in our laboratory has demonstrated admirable atomization characteristics for the direct elemental analysis of very refractory solid powders. Although analytical emission measurements in the expanding plasma plume provide reasonable powers of detection, independent control over atomization and excitation conditions is not possible with this single source. We have been studying the utility of microwave induced plasmas (MIPs) as re-excitation devices for use with the plasma gun for direct solid sampling. We have developed a microwave generator (based on a microwave oven magnetron) which can be operated either to produce steady-state or pulsed MIPs using the highly efficient cavity developed by Boss and co-workers at North Carolina State University. Plasma gun vapor has been successfully coupled with 100-watt argon and helium steady-state plasmas produced with this system, but the rapid expulsion of vapor from the plasma gun necessitated connection of the two plasmas via a long length of tubing. The lengthy transport time resulted in significant analyte losses in the tubing and inefficient excitation of the plasma gun effluent by the low-power MIP. We were able to reduce tubing length and transport time drastically by operating the MIP in pulsed mode (repetitive or single-shot) at much higher powers (ca. 1 kW). Using helium as both carrier and plasma gas, the pulsed MIP is self-igniting and single-shot microwave discharges as long as 20 ms in duration were readily used for plasma gun re-excitation. The results of time resolved emission studies using both steady-state and pulsed MIPs for plasma gun re-excitation will be presented along with design details of the pulsed microwave system. The effects of pulsed plasma power, duration, and gas flow rate on *nearly in situ* plasma gun re-excitation will be discussed.

98 STRATEGIES FOR RF RE-EXCITATION OF VAPOR PRODUCED BY A PLASMA GUN ATOM SOURCE.

Garrett J. McGowan and J. M. Goldberg, University of Vermont, Department of Chemistry, Burlington, VT 05405-0125.

Although the plasma gun source developed in our laboratory is capable of efficiently atomizing very refractory solid powder samples, the highly-ionic line rich spectrum (on top of a relatively high continuum background) that it produces, limits its analytical utility. Consequently, we have been investigating the utility of a number of RF plasmas (non-ICP) for efficient re-excitation of the atomic/ionic sample vapor produced by the plasma gun. A 27 MHz RF generator was modified so that it could be operated in either steady-state (up to 2 kW) or pulsed (up to ca. 4 kW) modes. Experiments utilizing an ICP-type induction coil to couple pulsed RF power into the plasma gun vapor plume demonstrated limited coupling efficiencies. However, a capacitive coupling arrangement using parallel electrodes on opposite sides of an insulating cylindrical quartz vapor transport tube enabled ready formation of a pulsed RF plasma in the expelled plasma gun vapor. We will present the results of studies investigating the utility of both pulsed and steady-state capacitively coupled plasmas (CCPs) are re-excitation devices for use with plasma gun atom cells. We have been successful in using an ICP torch with these CCPs and will present the results of temporally resolved emission measurements comparing both pulsed and steady-state CCP re-excitation properties. Also, we will present the results of spatially and temporally resolved emission studies characterizing the propagation of vapor from the plasma gun at displacements as great as 80 mm from the plasma gun source. Plasma gun vapor propagation information from this study will be used to design CCP re-excitation systems with optimum temporal and spatial displacements from the plasma gun atom cell.

99 CHEMICAL SYNTHESIS THROUGH CONDENSED PHASE PLASMAS.

Vahid Majidi and Mark Meier, Department of Chemistry, University of Kentucky, Lexington, KY 40506.

Recently, the scientific community has witnessed the birth of a new class of compounds generated via plasma synthesis. These compounds are known as fullerenes and are generally synthesized in carbon arcs. Using a similar approach, we have utilized laser plasmas to generate new chemical species in condensed phase systems. Typically, a pulsed laser beam (8 ns duration, 100 mJ/pulse) is focused tightly into an organic liquid. The temperature of this plasma can reach as high as 20000 K and the plasma lasts approximately 8 ns. This in turn produces tremendous pressure and temperature gradients. UV-Vis spectroscopy and HPLC results show that the compounds formed within the liquid resemble larger fullerenes. These products are formed due to extensive atomization and ionization of the solvent molecules during the lifetime of the plasma. Due to intense pressures encountered by the post-plasma species, these atoms and ions rapidly coalesce to form stable products.

100 ANALYTICAL IMPLICATIONS OF PLASMA DYNAMICS IN THE HIGH VOLTAGE SPARK DISCHARGE.

Cheryl A. Bye and Alexander Scheeline; School of Chemical Sciences, 1209 West California Street, Urbana, IL 61801.

The effect of the high voltage spark's plasma dynamics on analyte excitation behavior will be discussed. The results of these continuing plasma diagnostic studies, probed by Stark electron density measurements, Boltzmann temperature measurements (both LTE and b-factor corrected measurements), and coupled Saha-Boltzmann temperature measurements will be presented. These results will include a comparison of analyte and plasma (Ar and Ar+) emission behavior. The temporal behavior, both average and resolved, has been investigated. In addition, the spatial character of both the analyte and plasma constituents has been probed. The results of an investigation into the spatial and temporal dependence of analyte excitation in several differing analyte matrices will also be presented. Comparisons will be made with earlier large bandpass echelle measurements. The analytical implications of both the analyte excitation and plasma dynamics will be discussed.

101 INFLUENCE OF SAMPLE HETEROGENEITY TO GRAPHITE FURNACE SOLID SAMPLING DATA.

Ulrich Kurfürst, University of Fulda (Fachhochschule), D-6400 Fulda, Marquardstr. 35, Germany.

With a subsample size in the milligram-range using graphite furnace solid sampling AAS the sample heterogeneity often is dominating the overall analytical error. Mostly normal distributed results are obtained. But when the sample contains rare grains of high analyte content ("nuggets"), a skew or multimodal distribution can appear. Examples and the statistical tools for the evaluation of solid sampling results depending from homogeneity of the sample and the calibrant (e.g. SRMs/CRMs) are shown and discussed.

102 THE ROLE OF EXTRACTION IN SLURRY ANALYSIS USING GRAPHITE FURNACE AAS.

M. T. C. de Loos-Vollebregt and P. van Oosten, Delft University of Technology, Laboratory of Materials Science, Division of Atomic Spectrometry, Rotterdamseweg 137, 2628 AL Delft, The Netherlands.

The results of the analysis of certified reference materials of soil, sediment and coal fly ash using slurry sample introduction and graphite furnace atomic absorption spectrometry were improved when the elements of interest were extracted into the liquid phase. A 100% recovery of Cr, Cu and Ni was obtained when the sample slurry was prepared in a medium of 3% HF and pretreatment during 4 hours of agitation with a stream of argon. Experimental results show that the atomization is not complete from particles larger than 10 μm. The analyte atoms arise from the smaller particles and the extracted part of the larger particles only. The accuracy and precision improved at higher degree of extraction.

103 ANALYSIS OF CARBON SLURRIES BY ETAAS AFTER TRACE METAL PRECONCENTRATION.

Kenneth W. Jackson and Tariq M. Mahmood, Wadsworth Center for Laboratories and Research, New York State Department of Health, and School of Public Health, State University of New York, P.O. Box 509, Albany, NY 12201-0509.

The accurate determination of metals at ultratrace levels in seawater presents a considerable challenge to the analytical chemist. It may require the combination of a difficult and time-consuming preconcentration step with analysis by a highly sensitive technique such as electrothermal atomic absorption spectrometry. A simple procedure will be described that allows preconcentration factors up to 800-fold. A suitable chelating agent is added to the water sample, followed by 6 mg of activated carbon. After shaking, the carbon is removed by filtration and made into a slurry with 5 ml of distilled-deionized water. The concentrated metals are then determined by direct injection of the carbon slurry into the electrothermal atomizer. Recoveries and detection limits for several elements will be presented, and it will be shown that the normally troublesome chloride interference is completely removed by this procedure.

104 THE ANALYSIS OF PAINT CHIPS USING SLURRY SAMPLE INTRODUCTION FOR GRAPHITE FURNACE AAS.

D. K. Bradshaw. Perkin-Elmer Corp., 400 Technology Park, Lake Mary, FL 32746.

The most common pediatric health problem today is due to lead poisoning. With the increased concern over juvenile lead poisoning, finding the source is critical to treatment. The most wide spread and dangerous source of lead poisoning is lead based paints. There are three means to measure levels of lead in painted surfaces in the home. The chemical spot test is qualitative, not quantitative, and results can be subjective. Portable x-ray fluorescence units are often not available, especially to home owners, require trained and experienced personnel, and results can be ambiguous. Laboratory testing can be time consuming and expensive. Much of the time, and therefore the expense, of the laboratory analysis by atomic absorption spectrometry is tied to sample preparation. Sample decomposition can require several hours to days depending on the type of paint. One alternative to reduce sample prep time and cost is to use graphite furnace AAS and analyze the solid directly to determine the lead content. This procedure can also be automated by introducing the sample into the furnace in the form of a slurry. Standard reference materials are analyzed using this technique and compared to results obtained with decomposition procedures.

105 COMPARISON OF DIRECT ANALYSIS OF SOLID POLYMERS BY GRAPHITE FURNACE AAS WITH MICROWAVE DIGESTION AND CONVENTIONAL ASHING.

D. A. Anderson and E. M. Skelly Frame, GE Corporate Research and Development, P.O. Box 8, Bldg. K-1, Room 2A32, Schenectady, NY 12301.

The determination of lead in polymer samples was accomplished by direct analysis of the sample by graphite furnace AAS, microwave digestion in sealed vessels and by conventional dry ashing. The direct graphite furnace method using an aqueous calibration curve gave a fast, semiquantitative determination of lead in samples that were extremely difficult to acid digest.

106 MULTIVARIATE CALIBRATION: OVERVIEW, CHALLENGES, AND PITFALLS.*

David M. Haaland, Sandia National Laboratories, Albuquerque, NM 87185.

Multivariate calibration methods have been shown to be extremely useful for improving the precision, accuracy, and reliability of quantitative spectral analyses. The methods can be applied in the presence of unknown interfering species and when deviations in Beer's law exist. An overview of the common factor analysis methods of partial least squares (PLS) and principal component regression (PCR) will be presented. Primary to the potential success of these chemometric methods is the design of the calibration samples upon which the calibration model is based. The proper design of calibration sets includes orthogonal statistical designs with special care paid to the quality and precision of the reference concentrations. Several statistical designs will be presented for two different data sets. Once the calibration data has been collected, care must be taken to assure the quality of the resulting data and calibration model. The ability to detect outlier samples is crucial to this phase of the analysis. If poor quality calibration data are detected and corrected, then the precision, accuracy, and sensitivity to future outliers will be improved. Multiple outlier detection methods will be demonstrated with data from real systems illustrating the importance of cross-validation procedures in the calibration step. Outlier detection is also crucial to assuring the quality of the analyses of unknown samples. Finally, the ability to maintain calibrations even when the spectrometer drifts or is altered or if multiple spectrometers are to be used in analyses will be discussed. If attention to these details are maintained, then the application of multivariate calibration to quantitative spectroscopy will generally result in success.

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107 THE ROLE OF DIAGNOSTIC TOOLS IN MULTIVARIATE CALIBRATION.

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The dangers of treating multivariate calibration methods such as PLS or PCR as black box systems are well known. Fortunately diagnostic tools are available to guide the inexperienced user and to prevent the generation of misleading results. The most important of these are outlier detection in developing a training set and validation to determine the optimum regression equation. When fresh samples are analyzed the mahalanobis distance can be used to verify that the samples lie within the range of the calibration. However, uncritical reliance on these tools can generate unjustified confidence in the analytical results. The number of samples of available for calibration is generally limited. Tests designed for normal distributions are often inappropriate so that graphic displays may be more informative. The use of replicate measurements to enlarge the training set must be treated cautiously because the resulting SEP values may be unrealistic. We have found that anomalous features in spectra can generate significant errors in quantitative results without being detected in the mahalanobis distance. Spectral residuals are generally a much more sensitive test. Various approaches have been tried to estimate the accuracy associated with individual analyses. The only reliable values are those derived from the calibration SEP when both the mahalanobis distance and spectral residual are acceptable.

108 COMPARISON OF ALGORITHMS FOR TRANSFERRING MULTIVARIATE CALIBRATIONS BETWEEN SPECTROMETERS.

Kenneth Beebe, The Dow Chemical Company, 1879H, Midland, MI 48667. Scott Ramos, Infometrix; David Haaland, Sandia National Laboratory.

The transfer of calibration models is receiving more attention from the analytical chemistry community as the utility of this technology becomes more well known. Recent publications have demonstrated the feasibility of re-calibrating an instrument using a subset of the original calibration samples (1) and transferring a calibration model from an instrument with good signal to noise to a poorer instrument with the result of improving predictive quality (2). Taking a slightly different approach, Adhihetty et al. (3) examined the instrument parameters that affected the model tranferability and used this information to build more robust calibration models. The present work examines how well the calibration transfer algorithms work on a variety of data sets. Four algorithms discussed in reference 1 were applied to data sets comprised of aqueous and organic samples. A systematic approach to comparing the results from each of the algorithms was used that demonstrated their effectiveness in achieving good transfers. Samples were analyzed on several instruments from different manufacturers all operating in the near infrared region. The ability of the techniques to identify the specific differences that exist between individual instruments of a given model was examined. A discussion of the transferability within and across manufacturer lines is also included.

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109 SOME COMPARATIVE INVESTIGATIONS OF NEURAL NETWORKS IN CALIBRATION.

Steven D. Brown and Thomas B. Blank, Department of Chemistry and Biochemistry, University of Delaware, Newark, DE 19716.

Traditional multivariate calibration methods are based on linear relations between the measured signal and the predicted result. Nonlinear calibration is performed using modified versions of the linear methods. Backpropagation neural networks relate multivariate input signals, entered at the input layer, to a predicted result by means of a series of connections from the signal input layer to one or more "hidden layers," where appropriately weighted inputs are combined, and then to the output layer, which determines the predicted result. Interlayer connections are weighted by a series of transfer functions, which can take various shapes, but are often sigmoidally shaped. The selection of suitable combinations of transfer functions should permit the modeling of a wide array of linear and non-linear relations using neural networks. This talk will review the nature of neural networks and goals of neural network modeling of continuous and discrete systems. Specifically, it will compare backpropagation neural networks with linear and nonlinear variants of PLS and PCR in multivariate calibration.

110 NIR ANALYSIS OF COMBINED AROMATIC-ALIPHATIC HYDROCARBON MIXTURES.

Edward W. Stark and Karen Luchter, KES Analysis, 160 W. End Ave., New York, NY 10023.

Our earlier investigation on separate aromatic and aliphatic mixtures provided quantitative determination of the three isomers of xylene to within 0.15% RMSD from gravimetric values. The determination of the constituents of the four component aliphatic mixtures provided prediction results to within 0.06% RMSD. This next stage extends the model to simultaneous measurement of aromatic and aliphatic compounds in the first and second combination and overtone regions under varying conditions. A statistically designed set of eight component mixtures of aromatic and aliphatic hydrocarbons was prepared with gravimetrically determined composition. The constituents include isomeric mixtures of xylene, toluene, benzene, ethylbenzene, 1-hexene, 2,2,4 trimethylpentane (isooctane), n-nonane, and methylcyclohexane. The concentration ranges were chosen for their usefulness in demonstrating the performance of NIR in the analysis of petroleum refinery streams. Interferograms were recorded at 4 cm^{-1} resolution on a Bomem MB155 FT-NIR using two detectors, InGaAs and InAs. The interferograms were Fourier transformed with cosine apodization to generate spectra at 4, 8, 16, 32, and 64 cm^{-1} resolution. Various data pretreatments, including derivatives and extended multiplicative signal correction (EMSC), and calibration models (PCR, PLS-1 and PLS-2) were investigated in both the 1st overtone and combination region (3600–6000 cm^{-1}) and the 2nd overtone and combination region (6000–9000 cm^{-1}). Calibrations were done at each of these resolutions, in each of the two wavenumber ranges, and, of course, for each of the mixture components. Comparisons were made between experimental conditions using sample prediction by cross validation techniques.

111 MOLECULAR TRANSPORT AND KINETICS AT SILICA/SOLUTION INTERFACES. J. M. Harris, W. B. Lacy, S. W. Waite, and H. Wang, Department of Chemistry, University of Utah, Salt Lake City, Utah 84112; D. B. Marshall, Department of Chemistry and Biochemistry, Utah State University, Logan, UT 84322.

The selective retention of molecules at chromatographic surfaces involves challenging questions concerning the structure of the liquid/solid interface and kinetics of sorption and desorption. In this talk, three methods to probe kinetics at such interfaces are described: temperature-jump, stopped flow, and nanosecond photoexcitation. Time-resolved fluorescence provides information from excimer formation and quenching which can be used to study the distribution of molecules at the interface and the rate of encounters between them. We employ these methods to measure rates of surface diffusion of adsorbed molecules; we also report the first observation of migration of covalently-bound siloxane species on silica surfaces. Stopped-flow methods are used to measure adsorption and binding. Temperature-jump relaxation techniques are adapted to measuring the reversible kinetics at liquid/solid interfaces using Joule-discharge heating. Initial studies of sorption/desorption kinetics under reversed-phase conditions indicate that changes in the rate of sorption play a major role in governing the dependence of the partition equilibrium on solution composition.

112 Abstract not received at time of printing.

113 SELECTIVITY CONTROL IN REVERSED PHASE LIQUID CHROMATOGRAPHY. John G. Dorsey and Steven R. Cole, Department of Chemistry, University of Cincinnati, Cincinnati, OH 45221-0172.

The chromatographic stationary phase has been shown to contribute significantly to the quality of separations achievable in reversed-phase liquid chromatography. Commercially available C_{18} columns exhibit wide differences in their surface chemistries, and in their durability, inter-column reproducibility, degree of tailing for amine solutes, and chromatographic selectivity. We have previously shown that shape selectivity is linearly related to bonded phase chain density, and that separations on high chain density monomeric phases are similar to separations achieved on commercial polymeric phases. Our current interests are in identifying and characterizing mobile phase additives that, when added in a low percentage to typical mobile phases, can modify the stationary phase to allow improved separation selectivity and efficiency for specific classes of compounds. We have found that cholesterol is an especially effective additive for improving shape selectivity of commercial columns, and cholesterol coated monomeric columns mimic separations achieved on polymeric columns. We have also found that these coated columns are stable at mobile phase compositions $\leq$70% organic modifier, and for compositions $\geq$70%, the additive is made part of the mobile phase.

114 ORIENTATIONAL DYNAMICS OF MOLECULES INTERACTING WITH CHROMATOGRAPHIC SURFACES. Mary J. Wirth, Malcolm E. Montgomery and John D. Burbage, Department of Chemistry & Biochemistry, University of Delaware, Newark, DE 19716.

Fluorescence spectroscopy is used to measure the reorientation of adsorbed molecules through in-plane and out-of-plane angles. The method is applied to C_{18} chromatographic surfaces to understand the molecular basis of wetting by short-chain alcohols and the surface modification by micelles. Two fluorescent probes are studied: a hydrophobic probe which resides inside the C_{18} monolayer and an amphiphilic probe which resides at the interface. The fluorescence technique allows direct observation, in laboratory coordinates, of the motions of chromatographically adsorbed species.

115 SELECTING MOBILE PHASES AND COLUMNS FOR SUPERIOR REVERSED-PHASE HPLC SEPARATIONS. J. J. Kirkland, Rockland Technologies, Inc., 538 First State Blvd., Newport, DE 19804.

Previous studies on systematically changing band spacing in HPLC usually involved altering the strength or composition of the mobile phase. Effective procedures now are available for conveniently modifying the mobile phase to achieve the needed separation. However, situations occur when altering separation selectivity is best achieved by changing the column rather than the mobile phase. A better approach than testing columns of the "same" type (e.g., C18) from different manufacturers is to investigate columns with different functionality. Greatest differences in band spacing often occur with C8, phenyl and cyano (CN) columns. Unfortunately, because of problems with the instability and irreproducibility of short chain phases (e.g., phenyl, CN), columns of these materials are not widely used in method development. The stability and reproducibility of these columns now are significantly enhanced by using "sterically-protected" silane bonded phases. Stable stationary phases are especially important for repeatable separations of many basic drugs, and particularly peptides and proteins, typically separated at pH ~2 by gradient elution. Metal-free, "non-acidic" silica supports reduce unwanted silanol interactions to improve column reproducibility further, particularly for separating basic compounds.

116 FASCINATING EXPERIENCES IN PREPARATIVE CHROMATOGRAPHY. Robert Sitrin, Merck Research Laboratories, West Point, PA 19486.

Preparative chromatography has evolved in the past 20 years into a powerful technique widely applied to the purification of synthetic and natural products. With the recent explosive growth in high value-added products produced by biotechnology, it is clearly the method of choice for the manufacture of highly purified products for human use. This presentation will describe some challenging experiences encountered when laboratory analytical separations were scaled-up to preparative levels during the course of developing and validating manufacturing processes. In one case involving the isolation of a cell culture product using metal chelation chromatography, an erratic breakthrough problem was attributed to lack of control of the metal ion concentration. The solution to successful scale-up in this case was to add small quantities of metal ion to the column feed stock to compensate for the continuous bleeding of metal in the eluate. In a second example, the capture step for a hepatitis B vaccine antigen posed complex scale-up problems. Adsorption of the antigen was originally carried out by batch treatment with fused silica followed by manual centrifugation to separate the liquid and solid phases. Desorption was carried out with hot borate buffer, again followed by manual centrifugation. This procedure was successfully scaled-up using a conventional chromatographic column packed with very wide pore silica (1500 Angstrom). Elution was achieved with a hot borate buffer. Scale-up aspects of this novel "thermal elution chromatography" will be described. In both cases, a thorough understanding of the underlying mechanisms involved in the separation was required in order to properly scale-up the process.

117 DESIGN AND CHARACTERIZATION OF A NOVEL HYDROLYTICALLY STABLE C_{18} STATIONARY PHASE. H. O. Fatunmbi and M. J. Wirth, Department of Chemistry & Biochemistry, University of Delaware, Newark, DE.

The technique of monolayer self-assembly was used to combine the high hydrolytic stability of self-assembled monolayers with the selectivity of a monomeric C_{18} chromatographic stationary phase. A mixture of n-octadecyltrichlorosilane and n-propyltrichlorosilane in n-hexadecane were reacted with silica under anhydrous conditions, except for a monolayer of water on the silica. This self-assembly process occurs through horizontal polymerization, which results in a very high density near the surface. The propyl chains are used to spaced the octadecyl chains to achieve the appropriately lower chain density a few angstroms away from the surface. The surface exhibits monomeric selectivity with C_{18} coverages comparable to those of monomeric stationary phases. The surfaces exhibits very high stability to both acid and base hydrolysis. The method is applicable to virtually any type of functional group desired in chromatographic applications. A U.S. patent application is pending for this bonding process.

118 Abstract not received at time of printing.

119 Abstract not received at time of printing.

120 COPOLYMERIC BONDED PHASE EXTRACTION OF COMPOUNDS FROM BIOLOGICAL MATRICES.

Deborah J. Fox, Edward T. Heebner, Michael J. Telepchak, Worldwide Monitoring, 417 A Caredean Drive, Horsham, PA 19044.

A novel copolymeric, multimodal bonded-phase silica was developed in 1986 by research scientists at Worldwide Monitoring in Horsham, PA. It was initially designed for use as a bonded-phase extraction column to be used in the drug of abuse testing industry, which demanded a product that would work for a wide range of compounds, produce a clean extract, give high recovery, and be quick, easy to use, and cost effective. It has since become the standard of the industry and is used by one-third of the NIDA approved labs for drug testing. Clean Screen® extraction columns allow the scientist to use mixed mode interactions to selectively retain and elute all compounds of interest while washing away the extraneous background interference and/or leaving the impurities on the column. This unique sorbent exhibits hydrophobic properties due to a non-polar carbon chain, and cation exchange properties due to a benzene sulfonic acid functional group. Many analytical procedures have been developed for the extraction of abused and therapeutic drugs from biological matrices on Clean-Screen® in the past five years. This paper will cover historical Clean-Screen® applications as well as current methods under development. Analyses are by GC/MS, HPLC and GC/FID. Chromatograms will be shown to demonstrate extract cleanliness and recovery.

121 Abstract not received at time of printing.

122 CHIRAL SEPARATIONS IN SUPPORT OF NEW DRUG DISCOVERY.

K. M. Kirkland, K. L. Neilson and D. A. McCombs, ICI Pharmaceuticals Group, A Business Unit of ICI Americas Inc., Wilmington, Delaware 19897.

The chiral separation of drug enantiomers has become an important issue facing the pharmaceutical industry today. Increased regulatory pressures coupled with stereoselective bioprocesses require the development of chiral-specific analytical methods as early as possible in the drug discovery/development process. At present there are several choices of chiral stationary phases (CSP) that can directly separate enantiomers. We have primarily focused on the immobilized protein, ovomucoid-based CSP (OVM). However, we have found the derivatized cellulose supports to be highly complementary in our methods development approach. Greater than 80% of the acidic, basic and neutral drug enantiomers investigated were well separated on OVM. The effect of pH, type of organic modifier, buffer concentration and temperature on resolution and selectivity factor, alpha, has been studied and a simplified optimization scheme for achieving rapid methods development on OVM has been defined. Both column types have been successfully used to solve problems in support of new drug discovery and for examining the stereoselective metabolism of racemic drugs.

123 EXPERIMENT AND SIMULATION OF ION BEHAVIOR IN A QUADRUPOLE ION TRAP.

R. Julian and R. G. Cooks, Department of Chemistry, Purdue University, West Lafayette, IN 47907-1393.

A large scale simulation is used to compute the trajectories of 10^4 ions within the quadrupole ion trap, to produce simulated mass spectra which are compared to experimental results. Two recent simulations predict improved instrument performance during resonant ejection. In the first simulation, on the effects of buffer gas collisions during the mass analysis scan, peak broadening is observed. Experiments indicate that improved performance is achieved by controlling the presence of the buffer gas during mass analysis using a pulse valve. A second simulation shows a strict RF/AC phase relationship is required for ions to be ejected to the detector during resonance ejection. Normally, the AC frequency is selected to achieve the mass range extension factor desired. This results in a rotating RF/AC phase relationship which produces poor ejection characteristics because the prerequisite RF/AC phase does not occur every AC cycle. By carefully choosing the AC frequency, a fixed RF/AC phase relationship can be achieved which forces ions to be ejected every AC cycle. By selecting the initial RF/AC phase angle, the ion ejection characteristics are improved further, forcing all ions of a single M/Z to be ejected over a few AC cycles. The optimum initial phase angle does not correspond to a maximum coupling between the ion motion and the AC potential, but rather creates a condition which allows a large number of ions to be ejected each AC cycle. It is possible to construct an external AC source which generates a fixed RF/AC phase angle and allows the initial phase angle to be selected, allowing the simulated results to be compared to experiment.

124 LASER PHOTODISSOCIATION PROBE OF ION MOTION IN THE ION TRAP.

P. H. Hemberger, M. L. Alexander, M. E. Cisper, & N. S. Nogar, Chemical & Laser Science Division, Los Alamos National Laboratory, Los Alamos, NM 87545. J. D. Williams & R. G. Cooks, Department of Chemistry, Purdue University, W. Lafayette, IN 47907. J. E. P. Syka, Finnigan MAT, San Jose, CA 95134.

We use spatially-resolved photodissociation of ions to map ion trajectories in a Finnigan ion trap mass spectrometer. Distributions measured in the present fashion are both radially-averaged and averaged with respect to the phase angle of the drive RF. Previous studies have been based on the photodissociation of benzoyl ion (from electron impact of acetophenone) at 308 nm. We have extended these measurements to a number of other ions to demonstrate the validity and generality of this technique and to investigate the effects of mass and chemical parameters on the distributions. Ion distributions can also be perturbed by applying a "tickle" voltage on the end caps of the ion trap to resonately excite ions in the z-direction. Tickled ion distributions can be then be measured as a function of excitation voltage and trapping potential well depth. The relaxation of the distribution following excitation can be related to collisional cooling parameters. Finally, the effect of other ions (e.g., Xe^+) on the distribution of benzoyl ions can be measured and described in terms of ion-ion interactions within the ion trap.

125 "PARTICLE BEAM LC/MS ON THE QUADRUPOLE ION TRAP."

Brent L. Kleintop, Donald M. Eades, and Richard A. Yost, Univ. of Florida, Gainesville, FL, 32611. Thomas D. Behymer and William L. Budde, U.S. EPA/EMSL, Cincinnati, OH 45286.

Particle beam (PB) LC/MS interfaces have recently attracted widespread attention largely because of their ability to generate library searchable EI mass spectra of a wide range of analytes introduced via LC. The vast majority of PB systems currently in use employ quadrupole mass analyzers due to their ruggedness and low cost. Ion traps have seen little use in LC/MS systems primarily because of the large amount of solvent introduced by most LC/MS interfaces. The residual solvent can cause undesired ion/molecule reactions and frequently can lead to space charging resulting in poor spectral quality and sensitivity. Fortunately, these adverse effects can be minimized by ejecting solvent ions prior to mass analysis [1]. This allows acquisition of EI mass spectra from LC/PB/ITMS analyses which compare favorably to library spectra. This talk will report the application of an LC/PB/ITMS system for environmental LC/MS analyses. Included will be an evaluation of the capability of the system to perform gradient elution analyses. Also, the performance of this system will be compared to PB systems which employ quadrupole mass analyzers with regards to detection limits, linear dynamic ranges, and overall spectral quality.

1. Kleintop, B. L.; Eades, D. M.; Yost, R. A., Presented at the 43rd Pittsburgh Conference on Analytical Chemistry and Applied Spectroscopy, New Orleans, LA, March 9–13, 1992.

126 LASER DESORPTION AND SELECTIVE ION-MOLECULE REACTIONS IN A QUADRUPOLE ION TRAP MASS SPECTROMETER.

Jennifer S. Brodbelt, Aubrey McIntosh, Tracy Donovan, Chien-Chung Liou, Department of Chemistry, University of Texas, Austin, TX 78712.

The implementation of a versatile new laser desorption interface and a probe-mounted electron ionization source in a quadrupole ion trap mass spectrometer allow desorption of biomolecules, metal cations, and reactive polyatomic species. For example, laser desorption can be used to generate metal ions for association reactions with macrocyclic substrates, allowing evaluation of host-guest chemistry in the gas phase. Collisional-activated dissociation techniques allow structural characterization of the laser-desorbed ions and may be used to derive orders of ligand affinities of macrocyclic ion-complexes. The host-guest complexes that are bound by multiple interactions have high activation barriers to dissociation and undergo different types of dissociation processes than loosely-bound complexes. Models that allow evaluation of hydrogen-bonding interactions consist of crown ether/ammonium ion complexes with several hydrogen-bond donating and accepting sites.

127 RAPID ANALYSIS USING DIRECT SAMPLING ION TRAP MASS SPECTROMETRY,*

Michelle V. Buchanan, Stacy A. Rossi, Marcus B. Wise, Cyril Thompson and Roosevelt Merriweather, Analytical Chemistry Division, Oak Ridge National Laboratory, Oak Ridge, TN 37931-6120.

New analytical methods employing direct sample introduction into an ion trap mass spectrometer (ITMS) have been developed for the rapid detection of trace compounds in complex matrices. In this approach, sample preparation steps have been minimized or even eliminated to reduce analysis times to a few minutes, as compared to conventional methods which are often quite time-consuming (hours). In the area of environmental analysis, volatile organics in water can be quantitatively measured at levels of 5 ppb in less than three minutes, by purging the volatiles directly into the ITMS with no trapping or chromatographic steps. Detection of drugs in physiological matrices, such as urine and milk, has been accomplished using thermal desorption into the ITMS. Detection limits in the low part per billion range have been achieved for the determination of phenothiazine in milk and nicotine in urine, with total analysis times of less than five minutes. This approach has been successfully used in a variety of other applications, clearly demonstrating its potential for reducing both the time and cost required for analysis.

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128 RECENT ADVANCES IN BIOMOLECULE ANALYSIS USING AN ION TRAP MASS SPECTROMETER.

Scott A. McLuckey, Gary J. Van Berkel, Roswitha S. Ramsey, Doug E. Goeringer, and Gary L. Glish, Analytical Chemistry Division, Oak Ridge National Laboratory, Oak Ridge, TN 37831-6365.

Electrospray ionization combined with mass spectrometric detection has revolutionized the field of biological mass spectrometry. ES-MS has proven useful for the analysis of polar, involatile and thermal labile compounds, and has been especially successful in the analysis of high molecular weight biopolymers such as proteins and oligonucleotides. This paper will describe the recent advances we have made in the analysis of ES derived ions using an ion trap mass spectrometer (ITMS). The small size, relatively low cost, high sensitivity, ion storage capability, and MS^n capability, along with other recent advancements in its analytical capabilities, makes the ITMS well suited for the analysis of ES derived ions. Topics to be covered include the use of ion-molecule reactions to probe the structure and determine the charge state of multiply charged gas-phase biomolecules, the promise and compromises of on-line coupling of condensed-phase separations to the ITMS via ES, and the use of random noise collisional activation (CA), rather than single frequency CA, in MS/MS experiments.

Research Sponsored by the U.S. Department of Energy, Office of Basic Energy Sciences, under contract DE-AC05-84OR21400, with Martin Marietta Energy Systems, Inc.

129 AN ION TRAP STORAGE/TIME-OF-FLIGHT MASS SPECTROMETER.

S. M. Michael, M. Chien, D. M. Lubman, University of Michigan, Department of Chemistry, Ann Arbor, MI 48109.

An ion trap/time-of-flight mass spectrometer combination was developed coupling the storage capabilities of an ion trap with the speed and resolution of a time-of-flight device. The ion trap is an RF quadrupole trap operated in the total storage mode, i.e. with a DC voltage = 0 on both endcaps and an RF voltage on the ring electrode. The stored ions are ejected into the time-of-flight device via a −150 V DC pulse on the exit endcap which causes the ion trajectories in the trap to become unstable. The ions are then mass analyzed in a reflectron time-of-flight. A maximum storage time of >1 sec and a resolution of 1300 at M/Z 93 were achieved. The storage capabilities of this device may have significant applications towards enhancing sensitivity, the study of slow metastable decay, and photodissociation mass spectrometry.

130 ATMOSPHERIC PRESSURE IONIZATION OF BIOLOGICAL COMPOUNDS USING AN ION TRAP STORAGE/TIME-OF-FLIGHT MASS SPECTROMETER.

M. Chien, S. M. Michael, D. M. Lubman, University of Michigan, Department of Chemistry, Ann Arbor, MI 48109.

An ion trap/time-of-flight mass spectrometer configuration has been designed which can be interfaced to continuous ion beam sources produced at atmospheric pressure such as glow discharge ionization or electrospray ionization. The ion trap is an RF quadrupole trap operated in the total storage mode, i.e. with a DC voltage at ground potential on both endcaps and an RF voltage on the ring electrode. Ions produced at atmospheric pressure are sampled into the ion trap device region and trapped for ~ 1 sec. The stored ions are ejected via a DC pulse on the exit endcap into the reflectron time-of-flight device and mass analyzed. This work demonstrated the ability of this new ion trap storage/time-of-flight mass spectrometer configuration as an detector for many on-line liquid injection techniques.

131 PHOTODISSOCIATION OF Ag(BENZENE)$^+$ AND Ag(TOLUENE)$^+$ IN A FOURIER TRANSFORM MASS SPECTROMETER;

S. Afzaal, Y. Huang, B. S. Freiser, Department of Chemistry, Purdue University, West Lafayette, IN 47907.

Ag(benzene)$^+$ and Ag(toluene)$^+$ are photodissociated using several different light sources to explore the thermodynamic thresholds for the two possible dissociative pathways, simple cleavage of the Ag$^+$-ligand bond to form Ag$^+$ and dissociative charge transfer to form the organic ion. The ions are generated and stored in the ion trap of a Fourier transform ion cyclotron resonance (FTICR) mass spectrometer. When these ions are irradiated with the output of a mercury-xenon arc lamp, using energy cutoff filters for wavelength selection, both processes are observed at wavelengths below 300 nm and only Ag$^+$ is observed at wavelengths above 330 nm. Irradiation by an Excimer pumped dye laser at 343 nm results exclusively in the dissociative charge transfer process for Ag(toluene)$^+$. Small amounts of silver$^+$ production through the simple photodissociation process is observed when the ions are irradiated with individual lines of an argon ion laser from 476 to 528 nm. This process is observed to fall off sharply at 514 nm. Multiphoton excitation of the ions using the 10.6 μm output of a cw infrared laser also yields Ag$^+$, exclusively. The thermodynamic information obtained from these experiments is compared with the recent work of Duncan and co-workers on the photodissociation of Ag(benzene)$^+$, prepared in a supersonic molecular beam and mass selected in a reflectron time-of-flight (TOF) mass spectrometer.

132 COMPACT RAMAN SENSOR USING HOLOGRAPHIC OPTICAL COMPONENTS.

Harry Owen, Kaiser Optical Systems, Inc., 371 Parkland Plaza, P.O. Box 983, Ann Arbor, MI 48106.

The presentation will examine an analysis of how several Holographic Optical Components can be integrated together to form the basis of a high performance and robust Compact Raman Sensor for process control applications.

133 RECENT DEVELOPMENTS WITH THE PORTABLE RAMAN FIBER OPTIC SPECTROMETER.

A. Leugers, R. McLachlan, D. Lafevor, L. Wright, Analytical Sciences, 1897F Building, Dow Chemical Company, Midland, MI 48667.

Improving holographic rejection filter technology and laser sources are making fiber optic Raman spectroscopy attractive for a wider array of analyses. New developments with our portable Raman spectrometer have enabled us to measure and analyze Raman spectra of highly scattering powders and pellets through the sample vial. Multiplexed Raman probes allow the same instrument to be used at several sites in the same plant to obtain fast on-line analyses of various materials. New software developments allow a plant technician to quickly build a spectral library of products and raw materials and then to identify each material at any of several remote probes, all multiplexed to the same instrument, with the push of two buttons. These developments and analytical capabilities of the instrument will be discussed.

134 SENSITIVE, COMPACT RAMAN SPECTROMETERS BASED ON DIODE LASERS, CCD'S AND IMAGING SPECTROGRAPHS. R. L. McCreery, C. Frank, M. Fryling, The Ohio State University, 120 West 18th Ave, Columbus, OH 43210.

A variety of technological developments occurring over the past ten years have made routine Raman spectroscopy much more feasible. These include near IR excitation, CCD detectors, compact spectrographs, holographic band rejection filters, diode lasers, and fiber optic sampling. A spectrometer based on these innovations will be discussed, as well as some important issues affecting background and signal/noise. Of particular interest are off-peak laser emission and overall spectrometer response function. Spectra of a variety of materials will be presented, in order to demonstrate spectrometer performance.

135 TURN-KEY RAMAN SYSTEMS FOR THE CHEMICAL ANALYST. Fran Adar, Frank Purcell, Roy Grayzel, Spex Industries, Inc., 3880 Park Ave., Edison, NJ 08820.

With the availability of effective notch filters, it is now feasible to tailor a high throughout Raman instrument for specific applications. Issues that will define an instrument for a particular chemical system will include: choice of excitation wavelength to avoid fluorescence; focal length/grating combination to define resolution and dispersion; choice of sampling optics: macro, micro, fiber optic; choice of detector: CCD vs. PMT for speed vs. cost, size of CCD for coverage vs. cost. Application of these systems that will be considered include—routine chemical analysis (for quality control of incoming chemicals, for example), in-situ monitoring of chemical reactions, and materials structural analysis.

136 COMPACT LINE-OF-SIGHT REMOTE RAMAN SPECTROMETER FOR INTERMEDIATE-RANGE CHEMICAL DETECTION AND MAPPING. Thomas J. Kulp, S. Michael Angel, and T. Vess, Lawrence Livermore National Laboratory, P.O. Box 808, L-524, Livermore, CA 94550.

Recent improvements in low-noise focal-plane array detectors, imaging spectrographs and holographic rejection filters have been utilized to produce extremely powerful and compact Raman spectrometers for remote fiber optic applications. These advances can also be applied to line-of-sight remote Raman measurements. In this paper, a compact remote Raman spectrometer will be discussed that allows Raman spectral measurements to be made of solid, liquid, and gaseous samples at distances of up to 100-m. The instrument uses a cooled two-dimensional CCD array in conjunction with an imaging spectrograph and relatively low-power (<100 mW) CW lasers. Collection of the return signal is achieved using a small-diameter (22-mm) collection lens. Applications of the instrument to the detection of chemicals in hazardous waste storage tanks, and to the two-dimensional mapping of chemical distributions will be discussed.

137 MICRO RAMAN SPECTROSCOPY: C. L. R. CONFOCAL LASER RAMAN NEAR IR EXCITATION. B. Lenain, J. Barbillat, E. Dasilva, M. Delhaye, EG&G/PARC—Dilor, P.O. Box 2565, Princeton, NJ 08543-2565.

The entry of Raman spectroscopy into the field of microanalysis represented a significant opportunity in that Raman scattering provides information which, up to this time, has not been available from any other widely used micro analytical techniques. With the ongoing developments in instrumentation for the optical spectroscopy, new development enhance and expand the application field of Raman microscopy: "Confocal scanning laser Raman—a new concept of entrance optics which extends the well known capabilities of confocal microscopy to Raman microprobing. This accounts for the Raman microprobe's ability to benefit from a better spatial and axial resolution. The confocal advantages are efficiently used in an original scanning system which permits "confocal Raman mapping". The originality of this scanning system is the possibility to continuously change the "spread" factor while rigorously conserving the confocal performances. *Near infrared Raman spectroscopy—it is important that near infrared Raman spectroscopy not only minimize fluorescence by near infrared excitation, but also that it offer the same level of analytical capabilities provided by modern Raman spectrometers. For several years, we have been working on the development of the multichannel Raman laser in the near infrared (YAG 1.06 μm). Some decisive steps have been taken in this field and we have demonstrated that such an instrument achieves superior performance to that of fourier transform interferometry in microscopy and in the low frequencies range. The advantages and the performances of those new developments are discussed and illustrated by some examples.

138 CRITICAL FACTORS IN RAMAN AND FT-RAMAN MICROSPECTROSCOPY. A. J. Sommer and J. E. Katon, Molecular Microspectroscopy Laboratory, Department of Chemistry, Miami University, Oxford, OH 45056.

The successful employment of Raman and FT-Raman microspectroscopy depend upon a critical assessment of spatial resolution, rejection of inelastically scattered light and sample heating. Although these factors are common to each technique, the excitation wavelength and instrument design dictate the extent which each affect the performance of a system. Theoretical and experimental results will be presented which contrast each of these factors for near-infrared and visible Raman microprobes. The extent to which instrument design affects these factors will also be discussed.

139 FT-RAMAN SPECTROSCOPY AS AN ANALYTICAL TOOL FOR INORGANIC AND ORGANOMETALLIC COMPLEXES. T. J. Johnson and N. T. Kawai, Bruker Instruments, Inc., Manning Park, Billerica, MA 01821.

We demonstrate the feasibility of FT-Raman spectroscopy as an analytical tool for investigation of inorganics and organometallics. For inorganic and alkali substances FT-Raman retains the advantage of conventional dispersive Raman, i.e. the ability to probe the low frequency-shift fundamentals associated with the heavier atoms; yet the spectra are much easier to obtain. For organometallic and coordination complexes, the advantage of the near-IR excitation (with high sensitivity FT-detection) comes to the fore in that the fluorescence and photodecomposition of these often-colored complexes under visible laser excitation are avoided. Several examples of inorganic and organometallic FT-Raman spectra including those of coordination complexes, catalysts, glasses, semi-conductor materials and others are presented. Polarized FT-Raman spectra are used to distinguish between symmetric and non-symmetric modes of vibration.

140 MICRON AND SUBMICRON ELECTRODES FOR USE IN SURFACE-ENHANCED RAMAN SPECTROSCOPY. Elizabeth A. Todd, Will K. Kowalchyk, Kevin L. Davis, Michael D. Morris, Department of Chemistry, University of Michigan, Ann Arbor, MI 48109-1055.

Insofar as a laser beam can be focused on a surface, the SERS signal from that surface is independent of the surface area. The use of microscope optics allows generation of intense SERS spectra from small probes, down to the micron level. Depending upon the numerical aperture of the objective and the incident wavelength, minimum spot sizes, and therefore minimum useful probe diameters, range from about 5 μm down to about 0.5 μm. Although tightly focused laser beams can damage the silver surfaces, this problem can be circumvented by the use of low incident power, an efficient collection system, and a high throughput spectrograph. Red illumination can also be employed to minimize surface damage. We describe the construction of micron and submicron diameter silver surfaces for SERS. Typical fabrication techniques are epoxy-sealing of silver wire into 0.5 mm i.d. glass capillaries followed by chemical etching to the desired diameter, or pulling of silver wire/glass capillaries in a micropipet puller. These surfaces can be used as electrodes, or can be used without potential control. They can be overcoated with membranes which prevent fouling, or with self-assembled thiol monolayers which stabilize the Ag surface and increase sensitivity and selectivity towards various chemical species. We will discuss application of these surfaces to several systems of contemporary chemical interest.

141 RAMAN MICROPROBE WITH HOLOGRAPHIC OPTICAL ELEMENTS. David M. Pallister, Kei-Lei Liu, Anurag Govil, M. D. Morris*; Department of Chemistry, University of Michigan, Ann Arbor, MI 48109-1055.

As spectrograph prefilters, holographic optical components have demonstrated high performance in Raman spectroscopic instrumentation. In this talk we will discuss the design and applications of a Raman microprobe incorporating a holographic notch filter in the spectrograph stage, a holographic band pass filter on the laser and a holographic beamsplitter in the microscope itself. The band pass filter has a narrower pass band and higher throughput than conventional designs. The beam splitter allows insertion of 90% of the incident laser beam, while transmitting up to 85% of the incident Raman scatter. Together these components allow acquisition of Stokes and anti-Stokes Raman microprobe spectra as close as 50 cm^{-1} from the exciting line, using low power lasers. We will discuss the design requirements imposed by the very sharp tuning and the polarization properties of holographic beam splitter. Procedures for correction of very low frequency spectra for filter and beam splitter attenuation will be described. We will illustrate the performance of a holographic optics microprobe with Raman spectra of materials of scientific and commercial interest. We will include some work on time-resolved measurements on a microscope scale.

142 DETECTION OF TRACE EXPLOSIVE EVIDENCE BY ION MOBILITY SPECTROMETRY.

Dean D. Fetterolf, Forensic Science Research, FBI Academy, Quantico, VA 22135.

The continuing threat of worldwide terrorism has prompted the need for new and innovative explosives detection systems. As part of an ongoing research effort, the FBI Laboratory has been evaluating new technology and the innovative adaptation of existing technology for use in counterterrorism and counternarcotics investigations. We have been examining the application of ion mobility spectrometry (IMS), for its role in explosives detection. The explosives residue is collected on a membrane filter by a special attachment on a household vacuum. Subsequent thermal desorption and analysis requires 5 seconds. Experimental results have determined the limits of detection for most common explosives to be approximately 200 pg. The vacuum sampling method permits the collection of trace physical evidence transferred to hands or surfaces through contact or post blast residue. The persistence of explosives on hands and transfer to other surfaces has been examined. Post-blast residue of NG was detected on fragments of improvised explosive devices constructed with double-based smokeless powder. Post-blast residue from C-4, Deta Sheet, SEMTEX, and ammonium nitrate explosives have also been detected on items of forensic and evidentiary value.

143 INFRARED ANALYSIS OF EXPLOSIVES.

Edward G. Bartick and Rena A. Merrill, Forensic Science Research and Training Center, FBI Academy, Quantico, VA 22135.

The identification of both preblast and postblast explosive materials is important for investigative work and forensic testimony. A wide variety of sampling methodologies are applicable to infrared analysis, permitting rapid analysis of a range of explosives types. Low explosive materials have been analyzed by diffuse reflectance spectrometry (DR). Preblast materials have been measured directly in KBr powder, while an extraction method has been used for postblast residues. Plastic bonded explosives have been measured by internal reflectance spectroscopy (IRS, ATR). As an aid to analysts, digital spectral libraries have been developed for searching unknown spectra. These methods of forensic explosive analysis will be described.

144 DETECTION OF THE ORGANIC CONSTITUENTS OF EXPLOSIVES AND GUNSHOT RESIDUES USING MICELLAR ELECTROKINETIC CAPILLARY ELECTROPHORESIS (MECE).

D. M. Northrop, and W. A. MacCrehan, WSP-Crime Lab, Rt. 7, Box 12450, Kennewick, WA 99337.

A MECE technique has been developed to separate and identify the organic components of explosive and gunshot residues (GSR). A standard mixture of 26 common constituents can be separated in under 10 minutes using an SDS/borate buffer and a 100 μm diameter capillary, providing efficiencies of 300,000 plates/m. Selected wavelength uv/visible detection provides detection limits in the low pg range and can be used to provide positive compound identification by comparison to tabulated absorbance profiles. Characteristic propellants, stabilizers and plasticizers of four plastic explosives and six reloading powders were determined by MECE. Application of MECE to GSR detection has been the focus of our work, however, MECE shows much promise for the detection of residues from commercial plastic and illicit gunpowder explosive devices. Masking tape sample collection has been found to minimize analyte losses and coextracted matrix interferences that were found with the use of solvent swabs. The addition of a non-volatile "keeper", ethylene glycol, to the tape extraction solvent prevented analyte loss upon evaporative concentration of the extract. An internal standard, β-naphthol improved quantitative precision of the MECE analysis. In test handgun firings, GSR's (amounting to less than 0.1 μg) were collected from the shooting hand and analyzed by MECE. GSR constituents including nitroglycerin and ethylcentralite could be detected and the pattern could be matched to the unfired gunpowder used. However, we found that the constituent pattern varied somewhat between gunpowder particles, necessitating careful sampling and interpretation if matches of the GSR to the gunpowder manufacturer and lot are to be made.

145 CAPILLARY ELECTROPHORESIS OF LOW EXPLOSIVE RESIDUES.

Kelly A. Hargadon, Materials Analysis Unit, FBI Laboratory, Washington, DC 20535, Bruce R. McCord, Forensic Science Research Unit, FBI Academy, Quantico, VA 22135.

A complex series of chemical reactions occurs during the deflagration of a low explosive which yields trace amounts of anions and cations. Traditionally, the forensic analysis of these reaction products has been performed by ion chromatography (IC). Recently, a new separation technology, capillary electrophoresis (CE), has been developed. CE serves as a complementary technique for IC peak confirmation while providing greater sensitivity and faster separation. Analyses of anionic residues from various types of explosive devices will be presented which demonstrate the utility of this technique.

146 THE ANALYSIS OF ALKYL AMINE NITRATES IN EMULSION AND WATER GEL EXPLOSIVES.

E. C. Bender, Bureau of Alcohol, Tobacco and Firearms, National Laboratory Center, 1401 Research Boulevard, Rockville, MD 20850.

Emulsion and water gel explosives are gradually replacing nitroglycerin dynamites. This increases the possibility of these explosives being used in terrorist bombings. Emulsions generally consist of an oxidizer(s) fuel, water, and emulsifying package. The water gels also have an oxidizer(s) fuel, water and a gelling agent to bind the materials together. These materials are relatively ubiquitous making post blast identification of these explosives difficult. However, some alkyl amine nitrates which are peculiar to a manufacturer are used as oxidizers in some of these formulations. Methyl amine nitrate is an ingredient in the explosives technologies international (fomally Dupont) "Tovex" water gel series. Ethylenediamine dinitrate is a component of the atlas powder company "7D" emulsion. The analysis of these amine nitrates, ethanolamine, and ammonia as their trinitrobenzenesulfonic acid (TNBS) derivatives by high performance liquid chromatography will be discussed.

147 SMOKELESS POWDER CHARACTERIZATION—AN INVESTIGATIVE TOOL IN PIPE BOMBINGS.

Cynthia L. Wallace and Edward C. Bender, Bureau of Alcohol, Tobacco & Firearms, Forensic Science Laboratory, 1401 Research Blvd., Rockville, MD 20850.

Smokeless powder is the filler in more than 50% of U.S. pipe bombings. The physical and chemical characteristics of smokeless powder may indicate manufacturer, identify the specific powder used, or link powder in a suspect's possession to that in a bomb. Since the manufacturing and blending processes have a significant impact on forensic comparisons, effects of sampling and lot-to-lot variation will be examined. Changes in manufacturing and marketing can date a smokeless powder. Case examples will illustrate the types of information which can be developed and how this information may be used to provide investigative leads or associative evidence in a pipe bombing.

148 TRACE ANALYSIS OF NITRATE ESTERS IN INDUSTRIAL WASTEWATER STREAMS.

Bruce P. Thomas, Naval Surface Warfare Center, Code 33300, 101 Strauss Avenue, Indian Head, MD 20640.

This study examines the trace analysis of nitrate esters, specifically TEGDN, PGDN, NG and TMETN, in wastewater streams. The quantitative method of choice is high performance liquid chromatography with ultraviolet detection. Confirmational techniques include gas chromatography, GC/MS and LC/MS with particle beam interface.

149 RECENT ADVANCES IN PROPELLANT STABILIZER ANALYSIS.

Gail Y. Stine, NSWC/IHD, Code 3320E, 101 Strauss Ave., Indian Head, MD 20640-5000.

Gun propellants are currently analyzed for percent stabilizer content utilizing classic solvent extraction followed by HPLC. This paper will cover recent advances in extraction techniques using supercritical fluid extraction. The paper will discuss changes in method parameters as they relate to quantitative extractions the use of methanol modified carbon dioxide as a supercritical fluid will also be discussed.

150 A NEW GENERATION OF COMBINED OPTICAL EMISSION ICP MASS SPECTROMETRIC INSTRUMENTATION

M. Bonner Denton, Department of Chemistry, University of Arizona, Tucson, AZ 85721.

Ion trap mass spectrometry offers significant and powerful capabilities in atomic analysis. A variety of unique operating modes allows storage of specific masses, a range of masses, as well as collisional dissociation of molecular species and even high resolution readout. The potential inherent in combining ICP M.S. with array optical emission spectroscopy will be discussed.

151 THE HIDDEN INFORMATION IN ICP-OES MULTICHANNEL DATA

A. Lorber, Nuclear Research Centre Negev, P.O. Box 9001, Beer-Sheva, ISRAEL.

Chemometrics techniques which exploit the multiwavelength information to improve precision, accuracy and reliability are now common place in numerous spectrometry based analytical techniques. In ICP-OES the degree of penetration of such techniques is negligible for unknown reasons. Our laboratory applies chemometric techniques for the data obtained from direct-reading ICP-OES. Few key achievements are: (a) accuracy of better then 0.5% RSD in routine analysis, (b) elimination of spectral interferences and (c) enhanced reliability in determination. The presentation will demonstrate the benefits of applying chemometrics techniques to ICP-OES for several applications.

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Abstract not received at time of printing.

153 MULTIVARIATE METHODS APPLIED TO SIMULTANEOUS EMISSION SPECTRA FROM THE INDUCTIVELY COUPLED PLASMA

Juan C. Ivaldi, Thomas Barnard, David Tracy, Walter Slavin, The Perkin-Elmer Corporation, 761 Main Avenue, Norwalk, CT 06859-0293.

Inductively Coupled Plasma (ICP) atomic emission spectra collected using a customized charge coupled device (CCD) detector are well-suited to the application of multivariate methods to treat the spectra. With this detection system, the spectral background and the analyte emission data are recorded simultaneously [1]. A multivariate treatment of these emission spectra provides a means to take advantage of the information content in the spectra. The combination of simultaneous spectral data collection and multivariate processing techniques introduces the potential for improved analytical performance compared to peak height methods with off-line background correction and systems without the capability to record a spectrum simultaneously. The improvements come primarily from the use of more information which is available in the spectrum. Additionally, simultaneous spectral data collection reduces the contribution of correlated noise in the background and the analyte signals. The net benefits are improved precision and detection limits, automatic background correction, and correction of spectral overlaps from interfering species [2]. These improvements are discussed in the context of SBR-RSDB detection limit theory developed by Boumans. Investigations were conducted using real data from the ICP system and simulated data generated in the computer. The results are presented in this paper.

1. T. W. Barnard, M. I. Crockett, J. C. Ivaldi, P. L. Lundberg, Paper #991, Pittsburgh Conference, March, 1992.
2. J. C. Ivaldi, D. Tracy, W. Slavin, FACSS October, 1991.

154 THE CHALLENGE OF DIGITAL FILTERING TECHNIQUES IN MULTIELEMENT ICP-AES

M. T. C. de Loos-Vollebregt and E. H. van Veen, Delft University of Technology, Laboratory of Materials Science, Division of Atomic Spectrometry, Rotterdamseweg 137, 2628 AL Delft, The Netherlands.

A survey of digital filtering techniques will be presented for ICP-optical emission spectrometry, with critical discussion of the possibilities and limitations of the various approaches. Applications will be presented of Kalman filter-based software used for the determination of different elements in a matrix of uranium, in tungsten and in environmental samples. It is concluded that line selection is easy and detection limits are better than the theoretical detection limits in many cases where overlapping lines cause problems in conventional data processing. Simulation studies demonstrated that the Kalman filter software is also promising for echelle spectrometers with charge coupled device detector or photodiode arrays.

155 FUNDAMENTAL ATOMIC REFERENCE DATA—WHERE HAVE WE COME IN 5 YEARS?

A. Scheeline, School of Chemical Sciences, University of Illinois, 1209 W. California St., Urbana, IL 61801.

Transition probabilities, energy levels, line-broadening and -shifting parameters, and wavelengths are the fundamental data upon which the spectroscopic edifice is built. The author has been an advocate of improved, computer-accessible reference data, and (with P. W. J. M. Boumans) chaired a workshop in 1987 to survey the status of reference data at that time. Now, five years later, there has been notable progress in several areas relevant to the needs of analytical spectroscopists. Definitive transition probability data have been obtained or tabulated on several important systems including Ar I, Ar II, Fe I, Fe II, and Mo I, with additional (though less comprehensive) data on many other neutral metallic species. Ionization potentials have been remeasured with greater precision for Ti, Fe, and several other transition elements. Much of NIST's data is now available on diskette, making access via spreadsheet or data base manager simple. Recent results, reported at a meeting at NIST the week before FACSS, will be presented. Progress in the last five years has been more limited with respect to line shapes and shifts than with respect to transition probabilities and energy levels. Thus, the needs in atomic absorption have been less well met than those in emission, fluorescence, and laser-enhanced ionization.

156 ELECTRONIC PUBLISHING IN SPECTROSCOPY: CURRENT STATUS AND FUTURE PERSPECTIVES OF SPECTROCHIMICA ACTA ELECTRONICA (SAE)

P. W. J. M. Boumans, c/o Philips Research Laboratories, P.O. Box 80.000, 5600 JA Eindhoven, The Netherlands.

Spectrochimica Acta Electronica (SAE) has been launched at the FACSS 1991 in Anaheim as an electronic supplement of Spectrochimica Acta B (SAB). The idea was to establish, in spectroscopy and related areas of analytical chemistry, a formally structured way for disseminating programs and/or data on diskettes to facilitate scientific communication. An SAE publication consists of a hardcopy paper in SAB format and electronic material on a diskette. Four types of papers are considered: (1) programs and data related to work in which the computer plays such a vital role that the only satisfactory way of publishing is to make the program and data in electronic form available to others, (2) data connected with new work reported in classical hardcopy form but far more extensive than the small selection made for the hardcopy, (3) fundamental reference and other data in tabular or graphical form for general use, (4) applied or tutorial programs and data related to earlier publications, in particular fundamental work. Since SAE is published as a section of SAB, the emphasis is on electronic publications (EP) in the field of analytical atomic spectroscopy. However, EPs in the fields of molecular spectroscopy, physical atomic spectroscopy, and general analytical chemistry or chemometrics are also considered. It has turned out that the SAE concept appeals to scientists, its formula being accepted. The present paper will briefly review the objectives and mode of operation of SAE and discuss its status and perspectives with reference to recently published and forthcoming papers.

157 MULTIELEMENT LINE SELECTION IN INDUCTIVELY COUPLED PLASMA ATOMIC EMISSION SPECTROMETRY (ICP-AES)

P. W. J. M. Boumans, c/o Philips Research Laboratories, P.O. Box 80.000, 5600 JA Eindhoven, The Netherlands.

Multielement lines selection in analytical atomic spectroscopy in general and in ICP-AES in particular has been a topic of much discussion and study in the past years. Although, conceptually great progress has been made, adequate practical application of the rules developed and full implementation of the insights gained are still hampered by the lack of the required spectroscopic data and apparatus. The purpose of this paper is not to lament the present situation and to shed tears about what we do not have available and are not likely to get available in the near future. In contrast, the author will review and assess recent developments with emphasis on their positive aspects in order to point out the trends that may lead us out of the abyss. In this context the author will discuss, inter alia, the following issues: (a) the concept of true detection limit ($c_{L,true}$) as a criterion for line selection in trace analysis, (b) the relationship between $c_{L,true}$ and the error in an interfering line signal, (d) means for improving $c_{L,true}$ and/or making line selection less dependent on sample composition including multicomponent analysis such as Kalman filtering, (e) facts and fiction about high-resolution spectroscopy, (f) spectrum simulation in connection with spectral interferences and line selection, (g) software for automatic line selection designed as expert system, (h) the future: on-line line selection using multiline measurements and chemometric approaches.

158 NEW APPROACHES TO THE ANALYSIS OF SMALL SAMPLES.

M. W. Blades, T. Hettipathirana, C. LeBlanc, C. Gill. University of British Columbia, Department of Chemistry, Vancouver, British Columbia, Canada. V6T 1Z1.

The method of choice for carrying out elemental analysis on small sample volumes (1–50 μL) has traditionally been graphite furnace atomic absorption specrometry. A variety of approaches has been investigated for developing the graphite furnace into a source capable of carrying out simultaneous, multielement analysis. The primary thrust behind these approaches has been to combine the excellent sample transport (and residence time) characteristics of the graphite furnace with some means of exciting the atomized analyte vapour directly inside the furnace. In this way atomic emission spectrometry can be used as a detection method. In 1989 our group and that of Ralph Sturgeon at National Research Council (Ottawa) described the use of a concentric geometric arrangement of graphite furnace and central graphite rod, powered using a radio-frequency generator, enabling the formation of a plasma inside the graphite furnace at atmospheric pressure. This device has been given the acronym FAPES (furnace atomization plasma excitation spectrometry). A characteristic of FAPES is that analyte vaporization, excitation, and emission take place in the same volume. For this reason it is important to understand the role of condensed and gas phase species on the analytical signal. This talk will address these aspects of FAPES.

159 A CRITICAL LOOK AT THE THERMODYNAMIC AND KINETIC FEATURES OF ATOM FORMATION FOR ANALYTICAL SPECTROMETRY.

Julian Tyson, Department of Chemistry, University of Massachusetts, Amherst, MA 01003.

The conversion of samples for analysis into atomic vapor is such a commonplace procedure in the analytical laboratory that many analysts hardly give the matter a second thought. However, the truth is that this combination of physical and chemical processes requires the exercise of considerable ingenuity and the need for improvement in the procedure, particularly for samples for which there are matrix interference effects, has been a major driving force in analytical atomic spectrometry research for many years. The goals are quite clear, a representative sub-sample of the material examined must be converted entirely to atoms with sufficient residence time in the observation volume to give a large, noise-free signal. Residence time is a function of the kinetics of the mass transport in, the transport out and of the various atom forming and removing reactions. For practical atom sources, attempts to increase the rate of appearance of atoms by increasing the rate of introduction of atom precursors are often counter productive as this strategy may reduce the rate of atom formation and increased noise. Given the effort that has been put into research into this area for flames, furnaces and plasmas, it is tempting to consider that the performance limit of conventional sample introduction (dissolve and spray) has been reached. It is time, therefore, to consider the potential of some alternative forms of bond-breaking, such as the use of two-stage thermal processes (electrothermal vaporization or laser ablation) or ion-bombardment (arcs, sparks and glow discharges). The role of chemistry for the removal of matrix interferences and analyte preconcentration should not be overlooked.

160 ON THE REALIZATION OF EXPERT SYSTEMS FOR ATOMIC SPECTROCHEMICAL ANALYSIS.

M. Bonner Denton, Department of Chemistry, University of Arizona, Tucson, AZ 85721.

An overview will be presented into the integration of state-of-the-art technologies for implementing automated atomic spectrochemical analysis. The potential merit of combining array detector-based optical emission spectroscopy in conjunction with ICP mass spectrometry will be discussed. Potential synergistic interactions between optical emission spectroscopy employing the latest generation in multi-wavelength array detectors with recent concepts in mass spectrometry will be presented. The ability to establish an analytical protocol for each specific sample based on the unique characteristic of that sample will be considered.

161 THE SEARCH FOR A SOLID SOLUTION.

E. Salin, J. M. Ren, C. Skinner, L. Blain, G. Légère, Department of Chemistry, McGill University, 801 Sherbrooke St. W., Montreal, P.Q., Canada, H3A 2K6.

Over the last decade our laboratory has studied the solid sample analysis problem from a wide perspective. Our initial work involved extensive work with Direct Sample Insertion (DSI). This work started with wire loops and then evolved through cups to pellets. We will discuss our most recent work with pellets and chemical modifiers. The DSI work, while successful, has pointed out some important limitations. These, in turn, have pushed us towards the use of electrothermal vaporization (ETV) techniques. We will discuss our conclusions from our most recent solid ETV-ICP work including the determination of Pb in soil at natural urban levels. In hindsight, maybe liquids do offer some advantages. We will mention an alternative approach to converting solids to liquids which we hope will revolutionize liquid sample preparation.

162 DIRECT ANALYSIS OF SOLID SAMPLE IN INDUCTIVELY COUPLED PLASMA SPECTROCHEMISTRY.

J. M. Mermet, Laboratoire des Sciences Analytiques, Université Lyon I, 69622 Villeurbanne Cedex, France.

Pneumatic nebulization is the standard method for sample introduction in inductively coupled plasma (ICP) spectrochemistry. As a solution is required for aerosol production, prior dissolution of solids must be carried out. However, dissolution is tedious and time-consuming with a risk of contamination and incomplete dissolution. There is therefore a need for direct solid analysis. This type of analysis is based on the introduction of fine particles into the ICP. These particles can be obtained either by grinding or by ablation and are injected either as a suspension or in a stream of gas. Due to the limited residence time and the poor thermal conductivity of argon, the size of the particles must be limited to a few micrometres. Experimentally, this is a severe limitation, in particular when the calibration is performed with solutions. The obtaining of submicron particles by grinding is not an easy task. An alternative is the production of electrically-dispersed particles with the use of a metal as an electrode for spark ablation in pure water. Another alternative is the direct ablation of the metal. Spark ablation can be used but does not provide any spatial information. Laser ablation permits local analysis and can be applied on any type of material. Advantages and analytical performance will be discussed for each method.

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164 MECHANISM OF ALUMINIUM ATOMIZATION IN GRAPHITE FURNACE ATOMIC ABSORPTION SPECTROMETRY.

C. L. Chakrabarti,[1] A. Kh. Gilmutdinov,[1,2] D. C. Grégoire,[3] J. C. Hutton[1] and M. M. Lamoureux,[1] [1]Centre for Analytical and Environmental Chemistry, Department of Chemistry, Carleton University, Ottawa, Ontario, K1S 5B6 Canada, [2]On leave from the Department of Physics, University of Kazan, Kazan, 80111 Russia, [3]Geological Survey of Canada, Department of Energy, Mines and Resources, Ottawa, Ontario, K1A 0E8 Canada.

The mechanism of atomization of aluminium has been investigated using two independent approaches under conditions for formation of Al spikes. The spatial and temporal behaviour of aluminium atoms and molecules generated in the graphite furnace were studied by the Spectral Shadow Filming technique. The experimental results have shown that Al atoms are in greater concentrations near the surface of the graphite tube while the Al molecules are located in the central axis of the tube. The temporal distribution of Al and Al-containing species have also been studied with a modified graphite furnace coupled to an ICP-MS. This configuration allows the simultaneous recording of the atomic absorption or the molecular absorption signals, and the ICP-mass spectrometric signals of Al atoms and Al-containing molecules. The experimental results obtained simultaneously by ICP-MS and GFAAS show that Al_2O appears simultaneously with Al during each spike. On the other hand, the temporal distribution of Al carbides is not correlated with the observed Al-spikes. A new mechanism for the aluminium spike formation will be proposed on the basis of the above results.

165 ATOMIZATION OF Al, Ga, In, Tl IN ETA-AAS

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To verify the validity of the theory of carbothermal reduction of metal oxides by gaseous carbides the process of atomization of Al, Ga, In, Tl has been studied theoretically and experimentally. The Langmuir model of vaporization from the open surface at normal pressure and calculation results of the equilibrium composition of vapors over oxides with the concentration of the oxygen impurity in the sheath gas taken into account form the basis of the estimations. Main experimental studies have been performed with the use of laboratory-made setup comprising a double-channel spectrometer with spectrum scanning, a combined atomizer with independent temperature control of the furnace and vaporizer made both of Ta, W, Mo or graphite, a sistem of automatic vaporizer temperature control by means of analytical signal feedback. It has been shown that the basic vapor com-components at M2O3 atomization are M, M2O, MO. The relation between them is determined by the content of oxygen in the sheath gas. The results of recording of the same molecular absorption bands in the carbon and free-of-carbon furnaces make it possible to identify them as belonging to molecules of oxides. The results obtained enable one to reject the assumption of the existence of high-volatile carbides in the atmosphere of graphite furnace.

166 MASS SPECTROMETRIC ELUCIDATION OF MECHANISMS THAT CONTROL THE ELECTROTHERMAL ATOMIZATION OF TIN.

G. N. Brown, D. L. Styris, Pacific Northwest Laboratory, Richland, WA 99352.

Mechanisms that control the electrothermal atomization of tin oxide and tin chloride were investigated by monitoring real-time mass spectra of gaseous species generated in pyrolytic graphite coated graphite furnaces. Atmospheric pressure and vacuum vaporization were used to separate homogeneous gas phase and condensed phase interactions. During atmospheric pressure vaporization the observed molecular species consisted of tin hydroxides, chlorides and monoxide. Free Sn was absent from the center of the furnace as determined by mass spectrometry but was present at the cooler end regions as determined by atomic absorption spectroscopy integrated over the length of the graphite atomizer. During vacuum vaporization free Sn was not observed and the only molecular species detected were Sn0 and SnC1$_2$. This paper presents these data, and proposes and discusses the associated mechanisms.

167 DIGITAL IMAGING AND COMPUTER SIMULATION OF ATOM FORMATION AND DISSIPATION IN A GRAPHITE FURNACE FOR ANALYTICAL ATOMIC SPECTROMETRY.

J. C. Hutton and C. L. Chakrabarti, Centre for Analytical and Environmental Chemistry, Department of Chemistry, Carleton University, Ottawa, Ontario, K1S 5B6, Canada. A. Kh. Gilmutdinov and R. Mrasov, Department of Physics, University of Kazan, 18 Lenin Str., Kazan, 420 008, Russia.

The understanding of the distribution of atomic and molecular species in electrothermal atomizers for atomic absorption spectrometry (ETA-AAS) has increased recently because of the results obtained by the Shadow Spectral Filming (SSF) technique.[1] Measuring the analyte distribution in ETA-AAS is important, not only because of the information that it can give us about the mechanisms of atom formation, but also because it has been shown that the analytical signal that is measured in atomic absorption spectrometry is affected by non-uniform distributions of the analyte.[2] Although SSF provides good qualitative results, the photometric accuracy of photographic film is quite low and therefore the quantitative results provided by SSF are less than ideal. This major shortcoming of the SSF technique has been removed by using a digital charge-coupled device (CCD) detection system instead of the movie camera used in SSF. Investigations of the atomization of aluminum will be presented and the results will be compared with those obtained using SSF. A complete understanding of the distributions obtained is only possible if they can be described theoretically. A computer model that generates a three-dimensional distribution of analyte atoms from the elementary processes that are occurring within the graphite tube atomizer will also be presented. The distributions obtained by the computer modelling and by the CCD digital imaging will be compared.

1. A. Kh. Gilmutdinov, Yu. A. Zakharov, V. P. Ivanov and A. V. Voloshin, *Journal of Analytical Atomic Spectrometry*, 1991, **6**, 505.
2. A. Kh. Gilmutdinov, T. M. Abdullina, S. F. Gorbachev and V. L. Makarov, *Spectrochimica Acta, Part B*, in press.

168 SURFACE STUDIES USING TUBE-IN-TUBE ELECTROTHERMAL ATOMIZERS.

Rodney W. Fonseca, James A. Holcombe, Department of Chemistry and Biochemistry, University of Texas at Austin, Austin, Texas 78712.

It is possible to study desorption processes for different metals using a system that combines concepts of two known techniques, temperature programmed desorption (TPD) and ETA-AAS. To do this, tubes of different materials were introduced into a Varian GTA-95 furnace and heated by thermal radiation from the outer tube. The heating program for the outer furnace was chosen to obtain a linear heating of the inner tube. A Ta liner was inserted between the tubes in order to improve isothermality along the length of the inner tube. The temperature along the length of the tubes was measured by means of a thermocouple. The inner tube was provided with a dosing hole to allow for sample introduction and temperature measurement. The materials used for the inner tube include graphite, Ta, and a non-conductive surfaces like alumina (ceramic). Atomization of Cd, Cu, Ag and Au was studied. The alignment of the peak maxima at increasing concentrations were observed to approximate the order of release. Activation energies of release were obtained by using Arrhenius plots. This technique is able to provide useful surface information during the actual heating of the sample and under atmospheric pressure which is a difficult task for common surface techniques. It is also possible to extend this approach to the desorption of molecular species at comparable surface coverages.

169 TEMPORALLY AND SPATIALLY RESOLVED GAS PHASE TEMPERATURE MEASUREMENTS IN ELECTROTHERMAL ATOMIZERS.

B. Welz, M. Sperling; Department of Applied Research, Bodenseewerk Perkin-Elmer GmbH, W-7770 Ueberlingen, Germany; J. Hertzberg, Fraunhofer-Institute for Laser Techniques, W-5100 Aachen, Germany; G. Marowsky, Max-Planck-Institute for Biophysical Chemistry, W-3400 Goettingen, Germany.

Coherent anti-Stokes Raman Spectroscopy (CARS) has been used successfully to measure the temperature distribution in the gas phase of a Massmann-type electrothermal atomizer over the length and the diameter of a graphite tube over time. A L'vov platform inserted into the graphite tube delayed the increase of the gas temperature and reduced the heating rate but not the maximum temperature. The lower the starting temperature the more pronounced was the "platform effect" i.e. the delay in heating. However, the effect was restricted to the central part of the tube in which the platform is situated. No influence of the starting temperature was observed on the gas temperature towards the tube end, and the temperature distribution over the tube length was under no conditions flat.

170 METAL-SURFACE REACTIONS AT ELEVATED TEMPERATURES ON VARIOUS SURFACES.

Jason G. Jackson, James A. Holcolmbe, Department of Chemistry, University of Texas at Austin, Austin, TX 78712.

Electrothermal atomization atomic absorption spectrometry (ETA-AAS) is the current technique of choice for ultratrace and microtrace analysis because of its part-per-billion detection limits and small (less that 10 μl) sample size. In order to gain a more fundamental understanding of ETA processes, most early research employed optical atomic and molecular spectroscopy of the vapor phase. Later, mass spectrometry, principally temperature programmed thermal desorption mass spectrometry (TP-TDMS) of the vapor phase was used to elucidate gas phase reactions and by inference, surface reactions. Several different analytical techniques have been used to gain insight into surface reactions. The techniques employed were useful in many mechanistic studies, but they are relatively insensitive to the ng and sub-ng analyte quantities usually encountered in ETA-AAS. These techniques also could not study the reactions during actual heating of the surface. In order to be able to investigate surface reactions at elevated temperatures, a temperature programmed static secondary ion mass spectrometer (TPS-SIMS) was constructed. Static SIMS was chosen because of its superior sensitivity and minimal surface perturbation. Molecular and isotopic information is also more readily obtained than with other surface analysis techniques. These characteristics permit surface studies using parameters and analyte concentrations typical of ETA-AAS. Discussion of various metal-surface reactions will be presented.

171 Abstract not received at time of printing.

172 SOLID SAMPLE SPECIATION USING PRESSURE REGULATED ELECTROTHERMAL ATOMIZER ATOMIC ABSORPTION.

P. Wang and J. A. Holcombe; Department of Chemistry and Biochemistry; University of Texas; Austin, TX 78712.

Electrothermal atomization with atomic absorption detection is becoming more routinely employed for solid samples without the need for complete dissolution. Use of slurries and the direct introduction of solids into the furnace have both exhibited success. Using an IC cuvette graphite furnace enclosed in a chamber to permit reduced pressure operation, it is possible to extract additional information about some solid samples. Specifically, different chemical forms and/or spatial locations (e.g. surface vs bulk) of concomitants in the sample may be elucidated from the temperature dependent release of the analyte. This talk will consider a study of a 99% pure Cu sample (SRM 1253) containing trace amounts of Pb (240 ppm). Three distinct Pb absorbance peaks can be resolved when atomizing at 0.01 torr. These have been tentatively assigned to surface (or near surface) Pb, Pb grains in the Cu and Pb which vaporizes with the bulk of the Cu matrix. While the surface Pb is easily determined with ETA-AAS, Auger and SEM with XRF detection both lacked sufficient sensitivity to detect the Pb on the surface of this sample. Discussion will consider the feasibility of using this approach to quantitatively speciate the Pb and possibly discern the Pb grain size in the original sample.

173 COMPUTER MODELING IN LIQUID CHROMATOGRAPHY METHOD DEVELOPMENT.

M. K. Watkins, J. D. Dolan, and T. Jupille, L. C. Resources, 2930 Camino Diablo, Walnut Creek, CA 94596.

The increased emphasis on method development and optimization has been due in large part, to the ability to automate various aspects of the HPLC process. This automation includes; collecting and analyzing data; organizing retention data for further interpretation; fitting these data to various models to predict new experiments; and finding the best conditions for a particular analysis. Although many types of procedures have been described for computer-aided HPLC method development, this paper will discuss the two main approaches used in most commercially available software. The experimental-design approach assumes some knowledge of the retention process and uses a predetermined experimental design to gather data. These data are fit to some model leading to predictions for an optimum separation. Alternatively a learning approach can be used to carry out experimental runs. Based upon the results, the computer predicts experimental conditions for subsequent runs. These runs are carried out in turn, and the process is repeated until a desired separation is obtained. This paper will give an overview of the commercially available software packages that fit each of these approaches.

174 MULTIVARIATE APPROACHES TO PEAK PURITY DETERMINATIONS IN HPLC.

Benedict G. Archer, Beckman Instruments Inc., 2500 Harbor Blvd., Fullerton, CA 92634.

Assessing peak purity in HPLC remains an important need in several analytical contexts. Two of the more challenging are peak tracking in methods development where the retention and spectral characteristics may be unknown, and relative analyte amounts are often similar, and purity validation in development and production of pharmaceutics where spectral and retention characteristics are usually known and often very similar, but impurities may be present in small, 1% or lower, amounts. The commonly used absorbance ratio method to detect inapparent coelution is inadequate in the first instance because spectral properties may be unknown, and too insensitive to be generally useful in the second. A multivariate method which makes use of the sequential spectral data produced by a diode array UV absorbance detector, and significantly enhances impurity detection was developed by Ramos[1,2] et al., and recently studied by Keller et al.[3,4] The central idea of this method is to estimate the pseudorank of a matrix comprising a fixed number of spectra taken sequentially during a chromatographic run, and to identify this result with the number of components in the column effluent at each corresponding time during a run. In a real time implementation, the matrix is continually updated by adding new spectra as each is acquired, and deleting the oldest. This presentation will include a review of the method including critical aspects of the algorithm, description of results obtained with actual and synthetic data which establish its capabilities under conditions of varying chromatographic resolution, spectral differences and signal to noise ratio, and discussion of sample and instrumental conditions that can cause erroneous results.

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2. B. G. Archer, L. S. Ramos and T. Hill, PittCon '90, paper 1179, Mar. 5–9, 1990, NY, NY.
3. H. R. Keller and D. L. Massart, *Analytica Chimica Acta*, **246** (1991) 379.
4. H. R. Keller, D. L. Massart, P. Kiechle and F. Erni *Analytica Chimica Acta*, **256** (1992) 125.

175 INVESTIGATION OF WINDOW FACTOR ANALYSIS AND MATRIX REGRESSION ANALYSIS IN CHROMATOGRAPHY.

Kathleen J. Schostack, Hoffman-La Roche, Nutley, NJ 07110, and Edmund R. Malinowski, Dept. of Chem. and Chem. Eng., Stevens Inst. of Tech., Hoboken, NJ 07030.

Window factor analysis (WFA), a self-modeling, chemometric method for obtaining the concentration profiles of individual components from evolutionary processes, is applied to unresolved liquid chromatograms. WFA makes use of the fact that each component lies in a specific region along the evolutionary axis, called the "window." Various mixtures of toluene, ethylbenzene, m-xylene and naphthalene, in methanol solvent, were pumped through a Whatman Partisil column using a 9:1 methanol-water mobile phase. Ultraviolet absorbance spectra consisting of 35 wavelengths from 215 to 385 nm were recorded at 2 second intervals with a Perkin Elmer HPLC/DAD System. The chromatograms exhibited severe overlap. Principal factor analysis (PFA) of the resulting data matrices gave evidence that at least 13 factors were responsible for the data. "Uniqueness tests" indicated that the absorbances at the first 7 wavelengths were unique. Examination of the absorbances at these wavelengths showed values greater than 2 a.u.; thus these absorbances are not reliable. These seven wavelengths were deleted from the data matrices. PFA of the reduced data indicated seven factors. The three "ghosts" factors were identified as: (1) baseline wave, (2) pump oscillation, and (3) methanol. The chromatograms were completely resolved by WFA without the use of any external information. Quantification required chromatograms of the pure components obtained under the same experimental conditions. Although the quantitative results obtained by WFA did not agree exactly with the known concentrations, the results were in agreement with those obtained by rank annihilation factor analysis (RAFA) and matrix regression analysis (MATRA). Derivation of matrix regression analysis, developed during this investigation, is presented.

176 PATTERN RECOGNITION OF CHROMATOGRAPHIC PROFILES FOR PRODUCT MONITORING.

D. R. Burgard, The Procter and Gamble Company, P.O. Box 398707, Cincinnati, OH 45239-8707.

Spectroscopic techniques can provide much useful information but have limited utility for the quantitation of individual components in complex mixtures. Chromatographic techniques can provide more detailed information for complex samples. High resolution chromatographic profiles contain distinctive patterns that can be used for comparative analysis. The value of such comparisons is limited by the quality of the measurements and the ability to identify and use the appropriate information. Pattern recognition techniques can be used to systematically identify differences in the levels of compounds allowing routine comparative analysis. Applications include process development studies, product monitoring for quality control, raw material qualifications, competitive product checking and performance versus composition testing. A discussion of chromatographic data handling considerations and examples using chromatographic data for product monitoring will be discussed.

177 PATTERN RECOGNITION METHODS APPLIED TO CHROMATOGRAPHIC DATA FOR FISH SPECIATION.

B. J. Tenge,[1] L. S. Ramos,[2] S. J. Kwolek,[1] N-L Dang,[1] J. A. Nolan,[3] J. D. Barnett,[1] M. M. Wekell.[1] [1]U.S. Food and Drug Admin., SPRC SB SEA-DO, P.O. Box 3012, Bothell, WA 98041-3012. [2]Infometrix, Inc. 800 Denny Building, 2200-6th Ave, Seattle, WA 98121, [3]Beckman Instruments, Inc. P.O. Box 3100, Fullerton, CA 92634-3100.

The pattern recognition method, Soft Independent Modeling of Class Analogy (SIMCA), as embodied in the Pirouette© chemometrics package, is applied to a fish speciation problem that involves identification of economic fraud. Specifically, less expensive members of the *Sebastes* (rockfish) genus are substituted for the more expensive *Lutjanus campechanus* (red snapper) and, in certain U.S. markets, are misbranded as red snapper. A database of gas chromatography fatty acid methyl ester (GC-FAME) profiles and/or capillary electrophoresis (CE) molecular weight protein profiles can be constructed from the flesh of many known samples of these species, and SIMCA can perform the classifications and provide confidence levels for these classifications. Subsequently, prediction samples can be rapidly analyzed by either instrumental method and can have their membership quickly calculated with the prediction module of this SIMCA routine. Furthermore, data from highly controlled GC-FAME experiments indicate the ability to use fatty acid methyl ester profiles for speciation of individual rockfish species.

178 PREDICTION OF CHROMATOGRAPHIC RETENTION OF ORGANIC COMPOUNDS FROM MOLECULAR STRUCTURE.

P. C. Jurs, T. F. Woloszyn, Chemistry Department, Penn State University, University Park, PA 16802.

The relationship between the molecular structure and Kováts retention index was investigated using computational techniques for a dataset comprised of fifty-one alkylbenzenes, fourteen styrenes, and sixteen associated aromatic and non-aromatic cyclic compounds. All of the compounds were products of pyrolysis naphtha and fluid catalytically cracked naphtha and were separated on two stationary phases, SE-30 and Carbowax 20M. The compounds were submitted to molecular modeling and descriptors generated that numerically encode the structural features of the molecules. These descriptors were either topological, geometrical, electronic, or physiochemical in nature. Multiple linear regression was used to develop linear models. The models were validated with an external prediction set and found to be robust and of high quality. Each stationary phase was modeled separately. A four descriptor model was generated for the SE-30 column with $R = 0.983$ and $s = 18.6$, which corresponds to a 1.8% error at the mean of the range. An additional descriptor was necessary to model the more polar Carbowax 20M column. This charged partial surface area descriptor accounted for the more polar interactions between the solute and the stationary phase. The five descriptor model for the Carbowax column has an $R = 0.987$ and a $s = 23.3$, which corresponds to a 1.9% error at the mean. Previous research has indicated that modeling chromatographic retention is more difficult on more polar stationary phases such as Carbowax 20M. Also investigated was the implementation of boiling points as a physiochemical descriptor. Boiling point have been found to be highly correlated with Kováts retention index. These models were statistically stable, and they were compared with previous work which modeled alkylbenzenes.

179 EXPLORING THE SOLUTION SPACE VIA CONSTRAINED NONLINEAR OPTIMIZATION.

S. Neal, Dept. of Chemistry, University of California, Riverside, CA 92521.

The resolution of component spectra from multicomponent bilinear matrix-formatted data by Self-Modeling Curve Resolution has been generalized to n components using constrained nonlinear optimization to control the combination of singular vectors to form component spectra while maintaining their nonnegativity, convexity and conjugacy. This approach only generates an exact solution when each of the component spectra (in both row and column spaces) has a zero response to a wavelength region which the remaining components respond to independently. In the absence of this feature, an infinite number of possible solutions exist forming regions of feasible solutions. Unique solutions have been extracted from feasible regions using a variety of criteria, especially maximum entropy and dissimilarity. The application of these additional constraints has been heuristic since no correlation has been established between the nature of the spectral overlap producing the feasible region and the features imposed on the solution using the additional constraints. In the work described in this presentation a series of objective functions for constrained nonlinear optimization based resolution that extract a variety of solutions from the feasible region designed and the properties of these solutions in the feasible region as a function of spectral overlap are monitored using synthetic data. Graphical and mathematical descriptors of the feasible regions are used as aids in evaluating solution properties. The utility of the various kinds of additional constraints will be illustrated using experimental fluorescence excitation-emission matrices.

180 A NEW APPROACH TO CHROMATOGRAPHY PATTERN RECOGNITION USING THREE-DIMENSIONAL MULTIVARIATE PLOTS.

F. O. Geiser, Geiser Scientific, Inc., 287A Wilson Ave., Glen Mills, PA 19342; C. Golt and L. Kung, Jr., Agriculture Experiment Station, University of Delaware, Newark, DE 19716; J. D. Justice, Justice innovations, Inc., 465 El Capitan Place, Palo Alto, CA 94306; and L. Fluckiger, Echo Data, Inc., 1010 N. State St., Orem, UT 84057.

Principal-component analysis as automated in Echo Data's Datamax™ software was used to correlate, visualize, and verify the relationships of chromatography data. Many dimensional data were plotted by relaxing the usual 90-degree axes and by using nonperpendicular vectors. The arccosines of the correlation coefficients were used as the vector angels. Bacterial treatments of bovine ruminal fluid were plotted in order to determine if bacterial inoculation in lieu of antibiotic treatments could enhance ruminal fermentations by increasing concentrations of acetic and propionic acids. A total of 160 chromatograms consisting of 20 replicated treatment protocols were merged into a 160×6 matrix using Justice Innovations' Chrom Perfect™ software. The Datamax™ software verified: (1) optimum concentration, (2) time-course effects, (3) replicate reproducibility. Applications for visualizing multidetector, multiwavelength, multicolumn data will be discussed.

181 DISPERSION IN ELECTROKINETIC SEPARATIONS.

Scott L. Delinger and Joe M. Davis, Department of Chemistry and Biochemistry, Southern Illinois University at Carbondale, Carbondale, IL 62901.

The extensive application of micellar electrokinetic separations has been accompanied by theory for the retention processes responsible for separation. Several detailed experimental programs have tested this theory. Regrettably, a theoretical interest in dispersion is not as developed. Explanations for the nonequilibrium-like dispersion observed in some publications of micellar electrokinetic data in the late 1980's have been limited. We are developing an experimental program to determine if this dispersion is real, as opposed to being an artifact, and to determine its origin, if it is real. The program is based on the construction of van-Deemter like graphs of plate height vs. applied voltage for a number of analytes, which previously have shown nonequilibrium-like dispersion at high voltages in micellar electrokinetic chromatography. Experimental values of plate height will be to fit to a model of dispersion, which includes detailed expressions for injection effects, longitudinal diffusion, and, if necessary, Joule heating. In addition, a generic nonequilibrium term, equal to the product of a coefficient and the applied voltage, will be included in the expression for plate height. This coefficient will be determined by the fitting and then compared to values predicted by existing theories. Adjustments to theory will be made on the basis of new experimental evidence.

182 CAPILLARY ZONE ELECTROPHORESIS OF BIOPOLYMERS WITH COUPLED FUSED-SILICA CAPILLARIES.

Ziad El Rassi and Wassim Nashabeh, Department of Chemistry, Oklahoma State University, Stillwater, OK 74078-0447.

The analysis of biopolymers by capillary zone electrophoresis (CZE) most often requires the use of capillaries with coated surfaces in order to minimize solute-wall interactions. However, the surface modification is always accompanied by a certain reduction in the electroosmotic flow (EOF). This usually leads to an increase in the analysis time and in some cases restricts the ability of the CZE system to analyze only similarly charged solutes. In this paper, we wish to introduce ways by which the EOF can be either tuned to any desired level or changed during the run independently of the applied voltage while keeping solute-wall interactions to a minimum level. In one approach, the flow is adjusted through coupled capillaries with different magnitude of flow. In a second approach, a multiport sliding valve which permitted the switching between several coupled capillary systems having different magnitude of EOF was developed. It allowed stepwise increase in EOF during analysis. Both approaches afforded the rapid analysis of bipolymers at low field strength without sacrificing the high separation efficiency obtained with surface modified capillaries. A general equation relating the average EOF velocity in the multiple capillary systems to the intrinsic electroosmotic velocity of the connected segments and their corresponding lengths has been derived and verified experimentally. In addition, the multiport sliding valve permitted the collection of the separated analytes, that were further analyzed by reversed-phase liquid chromatography and liquid secondary ion mass spectrometry. These schemes were evaluated with proteins and bioactive peptides.

183 OPTIMIZATION OF SELECTIVITY IN CAPILLARY ELECTROPHORESIS.

M. R. Hadjmohammadi, B. Ye, and M. G. Khaledi, Department of Chemistry, North Carolina State University, Raleigh, NC 27695-8204.

The enormous separation power of HPCE stems from the possibility of generating a very large number of theoretical plates in a short period of time. An important advantage of HPLC, on the other hand, is the feasibility of enhancing separation selectivity through careful manipulation of mobile phase composition. It is simply more rewarding to achieve a better resolution in chromatography by optimizing selectivity rather than efficiency. For HPCE separation of compounds with nearly identical mobilities, the high efficiency might be inadequate and selectivity enhancement would be the only alternative to achieve a satisfactory separation. In addition, optimization of selectivity in HPCE would reduce the need for generating very large number of theoretical plates which imposes restrictions on capillary dimensions and consequently on sample size and detectability. In this presentation, the influence of different selectivity parameters in CZE and MECC (especially pH, organic solvents, and micelles) will be discussed and appropriate strategies for their optimization will be presented. In addition, the usefulness of performing HPCE separations in mixed micellar media and purely non-aqueous solvents will be discussed.

184 OPTIMIZATION OF EXPERIMENTAL PARAMETERS IN CAPILLARY ZONE ELECTROPHORESIS. H. J. Issaq, K. C. Chan, G. M. Janini, G. M. Muschik; Program Resources, Inc./DynCorp, NCI-FCRDC, P.O. Box B, Frederick, MD 21702.

The effect of experimental parameters such as applied voltage, buffer type, concentration and pH, and of inorganic and organic additives on mobility, resolution, selectivity and efficiency were studied. Solute migration time in CZE is linearly proportional to the square root of the buffer concentration and inversely proportional to the applied voltage and the charge density of the buffer's cation. Column efficiency and resolution in CZE are enhanced by increasing the buffer concentration at a moderate voltage. Literature citations on the effect of the addition of organic modifiers, methanol and acetonitrile, to the buffer show contradictory results. We critically and systematically examined this effect on migration time and separation efficiency. The results will be presented and discussed. Research sponsored by the National Cancer Institute, Department of Health and Human Services, under contract number NO1-CO-74102 with PRI/DynCorp.

185 Abstract not received at time of printing.

186 RECENT ADVANCES IN MOLECULAR-WEIGHT-SENSITIVE DETECTORS FOR SIZE EXCLUSION CHROMATOGRAPHY. Howard G. Barth, Wallace W. Yau, and Christian Jackson, E. I. du Pont de Nemours and Company, Experimental Station, E228/238, P.O. Box 80228, Wilmington, DE 19880-0228.

Molecular-weight-sensitive detectors for size exclusion chromatography are becoming increasingly popular for the characterization of polymers. These detectors are based on light scattering and intrinsic viscosity measurements. With these types of detectors, polymer conformation and branching can be determined, as well as molecular weight. This talk will review the latest developments in this area including the combination of light scattering and viscosity detectors. Also discussed will be difficulties of and approaches for characterizing complex polymers.

187 THE "SIZE" OF MOLECULES AND INSTRUMENTAL BROADENING. Phillip J. Wyatt, Wyatt Technology, 802 E. Cota St., P.O. Box 3003, Santa Barbara, CA 93130.

For sufficiently large molecules, the direct measurement of the mean square radius, $\langle r_g^2 \rangle$, from light scattering measurements of fractions eluting from a GPC column permits the additional direct determination of molecular conformation, the detection of branching, and an explicit measurement of instrumental broadening (sometimes called "band broadening"). With only a few exceptions (e.g. heterogeneous copolymers), the light scattering technique for such "size" measurement does not require a concentration detector, a measurement of the refractive index increment, dn/dc, nor a knowledge of the eluting species' molecular weight. Modern analytical procedures to extract such size information incorporates all measured Rayleigh excess ratios and do not depend on linear extrapolations. As confirmed recently by Van Zanten and Monbouquette, even the determination of hydrodynamic radii by these classical LS methods agree to within experimental error with the results obtained from the more demanding QELS procedures.

188 CHARACTERIZATION OF SEMI-FLEXIBLE POLYMERS BY SIZE EXCLUSION CHROMATOGRAPHY WITH MULTI-ANGLE LIGHT SCATTERING. Patricia M. Cotts, IBM Research Division, Almaden Research Center, 650 Harry Rd., San Jose, CA 95120-6099.

Semi-flexible polymers are polymers for which the usual assumption of Gaussian chain statistics does not hold. The analysis of these polymers by Size Exclusion Chromatography (SEC) is complicated by the *stiffness* of the polymer backbone. Light scattering detectors which permit measurement of both the molecular weight and the size (radius of gyration) of fractions eluting from the column are now available. These measurements eliminate the need for calibration standards which may be inappropriate for stiff polymers. Results for several semi-flexible polymers such as polyimides and polysilanes are presented.

189 SYSTEM REQUIREMENTS FOR MULTIPLE DETECTOR CHARACTERIZATION OF POLYMER SYSTEMS. J. Lesec, R. Nielsen, and T. Havard, Waters-Millipore, 34 Maple Street, Milford, MA 01757.

The development of on-line viscometry detectors for gel permeation chromatography (GPC) has focused attention towards the use of information derived from a GPC/Viscometry system to calculate accurate (absolute) molecular weight averages and branching information. The objectives of this paper are to examine how the system parameters and instrument design affect the performance of a GPC with multiple detectors. This technique will be applied to commonly available narrow and broad distribution polymers.

190 CHARACTERIZATION OF HIGH MOLECULAR WEIGHT POLYETHYLENES USING GPC, GPC-LALLS AND GPC-DV. A. Willem deGroot, Wayne U. Hamre, and Harolyn Perkins, Dow Chemical Co., Texas Operations, B-3833 Bldg., Freeport, TX 77541.

Gel permeation chromatography, gel permeation chromatography/low angle laser light scattering, and gel permeation chromatography/differential viscometry have been applied to the characterization of high molecular weight polyethylene. GPC columns having a wide variety of particle sizes and various flow rates were investigated. The data indicates that severe shear degradation takes place during the GPC experiment. Larger particle size columns and slow flow rates can minimize this effect.

191 MEASURING PHARMACOLOGICAL EVENTS IN VIVO WITH LCEC: NEW CHALLENGES AND OPPORTUNITIES. Ronald E. Shoup, Chester Duda, James Gitzen, Peter Kissinger, Bioanalytical Systems, Inc., 2701 Kent Avenue, West Lafayette, IN 47906.

Contrary to the symposium title, there remain many unexplored LCEC applications areas, even in the area of catecholamines. With the advent of microdialysis as a useful in vivo monitoring technique, demands on the sensitivity and reliability of sub-picogram LCEC assays are high. From a dual perspective as both a manufacturer and FDA-regulated analytical laboratory, we will attempt to show how these new challenges are being met and also introduce other new applications which have been validated, most over the course of several thousand injections. Examples will be taken from our work in protein analysis, bioanalytical methods development, and pharmaceutical analysis.

192 IDENTIFICATION AND QUANTITATION OF PEPTIDES AND PROTEINS BY LIQUID CHROMATOGRAPHY-ELECTROCHEMICAL DETECTION WITH POST-COLUMN, PHOTOLYTIC DERIVATIZATIONS (HPLC-hv-EC). Ira S. Krull, Lin Dou, Ling Chen, and Jeff R. Mazzeo, Department of Chemistry and The Barnett Institute (341MU), Northeastern University, 360 Huntington Avenue, Boston, MA 02115.

Electrochemical detection in liquid chromatography for amino acids, peptides, and proteins has been a long-neglected area of research. It has generally been assumed that most biopolymers are not suitable analytes for LCEC, unless chemical derivations or chemically modified electrodes are employed. We have shown that post-column photolysis can be easily and reproducibly employed to greatly improve the EC detection (GC) of many aromatic and sulfur-containing amino acids and peptides, even when these have no native EC properties. Proteins also become EC active under such photolytic conditions, leading to new species/products, having both UV and/or EC properties different from the starting biopolymers. We will discuss these results for a variety of peptides/proteins, and the possible mechanism(s) operative in the EC detection of such analytes, at times, in biofluids, such as plasma. The ability to use LCEC for drugs and peptides in biofluids without sample preparation, will also be described, with applications.

193 NEW ELECTRODE MATERIALS AND STRUCTURES FOR CHEMICAL ANALYSIS, R. P. Baldwin, P. Luo, X. Qi, and J. Ye, University of Louisville, Department of Chemistry, Louisville, KY 40292.

Throughout its long history, electroanalytical chemistry has been largely dominated by a reliance on mercury and carbon electrodes. However, recent years have seen the emergence of a wide range of new electrode materials and structures which offer improved performance and extended applications compared to the traditional choices. In particular, the new generation of electrodes—which provides the opportunity to create detection systems tailored to meet the demands of specific analytical problems—includes both transition metal-based electrodes and chemical modifications of conventional electrodes. Examples from both categories will be considered, with emphasis on LCEC applications.

194 SCANNING ELECTROCHEMICAL DETECTION IN NARROW-BORE CAPILLARY ELECTROPHORESIS.

S. E. Sloss and A. G. Ewing, Department of Chemistry, Penn State University, 152 Davey Laboratory, University Park, PA 16802.

A major limitation to the full application of capillary electrophoresis (CE) for the direct analysis of biological microenvironments is the need for sensitive detectors. Electrochemical methods offer both sensitivity and selectivity for detection in CE. End-column amperometric detection has been shown to be a very sensitive scheme for the detection of catecholamines. This technique has been further developed to include high potential electrochemistry in nonaqueous solvents for the detection of peptides, pulsed amperometric detection for the analysis of amino acids and carbohydrates, and scanning electrochemistry for added selectivity in CE.

195 ULTRAMICRO AMPEROMETRIC BIOSENSORS.

Alexander M. Yacynych and Eugene R. Reynolds, Department of Chemistry, Rutgers, The State University of New Jersey, New Brunswick, NJ 08903.

Electrode surface modification techniques are used to make ultramicro amperometric glucose biosensors. Ultramicro electrodes made from platinum wire and carbon fiber (25 µm or less in diameter) are used for biosensor construction. Both disk and cylindrical configurations were used. Construction consisted of the following techniques: Platinization of carbon electrodes, glucose oxidase immobilization, and electropolymerization to eliminate interferents and electrode fouling. The polymer films were also examined for their effects on the working lifetime of the sensor. The results obtained for bovine serum samples showed good correlation.

196 COLONIAL CHEMISTRY: THE AGE OF GASES.

Alvin Bober, State of Maryland, Lab. Adm., Envir. Chem. Div., 201 West Preston Street, P.O. Box 2355, Baltimore, Maryland 21203.

Colonial times in the western world was an age of chemical discovery. Specifically, the development and evolution of the gas laws took place. This paper will attempt to highlight the work of Priestly, Charles, Henry, Dalton, Avogadro and others. The multifaceted genius of these pioneers has affected generations of future scientists. There is a strong heritage and legacy from this effort still visible in the greater Philadelphia area.

197 LIMELIGHTS TO SEMICONDUCTORS—INDUSTRIAL GASES FROM A HISTORICAL PERSPECTIVE.

Allan J. Ellgren, BOC Group Inc., 100 Mountain Avenue, Murray Hill, NJ 07974.

Our presentation will trace the development of industrial gas technology from the time of Joseph Priestly and Antoine Lavoisier to the present.

198 LINDE'S CONTRIBUTIONS TO THE U.S. INDUSTRIAL GAS INDUSTRY.

T. F. Fisher, Linde Division, Union Carbide Industrial Gases, P.O. Box 44, Tonawanda, NY 14151-0044.

Karl Von Linde's work in Germany during the late 19th century laid the foundation of the industrial gas industry. He enlisted support from U.S. "Captains of Industry" to found the Linde Air Products company in 1907. Under leadership of Cecil Lightfoot, from Linde British Refrigeration, the American company grew to be the largest undertaking within the oxygen industry by time of U.S. entry into the first World War. Gradual withdrawal of European interests left American capital in complete control. Linde was one of five founding companies of Union Carbon and Carbide in 1917. Work under Leo Dana at Linde's Buffalo/Tonawanda Laboratories advanced cryogenic technology beyond its European roots. Thermodynamic properties were established and methods of storage transfer and distribution were improved. A four orders of magnitude increase in insulation was achieved. Work on olefins separations, continuous production of polyethylene, permanent antifreeze, synthetic gems and uranium extraction resulted in formation of new carbide businesses. Milton's invention of molecular sieves was applied to pressure swing adsorption and catalysis needs. Advances in cryogenic distillation and heat transfer equipment led to use of Linde trays and high flux exchangers throughout the chemical industry. Novel gas application processes were developed. Major improvements were made in turbomachinery. The use of membranes in air separation is undergoing rapid growth. These and other significant Linde developments are traced through the U.S. industry's 85 years.

199 DISCOVERING THE HALOGENS.

Andrew J. Woytek and Frank K. Schweighardt, Air Products and Chemicals, Inc., 7201 Hamilton Blvd., Allentown, PA 18195-1501.

Fluorine (F_2; L. flou, flow), Chlorine (CL_2; Gr. chlorous, greenish-yellow), Bromine (BR_2:Gr. bromos, stench), Iodine (I_2:Gr. iodes, violet) and Astatine (At^-;GR.astatos, unstable) are the halogens. Their history is an exciting and dangerous tale of discovery and controversy. One of the fiercest controversies in science is the rightful discovery of chlorine as an element. From its serendipitous finding by Scheele in 1774, chlorine has been misunderstood, as by Berthollet, who's zeal for Lavoisier's doctrines labeled it Dephloigisticated Marine Acid, a compound. Some credit Gay-Lussac and Thenard (1811) for establishing the elementary nature of chlorine. But Davy first concluded chlorine contained no oxygen and was itself an element. The first halogen to be produced and sold in America was Bromine in 1846 from Freeport, Pennsylvania, 20 years after its discovery by Balard in France. Iodine, discovered in 1811 by Courtois, was first used in the American Civil War to treat wounds. Fluorine's second birth, after Moissan's discovery in 1886, took place in WWII during the Manhattan Project to refine uranium. Astatine was created in 1940 from the cyclotron bombardment of bismuth with helium. The Group VII elements are colorful and active members of Mendeleeff's periodic table of elements.

200 EXPERIMENTAL PARAMETERS IN LDMS ION SOURCES.

Ronald C. Beavis, Dept. of Physics, Memorial University of Newfoundland, St. John's, Newfoundland, Canada A1B 3X7.

An ion source designed for matrix-assisted laser desorption is a simple, but subtle, arrangement of ion optics and laser optics. The laser system provides a short (nanosecond) pulse of ultraviolet light, with a fluence of approximately 20 mJ/cm^2. The ion optics are an extraction and acceleration system that take the ion produced by the laser pulse and transform them into a collimated, monoenergetic beam. This talk will discuss the individual parameters available to an ion source designer and how best to use these parameters, in light of what is currently known about the matrix-assisted laser desorption process. In particular, the effects of the ions' initial velocity distribution on the final beam collimation and energy will be dealt with in detail. The effect of the illumination system also will be discussed, with emphasis on the necessity for uniform sample illumination. The growing use of pulsed, ultraviolet gas lasers as light sources means that careful optical design is important to obtain predictable results from an ion source. These lasers produce beams with non-uniform spatial fluence distribution and pulse-to-pulse energy variations of up to ±10%, which can result in poorly defined sample illumination conditions.

201 VELOCITY AND TIME SPREADS IN MATRIX-ASSISTED LASER DESORPTION.

Werner Ens and Ken Standing, University of Manitoba, Department of Physics, Allen Physics Building, Fort Garry Campus, Winnipeg, Manitoba, R2T 2N2, CANADA.

Many of the important physical parameters of ions leaving a matrix assisted laser desorption ion source are unknown. This talk will deal with recent measurements that attempt to determine the velocity and temporal distributions of protein ions emitted by an LD ion source.

202 MASS SPECTROMETRIC INVESTIGATION OF PROTEINS SEPARATED BY TWO-DIMENSIONAL GEL ELECTROPHORESIS.

Wenzhu Zhang and Brian T. Chait, Rockefeller University, 1230 York Avenue, New York, NY 10021.

This talk will be a report on ongoing research to couple two-dimensional gel electrophoresis with matrix-assisted laser desorption mass spectrometry. This coupling is being performed off-line. The use of a mass spectrometer to determine molecular mass is expected to greatly increase the interpretation of anomalously migrating bands in two-dimensional gel electrophoresis.

203 MATRIX-ASSISTED LASER DESORPTION OF PROTEINS: CURRENT STATUS. Peter Williams, Arizona State University, Department of Chemistry, Tempe, AZ 85287-1604.

Matrix-assisted laser Desorption has become a versatile methods for the analysis of high molecular mass proteins, but the methods has not yet shown the same utility for nucleic acids. The current "state-of-the-art" in analyzing DNA and RNA using matrix-assisted laser desorption will be discussed, along with current directions of research in this area.

204 USE OF CAPILLARY ELECTROPHORESIS-ELECTROSPRAY IONIZATION MASS SPECTROMETRY TO CHARACTERIZE BIOMOLECULES. D. R. Goodlett, J. H. Wahl, H. R. Udseth, R. D. Smith, Battelle PNL, P.O. Box 999, P8-19, Richland, WA 99352.

The combination of capillary electrophoresis (CE) with electrospray ionization mass spectrometry (ESI-MS) created a powerful on-line technique for separation, detection, and structural analysis of compounds of disparate chemistries and masses. Recent progress with CE/ESI-MS has focused on increasing the limits of detection. Detection limits for peptides in the attomole range have been demonstrated. Parameters that affect and limit further increases in the sensitivity and efficiency of mass spectrometric detection during CE/ESI-MS will be discussed.

205 NANOSECOND VERSUS PICOSECOND MATRIX-ASSISTED LASER DESORPTION/IONIZATION. Timothy King, Steven Colby, James Reilly,* Department of Chemistry, Indiana University, Bloomington, IN 47405, Richard King, Robert Goldschmidt, Kevin Owens,* Department of Chemistry, Drexel University, Philadelphia, PA 19104.

A dual head picosecond/nanosecond Nd:YAG laser (Quantel International, Inc.) operating at 355 nm is used to explore the effect of laser pulse duration on the matrix-assisted laser desorption/ionization process. With ferulic acid as the UV absorbing matrix for several peptide samples (including leucine-enkephalin, bradykinen, insulin and lysozyme), enhanced ion signals are observed with the picosecond laser. Additionally, the thresholds for the observation of matrix and analyte ions occur at similar pulse energies in both cases.

206 MULTICHANNEL RAMAN SPECTROSCOPY: MAKING THE MOST OF MANY CHANNELS. M. J. Pelletier, Procter & Gamble, P.O. Box 398707, Cinncinnati, OH 45239-8707.

In the beginning Raman spectrometry used photographic films for detection. The benefits of parallel detection were largely overcome by limitations such as nonlinear response, reciprocity failure, and darkroom processing delays. The photomultiplier became the detector of choice. Recently, array detectors with nearly ideal performance became available, and are becoming the new detectors of choice for many Raman applications. This talk will review the incorporation of modern array detectors into Raman instruments and some new applications of these instruments. Optical intensities can be imaged on the array detector to give spectral, spatial, and/or temporal information. One type of imaging allows the array detector to collect spectra from many stations at once. Another may rapidly collect Raman images. Still another imaging method can yield wide spectral coverage with high resolution in a single measurement. Optics for encoding these measurements into images on the multichannel detector, including holographic filters, multi-functional holographic elements, atomic vapor filters, fiber optics, and echelle gratings, will also be reviewed.

207 CURRENT STATUS OF RAMAN SPECTROSCOPY AT 1 MICRON AND BEYOND. Bruce Chase, The Du Pont Company, Corporate Center for Analytical Sciences, P.O. Box 80328, Wilmington, DE 19880-0328.

There have been several effects of the growing interest in FT-Raman spectroscopy for both research and analytical applications. The technique itself is constantly seeing improvements in sensitivity. These gains arise from changes in detectors, filters, and lasers. Enhancements such as holographic filters and diode pumped lasers have helped to make the measurements faster with a broader spectral coverage. These new components will be reviewed and the limiting factors for sensitivity will be discussed. A second effect has been the development of other dispersive technologies for Raman spectroscopy. High sensitivity CCD detectors coupled with diode lasers offer a real alternative to FT-Raman techniques. The advantages and disadvantages of these two approaches will be reviewed, along with a discussion of the newer, non-silicon array detectors for operation beyond 1 micron.

208 ADVANCES IN REMOTE RAMAN SPECTROSCOPY. S. Michael Angel, T. Vess, T. J. Kulp, and Michael M. Carrabba, Lawrence Livermore National Laboratory, P.O. Box 808, L-524, Livermore, CA 94550.

Raman spectroscopy is ideally suited for characterizing and quantifying a wide variety of materials at relatively high concentrations. Recent advances in solid-state laser technology, high efficiency laser rejection filters, and CCD detectors now makes small compact Raman instruments possible, and developments with imaging spectrographs has made it possible to use the two-dimensional CCD detector to full advantage. New developments include, simultaneous measurements at ten or more locations using optical fibers, full spectral coverage with high resolution using two-dimensional dispersion, and non-contact Raman at intermediate ranges (100 m) using small detector optics and low-power CW lasers.

209 WAVEGUIDE RAMAN SPECTROSCOPY OF POLYMER LAMINATES. C. G. Zimba and F. Chen, Polaroid Corporation, Media Research Division, 750 Main St., Cambridge, MA 02139.

The investigation of the structure of thin films has had a considerable impact on the fields of optics, microelectronics, coating technology, and imaging. To better understand the nature of the chemistry of the thin films and interfaces, several methods of characterization have been developed recently. Of these waveguide Raman spectroscopy (WRS) has been demonstrated to have a large potential for investigating a wide array of surface and interfacial chemistry. The application of Raman spectroscopy to the characterization of structure, orientation, and morphology of polymers has until recently been severely limited by the presence of high levels of fluorescence. Near-infrared excitation provides a method to eliminate the fluorescence, making the measurement of the Raman spectra of polymers much easier. The long wavelength excitation also allows the Raman spectra of highly colored materials, such as dyes and colorants, to be measured without any contributions of resonance enhancement, thus reflecting the molecular structure away from the chromophore. Combination of FT-Raman spectroscopy with integrated optics techniques has made the measurement of thin polymer films more tractable. In this presentation, the principles of both FT-Raman spectroscopy and waveguide Raman spectroscopy will be discussed. The influence of wavelength and refractive index upon the waveguiding characteristics of thin films will be discussed. Applications of waveguide techniques to laminated polymer films will be used to illustrate the various advantages to this approach.

210 DIRECT POWDER INTRODUCTION—INDUCTIVELY COUPLED PLASMA EMISSION SPECTROMETRY WITH A PHOTODIODE ARRAY SPECTROMETER. Nimalasiri De Silva, Mineral Resources Division, Geological Survey of Canada, 610 Booth Street, Ottawa, Ontario, Canada, K1A 0E8; and Roger Guevremont, National Research Council of Canada, Institute for Environmental Chemistry, Montreal Road, Ottawa, Canada K1A 0R6.

In spite of its numerous potential advantages, direct powder introduction (DPI) has not yet gained popularity as a routine sample introduction technique in ICP-ES due to several technological problems. Some of the important requirements which need to be satisfied for the successful adoption of DPI-ICP-ES as a qualitative analytical technique are: (a) the ability for controlled delivery of the powder at a predetermined uniform flow rate; (b) total consumption of known masses of material; and (c) simultaneous measurement of the background intensities and the emission signals. A DPI-ICP-ES system which satisfies the above features will be described along with its application to geological and other powder materials.

211 SPECIAL CONSIDERATIONS IN THE SELECTION OF INTERNAL STANDARD FOR THE ANALYSIS OF SLURRY SAMPLES BY ICP-AES. Alan Merrick and Debbie Schatzlein, Spectro Analytical Instruments, Inc., 160 Authority Drive, Fitchburg, MA 01420.

The analysis of slurries by ICP-AES has long been considered an attractive alternative to dissolution procedures. Applications have included, but not been limited to, refractory and abrasive materials, which are notoriously hard to dissolve. Modern high solids nebulizers are easily able to put these slurry particles into the plasma, but problems lie in doing so with sufficient precision to meet quality control tolerances. The key to overcoming these difficulties is in the use of the internal standardization technique. The presentation explores this in terms of reference element and wavelength selection, measurement considerations, improvement in results, and common pitfalls to be avoided.

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CHARACTERIZATION OF A PLASMA GUN DIRECT SOLID SAMPLING SOURCE FOR ICP-AES. James L. McKinstry and J. M. Goldberg, University of Vermont, Department of Chemistry, Burlington, VT 05405-0125.

A high-energy plasma gun atomic emission source has been developed in our laboratory and has shown considerable promise as a direct solid sampling device for refractory materials. Real sample emission spectra from the expanding plasma gun vapor plume, however, are very complex and line-rich, making qualitative and quantitative analyses prone to spectral interferences. Using a specially designed low-volume plasma gun chamber, we have been able to rapidly transport the sample vapor produced by the plasma gun into a steady-state inductively coupled plasma (ICP). Initial studies of the ICP spectra from the plasma gun sampled vapor showed decreased spectral complexity, significantly lower continuum background levels, and much narrower emission linewidths. Subsequent work has been directed towards the characterization of the vapor transport properties of the plasma gun/ICP system as well as evaluation of the analytical utility of the system for direct solid sampling methods of elemental analysis. The results of time resolved emission studies of ICP excited plasma gun vapor will be presented along with the results of some initial quantitative determinations of trace metal constituents in refractory NIST Standard Reference Materials.

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SPECTROCHEMICAL ANALYSIS OF DIFFICULT SAMPLES BY ICP-AES USING A NEW HIGH EFFICIENCY HIGH SOLIDS NEBULIZER. Gerhard A. Meyer, Battelle, 505 King Avenue, Columbus, OH 43201. Lisa C. Goldstone and Didier Arniaud, Jobin Yvon Division of Instruments, S.A. Inc., 6 Olsen Avenue, Edison, NJ 08820.

A glass nebulizer for the analysis of liquid samples by inductively coupled plasma atomic emission spectrometry (ICP-AES) has recently been introduced. The nebulizer is similar to a modified lichte design. It utilizes a dual bore glass capillary tubing for transportation of the sample and pneumatic gas in one embodiment. The nebulizer has been used for the determination of metals in a variety of matrices such as organic solvents, plating bath solutions, urine, 25% ammonium hydroxide, lactic acid formulations, pharmaceuticals, and others. A comparison of detection limits in water has been made using a JY-24 sequential ICP on elements of the U.S.E.P.A. contract laboratory program (CLP). Initial results indicate a general improvement in detection limits with no loss of performance in comparison to the conventional concentric nebulizer. This data provides the basis for additional benefits such as using a high solids nebulizer for all types of samples, thus eliminating the need for changing nebulizers from matrix to matrix. Data from this comparison, along with data from experiments measuring the affect of nebulizer performance on the intensity of emission lines of varying excitation energies will also be presented.

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ANALYSIS OF LOW-VOLUME NEBULIZED SAMPLES BY INDUCTIVELY COUPLED PLASMA ATOMIC EMISSION SPECTROMETRY. Laura J. Thompson and Charles B. Boss, North Carolina State University, Department of Chemistry, Raleigh, NC 27695-8204.

Typically, analysis by the Inductively Coupled Plasma (ICP) requires a minimum of 1–2 mL of sample. In this study, a method is presented to reduce this minimum volume to the μL range. A small funnel is inserted in the end of the aspiration tubing allowing sample introduction with a micropipette. After injection, the sample travels into the nebulizer as a small plug. In the normal aspiration mode, the signal produced is a wide peak that reaches a plateau region that indicated maximum intensity. As the volume of the sample decreases, the width of this peak as well as the width of the plateau region decreases. This signal becomes a small pulse when using μL volumes. The area of this pulse is then used as an indicator of sample concentration. Using the ICP in this manner, accurate sample analysis can be performed on samples smaller that 100 μL without significant loss in precision. Conceivably, using this method, 10–15 separate analyses could be run with the same volume of sample required for one analysis using continuous aspiration.

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ANALYSIS OF SMALL VOLUME HYDROFLUORIC ACID SAMPLES BY DIRECT INJECTION NEBULIZATION ICP SPECTROMETRY. Daniel R. Wiederin and Thomas L. Pinkson, Cetac Technologies, 5600 S. 42nd Street, Omaha, NE 68107.

There is considerable interest in the determination of trace metals in small volume (<0.2 ml) HF samples, especially in the semiconductor industry. A direct injection nebulizer (DIN) constructed from materials resistant to HF allows multielement determinations to be performed with less than 100 μL of HF by ICP spectrometry. Typically, a steady-state is achieved with less than 20 μL of sample. Detection limits, precision, and effects of HF concentration will be presented.

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FLOW INJECTION DONNAN DIALYSIS PRECONCENTRATION FOR TRACE METALS ANALYSIS BY ICP-AES. K. Narasimhan and J. A. Koropchak, Department of Chemistry and Biochemistry, Southern Illinois University, Carbondale, IL 62901.

Donnan dialysis is a process which can preconcentrate a given ionic species, either cation or anion, into a concentrated electrolyte solution by establishing an ionic strength gradient across an ion exchange membrane.[1] Studies with flame atomic absorption (FAAS) indicated that a flow injection approach to Donnan dialysis (FIDD) is the optimum configuration to rapidly provide high preconcentration factors and large improvements in LOD.[2] The lower LOD's and sample flowrates for ICP-AES compared to FAAS make ICP-AES particularly attractive as a detector for FIDD. Using tubular membranes and a flow injection approach (FIDD), we have shown that sensitivity enhancements of over a hundred fold versus direct aspiration can be achieved with ICP-AES using short dialysis times (∼5 minutes) for a few cations.[3] In this presentation we will describe the optimization of this technique for ICP-AES, applicability of FIDD for a wide variety of cations, and the analysis of environmental samples for trace metals. In addition, we will describe the use of FIDD for on-site preconcentration. Finally, we will compare results for FIDD-ICP-AES to preconcentration studies performed with packed column Chelex 100 ion-exchangers.[4]

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RECENT INVESTIGATIONS OF MEINHARD CONCENTRIC NEBULIZERS. Hsiaoming Tan, B. A. Meinhard and J. E. Meinhard, J E Meinhard Associates Inc., 1900-J E. Warner Ave. Santa Ana, Ca 92705.

The MEINHARD nebulizer has been the most popular sample introduction system because of its simplicity and low cost while providing satisfactory performance for inductively coupled plasmas atomic emission and mass spectrometry. In this work, systematic parametric studies of the nebulizer were conducted to understand the effects of nebulizer geometries, nebulizing gas flow rates, and sample uptake rates on the analytical performance of Ar ICP-AES. Results for the nebulizer in handling difficult matrices also will be presented.

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MONODISPERSE DRIED MICROPARTICULATE INJECTION. B. Etkin, J. B. French and R. Jong, Institute for Aerospace Studies, University of Toronto, 4925 Dufferin Street, Downsview, Ontario, Canada M3H 5T6.

A liquid sample injection system for r.f. plasmas is being studied. A drop-on-demand micropump injects a monodisperse stream of 57 micron drops at typically 1 KHz (8 microlitres/minute) into a laminar flow oven operating at 700° C. The drops are calculated and observed to go to dryness at a position which can be adjusted to be just ahead of entry into the plasma by independent control of oven temperature or sample carrier gas flow rate. In tests on a SCIEX Elan 5000 ICP-MS system, sensitivities varied linearly with drop frequency up to 2500 Hz, and were approximately equivalent to those achieved with a standard Meinhardt nebulizer at 1 KHz, operating with argon carrier flow for optimum response. Oxides were reduced by a factor of at least five, operating near optimum conditions. The effects of high salts content (to 1%) and variation in sample surface tension (via alcohol addition) were observed to be negligible. Signal noise was reduced several-fold below that present with a Meinhardt nebulizer, so long as care was taken to preserve the orderly nature of the microparticulate stream. The system is proving to be useful in studying sample ionization processes, and results to date, particularly on oxide formation mechanisms, support the observations of Olesik et al which suggest a cooler, oxygen-rich microregion around drops if injected wet.

219 "PROMOTING USEFUL KNOWLEDGE": BENJAMIN FRANKLIN AND THE AMERICAN PHILOSOPHICAL SOCIETY. Roy E. Goodman, American Philosophical Society, 105 South Fifth St., Philadelphia, PA 19106.

In 1743—nearly 250 years ago—Benjamin Franklin, America's first internationally-known scientist, founded the American Philosophical Society (APS) in Philadelphia. This paper describes Franklin's role in fostering science through the APS, which became the leading promoter of "useful knowledge" in the New World. It will also discuss Franklin's scientific relations with John Bartram, John Ellis, Antoine Lavoisier, and A. F. Antoine Cadet de Vaux, all members of the APS, and all involved in the study of economic botany and food chemistry.

220 Abstract not received at time at printing.

221 ELECTRICIANS AND ELECTRICAL ENGINEERS: CHANGES SINCE THE TIME OF FRANKLIN. Jane Mork Gibson, Consultant, 32 Rex Avenue, Philadelphia, PA 19118.

The gentlemanly pastime of scientific experimentation changed to serious industrial research and development by scientists and electrical engineers in the one hundred and fifty years after Benjamin Franklin first witnessed experiments in electricity in Boston in 1743. During his ten years of electrical experimenting Franklin established certain basic concepts and terms still in use, but others were found to be mere hypotheses. The American Institute of Electrical Engineers was founded in 1884 to establish the professionalism of "practical electricians" as opposed to the "pure scientists" who were theorizing about electricity and were called "electricians." At the 1884 national conference of electricians in Philadelphia both groups expressed themselves on electric theory and practice, and both were equally in the dark about the electron theory which was not developed until 1897. The concurrent international electrical exhibition in 1884 was a snapshot of the state of the art, displaying both the inventiveness of the practical electricians and the need for electrical standards in terminology, units, and instruments of measurement. Here Edison's "tri-polar lamp" was first shown publicly, but neither scientist nor engineer recognized its usefulness as the basis of today's electronics. By 1893 independent inventors in the United States were associated with one of the two large electrical corporations, General Electric and Westinghouse, and the small independent laboratory became the exception. The activities of the electrician of the earlier period were taken over by the physicist and by the electrical engineer, and the skilled workman inherited the title, "electrician."

222 THE BEN FRANKLIN PARTNERSHIP: BEN'S SPIRIT SURVIVES IN PENNSYLVANIA'S TECHNOLOGY DEVELOPMENT PROGRAM. Mark S. Lang, NET Ben Franklin Technology Center, 125 Goodman Drive, Bethlehem, PA 18015-3715.

In the modern parallel of Franklin's inventive spirit, the State of Pennsylvania has established a cooperative State-Academic-Industrial program for technology commercialization. Ben Franklin Partnership Centers in Philadelphia, Pittsburgh, State College, and Bethlehem bring together companies, academic researchers, and State seed money in a vibrant synergy that has already brought new products and technologies to the marketplace.

223 Abstract not received at time of printing.

224 CHALLENGES OF DATA COLLECTION AND DIFFUSION IN TOXICOLOGY. Caroli, Istituto Superiore di Sanitá, Viale Regina Elena 299, Rome 00161, ITALY.

Benefits and drawbacks consequent to the widespread use of chemicals are inextricably interwoven. According to recent estimates, more than 8 million chemical substances are presently known, 70,000 of which are in common use as industrial compounds, pesticides, pharmaceuticals, food additives, cosmetics and the like. Their annual increase rate is calculated to number about 1000. The deleterious consequences deriving from their exploitation pose tremendous challenges to the scientific community for protection of human health and the environment. It is therefore of utmost priority to appropriately select valid information generated in this investigation area and to correctly convey it to the users. Here the adoption of the principles of good laboratory practice in experimental activities is essential as well as the setting-up of global networks for data exchange on the safe use of chemicals. The structure and goals of the International Register of Potentially Toxic Chemicals (the data bank of the United Nations Environmental Programme) are detailed to give an example of such undertakings. Moreover, the seventeen fields covered therein are illustrated, i.e. identifiers, properties and classification, production/trade, production processes, use, pathways into the environment, concentrations, environmental fate tests, environmental fate, chemobiokinetics, mammaliam toxicity, special toxicity studies, effects on organisms in the environment, sampling/preparation/analysis, spills, treatment of poisoning, waste management, and recommendations/legal mechanisms.

225 APPLICATION OF LABORATORY DATA MANAGEMENT SYSTEMS FOR INORGANIC ENVIRONMENTAL ANALYSIS. Arthur F. Ward, Ward Scientific, Ltd., 2 Ray Avenue, Burlington, MA 01803.

With the increase in the number of samples being analyzed and the more stringent requirements for data integrity and quality control, data management is becoming essential to the efficient operation of the laboratory. Integrating various laboratory instruments and sample preparation stations provides a challenge due to the lack of standardization of data formats between different instruments. The design and use of a translation program to convert raw instrument data base designs will be described. Data base design will also be discussed with particular emphasis on the advantages and disadvantages of customized reporting systems and universal reporting systems with regards to data size, speed of reporting and ease of use. The use of a customized report generator that generates strictly compliant EPA CLP protocol reports as well as allowing the user to readily customize the reports for different applications based on the same protocol will be discussed.

226 AN INTELLIGENT DATA MANAGEMENT SYSTEM FOR WATER QUALITY STUDIES. Dale B. Peart and Howard E. Taylor, USGS-WRD, 3215 Marine Street, Boulder, CO 80303.

A network of PC's and Unix workstations has been established to process the vast amount of data generated by multiple, concurrent water-quality studies. By selection of a Unix based database management system that can utilize all of the standard Unix commands, the Unix shell languages and a simple ASCII format for storing the datafiles and integrating the PC's with the Unix workstations over a network connection, both PC users and Unix users can process and manipulate the datafiles as if they were native to their own systems. This approach eliminates time consuming problems generated when files must be translated between various proprietary forms when moving data between different applications for processing. It also eliminates loss of accuracy that may occur during translation processes. The database management system allows for sophisticated data processing and report generation using standard Unix commands, shell scripts or C language programs. Self explanatory menu's can be written to make the more sophisticated details of Unix and the database system transparent to the less knowlegeable user.

227 INTERPRETATION OF MULTI-ELEMENT ANALYTICAL DATA USING PRINCIPAL COMPONENTS ANALYSIS. Dennis A. Yates* and Rupert Aries, The Perkin-Elmer Corporation, Norwalk, CT.

Multi-element detection techniques such as ICP and ICP-MS have good sensitivity for a broad spectrum of elements. In addition to allowing interesting "semi-quantitative" analysis, it is proposed that the Multi-element spectra may offer sufficient sensitivity to provide a unique elemental "signature" that can be used to differentiate various sample types within groups of similar types as well as characterize differences. Principal Components Analysis (PCA) techniques provide a way to reduce a large set of analytical data into distinct linear combinations of independent terms. Each individual Principal Component describes some portion of the variance in the data set. Together the Principal Components represent the sum of the spectral variance in the data set. In this paper the analysis of several types of samples was undertaken using Inductively Coupled Plasma Mass Spectroscopy and ICP Optical Emission Spectrometry. Although standardization is not required within PCA, the use of standards in the data set provides a check on the validity of the procedure. The influence of each spectral component on the PCA results will be examined.

228 USE OF ICP/AES AND ICP/MS FOR MULTIELEMENT DETERMINATION IN GEOCHEMICAL PROSPECTING. M. Borsier, BRGM, BB 6009, 45060 Orleans France. I. B. Brenner, Geological Survey Israel, 30 Malkhe Israel Street, Jerusalem 95501, Israel.

Multielement analysis is essential during geochemical prospecting because most of the data is obtained for the sample collected. Our team has developed automated digestion and ICP/AES analytical procedures using a sodium peroxide procedure for a simultaneous determination of major and trace elements (34). Although this procedure gives detection limits sufficient for most of the elements? It has proved not to be low enough for REE and gold or pg elements. The development of ICP/MS gave the opportunity to enhance detection limits while working with the same digestion. The high salt content of solution prevents from working directly with the solution and a FIA procedure has been developed to reach the necessary detection limits without disturbing the plasma or clogging the interface with the salt content. Contribution of both techniques are now used to get full information from the samples collected.

229 QUALITY-CONTROL PROCEDURES FOR INDUCTIVELY COUPLED PLASMA-OPTICAL EMISSION SPECTROMETRY AT THE U.S. GEOLOGICAL SURVEY NATIONAL WATER QUALITY LABORATORY.

Edward J. Zayhowski, Thomas J. Bushly, U.S. Geological Survey, 5293 Ward Road, Arvada, Colorado, 80002. Christine A. Gable, National Park Service, 301 S. Howes St., Fort Collins, CO 80521.

In 1991, the U.S. Geological Survey's (USGS) National Water Quality Laboratory (NWQL) performed several levels of quality control to analyze about 14,000 natural water samples for about 130,000 analytes by inductively coupled plasma-optical emission spectroscopy (ICP-OES). Since the Plasma Unit of the NWQL first used the ICP-OES technique in the mid-1970s, many advances in computer software and hardware technology have come into use. These advances have helped to improve productivity without sacrificing quality, enabling fully automated sample analysis and quality-control procedures. On-line quality control for ICP-OES analysis consists of calibration check standards, blanks, and standard reference water samples from the USGS and National Institute of Standards and Technology. In addition, analytical results are run through an ionic check program before the analyses are released by automatic data transfer to the NWQL's Laboratory Information Management System and prior to review by the Quality Management Group (QMG), which is separate from the Plasma Unit but part of the NWQL. The on-line quality-control data are reviewed periodically by the Plasma Unit and the QMG to identify quality-control trends and to evaluate any potential inconsistent reference material. The QMG also submits blind quality-control samples and blanks to the Plasma Unit to further monitor quality control. In addition, the Branch of Quality Assurance, which is external to the NWQL, monitors the Plasma Unit by submitting blind reference samples to ensure that analytical results are of the highest quality.

230 CHEMICAL MODIFICATION IN GRAPHITE FURNACE ATOMIC ABSORPTION SPECTROMETRY INVESTIGATED BY INDUCTIVELY-COUPLED PLASMA MASS SPECTROMETRY.

J. P. Byrne, Department of Applied Chemistry, University of Technology, Sydney, Australia. C. L. Chakrabarti, M. M. Lamoureux, and T. Ly, Centre for Analytical and Environmental Chemistry, Department of Chemistry, Carleton University, Ottawa, Ontario, K1S 5B6 Canada. D. C. Grégoire, Geological Survey of Canada, Department of Energy, Mines and Resources, Ottawa, Ontario, K1A 0E8 Canada.

The mechanisms of interferences by the $MgCl_2$ and the NaCl matrix with the atomization of Mn and of the removal of these interferences by ascorbic acid in the graphite furnace atomic absorption spectrometry were investigated using a graphite platform electrothermal vaporizer in inductively-coupled plasma mass spectrometry (ETV-ICP-MS). The $MgCl_2$ matrix undergoes rapid hydrolytic decomposition that releases $HCl_{(g)}$ at temperatures greater than 700° C, resulting in the loss of Mn from the graphite furnace during the charring step by expulsion with the rapidly expanding HCl gas. The ETV-ICP-MS results show that ascorbic acid chemical modifier retards the hydrolysis reaction, and consequently, little $HCl_{(g)}$ is formed during the charring step and no Mn is lost in the charring step. The NaCl matrix interferes with Mn by forming undissociated manganese chloride in the vapour phase during the atomization step. The experimental results show that the chemical modification of the NaCl interference with Mn does not involve a gas-phase reaction. In fact, the ETV-ICP-MS results clearly show that the ascorbic acid chemical modifier removes chloride preferentially at two distinct stages of the heating cycle. Ascorbic acid allows chloride to be removed as $HCl_{(g)}$ during the heating ramp of the charring step and at temperature above 900° C, further chloride is removed during the heating ramp between the charring and the atomization step. This chloride removal occurs at a temperature about 350° C lower than the appearance temperature for manganese, thereby preventing the formation of gaseous manganese chloride species during atomization.

231 MECHANISM OF PALLADIUM MODIFICATION FOR THE REMOVAL OF CHLORIDE INTERFERENCE IN ETAAS.

Kenneth W. Jackson and Huancheng Qiao, Wadsworth Center for Laboratories and Research, New York State Department of Health, and School of Public Health, State University of New York, P.O. Box 509, Albany, NY 12201-0509.

Interference by chloride is especially severe in the determination of thallium by ETAAS. It occurs through the formation of volatile TlCl, which is lost during the pyrolysis stage of the atomization cycle. A palladium/magnesium mixture has been shown to be successful as a modifier to reduce this interference (1). Previously, we proposed a physical mechanism to account for the modifying action of mixtures containing palladium (2). During the atomization cycle, analyte metals are stabilized by becoming embedded in molten palladium, and the rate-limiting step during atomization is diffusion of the analyte out of palladium droplets. Results of pyrolysis experiments will be presented to show that this physical mechanism can explain the effect of palladium in reducing the interference by chloride.

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232 A STUDY OF MATRIX MODIFIERS ON HEATED GRAPHITE SURFACES.

Corinne Eloi, J. David Robertson, N. Xu and Vahid Majidi, Department of Chemistry, University of Kentucky, Lexington, KY 40506.

Although, GF-AAS is one of the most sensitive analytical techniques available for elemental analysis, it is often plagued by various matrix interferences. These interferences are generally minimized by the addition of matrix modifiers. While these matrix modifiers greatly improve the detection limits, the chemistry involved in the signal enhancement process is unclear. In this study, a series of Rutherford backscattering (RBS) experiments were performed to investigate the interaction of phosphate modifiers with Cd, Pb, and Ag on heated graphite surfaces. Surface characteristics of these analytes are determined in the absence and the presence of phosphate modifiers. Furthermore, the depth of analyte penetration into the graphite substrate is evaluated. In a second set of experiments the influence of oxygenated surface at two different treatment temperatures was evaluated. The results for Cd, Pb, and Ag on the oxygenated graphite will also be presented.

233 BULK DIFFUSION INDUCED ANALYTE LOSS IN GRAPHITE ATOMIZERS.

D. L. Styris, Pacific Northwest Laboratory, Richland, WA 99352. J. A. Harris, D. A. Redfield, Northwest Nazarene College, Nampa, ID 83686.

Analyte loss by molecular and atomic diffusion through bulk pyrolytic graphite-coated graphite is investigated by mass spectrometric monitoring of the gallium species that vaporize in vacuo after diffusing through a 0.3 mm thick graphite diffusion barrier. The flat base of an inverted, capillary tube-like, graphite cup is used for this barrier to ensure that the monitored species is involved in the diffusion process and not species simply vaporized from the atomizer wall. By placing the inverted cup in a diametrical position in a tube atomizer so that the cup is contained completely, and the base is flush with the dosing hole, it is possible to heat the cup radiatively (like a platform) and to sample species that diffuse only through the base from the cup interior. It is estimated, by comparing the resulting signal amplitudes with those from the open (noninverted) cup, that perhaps three to five percent of the analyte is lost through this bulk diffusion. Experimental details, data, and the implications of this mechanism will be discussed.

234 PRETREATMENT TIME AS A PARAMETER FOR THE EVALUATION OF MATRIX MODIFIERS IN ETA-AAS.

Gary D. Rayson, Mark R. Fresquez and Katrina Hall, Chemistry Department, Box 30001, New Mexico State University, Las Cruces, NM 88003.

Considerable attention has been focussed on the use of a variety of matrix modifiers to facilitate the determination of elements within several different types of samples. The selection of the appropriate mixture of added chemicals has been typically exemplified by the thermal stabilization of the analyte. Often this is demonstrated by the use of increased thermal decomposition (ash or char) temperatures with high recovery efficiencies. One operating parameter in the temperature program of a graphite furnace atomizer which is given less emphasis is the duration of the thermal pretreatment stage. The impact of pretreatment time on the measured atomic absorbance signal will be discussed for several representative metal analytes. The effect of magnesium and palladium matrix modifiers on the temporal behavior of these analytes during the pretreatment stage will be described. The utility of evaluating the temporal stabilizing characteristics of chemical modifiers will be discussed.

235 MECHANISM OF INTERFERENCES OF HYDRIDE-FORMING ELEMENTS ON THE DETERMINATION OF SELENIUM, B. Welz and P. Stauss, Department of Applied Research, Bodenseewerk Perkin-Elmer GmbH, W-7770 Ueberlingen, Germany.

The most severe interferences in hydride-generation atomic absorption spectrometry (HG-AAS) with a heated quartz tube atomizer are caused by other hydride-forming elements. The interference of antimony, arsenic, bismuth, tellurium and tin on the determination of selenium was investigated systematically using different accessories for HG AAS. In a flow injection (FI) system the prevailing mechanism was an analyte decay interference caused by an alteration of the quartz tube surface by the interferent. Interferences are much less pronounced in the FI system, compared to a batch system, because of the more efficient use of oxygen in the former system which makes a radical deficiency less likely to occur. Interferences can be further reduced by increasing the carrier gas flow rate without affecting the sensitivity significantly.

236 REAL WORLD APPLICATIONS OF A MULTI-ELEMENT GFAAS. G. R. Dulude, M. J. Dauzvardis and S. Karpova, Thermo Jarrell Ash Corporation, 8E Forge Parkway, Franklin, MA 02038.

The simultaneous determination of trace metals by GFAAS has long been a desirable goal of the analytical chemist due to the time consuming nature of conventional one-at-a-time AA's. Recently, the commercial availability of multi-element AA's has made it possible to test the practical utility of this technique for several applications. We have examined the performance, linear range, and interferences in the determination of lead and cadmium simultaneously in vegetable oil. In order to circumvent difficulties in sample introduction which usually result from the introduction of organic solvents with a discrete sampler, a tetrohydrofuran dilution of the oil was deposited into the graphite tube using an aerosol deposition system. The multi-element GFAAS system was also evaluated for the simultaneous determination of lead, copper, antimony, and thallium in drinking water. This application is particularly interesting today because of the tightening of federal and state regulations regarding these pollutants in drinking water.

237 DEVELOPMENT OF A MICROANALYTICAL METHOD FOR THE DETERMINATION OF SELENIUM IN BOVINE HEART TISSUE USING ZEEMAN GRAPHITE FURNACE ATOMIC ABSORPTION SPECTROMETRY. Chandra M. Tummalapalli and J. C. Williams, Department of Chemistry, Memphis State University, Memphis, TN 38152.

A microanalytical method for the determination of Se in bovine heart tissue is reported. Various modifications made in this method development include drying the tissue, digestion ratio of the dried tissue to the acid, heating temperature and heating pattern of the digestate, obtaining the density, volume and the acidity of the digestate, ratio of thus obtained digestate to the surfactant, ratio of the final sample solution to the modifier solution, cleaning the sampler tube, furnace parameters, and minimization of the memory effect. Comparison is made between the aqueous calibration method and the standard additions method using bovine liver powder as standard and extended to the bovine heart tissue. Two aspects of the Se concentration in bovine heart were studied. Both the right and the left ventricles are analyzed for the homogeneity of selenium distribution on the surface of both the interior and the exterior regions and the concentration gradient in the pattern of the distribution of Se across the myocardial tissue from epicardium to endocardium. Possible explanation for this observed pattern is offered. Also reported are the results of the multiple injection analysis performed on the solvent extract obtained during lyophilization.

238 ELECTROTHERMAL ATOMIZATION OF SOLID SAMPLES FOR ELEMENT CONCENTRATION DETERMINATIONS IN INDIVIDUAL HAIRS. Robert D. Koons, Forensic Science Research and Training Center, FBI Academy, Quantico, VA 22135. Charles A. Peters and Brian Donnelly, FBI Laboratory, Washington, DC 20535.

Electrothermal vaporization offers a convenient means of sample introduction and thermal isolation of elements of interest for segments of individual human hair. Quantitation of an element of interest can then be made using AAS, often by comparison with solution standards. Use of ICP-MS as a detector expands the capabilities to include simultaneous multielement characterization of sub-centimeter sized fragments of individual hairs. The use of these techniques to distinguish between chronic and acute exposure in cases involving intentional arsenic poisoning and to characterize hairs for purposes of eliminating suspects in several unusual crime scene scenarios will be discussed.

239 Abstract not received at time of printing.

240 Abstract not received at time of printing.

241 Abstract not received at time of printing.

242 THREE-WAY DATA ANALYSIS ON DIFFERENCES BETWEEN STATIONARY PHASES. Age K. Smilde* and Bruce R. Kowalski, Laboratory for Chemometrics, CPAC, Department of Chemistry, University of Washington, Seattle, WA 98195. Durk A. Doornbos, Research Group Chemometrics, University Centre for Pharmacy, University of Groningen, Groningen, The Netherlands.

Three-way analysis methods are rather new in chemometrics. General three-way models will be described, like the Tucker model, the PARAFAC model and the unfolding solution. The advantage of three-way models over conventional two-way methods is discussed briefly. Results of three-way analyses on different data sets originating from reversed-phase liquid chromatography are shown. The purpose of these analyses can be the prediction of retention values on new stationary phases or elucidating structural phenomena in the data. Special attention is paid to the role of outliers, the influence of different data preprocessing methods (centering) and nonlinearity. With the use of score and loading plots it will be shown that these aspects are related.

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243 EFFECTS OF RANDOM ERRORS ON GENERALIZED RANK ANNIHILATION METHOD. Karl Booksh and Bruce R. Kowalski, University of Washington, BG-10, Seattle, WA 98195.

With hyphenated techniques (LC-UV, GC-MS) the noise in the instrument response depends upon the random noise in each order. Random fluctuations in the first, or X, order (LC or GC) are correlated in each row of the instrument response matrix. However, random fluctuations in the second, or Y, order (UV or MS) are random throughout the instrument response matrix. As expected these errors propagate differently with the generalized rank annihilation method (GRAM). It is shown through propagation of errors and with simulations that the errors in the first, X, order have the larger effect on precision of estimating analyte concentrations, while precision in the second, Y, order have the larger effect on the precision of the estimated spectra of the pure components in each order. These results will be presented in the context of instrument optimization.

244 SIMILARITY TRANSFORMATIONS FOR THE GENERALIZED RANK ANNIHILATION METHOD. Shousong Li and Paul J. Gemperline, Department of Chemistry, East Carolina University, Greenville, NC 27858.

Generalized Rank Annihilation Method (GRAM) is a useful noniterative algorithm for the analysis of complex mixtures when only a few constituents are of interest, and the spectroscopic/chromatographic measurement process can not adequately resolve them from interfering components. Two bilinear sample matrices (standard and unknown) are necessary in the application of GRAM technique. When more than two bilinear sample matrices are combined together, the three-dimensional array can be considered as a trilinear data set. An extension of GRAM called the Direct Trilinear Decomposition Method (DTDM) was developed to treat these trilinear data sets. Recently several papers have described the GRAM and DTDM; however, none of these publications treated the cases where complex eigenvalues and eigenvectors may appear when the generalized eigenproblem is solved. When complex eigenvalues and eigenvectors are encountered, the results can not be used to estimate pure component profiles (e.g. spectra or chromatograms). In this presentation, Similarity transformations are used to transform complex eigenvalues and eigenvectors into real eigenvalues and eigenvectors, thereby permitting spectra and profiles of pure constituents to be estimated. The modified GRAM and DTDM methods are illustrated with simulated and real data and the results are successful when the modified GRAM technique is applied in determining hydrocortisone in real urine samples when many interfering components are present.

245 Abstract not received at time of printing.

246 SOME THEORETICAL ASPECTS IN SECOND ORDER CALIBRATION. Yongdong Wang and Bruce Kowalski, Department of Chemistry, BG-10, University of Washington, Seattle, WA 98195.

Two methods which have the potential of handling the second order nonbilinear data, nonbilinear rank annihilation (NBRA) and residual bilinearization (RBL), are studied through theoretical analysis and computer simulation. It is found that these two methods are mathematically equivalent with different noise and concentration nonlinearity handling properties, and the second order advantage, quantitation in the presence of the unknown interferences, can be carried over to nonbilinear data if a property defined as net analyte rank (NAR) holds for the analyte of interest.

247 THE ASSAY OF PEPTIDES USING MULTICHANNEL DETECTION IN CAPILLARY ELECTROPHORESIS. J. V. Sweedler, A. T. Timperman, S. E. Tracht, R. R. Fuller and L. Cruz, Department of Chemistry, University of Illinois, Urbana, IL 61801.

Detection schemes based on laser-induced fluorescence have greatly improved the measurement sensitivity obtainable with capillary electrophoresis. A unique detection scheme utilizing a charge-coupled device (CCD) to detect laser-induced fluorescence is described which further improves the detection sensitivity. Using the multichannel CCD with an imaging spectrograph, entire fluorescence spectra are simultaneously obtained allowing multiple fluorophores to be distinguished within a single electrophoresis run. The factors effecting ultimate sensitivity in this system including background sources, observation time, illumination power and photochemical properties of the fluorescent probe are described. Current results demonstrating the performance of several rhodamine derivatizing agents are presented for amino acid and peptide analyses, with limits of detection of 10^{-13} M for fluorescently tagged peptides. Progress in derivatizing and detecting trace levels of peptides in real world biological samples will be presented.

248 DIRECT CONTROL OF ELECTROOSMOSIS AND RETENTION WINDOW IN MICELLAR ELECTROKINETIC CAPILLARY CHROMATOGRAPHY. Bhisma Patel, Pei Tsai and Cheng S. Lee, Department of Chemical and Biochemical Engineering, University of Maryland, Baltimore Campus, Baltimore, MD 21228.

One key obstacle in the application of Micellar Electrokinetic Capillary Chromatography (MEKC) to the separation of the complex sample is its limited retention window. One way for varying the range of the retention window is the adjustment of electroosmosis. A novel instrumental approach involving the use of a radial electric potential gradient across the capillary wall for directly and dynamically controlling the electroosmotic flow will be presented. The effect of a radial potential gradient on the retention window will be discussed. The direct and dynamic manipulation and optimization of the separation efficiency and resolution during the separations of PTH-amino acids in MEKC will be demonstrated.

249 ULTRAMICRO ENZYME ASSAYS IN A CAPILLARY ELECTROPHORETIC SYSTEM. Jianmin Bao and Fred E. Regnier, Department of Chemistry, Purdue University, W. Lafayette, IN.

This paper describes an ultramicro method for achieving enzyme assays. Enzyme saturating concentrations of substrate, coenzyme when appropriate, and running buffer were mixed and used to fill a deactivated fused silica capillary in a capillary zone electrophoresis (CZE) apparatus. The enzyme glucose-6-phosphate dehydrogenase (G-6-PDH) was injected by either electrophoresis or siphoning and mixed with the reagents in the capillary by electrophoretic mixing. Enzyme activity was assayed by electrophoresing the product, reduced nicotinamide adenine dinucleotide phosphate, to the detector where it was detected at 340 nm. Under constant potential, the transport velocity of enzyme and the product was generally different. This caused product to be separated from the enzyme after it was formed. Because product formation was much faster than the rate of enzyme-product separation, product accumulated. The amount of accumulated product was inversely related to operating potential. At the extreme case, the operating potential was zero. Zero potential assays were generally carried out by electrophoresing the enzyme partially through the capillary and then switching to zero potential. The capillary was left at zero potential for several min to allow additional product to accumulate. After this additional amplification step, potential was again applied and the product transported to the detector. Product formed under constant potential appears as a broad peak with a flat plateau. When the voltage is switched to zero at intermediate migration distance, a peak will be observed on top of this plateau. Either the height of the plateau or the area of the peak may be used to determine enzyme concentration. The lower limit of detection was 4.6×10^{-17} moles of G-6-PDH.

250 SEPARATIONS OF POLYAROMATIC HYDROCARBONS USING MICELLAR ELECTROKINETIC CAPILLARY CHROMATOGRAPHY. Michael J. Sepaniak, Tracy D. Staller and Christine Copper, The University of Tennessee, Department of Chemistry, Knoxville, TN 37996-1600.

Highly efficient separations of polar compounds can be accomplished using micellar electrokinetic capillary chromatography (MECC). Unfortunately, hydrophobic molecules are difficult to resolve because they tend to completely associate with the micelles and exhibit capacity factors that are well beyond the optimum range. This limitation of MECC is particularly prevalent in the separation of polyaromatic hydrocarbons (PAHs), which constitute an important class of environmental toxins. We will illustrate the use of mixed aqueous-organic mobile phases, and various organized media as mobile phase additives, to enhance the separation capabilities of MECC for PAH mixtures. Laser flourimetry provides the sensitivity needed for trace level PAH detection.

251 STRUCTURED METHOD DEVELOPMENT IN CE/MECC: ANALOGIES AND DIFFERENCES WITH HPLC. Joost K. Strasters, Sterling Winthrop, 9 Great Valley Parkway, Malvern PA 19355. Morteza G. Khaledi, North Carolina State University, Dept. of Chemistry, P.O. Box 8204, Raleigh, NC 27695.

A number of approaches applied in HPLC for computer assisted method development are currently extended to CE and MECC. Like HPLC, the number of interacting parameters influencing selectivity is extensive, requiring simultaneous evaluation for an efficient design of a separation. This presentation will discuss a number of approaches, emphasizing interpretive strategies which require migration models for the individual components in a mixture. These models can range from very simple (linear) to more complex (e.g. models describing migration behavior as a function of several parameters such as pH, surfactant concentration, organic modifier concentration etc.). Additionally a choice has to be made regarding the initial experimental design: a limited number of experiments followed by refinement vs. a large number of measurements and direct prediction of optimum separation. Both analogies and differences with traditional applications in HPLC will be discussed and illustrated.

252 LOOKING AT PARTICULATES WITH CAPILLARY ELECTROPHORESIS. B. B. VanOrman and G. L. McIntire, Sterling Drug, Inc., 9 Great Valley Parkway, Great Valley, PA 19355.

Capillary electrophoresis has been used to separate solid polystyrene nanospheres in the size range $9 \text{ nm} < X < 1000 \text{ nm}$. This is possible regardless of the nature of the particle surface charge and with resolution in the area of several thousand theoretical plates per meter of capillary. Conditions necessary to effect these separations include careful pretreatment of the capillary with surfactant and the use of low ionic strength buffers such as borate or ACES. While results suggest that particle size plays a role in these separations, correlations with particle electrophoretic mobilities have also been proposed. Possible mechanistic considerations will be presented towards an understanding of these results.

253 CONTRASTING THE MECHANISMS OF SIZE EXCLUSION CHROMATOGRAPHY AND GEL ELECTROPHORESIS. David A. Hoagland and Evangelia Arvanitidou, Department of Polymer Science and Engineering, University of Massachusetts, Amherst, MA 01003.

Both size exclusion chromatography (SEC) and gel electrophoresis (GE) provide molecular weight separation during the forced migration of macromolecular solutes through porous supports. In SEC the migration is driven by a pressure gradient and in GE by a voltage gradient. The ratio R/ξ of solute size to pore size is widely accepted as the governing parameter for both separations. Similarly, it is known that solute entropy dominates in either case since separation quality is enhanced when enthalpic effects are suppressed. Despite the similarities, the underlying molecular mechanisms for SEC and GE are very different (except when $R/\xi \ll 1$). SEC is directed by the equilibrium partitioning of solute between a flow-dominated, interparticle void space of macroscopic dimension and a stagnant intraparticle void space of dimension ξ which is larger than R. R/ξ varies more widely in GE than in SEC and consequently different separation regimes are sampled. Clearly, solutes in GE must pass through pores rather than simply partitioning into them. Separation is governed by the rate of macromolecular transport through pores, and at low applied fields this transport is thermodynamically activated: the pores act as *Entropic Barriers*. Only at $R/\xi \ll 1$ is the passage rate dictated by solute size. With $R \geq 1$, molecular weight determines this rate, with molecules deforming to fit into pores. Comparable values of R/ξ, which require solute deformation, are not encountered in SEC and separation is thus by solute size alone.

254 ON THE MECHANISM OF SIZE EXCLUSION CHROMATOGRAPHY.

Martin Potschka, Porzellangasse 19 A-1090 Vienna, Austria.

The last decade has seen great advances in understanding the mechanism of separation in size exclusion chromatography. It is now clear that interfacial repulsion plays a dominant part in establishing the size of solutes in porous matrices. The ionic strength effect of elution has been fully accounted for both retention and dispersion. Conditions and role of shear deformation and degradation may be stated precisely. Convection may play some role in establishing permeation of the matrix but the principle of separation seems to be an equilibrium process. Available theory, however, lacks aggrement to experiment, partly due to inadequate description of the porous network. As a consequence there is still ongoing debate about the proper influence of solute shape on retention, viscosity radii beeing the favorite. At the same time Stokes radii may be obtained from dispersion data.

255 CARBOXYLATED STARBURST DENDRIMERS AS CALIBRATION STANDARDS FOR AQUEOUS SIZE EXCLUSION CHROMATOGRAPHY.

P. L. Dubin, S. L. Edwards, J. I. Kaplan, M. S. Mehta, D. Tomalia and J. Xia, Department of Chemistry, Indiana University-Purdue University, 1125 E. 38 Street, Indianapolis, IN 46205.

Standards commonly employed to calibrate size exclusion chromatography columns usually do not themselves have well-defined sizes. Carefully characterized spherical solutes in the appropriate size range are therefore of considerable interest. The chromatographic behavior of carboxylated starburst dendrimers—characterized by quasielastic light scattering and viscometry—on a Superose size exclusion column has been explored. Carboxylated starburst dendrimers appear to behave as non-interacting spheres during chromatography in the presence of an appropriate aqueous mobile phase. The dependence of the retention time on solute size seems to coincide with data collected on the same column for Ficoll, an uncharged, quasi-spherical polysaccharide. Chromatography of the dendrimers yields a remarkable correlation of the chromatographic partition coefficient with the generation number; this result is in part a consequence of the exponential relationship between the generation number and the molecular volume of the dendrimers.

256 INVESTIGATIONS OF POLY (VINYL ALCOHOL) USING DUAL DETECTOR SEC.

Lev Z. Vileuchik and George C. Kingston, Monsanto Chemical Company, 730 Worcester St., PASC, Bldg 43A, Springfield, MA 01151.

Size Exclusion Chromatography (SEC) coupled with both concentration and viscometric detection has been developed for molecular weight and structure characterization of poly(vinyl alcohol) (PVOH) in water solution. It was shown that values of Mark-Houwink coefficients for PVOH samples depend on degree of alcoholysis. Samples of PVOH from different commercial sources were compared and the length of the statistical segment for them was calculated from the SEC data.

257 SIZE EXCLUSION CHROMATOGRAPHY IN AN ANALYTICAL PERSPECTIVE.

Lars Hagel, Pharmacia Biotech, S-75182 Uppsala, Sweden.

Modern media for analytical size exclusion chromatography brings this separation technique close to its theoretical performance. However, after the separation step, analysis of sample component properties still remains. The system may be treated as a black box, i.e., the response is calibrated through the use of well defined standards and the analytical task is thus to accurately characterize these. This communication discusses the performance and applicability of modern SEC for rapid, simple, and accurate analysis of properties of sample components, with special reference to molar mass distributions.

258 MONITORING DYNAMIC CHEMICAL EVENTS AT INDIVIDUAL BIOLOGICAL CELLS.

R. M. Wightman, J. Jankowski and T. Schroeder, University of North Carolina at Chapel Hill, Department of Chemistry, CB# 3290, Chapel Hill, NC 27599-3290.

Secretion of chemical substances from biological cells often occurs by an exocytotic mechanism. In this case intracellular vesicles fuse with the plasma membrane of the cell, and the vesicular contents are extruded into the extracellular spaces. Recent advances demonstrate that the secretion process can be measured with microelectrodes placed adjacent to cells. Because the amounts are small (attomoles or less), high sensitivity techniques are required. The use of appropriate filtering and integrated circuit techniques is essential for these measurements.

259 MICROANALYTICAL LABORATORIES ON A CHIP: PROSPECTS AND PITFALLS FOR A FANTASTIC VOYAGE.

James L. Anderson, Department of Chemistry, University of Georgia, Athens, GA 30602.

We will speculatively discuss constraints and practical problems limiting the fabrication and eventual implementation of practical analytical microprobes suitable for implantation and remote monitoring of chemical processes and functions. Emphasis will be on the feasibility of monitoring remote or hostile sites, or in vivo monitoring of living organisms with minimal interference and with acceptable device lifetime. Major factors which we will consider are the robustness and durability of the device, compatibility with the medium, dimensional and materials constraints of feasibility devices, and limitations on the information obtainable from small sample regions with a finite probe.

260 CHEMISTRY FOR THE MICROSCOPIC MAPPING OF SYNAPTIC GLUTAMATE.

Lin LI and Mark A. Arnold, Chemistry Department, Jonathan S. Dordick, Department of Chemical and Biochemical Engineering, The University of Iowa, Iowa City, IA 52242.

The long term goal of our project is to develop a chemical sensor to monitor the spatial and temporal distribution of synaptic glutamate by microscopic mapping. The sensing scheme for glutamate is as follows:

$$\text{Glutamate} + O_2 \rightarrow \alpha\text{-ketoglutarate} + NH_3 + H_2O_2$$

$$2H_2O_2 + \text{Luminol} + OH^- \rightarrow \text{Aminophthalate} + N_2 + H_2O + h\nu$$

The first and second reactions are selectively catalyzed by glutamate oxidase and peroxidase respectively. The chemiluminescence signal is proportional to the glutamate concentration. A fraction of this light is collected by a microscope objective and detected by a photon counting detector. Two chemiluminescence reactions have been examined. The merits and disadvantages of these reactions will be discussed. The characterization and kinetic properties of this biocatalytic-chemiluminescence reaction sequence will also be presented. Additionally, a mathematical model for the luminol chemiluminescence reaction has been established and the utility of this model for the sensing scheme will be discussed. Finally, preliminary experimental results for the chemiluminescence signal collected from the microscope/photon counting system will be presented.

261 WONDERS OF MICROMACHINING: CHEMICAL ANALYSIS AND ELECTROPHORESIS ON A CHIP.

K. Seiler, D. J. Harrison and A. Manz, Department of Chemistry, University of Alberta, Edmonton, Alberta, Canada T6G 2G2.

The miniaturization of benchtop scale chemical analysis systems to the size of a microchip presents interesting possibilities and challenges. Such devices would resemble sensors in their size and ease of use, but they should offer improved performance and lifetime because a complete *system* of sample treatment is used. Silicon micromachining techniques provide a route to fabricating micro-three dimensional structures for such applications. We have realized a manifold of interconnected capillary channels for fluid handling on a chip. Electroosmotic pumping has been used to drive fluid flow in a flow injection analysis manifold for sample treatment. This is coupled to an electrophoresis capillary on the chip for sample separation, with over 70,000 theoretical plates and fluorescence detection of sub-femtomole quantities.

262 STABILIZED SURFACTANT FILMS—COATINGS FOR MULTIPLEX SENSORS. James F. Rusling, Department of Chemistry (U-60), University of Connecticut, Storrs, CT 06269-3060.

Ordered films of insoluble surfactants are easily prepared by casting on solid surfaces, such as underlying sensors or groups of sensors. These films undergo phase transistions between solid-like and liquid crystal phases. Incorporation of various agents in the films may lead to multiple sensors for many species. We are elaborating such sensor functions and also establishing structure-function relations for these films. Some functions of insoluble cationic surfactant films in the liquid crystal phase are: (1) they reject multiple anions; (2) they preconcentrate multiple cations and hydrophobic molecules from solutions; (3) with multianionic metal phthalocyanine redox catalysts incorporated, catalytic electrochemical signals for organohalides result; (4) molecular recognition agents might be incorporated for selective reactions; (5) redox proteins can be incorporated. Films are stabilized by making composites of surfactants with clay colloids, linear ionic polymers, metal phthalocyanine tetrasulfonates, and perhaps biomacromolecules. Structurally, most films consist of partly disordered, wavy stacks of bilayers.

263 APPLICATIONS OF MALDI-TOF TO BIOLOGICAL PROBLEMS. Randall W. Nelson,[1] Mathew A. McLean,[1] T. William Hutchens[2] and Marvin L. Vestal,[1] Vestec Corporation,[2] 9299 Kirby Drive, Houston, TX 77054 and the Protein Structure Laboratory,[2] USDA/ARS Children's Nutrition Research Center, Department of Pediatrics, Baylor College of Medicine, 1100 Bates St., Houston, TX 77030.

Matrix-assisted laser desorption/ionization time-of-flight mass spectrometry (MALDI-TOF) has been demonstrated in our laboratories to be a powerful new technique for: 1) the accurate determination of intact protein molecular weights (up to 500 kDa), 2) mass-dependent identification of intact proteins and enzymes in unfractionated mixtures (natural and chemically defined), 3) evaluation of protein structure homology (comparative peptide mapping and mass-dependent sequence identifications), 4) evaluation of various posttranslational modifications (e.g., phosphorylation, glycosylation, disulfide bond formation), 5) the evaluation of sequence-specific transition metal-binding capacity and stoichiometry. Examples of these applications will be presented and discussed with respect to both *qualitative* and *quantitative analyses*.

264 SIMULTANEOUS HIGH RESOLUTION-HIGH SENSITIVITY REFLECTRON MATRIX ASSISTED LASER DESORPTION OF PROTEINS. F. Laukien, K. Norbash and J. Wronka, Bruker Instruments, Inc., Manning Park, Billerica, MA 01821.

The analysis of high molecular weight samples has been an active area of research for many mass spectroscopists. Now peptides and proteins ranging in molecular weights form 2000 to >150,000 amu can be routinely analyzed by the technique of matrix-assisted laser desorption (MALD). Nearly all previous MALD work has been reported using relatively low mass resolution time-of-flight (TOF) mass spectrometers. We have developed a innovative gridless reflectron time-of-flight mass spectrometer to obtain improved high resolution on high molecular ions. The MALD technique coupled with TOF mass analysis has been used to study biologically interesting compounds. The objective of our current research was to develop a protocol to produce high resolution time-of-flight mass spectra of biological samples on a routine basis. Optimization of the choice of matrix, ratio of analyte to matrix, and laser wavelength has a large influence on the quality of the mass spectra obtained. The optimization procedure will be discussed in terms of the methodology to generate high quality results.

265 MODELS FOR LASER-PULSE DESORPTION. R. E. Johnson, Engineering Physics, University of Virginia, Charlottesville, VA 22903.

Although there is no complete quantitative description of the desorption process, the general qualitative picture given by most workers is roughly the same. Based on this picture, a quantitative description can be obtained by organizing data using an appropriate framework. Such a framework is given here for the total (ablation) yield and the imbedded molecule ion yield. Data to date suggest that ions predominantely come from the surface layer in most materials. The role of the plume in determining the internal energy and charge state of the yield is discussed, and molecular dynamics calculations are presented.

266 DEVELOPMENT OF HIGH PERFORMANCE TIME-OF-FLIGHT INSTRUMENTATION FOR ANALYSIS OF BIOLOGICAL MOLECULES. Timothy Cornish and Robert Cotter, Johns Hopkins University, Baltimore, MD 21205.

A double reflection time-of-flight mass spectrometer is currently under development to study peptides and small proteins (1000–5000 amu range) with unit resolution. This compact laser desorption instrument has been designed in order to determine the limitations of both resolution and performance in a miniature tandem TOF. A pulsed molecular beam collision gas source has been installed at the collision cell to minimize pumping requirements and reduce overall background pressure in the tandem mode. The development of this instrument has been divided into several stages with the initial goals focussed on testing the single and double reflection configurations. For small organic compounds, resolutions between 1000–2000 are commonly achieved using the first reflection only, and between 3000–4000 suing both reflections. Currently, we are investigating the performance of the tandem TOF configuration using high energy collisions with an inert gas but will eventually use low energy endothermic ion-molecule reactions for the fragmentation of proteins.

267 DETERMINATION OF INTRACELLULAR SPECIES AT THE LEVEL OF A SINGLE ERYTHROCYTE VIA CAPILLARY ELECTROPHORESIS WITH DIRECT AND INDIRECT FLUORESCENCE DETECTION. E. S. Yeung, B. L. Hogan and T. Lee, Department of Chemistry and Ames Laboratory-USDOE, Iowa State University, Ames, IA 50011.

Intracellular contents reflect the specific history of a cell including innate physiological heterogeneity as well as differing levels of exposure to environmental influences. A method capable of analyzing a variety of species from within a single human erythrocyte is demonstrated. Guided by a microscope, individual cells can be drawn into open capillaries of 10 μm i.d. On contact with a low ionic strength buffer solution, the cell lyses and releases its intracellular fluid. The ionic components are then separated by capillary electrophoresis. For glutathione, microderivation with a fluorescent reagent can be accomplished *in vitro* with monobromobimane. The effects of extracellular oxidizing and reducing agents on the glutathione levels can thus be followed. For sodium and potassium, or any other ionic species, charge displacement of a fluorescent cation results in indirect fluorescence detection. The two detection modes are suitable for intracellular components present at sub-attomole and subfemtomole levels, respectively. Native protein fluorescence is another useful detection scheme, providing attomole detectability. Carbonic anhydrase and hemoglobin A can be quantified in individual cells.

268 MULTIWAVELENGTH THERMAL LENS SPECTROPHOTOMETER BASED ON ACOUSTO-OPTIC TUNABLE FILTER, Chieu D. Tran, Mark Bartelt and Valerian Simianu, Department of Chemistry, Marquette University, Milwaukee, WI 53233.

The instrumentation development of a novel, all solid state, non moving parts, fast scanning and wide tuning range multiwavelength thermal lens spectrophotometer based on the acousto-optic tunable filter (AOTF) is described. Initially, the essential electronic driver was developed to facilitate the systematic characterization of the parateluride (TeO_2) AOTF and to demonstrate that this filter can be successfully and uniquely used as an all solid state, non moving parts dispersive device to rapidly diffract white incident light into a selected color beam, to amplitude modulate the diffracted monochromatic light and to keep its intensity constant. The multiwavelength thermal lens instrument was subsequently constructed using this AOTF and preliminary results on advantages of this spectrophotometer such as its ability to characterize trace chemicals and to analyze multicomponent samples are delineated.

269 A LASER-BASED OPTICAL POLARIMETER: COMPUTER SIMULATION AND EXPERIMENTAL EVALUATION. M. E. Johnson and E. Voigtman, University of Massachusetts, Amherst, MA 01003-0035.

Computer simulations are an important part of the analytical chemist's arsenal. As a case in point, we present results obtained with a solid-state optical polarimeter, based on the design of Yeung et al., with a diode laser source and faraday rotator modulation. The polarimeter was constructed in the lab and was modeled with a commercial computer simulation program (extend with the Voigt *f*X Libraries). Simulation of the full optical and electronic train, using realistic flicker noise on the source and non-ideal optical components, allowed evaluation of the polarimeter. The effects of various operating parameters on signal-to-noise ratio were

284 SAMPLE MATRIX INFLUENCES ON ATOMIZATION AND IONIZATION IN GLOW DISCHARGE MASS SPECTROMETRY.

J. Tend and F. L. King, Department of Chemistry, West Virginia University, Morgantown, WV 26505-6045.

Quantitative glow discharge mass spectrometry for the direct determination of trace elements in solid matrices is limited by the availability of suitable standards with which to define relative elemental sensitivities. Standard reference samples are employed to provide a measure of elemental sensitivities relative to a selected standard element. This measurement is termed a relative sensitivity factor and is employed as a correction factor in the quantitative analysis of unknown samples. It is assumed that sensitivities do not vary significantly between a standard and a sample. Often strict matrix matching is required to assure the validity of this assumption. A priori knowledge of a samples composition is needed to permit such matrix matching. The correlation of relative sensitivity factors with various observable plasma parameters is investigated to elucidate the influence of changes in atomization and ionization on elemental sensitivities. The effect of matrix on atomization is corrected for by use of relative sensitivity factors because the reference element in each sample is subject to the same atomization rate as other constituents. For a given matrix, relative sensitivities are found to correlate closely with the applied power. The ability to predict changes in relative sensitivities by measurements of argon excitation and ionization temperatures is examined. These measurements are employed to characterize the change in plasma energy partitioning as a function of the sample matrix. This change in energy can be observed also as a change in the relative ionization of analyte species.

285 TRACE ELEMENT ANALYSIS USING MODULATED GLOW DISCHARGES.

C. Pan and F. L. King, Department of Chemistry, West Virginia University, Morgantown, WV 26505-6045.

A modulated glow discharge atomization/ionization source was employed with atomic absorption and mass spectrometries for the direct determination of trace element concentrations in solid samples. Standard reference cathodes were formed by pressing graphite powders containing known concentrations of analyte elements. The concentration of elements in these powders was determined by the method of standard additions. The discharge was modulated at 50 Hz permitting temporal resolution between analyte and background signals. Whereas the ground state atom population was found to decay slowly following the termination of discharge power; atomic emission and analyte ion signals were observed to maximize within 1 millisecond of the discharge power termination. Time-resolved atomic absorption measurements were made during the decay regime to afford the determination of transition elements in a graphite matrix at the sub-ppm level with 5% precision. Excellent linearity was exhibited by the calibration curves used in this determination. The rapid recombination of argon ions with electrons leading to a surge in the metastable argon atom population during the discharge decay time regime was revealed by atomic emission and atomic absorption spectrometries. Penning ionization was maximized during this decay regime; thus, mass spectra were obtained in which the influence of discharge support ions was removed. Optimization of the mass spectrometric measurements is underway utilizing a time-of-flight mass spectrometry system designed to monitor modulated glow discharge plasmas.

286 CORRELATION BETWEEN PLASMA OBSERVALBES AND POLYATOMIC IONS IN GLOW DISCHARGE MASS SPECTROMETRY.

G. Chen and F. L. King, Department of Chemistry, West Virginia University, Morgantown, WV 26505-6045.

Polyatomic ions limit the utility of low resolution mass analyzers, such as quadrupoles, in glow discharge mass spectrometry. This limitation arises because some polyatomic ions can have the same nominal mass as analyte ions. To minimize the spectral contribution of polyatomic ions, it is necessary to understand their origin. The formation of metal-argide ions is the subject of this presentation. These species arise from associative ionization or three body collisions in which an argon ion participates. The relative contribution of metal-argides to a glow discharge mass spectrum correlates with discharge parameters, operating pressure and power, and is predictable. The population of metal-argide species tracks the relative ion temperature as determined from the ratio of singly to doubly charged argon ions. Modulation of the glow discharge plasma permits sorting of the relative contribution from the two mechanisms because processes involving metastable argon atoms, such as associative ionization, can be isolated in time from other ion formation processes. Atomic absorption, atomic emission, and mass spectrometric measurements, permit the characterization of the relative contribution of metal-argide formation processes as a function of discharge power and pressure.

287 TANDEM MASS SPECTROMETRY FOR THE CHARACTERIZATION OF GLOW DISCHARGES.

L. R. Meadows, F. Fotia and F. L. King, Department of Chemistry, West Virginia University, Morgantown, WV 26505-6045.

Tandem mass spectrometry is used to characterize glow discharge plasma chemistry. The glow discharge plasmas of interest are employed in the determination of trace elements and the deposition of thin films. The identification of isobaric polyatomic interferences in analytical glow discharge mass spectrometry is demonstrated. Spectral simplification is achieved through the removal of polyatomic ions with a concomitant reduction in sensitivity. Unique species generated in these glow discharge plasmas, such as metal-dimer and metal-argide ions, are characterized in energy resolved collision-induced dissociation experiments. In thin film deposition plasmas, the identity and energy content of film precursors are determined in similar experiments. The impact of discharge operating parameters, such as power, pressure, and gas composition, on film deposition is characterized as a function of the change in film precursor internal energies induced by changes in these parameters. Precursor internal energy is correlated with measurements of plasma energy content such as argon excitation and ionization temperatures. The plasma chemistry that is relevant to the growth of diamond thin films is inferred from the energy dependent dissociation of methyl species generated in glow discharge plasmas sustained in a 5% mixture of methane in hydrogen that is diluted with argon.

288 LOW LEVEL DETERMINATIONS OF COPPER AND ZINC IN WATER AND WASTEWATER BY GRAPHITE FURNACE ATOMIC ABSORPTION AND INDUCTIVELY COUPLED PLASMA ATOMIC EMISSION SPECTROSCOPY.

B. M. Patel, A. H. Ali, D. D. Johnson and C. T. Mansfield, Texaco Inc., Research & Development-PA, P.O. Box 1608, Port Arthur, TX 77641.

Graphite furnace atomic absorption and inductively coupled plasma atomic emission spectroscopic techniques were evaluated for accurate determinations of low concentrations of toxic metals copper and zinc in water and wastewater samples. The main features considered were detection sensitivity, influence of sample matrix and freedom from interferences. Various parameters evaluated for these techniques included sample preparation procedures, spike recoveries, certified sample analysis, precision and accuracy. Water samples were acid digested and/or diluted to permit measurements at low levels. Spike recoveries were quantitative and precision data were in the range from 2–6% RSD. Determinations of copper and zinc were carried out by both techniques at fractional parts per million levels. However, the graphite furnace technique in particular provided measurements of lower parts per billion (2–5 ppb) concentrations of these analytes in real world samples. Intercomparison of results for analysis of water and wastewater samples as well as analytical figures of merit data will be presented for both techniques.

289 INSTRUMENTATION FOR CURRENT CONTROL IN A PULSED HOLLOW CATHODE DISCHARGE.

James A. Moore, P. D. Mixon, C. W. Bray, S. T. Griffin and J. C. Williams, Departments of Electrical Engineering and Chemistry, Memphis State University, Memphis, TN 38152.

A constant current switch and differential high-voltage monitor designed to control and monitor a hollow cathode discharge (HCD) emission source are described. The purpose of a constant current switch is to maintain a constant discharge each time a sample is excited. A consistent discharge then yields a large improvement in the precision of spectroscopic measurements of the discharges. In observing the characteristics of the discharge, electrical measurements are often needed. For this task, a differential high voltage monitor was developed. Normally, differential measurements require at least two channels of an oscilloscope. The monitor described here reduces the requirement to only one channel. With improved instrumentation, HCD emission spectroscopy will come closer to becoming a valuable technique in the analysis of microsamples.

290 LOW PPB MEASUREMENTS USING A SEQUENTIAL ICP-AES WITH AN ULTRASONIC NEBULIZER.

Jerry Shkolnik, Tran Nham and Geoff Tyler, Varian, 201 Hansen Court, Suite 108, Wood Dale, IL 60191.

With the introduction of a new generation ultrasonic nebulizer trace element determination has entered a new era. The new ultrasonic nebulizer has overcome the limitations of instability and memory that have plagued ultrasonic nebulizers. This paper will present the data obtained with the new ultrasonic nebulizer and a high resolution sequential ICP-AES. Data will be presented on a variety of samples types including drinking water, seawater and urine. Long term stability data will be shown for copper, aluminum and barium. Stability data over a one hour period will be presented for manganese and cadmium in a one percent sodium chloride matrix. The wash out time for a one thousand ppm copper standard will also be discussed. It will be shown that the fast pump feature of the liberty ICP can reduce the wash out time by one third.

291 HYDRIDE TRAPPING ON PALLADIUM AND SUBSEQUENT DETERMINATION BY ELECTROTHERMAL VAPORIZATION INDUCTIVELY COUPLED PLASMA MASS SPECTROMETRY [ETV-ICP-MS].

Isam Marawi, Jiansheng Wang and Joseph A. Caruso, Department of Chemistry, Mail Location 172, University of Cincinnati, Cincinnati, OH 45221.

In recent years hydride generation has become a popular sample introduction method in the inductively coupled plasma with atomic spectroscopy [ICP-AES], and mass spectroscopy [ICP-MS]. Arsenic III is the most investigated element utilizing this technique simply because of it's toxicity. Even though the hydride generation method of sample introduction offers higher sensitivity than pneumatic nebulization, detection limits are still not satisfactory. In this study an electrothermal vaporization step was added to serve two purposes. One is to preconcentrate the analytes; and the second is to eliminate the hydrides by-products, namely the excess hydrogen. The analyte hydride was generated by mixing the analyte with the reagents in a porous polypropylene tubing (as a gas liquid separator) which is sealed in a glass sleeve with side arms for gas flow. The volatile hydrides were purged through a modified graphite furnace for preconcentration of hydrides onto palladium. Subsequent volatilization of the elements and determination by inductively coupled plasma-mass spectrometry may yield detection limits below what have been reported by using the ETV method alone. The instrumentation will be described, results of optimizations, detection limits and other figures of merits will be presented.

292 TRACE METAL ANALYSIS OF COAL FLY ASH BY RF GLOW DISCHARGE MASS SPECTROMETRY (RF GD/MS) AND INDUCTIVELY COUPLED PLASMA MASS SPECTROMETRY (ICP/MS).

Jeffrey J. Giglio, Jiansheng Wang and Joseph A. Caruso, University of Cincinnati, Department of Chemistry, Cincinnati, OH 45221-0172.

As the acceptable levels of environmentally interesting elements become lower and lower, the sample handling or lack there of, is of increasing significance. The results of analysis of Coal fly ash samples (NIST) by ICP-MS, with microwave digestion will be presented. In addition, a rf glow discharge device will analyze the same sample and comparisons will be made between the two techniques. These comparisons will include relative ease of sample analysis, sample handling involved, and analytical figures of merit.

293 DETERMINATION OF SELENIUM IN HUMAN RED BLOOD CELLS BY GRAPHITE FURNACE ATOMIC ABSORPTION SPECTROMETRY.

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Selenium plays an important part in the body's defense system and protects the cell against the damage caused by oxygen free radicals. Selenium status is an important clinical marker in many conditions, and there are many disease states in which selenium deficiency may play an important role. Selenium levels in blood are monitored in red blood cells (RBC), for preference, and/or plasma. We now report a method for RBC-selenium determination using Zeeman GFAAS and noble metal matrix modification. Washed RBC is diluted two fold with triton-EDTA mixture and a further two fold with modifier containing Pd(II) from palladium(II) chloride in 0.1 M nitric acid. The diluted RBC mixture is analysed by direct injection into the graphite furnace. Pyrocoated tubes with inserted L'vov platforms are used with an optimised furnace heating program. Oxygen is used in the post-atomisation cleaning stage (800 C). The analysis is calibrated by standard additions, against inorganic selenium in nitric acid. Interlaboratory standardisation is tested with a commercial quality assurance material (Seronorm/Nycomed). The method allows direct and rapid selenium determination at the low levels found in selenium-deficient patients, with sufficient accuracy (±5%) for clinical research purposes.

294 ATOMIC ABSORPTION SPECTROSCOPY WITH A FLAME EMISSION SOURCE.

Clifton P. Calloway, Jr. and Bradley T. Jones, Department of Chemistry, Wake Forest University, Winston-Salem, NC 27109.

Since the time that Alan Walsh proposed the use of atomic absorption (AA) methods for spectrochemical analysis, AA has experienced widespread use in modern instrumental laboratories. Traditional AA spectrometers have used hollow cathode lamp sources, and continuum sources have been used in order to perform multielement analysis. In this poster, an atomic absorption spectrometer that utilizes an alternative source, i.e. a second flame, for AA measurements is described and evaluated. The source flame uses a high concentration of the analyte to be studied aspirated into a burner equipped with a capillary burner head to create a stable, intense emission signal. The emission signal is modulated and focused through the sample flame. The unabsorbed photon flux is then focused onto the entrance slit of a 1.33 m high resolution monochromator equipped with either a photomultiplier tube and a lock-in amplifier or a 2" photodiode array detection system. The flame emission source provides a more convenient method for changing analytes as well as the ability to aspirate mixtures, which can be used to create a multiple line source for multielement analysis or for internal standard correction methods. Results, which are in some cases as good as hollow cathode lamp results, are presented and compared with conventional atomic absorption methods.

295 MATERIAL VERIFICATION OF 90/10 PLATINUM/IRIDIUM PARTS BY Zn FUSION-ICP/AES.

Kenneth D. Soderquist, Medtronic, Inc./Promeon Division, 6700 Shingle Creek Parkway, Brooklyn Center, MN 55430.

A procedure for analyzing PT/IR alloys by ICP/AES utilizing a zinc fusion to aid dissolution will be presented. Dissolution time has been reduced from approximately one week to one day. Analysis is performed for Ir (10%), Au, Pd, Rh and Ru at the 100 to 1000 ppm level. Preliminary work has been done to extend this procedure to the minor trace elements.

296 DETERMINATION OF SILOXANES IN SPENT SULFURIC ACID.

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An atomic absorption spectrometric method has been developed for the determination of residual siloxanes in "spent" sulfuric acid (used acid which is going to be recycled) evolved during a silicone manufacturing process. The spent acid is diluted with isopropanol and then aspirated directly into an atomic absorption spectrometer equipped with a nitrous oxide burner head. Silicon is measured, expressed as SiO_2. Calibration standards are prepared from octamethylcyclotetrasiloxane, reagent grade isopropanol and reagent grade sulfuric acid. The method is rapid, with a precision of 0.9% RSD and a sensitivity of 1.7 ppm Si, making it suitable for a quality control application.

297 IMPLEMENTATION OF A DIRECT INJECTION NEBULIZER (DIN) FOR ANALYSIS OF VOLATILE HYDROCARBON SAMPLES AND ANALYTES.

M. A. Shepherd, A. R. Forster and G. J. Kamla, Shell Development Co., P.O. Box 1380, Houston, TX 77251-1380.

Inductively coupled plasma atomic emission spectroscopy (ICPAES) using direct organic aspiration typically employs a conventional spray chamber sample introduction system. When samples with volatile matrices are aspirated using this sample introduction system, additional sample solution is directed to the plasma in the form of vapor. This results in excess hydrocarbon loading of the plasma. There are several techniques available to minimize the effect of a volatile sample matrix. However, analyte volatility presents a fundamental problem. Analyte vapor contributed from a volatile analyte component in the sample will result in a significant bias in quantitation relative to the non-volatile calibration standard. To circumvent this volatility bias, the spray chamber can be eliminated by employing the direct injection nebulizer (DIN).[1] The DIN, a concentric glass micro-nebulizer, is positioned in the aerosol tip of the ICP torch. This device allows the aerosol to be injected, wholly, into the plasma. A DIN and torch combination was designed and fabricated in order to aspirate the hydrocarbon matrices. This design has proven effective in analysis of hydrocarbon samples containing volatile matrices and analytes. Subsequent refinements in the design of the DIN torch have been made to resolve long term instability resulting from deposits noted to form on the micro-nebulizer. The resulting improvements in performance have allowed the automation of the technique.

1. Kimberly E. LaFreniere, Gary W. Rice, and Velmer A. Fassel, *Spectrochimica Acta*, 1985, Vol. 40B, Pg. 1495.

298 TWO STEP LASER ENHANCED ATOMIC FLUORESCENCE OF MERCURY.

Wifredo Resto, Raúl G. Badini and James D. Winefordner, Department of Chemistry, University of Florida, Gainesville, FA 32611.

Two step laser induced fluorescence study for Hg will be presented. The optical scheme involves excitation at $\lambda_1 = 253.7$ nm and a second step at $\lambda_2 = 435.1$ nm, while the fluorescence signal is detected at 546.1 nm. A strong Amplified Stimulated Emission (ASE) is found when the two exciting laser beams meet at the center of either a Hg filled vapor cell or a Hg injection in a graphite atomizer. The ASE signal shows a highly non linear response with the mercury number density and second power dependency upon the "pumping" laser energy. The ASE signal ends at Hg concentrations less than 10^{13} atom cm^{-3} in the vapor cell and for less than 2 ng in the graphite furnace. Linear behavior (fluorescence) is found as well and it prevails at lower Hg concentration. An alternative optical arrangement can also makes possible to separate the fluorescence from the ASE. A study of the dependency of the ASE signal upon foreign gases pressure is presented. The analytical usefulness of this system is discussed as an alternative to cold vapor determinations. The LOD for Hg using GFA-LEAFS is found to be in the low picograms.

299 LINEARIZATION OF ELECTROTHERMAL ATOMIC ABSORPTION CALIBRATION CURVES.

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Correction for non-linear calibration curves in electrothermal atomic absorption is usually attempted with completely empirical relations between integrated absorbance and concentration. Since the principal cause of curvature is stray light, light that is not as strongly absorbed as light on the center of the atomic line, a mathematical model of stray light should be a less empirical way to correct for non-linearity in electrothermal atomic absorption calibration curves. Stray light calibration curve linearization is more complicated in electrothermal AAS than in flame AAS since the concentration of analyte in the optical beam is a complicated function of time, as well as a function of solution concentration. A computer algorithm has been developed to linearize ETV-AAS calibration curves which makes two assumptions: one, some fraction of the light has a lower absorption probability than the center of the atomic line and two, that the total integrated, linearized absorbance should be directly proportional to the mass of analyte placed in the furnace.

300 USE OF PC/ABSORB TO COLLECT ATOMIC ABSORPTION DATA FOR STRAY LIGHT LINEARIZATION COMPUTATIONS.

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An algorithm for the linearization of non-linear transient atomic absorption (AA) data for stray light correction as described by Black et al.[1] has been developed by Boss.[2] Using the recorder output of an AA instrument, the analog instrument signal is digitized by an analog-to-digital board using the PC/Absorb software package within a personal computer. Lin nearization of this digital signal is just one feature of the PC/Absorb package. Conventional processing of transient and continuous modes of signal generation are also supported. PC/Absorb is a user-friendly, menu driven program that is applicable to laboratories that require high standards of data manipulation, archival, and reporting. Bracketed standards as well as standard addition modes of calculation support are included together with report generation capabilities and quality control options. The transient signal mode also allows for reintegration of graphic data, overlaying of peaks, and peak area and height modes of calculation.

1. Measurement of Stray Light in Atomic Absorption Spectrometry, S. S. Black, W. P. Robarge, and C. B. Boss, *Appl. Spectrosc.*, **44**, 280 (1990).
2. C. B. Boss, personal communication (1991).

301 Abstract not received at time of printing.

302 IMPLEMENTATION OF A DIRECT INJECTION NEBULIZER (DIN) FOR ANALYSIS OF VOLATILE HYDROCARBON SAMPLES AND ANALYTES.

M. A. Shepherd, A. R. Forster and G. J. Kamla, Shell Development Co., Westhollow Research Center, 3333 Hwy. 6 South, Houston, TX 77082.

ICPAES using direct organic aspiration typically employs a conventional spray chamber sample introduction system. When samples with volatile matrices are analyzed, components evaporating from the walls of the spray chamber are directed to the plasma along with the analyte containing aerosol resulting in excess hydrocarbon loading of the plasma. Similarly, volatile analytes in the sample will result in a significant bias in quantitation based on the relative volatility of the analyte component. Elimination of the spray chamber, by implementation of the DIN, permits reliable quantitation of hydrocarbon samples containing volatile matrices and/or analytes.

303 DETERMINATION OF RARE EARTH ELEMENTS (REEs) AND TRANSITION METALS IN NATURAL WATERS BY CHELATION PRECONCENTRATION-ICP-MS

Judy E. Vaive, Gwendy E. M. Hall and Jean-Claude Pelchat, Mineral Resources Division, Geological Survey of Canada, 601 Booth Street, Ottawa, Ontario, Canada, K1A 0E8.

The determination of REEs and transition metals in natural waters directly by ICP-MS can be difficult due to their low concentrations and interferences caused by the presence of alkali and alkaline-earth metals and various anions such as chloride. These problems are overcome using a Dionex Chelation Module which has been fully automated with a Gilson Model 222 Autosampler and a Foxy Fraction Collector. A set of Dionex MetPac CC-1 columns is used to clean on-line the 2 M ammonium acetate buffer and the sample buffer. These columns are regenerated after each sample allowing less expensive grades of acetic acid and ammonium hydroxide to be used. A separate MetPac CC-1 column is used to preconcentrate the REEs, Cu, Pb, Ni, Co, Zn, Mn, Al, Fe, Y, Ti, Cd, In and U while interferents such as anions, Na, K, Ca and Mg are not retained on the column. The sample is recovered in 5% HNO_3 for analysis by ICP-MS. Forty samples can be preconcentrated ten fold in less than 24 hours without operator assistance. Recoveries, detection limits and some of the current projects ongoing at the Geological Survey of Canada will be discussed.

304 NEW METHOD FOR THE DETERMINATION OF METALIC ELEMENTS BY ATOMIC ABSORPTION SPECTROPHOTOMETRY IN CRUDE OILS AND PETROLEUM PRODUCTS.

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A new solvents mixture, which allows the determination products and residual products, had been used for the development of analytical methods, both in flame and graphite furnace atomic absorption spectrophotometry (FAAS or GF-AAS). The mixture is composed by 2,6-Dimethyl-

TABLE I. Determination of V and Ni in Venezuelan Cerro Negro Crude Oil using a DIBK-ISOPOH matrix with inorganic aqueous standards by AAS.

Element-Conc. (1)	Method	Matrix Modificator
V:		
493.6 ± 9.1 ppm	FRX	—
964.0 ± 42.6	FAAS	NO
522.0 ± 18.6	FAAS	Aliquat 336 (1%)
522.3 ± 12.5	FAAS	Cetylpyridinium chloride (1%)
V:		
472.0 ± 5.2	FRX	—
460.8 ± 16.3	GF-AAS	NO
Ni:		
107.5 ± 2.1	FRX	—
56.0 ± 8.0	GF-AAS	NO
110.3 ± 1.9	GF-AAS	Dodecylbenzenesulfonic Acid (10%)

(1) Reported numbers are mean values for four independent determination.

4-heptanona (DIBK) and isopropanol (ISOPOH). The first of these compounds has an excellent solvent capability for the mentioned products, the second is completely miscible with DIBK. The mixture of DIBK + ISOPHO (1 + 4) can tolerate 30% of water in volume, this property allows the use of aqueous standards for the determination above mentioned. The results obtained for determination of vanadium and nickel in crude oil indicated the need of using a matrix modification agent is some cases, surface active agents have shown a good performance for some results are presented in Table 1.

305 THE NATURE OF THE $C_6H_4X^-$ IONS ($X = F$, Cl, Br, I) IN THE GAS PHASE.

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The gas phase acidieties of halobenzenes are known to lie between that of water and methanol. We have produred $C_6H_4X^-$ ions in a homemade FT-ICR spectrometer from the reaction of NH_2^{-6} with the halobenzenes. For $X = F$, Cl, CN, NO_2, the $C_6H_4X^-$ anions are unreactive towards the precursor halobenzene or ammonia but readily abstract a proton from more acidic alcohols. On the other hand, $C_6H_4Br^-$ and $C_6H_4I^-$ undergo further reaction with the parent halobenzene to yield $C_6H_5Br_2$ and $C_6H_5I_2^-$. A particularly important observation is the fact that $C_6H_4Br^{-6}$ and $C_6H_4I^-$ react readily with the more acidic methanol by halide transfer rather than by proton abstraction. Halide transfer has been verified for a large number of polar substrates. These observations strongly suggest that the structure of the $(C_6H_4)Br^-$ and $(C_6H_4)I^-$ correspond to that of a halide weakly bound to benzyne. An upper limit of 12.5 kcalmol^{-1} is proposed for the $C_6H_4.Br^-$ binding energy based on available thermochemical data. The stability of these species is proposed to arise from a favorable interaction between the doubly occupied p orbital of Br^- and the LUMO of benzyne. (Work supported by FAPESP and CNPq).

306 PHOTOPHYSICAL PROPERTIES OF POLYCYCLIC AROMATIC COMPOUNDS: CHARACTERIZATION AND PROBE CHARACTER.

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Identification and quantification of unknown polycyclic aromatic hydrocarbons (PAHS)/polycyclic aromatic nitrogen heterocycles (PANHS) mixtures requires accurate fluorescence emission intensity measurements and availability of a large spectral data file for comparing the unknown's spectrum against PAH/PANH standards. Mixtures of environmental/industrial importance contain isomeric or structurally similar PAHS/PANHS, which emit in approximately the same spectral regions. Utilization of discriminating solvents, such as quenching reagents and protonating solvents, can significantly simply observed emission spectra. Experimental measurements on roughly 150 PAHS benzenoids, PANHS, methylene-bridged PAHS, and cyclopenteno-PAH derivatives, utilizing nitromethane as a quenching reagent reveal that in most cases nitromethane selectively quenches fluorescence of alternant PAHS/PANHS (e.g. pyrene and 1-azapyrene) as opposed to non-alternate PAHS (e.g. fluoranthene), thus allowing one to distinguish these two chemical classes. A few notable exceptions will be presented, as will quenching studies involving other quenching media. To prevent misidentification, experimentally determined spectra must be free of chemical and instrumental artifacts that might unexpectedly reduce emission intensities; therefore, corrections for primary and secondary inner-filtering were taken into account. Discriminating solvents like $HClO_4$/acetonitrile can be used to protonate PANHS (and not PAHS). Protonation of the nitrogen lone pair by an hydrogen ion results in the loss of emission fine structure accompanied by a sizable redshift in emission wavelength(s). Degree of protonation should be reflected by both solvent acidity and PANH basicity. As expected the protonation is completely reversible and prevents photochemical quenching by nitromethane.

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307 DEVELOPMENT, CHARACTERIZATION AND APPLICATION OF EOF-DRIVEN CAPILLARY ISOELECTRIC FOCUSING.

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We have recently developed the technique of EOF-driven CIEF, whereby mobilization of the focused protein zones is due to residual electroendosmotic flow (EOF) present in the silica capillary. It is necessary that EOF be minimized such that proteins spend enough time in the capillary to be focused properly for high resolution. This is accomplished through addition of methyl cellulose to the sample/ampholyte mixture, with the methyl cellulose acting to reduce EOF by increasing viscosity and adhering to the capillary wall. Because very basic proteins focus in the region past the stationary detection point in the capillary, it was necessary to supplement the ampholyte gradient with temed, a PH gradient extender. Problems with broadening of acidic proteins were determined to be due to inherent anodic drift present in the ampholyte gradient and were minimized by increasing the concentration of phosphoric acid in the anode buffer. The method was applied to bovine hemoglobin forms and peptide mapping.

308 MOLECULAR ANALYSES OF FROZEN AQUEOUS SOLUTIONS USING ION-BEAM-INDUCED DESORPTION AND MULTIPHOTON RESONANCE IONIZATION.

Matthew H. Ervin, Mark C. Wood and Nicholas Winograd, Department of Chemistry, Penn State University, 152 Davey Laboratory, University Park, PA 16802.

The combination of ion-beam-induced desorption and multiphoton resonance ionization results in a very sensitive method for surface specific detection of molecules. Previously, femtomole detection limits have been demonstrated for biologically important molecules coated onto silicon wafers (Hrubowchak, et al., *Anal. Chem.* **63**, 1947, 1991). One exciting potential application of this methodology is to make molecular analyses of biological tissues in situ. With this in mind, we have applied our methodology to the analyses of frozen aqueous solutions which serve as model systems for biological tissues. When using a frozen millimolar solution of tryptophan/H_2O a time-of-flight mass spectrum for tryptophan in obtained which is virtually identical to that obtained for a submonolayer of tryptophan on a silicon wafer (ibid.). In order to simplify the production of a calibration curve, 4,4'-biphenol was used as an internal standard. A linear calibration curve and a detection limit of 2.03×10^{-6} M were obtained. Since our ion beam samples 0.1 cm^2 and we assume 10^{14} molecules/cm^2, this corresponds to a detection limit of about 3.6×10^5 molecules. If these 3.6×10^5 molecules are packed together on the surface they should cover an area of 0.36 μm^2. This indicates that sub-micron molecular imaging with a liquid metal ion source is feasible. Furthermore, there are a number of strategies available to improve on this detection limit. Among these, the extension of counting times will only be modestly effective, since the signal exhibits an exponential decay with time due to the accumulation of primary ion damage in subsurface molecules.

309 COMPARISON OF A NEW LIQUID EXTRACTION METHOD TO TRADITIONAL METHODOLOGY IN THE RECOVERY OF TRACE LEVEL ORGANICS FROM AQUEOUS ENVIRONMENTAL MATRICES.

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Most environmental water analyses employ one of three common extraction techniques: separatory funnel, continuous liquid/liquid, or solid phase extraction. The first two use large quantities of solvent, and are either labor intensive or slow. SPE is more rapid for some matrices, such as drinking water, but cumbersome for oily or particulate-laden samples. The RALLE™ (rapid, automated, liquid/liquid extraction) technique combines the rapid throughput of separatory funnels with the matrix-handling ruggedness of continuous liquid/liquid extraction. Introduced sample is dispersed by transient high-intensity electric fields as micron-sized droplets within the organic phase. The electric fields induce droplet distortions, translation, and coalescence; this promotes rapid phase transfer, then phase separation. Excellent recoveries are obtained for the methylene chloride extraction of organic compounds analyzed under EPA methods. GC/MS recovery data from RALLE passed EPA method 625 QC requirement. Compared to traditional labor intensive extraction methods (EPA SW-846 method 3520), equivalent or superior precision and accuracy is produced, with less solvent usage and exposure to hazardous substances. Analytical applications of this technique derive from technology transfer under U.S. Patent 4,767,515, "Surface Area Generation And Droplet Size Control In Solvent Extraction Systems Utilizing High Intensity Electric Fields", 1988, by T. Scott and R. Wham, at Oak Ridge National Laboratory (ORNL).

310 HIGH SENSITIVITY FLUORESCENCE DETECTORS AND THEIR APPLICATIONS IN HIGH SPEED DNA SEQUENCING ANALYSIS BY CAPILLARY GEL ELECTROPHORESIS.

D. Y. Chen and N. J. Dovichi, Department of Chemistry, University of Alberta, Edmonton, Alberta, Canada T6G 2G2.

Capillary electrophoresis (CE) has attracted much attention in separation and microchemical analysis. Laser induced post column fluroescence detection in a sheath flow cuvette is the most sensitive method of detection for CE. Using a 1 mW He-Ne laser operating at 543.5 nm as the excitation source, a photon counter with cooled PMT as the fluorescence detector, and appropriate digital signal processing, detection limit of 50 yoctomole (30 molecules, 1 yoctomole = 1×10^{-24} mole) of rhodamine is obtained. This is the state of the art detection limit in CE. Zeptomole (10^{-21} mole) detection limits are obtained with a simple PMT operating at room temperature. An Ar^+ laser gives similar detection limits for fluorescein in the same CE system. The very high sensitivity makes this a suitable detector for high speed DNA sequencing by capillary gel electrophoresis. Combining the color encoded base recognition introduced by Smith et al.,(1) and the peak height encoded base recognition by Richardson and Tabor,(2) a color and peak height encoded DNA sequencing technique is developed. Sequencing is achieved by using two lasers focused on two separate spots at the end of the capillary; each laser excites a different group of fluorescent dye labeled, peak height encoded DNA segments. Fluorescence is collected in two spectral channels, and the bases are determined by the color and height of the peaks. Less dependence on resolution, simpler data processing and more accurate base recognition are achieved.

1. L. M. Smith, J. Z. Sanders, R. J. Kaiser, P. Hughes, C. Dodd, C. R. Connell, C. Heiner, S. B. H. Kent, and L. E. Hood, *Nature* **321**, 674 (1986).
2. S. Tabor and C. C. Richardson, *J. Biological Chemistry* **265**, 8322 (1990).

311 DETERMINATION OF TRACE AND ULTRATRACE CHLORINE BY GRAPHITE FURNACE LASER EXCITED MOLECULAR FLUORESCENCE SPECTROMETRY OF INDIUM MONOCHLORIDE.

Evelyn G. Su and Robert G. Michel, Department of Chemistry, University of Connecticut, U-60, Storrs, CT 06269.

Trace and ultra-trace non-metals cannot be readily determined by direct atomic spectroscopic methods because their resonance lines tend to fall in the vacuum UV region, and they tend to form stable diatomic molecules in high temperature atomizers. As a result, indirect and molecular spectroscopic methods have often been used to determine non-metals. Determination of chlorine has been done by flame and graphite furnace molecular absorption spectrometry (MAS) of indium monochloride. In this work, laser excited molecular fluorescence spectrometry (LEMOFS) in a graphite tube furnace with front-surface illumination was used to investigate indium monochloride. High resolution excitation and fluorescence spectra, with different excitation and detection schemes, were obtained with the use of high spectral purity laser radiation and a high resolution monochromator. Vibrational transitions associated with the electronic transitions were also assigned. A comparison of analytical performance between these schemes under optimized experimental conditions was made. An improvement of two orders of magnitude in detection limit over MAS is expected to be achieved with the use of the best scheme. The effects of metal ions as chemical modifiers, and of non-metal ions as interferent ions will be reported. Determination of chlorine in real samples by LEMOFS of indium monochloride will be presented.

312 DIGITAL IMAGING IN ATOMIC ABSORPTION SPECTROMETRY.

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The use of imaging techniques in analytical atomic spectrometry as both a diagnostic tool and for fundamental studies is becoming widespread. Notable contributions to this area of research are the recent works of Gilmutdinov *et al.*,[1] who have studied the distribution of atoms in graphite furnaces, and Hieftje,[2] who has used imaging techniques for the understanding and control of inductively coupled plasmas. In this work, a Charge-Coupled Device (CCD) detection system that is based on the Shadow Spectral Filming (SSF) system of Gilmutdinov *et al.*,[1] has been used to investigate the distribution of atoms within two different types of atomizers for atomic absorption spectrometry. The primary advantage that the CCD detection system has over the movie camera employed by the SSF technique[1] is that the CCD camera provides photometrically-accurate, digital results. The digital nature of the results facilitates the manipulation and analysis of the nature of the enormous amount of data that is obtained. The two atomizers that have been investigated are: 1) a cathodic sputtering atomizer, and 2) a graphite furnace. Both of these types of atomizers are characterized by distinctly non-homogeneous distributions of the analyte. The design of the imaging system and the characteristics of CCDs that make them ideal for imaging applications will be presented. The effects of various experimental conditions on the measured analyte distributions will be presented and the information that can be obtained from these distributions will be discussed.

1. A. Kh. Gilmutdinov, Yu. A. Zakharov, V. P. Ivanov and A. V. Voloshin, *Journal of Analytical Atomic Spectrometry*, 1991, **6**, 505.
2. G. M. Hieftje, *Spectrochim. Acta*, 1992, **47B**, 3.

313 INVESTIGATION OF SUB-MOLECULAR LIQUID CRYSTAL DYNAMICS BY USE OF STEP-SCAN AND STROBOSCOPIC CONTINUOUS-SCAN FT-IR.

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The information that can be acquired by the implementation of vibrational spectroscopy in the study of reorientations of uniaxially aligned liquid crystals is of fundamental importance to the design and development of new types of liquid crystals for advanced display devices. We have used polarized, time-resolved step-scan FT-IR spectroscopy to observe the dynamic response of nematic and smectic liquid crystals to AC and pulsed DC electric field perturbations. Impulse-response time-resolved step-scan FT-IR experiments are used to analyze the rise dynamics of reorientation resulting from pulsed DC perturbations, whereas synchronous modulation time-resolved step-scan FT-IR experiments are used to monitor both rise and decay processes in response to AC electric fields. In the pulsed experiments the change is infrared transmission as an explicit function of time is used to extract the dynamic information, while in the synchronously modulated measurements the phase of the response signal and/or its in-phase and quadrature components, is determined. In both types of experiments the absolute and relative rates of reorientation of the separate functional groups of the liquid crystal molecules in response to the perturbation are observable in terms of intensity changes in their characteristic absorption bands. In the synchronous modulation measurements, the submolecular view of the dynamics of liquid crystal director reorientation is enhanced by frequency correlation analysis, to yield 2D FT-IR spectra. In preliminary studies (*Chem. Phys. Lett.*, **179**, 491 (1991)) we have shown how these techniques can be used to distinguish the reorientation behavior of the rigid and flexible parts of nematic LC molecules. In this paper we will present new and expanded studies of related nematic LC's as well as smectic *C (ferroelectric) LC phases studied both by step-scan and stroboscopic continuous scan IR techniques.

314 CHEMICAL IMAGING IN BIOLOGY AND MEDICINE USING ION MICROSCOPY.

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The ability to quantitatively map the distribution of elements on the micrometer scale and smaller with high sensitivity and isotopic discrimination is unique to ion microscopy. The information contained in ion images can be crucial to the study of the solid state, where chemical heterogeneity is often directly related to observed behavior. The tools of digital image processing allow the extraction of quantitative information from the image data. These techniques coupled with improved instrumentation for the detection of ion images drastically increase the problem solving capabilities of the ion microscope. The use of such methods and instrumentation in the ion microscopic analyses of cell cultures and tissues of biological and biomedical relevance will be discussed.

315 COMPOSITIONAL SIMS QUANTIFICATION USING THE CsM^+ MOLECULAR ION METHOD.

H. E. Smith and W. C. Harris, Digital Equipment Corporation, 77 Reed Road, Hudson, MA 01749.

In dynamic SIMS analyses using Cs^+ primary ion beams, cesium-containing molecular secondary ions (CsM^+) are formed with relatively high abundances for many elements (M). This offers an alternative to typical elemental quantification in which electronegative elements are detected as elemental M^- secondary ions using a Cs^+ beam, or electropositive elements are detected as M^+ using an O_2^+ beam. These CsM^+ ions have been shown in some instances to be far less susceptible to composition-induced secondary ion yield variations than the M^- and M^+ elemental ions, offering the promise of quantification without compositional effects ("matrix effects"). CsM^+ analysis has been particularly successful in quantitative compositional depth profiling of III-V compound semiconductors. However, CsM^+ ions are not free from matrix effects in all cases. The formation and yield of CsM^+ ions from various compositions using a CAMECA ims-4f SIMS instrument will be discussed and compared with the corresponding elemental ion species. Composition-dependent CsM^+ ion yield variations are related to variations in sputter yield and surface cesium concentrations on the sputtered surface. An empirical correction procedure is also proposed which takes these effects into account, providing quantification of CsM^+ depth profiles. Results for both major element profiling ($M > 1$ atom %) and dopant profiling ($M < 1\%$) in layered samples will be presented.

316 APPLICATIONS OF SIMS IN MODERN METALLURGY. Jennifer A. Jackman, Metals Technology Laboratory, Canada Centre for Mineral and Energy Technology, Energy, Mines and Resources Canada, 568 Booth St., Ottawa, Canada K1A 0G1.

Secondary Ion Mass Spectrometry is not a routinely used tool in metals research despite the obvious advantages of extremely good detection limits for almost the entire periodic table, coupled with imaging and depth profiling capabilities. The reasons for a reluctance on the part of the metals research community to adopt this technique stem from difficulties in interpretation and quantification of data. SIMS is based on an atomic sputtering process combined with ionization, and both the sputter rates and ionization probabilities are extremely variable and depend on impurities, crystallographic orientation and the presence of alternate phases. These problems are present to a lesser degree in semiconductors because they tend to be much purer, mono-crystalline and rarely include second phases. This talk, while illustrating some of the difficulties analyzing metals with SIMS, reviews the considerable effort which has been undertaken to overcome many of these problems, allowing researchers to access the rapid data acquisition rates and remarkable detection limits of SIMS. Examples of imaging and depth profiling to study diffusion and segregation of elements in metals and alloys demonstrates that SIMS can make a unique contribution to the understanding of modern metallurgical processes. Recent advances in instrumentation will also be discussed.

317 ANALYSIS OF TRAPPED AND QUENCHED SILICATE MELT BY SIMS: APPLICATION TO VOLCANIC ERUPTIONS. James D. Webster, Department of Mineral Sciences, American Museum of Natural History, Central Park West at 79 Street, New York, NY 10024-5192.

Volcanic glass occurs as inclusions within minerals in volcanic rocks, and these inclusions range from less than 1 micron to approximately 150 microns in diameter. Glass inclusions are trapped and quenched silicate melt (Magma), and in many cases are chemically representative of the Magma. To better understand the processes involved during volcanic eruptions, abundances of the volatiles H_2O, CO_2, F, Cl, and B in class inclusions from volcanic rocks have been determined by SIMS, because these volatiles provide the driving force for volcanic eruptions. The results of analyzing glass inclusions in volcanic rocks from Western North America, Ascension Island, and Ethiopia will be presented and discussed.

318 HIGH RESOLUTION SIMS IMAGING OF FCC CATALYSTS. J. K. Lampert, G. S. Koermer and M. Deeba, Engelhard Corporation, 25 Middlesex Tpke., Iselin, NJ 08830. R. Levi-Setti and J. Chabala, Department of Physics, The University of Chicago, 5640 South Ellis Ave., Chicago, IL 69637.

We have used a scanning ion microprobe to study the chemistry and morphology of fluid catalytic cracking (FCC) catalysts. Modern cracking catalysts used to convert heavy hydrocarbons into fuels are approximately 70 µm diameter microspheres of crystalline zeolite Y in an amorphous silica alumina matrix. High resolution (ca. 50 nm) element maps clearly distinguish the zeolite and matrix regions in the microspheres. Analysis of laboratory prepared catalysts show that phase morphology and composition depend on the precursor microsphere's method of synthesis and composition. This in turn affects the distribution of sodium and absorbed catalyst poisons nickel and vanadium. Preferential adsorption is observed for these elements, with some migration from one phase to another after hydrothermal treatment.

319 UNDERSTANDING OXIDE FORMATION ACROSS LIQUID SURFACES: AN IMAGING SIMS ANALYSIS. Jan M. Chabala and Riccardo Levi-Setti, Enrico Fermi Institute and Department of Physics, The University of Chicago, 5640 S. Ellis Ave., Chicago, IL 60637.

The lateral development of oxide over the surface of liquid metals has rarely been studied. This oversight is remarkable when compared to the extensive research focused on the oxidation of solids. Numerous questions concerning the initial stages of oxidation on both liquids and solids remain unanswered. We employ high spatial resolution imaging secondary ion mass spectrometry to monitor the growth and organization of oxide as it forms on a number of liquid metals (Ga, GaBi, GaIn, Al-based alloys). These in situ investigations are performed with the University of Chicago scanning ion microprobe, with a lateral resolution of ~50 nm. The oxide forms unanticipated fractal-like structures over the liquid. The development of these structures provides clues about the roles of impurities and surface imperfections on the oxidation process. In addition, information about the oxidation kinetics can be deduced from the oxide growth rate.

This research is supported by the NSF Materials Research Laboratory at the University of Chicago.

320 EFFECT OF HIGH INTENSITY SOURCE PULSING ON DETECTION LIMITS FOR GRAPHITE FURNACE AAS WITH A CONTINUUM SOURCE AND PHOTODIODE ARRAY DETECTION. James M. Harnly, USDA, Nutrient Composition Laboratory, Bldg. 161, BARC-East, Beltsville, MD 20705.

One method for obtaining increased intensity from a xenon short arc lamp is to pulse the current. An advantage over non-pulsed lamps is achieved because the intensity ratio (pulsed/non-pulsed) is proportional to the current ratios raised to the 2.3 power. In addition, if the burst of pulses lasts only a short period of time (eg. pulsing at 50 Hz for 5 s) and a long recovery period is allowed between bursts or (eg. 2 min while the furnace cools and the next sample is dried and ashed), then a 300 W lamp can be operated at close to 600 W during the burst. To date, 0.5 ms pulses of 20, 40, 60, and 80 A have been superimposed on a simmer current of 20 A. With 20 ms between pulses, the duty cycle is 2.5% and the power levels are 193, 304, 316, and 329 W, respectively. These pulses produced increases in the integrated intensities of 9, 19, 28, and 37%, respectively. The intensity ratios correspond to the current ratios raised to powers of 1.8, 1.7, 1.6, and 1.5, respectively. These values are lower than the manufacturers predicted value of 2.3. One reason for the poorer performance is a decrease in the simmer intensity during the pulsing regime. This decrease may be due to stress on the lamp induced by the pulses or a result of cross-talk between the power supplies. Pulsing at higher currents, higher duty cycles, and higher power levels will be reported.

321 SIMULTANEOUS DETERMINATION OF CADMIUM AND CALCIUM IN URINE BY CONTINUUM SOURCE ATOMIC ABSORPTION SPECTROMETRY. Reshan Fernando, Fanny K. Ennever and Bradley T. Jones, Department of Chemistry, Wake Forest University, Winston-Salem, NC 27109.

A new instrument will be described which provides for the simultaneous determination of Cd and Ca in urine samples. The continuum source atomic absorption spectrometer employs a xenon arc lamp, a graphite furnace atomizer, and a photodiode array detector. Detection limits for the new system are approximately one order of magnitude lower than those reported for previous continuum source AA instruments. For example, the detection limit observed for Cd is 0.01 ng/mL, the same level observed with commercially available line-source systems. By monitoring the strongest absorption line for Cd (228.8 nm) and a very weak absorption line for Ca (227.5 nm), the two elements are determined without the need for multiple dilutions, even though they are present in urine at drastically different levels. The multi-element capacity of the present system also provides for the use of Bi (227.7 nm) as an internal standard to correct for variations in the atomization procedure. The relationship between Cd body burden and increased Ca excretion in post-menopausal women has been investigated in an attempt to establish Cd exposure as a risk factor for osteoporosis.

322 CHARACTERISTIC MASSES AND DETECTION LIMITS FOR GRAPHITE FURNACE AAS WITH A CONTINUUM SOURCE AND A PHOTODIODE ARRAY DETECTOR. James M. Harnly, USDA, Nutrient Composition Laboratory, Bldg. 161, BARC-East, Beltsville, MD 20705.

Using a photodiode array, wavelength integrated absorbance, A, is computed as:

$$A = \Sigma \log(I_i/I_{Ref}) \quad i = 1, n,$$

where I_i is the intensity of each of the n sample pixels selected to cover the absorption profile and I_{Ref} is the average intensity of n reference pixels selected symmetrically from both sides of the profile. The number of sample pixels, n, is dictated by the entrance slit width but A is independent of the slit width. Propagation of errors shows that the uncertainty for the wavelength integrated absorbance is:

$$\sigma_A = (0.43\ \sigma_r/I)\sqrt{n + 1}$$

where σ_r is the pixel readout noise. The uncertainty of the temporally integrated absorbances, σ_{At}, is:

$$\sigma_{At} = \sigma_A\sqrt{T/f}$$

where T is the time necessary to integrate over the analytical signal and f is the data acquisition frequency. Thus, the absorbance noise can be computed for any wavelength and any slit width from the measured intensity. Character masses and detection limits will be reported for a series of elements.

323 MULTIELEMENT DETECTION BY ELECTROTHERMAL ATOMIZATION MASS SPECTROMETRY USING SECOND SURFACE TRAPPING.

Andrew J. Scheie and James A. Holcombe, Department of Chemistry and Biochemistry, The University of Texas at Austin, Austin, TX, 78712.

ETA/AA using a second surface atomizer[1,2] has proven to be an effective method for reducing matrix effects for ultra-trace analysis. However, with AA detection, it does not possess multielement or isotopic capabilities. This research attempts to couple the trapping advantages of the second surface with the detection advantages provided by mass spectrometry. A new ETA/MS system will be discussed involving a modified graphite furnace, an atmosphere/vacuum interlock, and MS with electron impact ionization. Within the MS chamber, the analyte is thermally desorbed from the Ta second surface.

1. T. M. Rettberg and J. A. Holcombe, *Anal. Chem.* **58**, 1462 (1986).
2. T. M. Rettberg and J. A. Holcombe, Anal. Chem. **60**, 600 (1988).

324 DETERMINATION OF ULTRA-TRACE AMOUNTS OF COPPER, CADMIUM, LEAD AND COBALT IN SEAWATER BY GRAPHITE FURNACE ATOMIC ABSORPTION AND LASER EXCITED FLUORESCENCE WITH A FLOW-INJECTION ON-LINE PRECONCENTRATION SYSTEM.

Mohui Wang, Alexander I. Yuzefovsky and Robert G. Michel, Department of Chemistry, University of Connecticut, Box U-60, Storrs, CT 06269.

Ultra-trace amounts of Cu, Cd, Pb and Co in seawater can be determined by graphite furnace atomic absorption and graphite furnace laser excited atomic fluorescence spectrometry following flow-injection on-line preconcentration. A micro preconcentration column packed with C18-bonded silica reversed-phase sorbent is used to extract metal-DDC complexes. The effects of flow rates, pH of the sample solution and the concentration of the complexing agent are studied. Columns with different shapes and volumes are compared. By this proposed system, matrix modifiers are not required, and at least an eight-fold preconcentration of the analyte can be expected.

325 USE OF RECIRCULATING LOOP FLOW INJECTION TECHNIQUES FOR SAMPLE INTROUCTION IN GRAPHITE FURNACE ATOMIC ABSORPTION SPECTROMETRY.

R. M. LaRue and J. F. Tyson, Department of Chemistry, University of Massachusetts, Amherst, MA 01003.

The combination of flow injection techniques and graphite furnace atomic absorption spectrometry (GFAAS) is not widely used due to the transient nature of the flow injection signal and the short analysis time of GFAAS. Through use of a recirculating loop, the timing problem is eliminated as, after complete dispersion has occurred, the concentration of analyte is the same throughout the loop. Sampling can then be performed by a GFAAS autosampler from the recirculating loop. This technique has been applied to the determination of Pb in water samples. Experiments involving partially and completely filled recirculating loops have been performed. Use of a partially filled loop is advantageous in that calibration of the recirculating loop volume is not needed, as a known volume is passed into the loop. It is also possible to preconcentrate the Pb in the water samples in order to increase sensitivity. Ion exchange resins and C-18 columns have been used to preconcentrate the Pb in the water samples. The analysis of spiked deionized water samples has shown close agreement between the experimental and the theoretical results with preconcentration on a cation exchange resin followed by release into the recirculating loop through an appropriate eluent. Cation exchange resins do not demonstrate the same efficiency for pond and tap water samples. Use of a C-18 column has shown more accurate results for the same type of analyses. Complexation of the Pb in the samples with DDC allows the Pb to be preconcentrated on the C-18 column, followed by release into the recirculating loop.

326 ON-LINE SEPARATION AND PRECONCENTRATION FOR ELECTROTHERMAL ATOMIC ABSORPTION SPECTROMETRY.

L. C. Azeredo, UFRRJ, Depto. de Quimica, Km 47 Antiga, Estr. Rio-SP., Rio de Janeiro, Brazil. R. E. Sturgeon, Institute for Environmental Chemistry, National Research Council of Canada, Ottawa, K1A 0R9, Canada.

Off-line preconcentration and separation of trace elements using batch procedures is an effective means of improving detection power and selectivity for atomic spectrometric techniques. Unfortunately, these approaches are often time consuming, require large sample volumes and clean areas for sample processing so as to minimize contamination. In contrast to this, on-line techniques are eminently suited to the problems of ultra-trace analyses as they exhibit none of the above deficiencies. A discontinuous micro-scale preconcentration system, based on chelation of trace metals with a 20 μl column of silica-immobilized 8-hydroxyquinoline, was interfaced with an electrothermal atomic absorption spectrometer. With 835 μl sample loop injections and elution of the trace metals directly into the furnace in 48 μl volumes of acid, quantitative recovery of Fe, Cd, Zn, Cu, Ni, Mn and Pb from open ocean seawater could be realized with a frequency of 10–20 per hour. Sensitivity is enhanced up to 250-fold over that achieved using direct injection of a 20 μl sample volume. Detection limits were 0.3, 6.9, 4.2, 1.8, 10.2, 5.7 and 1.8 pg for Cd, Cu, Fe, Mn, Ni, Pb and Zn, respectively, in a seawater matrix. The design, operation and performance of this system will be described.

327 DETERMINATION OF As AND B BY HOLLOW CATHODE-FURNACE ATOMIZATION NON-THERMAL EXCITATION SPECTROMETRY.

Clare Smith, Philip Riby and James Harnly, USDA, Nutrient Composition Laboratory, Bldg. 161, BARC-East, Beltsville, MD 20705.

Hollow anode-furnace atomization non-thermal excitation spectrometry (HA-FANES) with a high pressure He plasma was used to determine As and B. The analytical signal and the signal-to-noise ratio were measured as a function of the discharge pressure and current. For both As and B, a linear increase in the integrated analytical signal was observed with increasing pressure up to a 600 Torr. At a given pressure, the signal-to-noise ratio decreased at the highest and lowest currents. At intermediate currents the plasma was stable, while at the extremes, the plasma was less stable and the background noise levels were higher. The detection limits were 45 and 2 pg for As and B, respectively. The detection limit for As was within a factor of 2 of that for conventional graphite furnace AAS while the detection limit for B is 2 orders of magnitude better than that for conventional AAS.

328 FAPES: A BIASED APPROACH.

R. E. Sturgeon, V. T. Luong and S. N. Willie, Institute for Environmental Chemistry, National Research Council of Canada, Ottawa, K1A 0R9, Canada.

The analytical potential of FAPES appears to be well appreciated, yet fundamental information characterizing this new emission source is clearly lacking. Improved understanding is required before logical action can be implemented which will systematically optimize performance and minimize interferences. One noteworthy parameter appears to be the d.c. self-bias potential which develops in this asymmetric rf system. The effect of d.c. bias control on plasma gas and analyte excitation temperatures as well as analyte signals and background spectra will be presented which illustrate the influence this parameter plays on detection power.

329 CHARACTERIZATION OF A HELIUM PLASMA IN HOLLOW ANODE-FANES.

Philip G. Riby and James M. Harnly, USDA, Nutrient Composition Laboratory, Bldg. 161, BARC-East, Beltsville, MD 20705.

A helium plasma was characterized for hollow anode-furnace atomization non-thermal excitation spectrometry. Sensitivity, like residence time, was found to be directly proportional to pressure. This suggests that the efficiency of the plasma in exciting the analyte is not a function of pressure. Thus, stabilization of a plasma at higher pressures was an analytical advantage. It was possible to sustain a plasma at pressures as high as 900 Torr although analytical results were only obtained at pressures up to 600

Torr. Operation of the plasma at higher pressures also reduced the influence of the thermionic electrons on the excitation temperature. When the cathode temperature exceeds 1500° C the discharge potential drop from in excess of 200 V to 30–50 V. At a pressure of 200–600 Torr there is less than a 10% variation in the excitation temperature over the atomization cycle. A similar resistance of the high pressure He plasmas to large, low energy electron fluxes was observed for easily ionized elements. The effect of NaCl on the discharge potential at higher pressures was much less dramatic than at lower pressures.

330 EFFECTS OF WATER VAPOR ON PLASMA REACTIONS IN GLOW DISCHARGE MASS SPECTROMETRY (GDMS).

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Glow discharge mass spectrometry (GDMS) is a technique often used for the elemental analysis of solid materials. It has been shown that GDMS processes are susceptible to contaminant species that may be present in the mass spectrometer ion source. Some species that are often found in the GDMS ion source are water vapor and the products from its reactions. The presence of water vapor in the ion source, with a content of as little as 2.5%, will produce a spectrum that is dominated by ions at mass-to-charge 18 and 19 (corresponding to H_2O^+ and H_3O^+). Water vapor in the source may exhibit a variety of reactions, most of which are detrimental to mass spectral analysis by GDMS. Water vapor in the source has been found to depopulate the metastable argon atoms by an efficient transfer of energy from the metastable species to the water molecule. This greatly affects the ionization of sputtered species, since metastable collisions provide the primary ionization path. Glow discharge sputtering may also be affected since low mass dissociation products such as hydrogen may carry a large portion of the discharge current, but contribute little to sputtering. The removal of water species from mass spectrometer ion source will occur with sputtering time, but the efficiency and speed is dependent on the cathode material. These interactions as well as others will be discussed in this presentation.

331 DETERMINATION OF NON-METALS IN VAPORS BY GAS-SAMPLING GLOW DISCHARGE-ATOMIC EMISSION SPECTROMETRY.

Rosario Pereiro, Timothy K. Starn and Gray M. Hieftje, Department of Chemistry, Indiana University, Bloomington, IN 47405.

At present, the helium microwave induced plasma (MIP) and the helium ICP are viewed as the atomic emission detectors of choice for the determination of non metals, such as sulfur, carbon and the halogens. However, although relatively unexplored, the high excitation energy and low background of a glow discharge make it, too, a promising candidate for the measurement of non-metals. In the present report, a gas-sampling glow discharge device (GSGD) is investigated for the determination of non metals in vapor-phase samples. Details of construction, performance optimization, and analytical characteristics of the new source are evaluated for the determination (at the PG/S mass-flow level) of carbon, halogens (fluorine, chlorine) and sulfur. Finally, preliminary results obtained with the GSGD for the quantification of element ratios among C, S, Cl, F, in different organic compounds will be presented, along with an evaluation of the potential of this novel plasma source as a detector for gas chromatography.

332 THERMABEAM AQUEOUS SAMPLE INTRODUCTION INTO A HOLLOW CATHODE DISCHARGE.

J. You and R. Kenneth Marcus, Department of Chemistry, Clemson University, Clemson, SC 29634-1905.

The wide applicability of glow discharge sources to direct solids analysis has lead to growing interest. In addition to solids analysis, we are interested in this laboratory in the possible applications of the devices for the analysis of volume-limited solution samples. Towards this end, an interface for introducing aqueous samples from a liquid chromatograph into a hollow cathode discharge has been developed. Specifically, a particle beam interface has been employed to introduce analytes in particle form into the discharge volume. A thermal, concentric nebulizer serves to produce a fine aerosol directly into a heated spray chamber for efficient desolvation. Use of a differentially pumped momentum separator results in the introduction of analyte particles of <2 microns in diameter. The hollow cathode is mounted in a heated (50–200° C) block, inducing thermal dissociation of the analyte particles into free atoms which are subjected to excitation collisions within the glow discharge. Data will be presented illustrating the effects of nebulizer conditions on sample introduction efficiency and the role of discharge conditions on analyte excitation.

333 THE GLOW DISCHARGE AS AN ANALYTICAL EMISSION SOURCE FOR FOURIER TRANSFORM SPECTROSCOPY.

Michael R. Winchester, John C. Travis and Marc L. Salit, Inorganic Analytical Research Division, National Institute of Standards and Technology, Gaithersburg, MD 20899.

The Fourier transform spectrometer has long been recognized to possess several inherent advantages over the more traditional scanning monochromator instrument, including higher spectral resolution, higher throughput, and a more accurate and precise wavenumber registration. However, the multiplex advantage inherent in the infrared region of the spectrum is lost in the ultraviolet-visible region, due to the fact that multiplicative source noise is usually limiting in the latter. In fact, a multiplex disadvantage may exist, in which noise from intense spectral features is written in the transform process into all spectral regions to some degree, such that weaker spectral features are lost in noise. This is particularly cumbersome, since in most applications, the smaller features are the desired ones. As a result, it is doubtful that FTS in the UV-VIS will ever become a standard analytical technique for the general purpose laboratory. However, the technique still holds specific applicability in specialized problems in which the attributes, particularly the resolution, can be exploited. For this reason, there is a need to investigate methods to reduce the severity of the multiplex disadvantage. One possible partial solution for FT atomic emission spectroscopy is to employ the glow discharge as the emission source, instead of the more traditional inductively coupled plasma, due to the fact that the glow discharge is a relatively quiet source. Additionally, techniques such as ratio recording, dual channel subtractive noise cancellation, use of pooled data, and bandwidth limitation through the use of optical filters may be employed to reduce the effects of multiplicative noise. This talk will be concerned primarily with the application of pooled data and bandwidth limitation for this purpose. Specifically, the advantages of utilizing the glow discharge as the emission source will be discussed.

334 APPLICABILITY OF LOW-PRESSURE DISCHARGES TO THE ANALYSIS OF NON-CONDUCTING MATERIALS.

S. Caroli, O. Senofonte, M. G. Del Monte Tamba and I. Brenner, Istituto Superiore Di Sanita', Viale Regina Elena 299, 00161 - Rome, Italy.

The suitability of glow discharges for the analysis of major, minor and trace elements in a variety of matrices is well corroborated by experience accrued to date. To further elucidate the potential of these sources, their two basic versions, namely the hollow cathode and the flat cathode discharges, were tested in application areas not yet fully developed. In the first instance a hollow cathode tube was boosted by superposing a microwave field at 2450 MHz to better its detection power. Several analytes (Al, As, P, Pb, S, Sb, Si, Sn and Ti) were quantified in aqueous solutions after drying. This considerably enhanced the spectral emission compared to that of a conventional source, as demonstrated by Burn-off curves and calibration graphs. In the second case an investigation was carried out to assess the capability of the flat cathode glow discharge for characterizing and assaying electrically non-conducting powders. This sputtering mode was used to elucidate the mineral composition and morphological features of coastal maine sediments previously processed for preparing a new multielemental reference material. Assumptions on the ablation mechanism were also formulated. Both examples testify the wide range of possibilities offered by these types of discharge.

335 THE APPLICATION OF A MICROWAVE BOOSTED GLOW DISCHARGE LAMP TO THE ANALYSIS OF NON-CONDUCTING POWDERS.

Franz Leis, Institut für Spektrochemie und angewandte Spektroskopie, Bunsen-Kirchhoff-Straße 11, D-4600 Dortmund 1, Bundesrepublik Deutschland.

Non-conducting powders can be analyzed by different methods, for example X-ray fluorescence or optical emission spectroscopy using dc-arcs, ICPs, or glow discharges. Each method has some inherent limitations. Generally, the use of glow discharges is restricted to the analysis of electrically conducting samples. Non-conducting powders can be mixed with a conducting matrix (copper or silver powder) and pressed to a pellet of a suitable form. However, by this process the concentrations of elements in the original sample are diluted by a factor depending on the mixing ratio of sample to copper. This leads to difficulties if low concentrations have to be determined as, for example, in ceramic powders which are the basic substances for the production of sintered ceramics. In this situation the microwave boosted glow discharge source with its higher power of detection compared to conventional glow discharge sources appears to be a suitable means for overcoming these difficulties. Disk shaped samples were prepared by mixing different ceramic powders with copper powder and analyzed by optical emission spectroscopy using a high resolution monochromator.

336 PRACTICAL APPLICATIONS OF QUANTITATIVE DEPTH PROFILE ANALYSIS BY GLOW DISCHARGE ATOMIC EMISSION SPECTROMETRY. Joel Mitchell and Johnna Shirley, Leco Corporation, 3000 Lakeview Ave., St. Joseph, MI 49085. Vince Caldwell, Armco Research & Technology Center, Door 225, Middletown, OH 45043.

Techniques ranging from SIMS through wet chemical stripping have been employed to characterize coatings and coating interfaces. Glow discharge source (GDS) atomic emission analysis has developed into a rapid method for obtaining quantitative depth profile (QDP) information. GDS provides analytical results within one to ten minutes, and sub-micron depth resolutions. A variety of coatings and surface treatments have been characterized by GDS-QDP. These analyses range from the determination of coating thickness of electro-galvanized steel to the characterization of induced elemental migration in steel products. Results of these analyses will be presented along with some of the practical capabilities and limitations of the technique.

337 AN ON-LINE METHOD FOR THE ANALYSIS OF SEAWATER BY INDUCTIVELY COUPLED PLASMA MASS SPECTROMETRY. J. W. McLaren, M. A. Azeredo, J. W. H. Lam and S. S. Berman, Institute for Environmental Chemistry, National Research Council of Canada, Ottawa K1A 0R6, Canada.

The relatively high salt content of seawater generally precludes its direct analysis by ICP-MS. Even if the obvious problems of salt deposition on the torch, sampling interface, or ion lenses can be avoided by the use of flow injection techniques instead of continuous nebulisation, at least a 10-fold dilution is necessary in order to alleviate severe suppression of sensitivity by the high salt concentration. This unavoidable dilution will place the concentrations of all but a few of the elements of environmental interest too low for accurate determination. A method for the ICP-MS determination of trace elements in seawater which has been in use in our laboratory for several years involves a separation of the analytes from the major seawater ions by passage of a 500 mL sample through a small column of silica-immobilized 8-hydroxyquinoline (I-8-HOQ), followed by elution with 10 mL of an HCl/HNO$_3$ acid mixture. This paper will describe modifications made to the commercially available Dionex "IC/ICP" Chelation Concentration System for on-line preconcentration which permitted the simultaneous determination of Mn, Ni, Cu, Zn, Cd and Pb in 5 mL seawater samples in under 15 minutes. Results obtained with the standard MetPac CC-1 columns will be compared with results obtained with I-8-HOQ columns.

338 THE MEASUREMENT OF TRACE ELEMENTS IN LARGE RIVERS BY ICP-MS. Howard E. Taylor and John R. Garbarino, USGS-WRD, 3215 Marine Street, Boulder, CO 80303.

Inductively coupled plasma-mass spectrometry has been successfully used for the measurement of dissolved trace elements in the study of the water quality of large rivers. Techniques are described for the sampling and measurement of AL, As, B, Ba, Be, Cd, Co, Cr, Cu, Li, Mn, Mo, Pb, Sr, Tl, V and Zn at microgram and submicrogram per liter concentration levels in the Mississippi and Colorado rivers. Data is presented showing the significance of the occurrence and distribution of these low concentration dissolved constituents.

339 CHARACTERIZATION OF TRACE METALS IN GROUND WATER IN SOUTHERN NEVADA BY ICP-MS. K. Zarrabi, M. Amano, V. Hodge and K. Stetzenbach, Harry Reid Center for Environmental Studies, University of Nevada, Las Vegas, Las Vegas, NV 89154.

This study is developing an origin identification method for ground water by detailed chemical analysis ("fingerprinting") of the aquifers in the Yucca Mountain, Nevada region. A great deal of information can be obtained from the concentration profile of the rare earth elements and the transition metals. This information is relatively easy to obtain at the trace and ultra trace level by ICP-MS. We have collected ground water and spring water samples from the southern Nevada region, including the Nevada Test Site, the Spring Mountains, Amargosa Valley, and Death Valley National Monument. Samples are analyzed by ICP-MS, IC, and field measurement parameters such as pH, alkalinity, dissolved oxygen, TDS, etc., are also taken. This generates large volumes of data which are difficult to interpret. Computer data reduction techniques such as factor analysis are used to reduce the volume of data without losing the variability among the samples. The first tier of data analysis reveals distinct differences between waters of different origin (well water vs. spring water). The second tier data analysis reveals further classification of water within a region (Spring A vs. Spring B). The expanded data base will allow us to identify blind water samples using this approach.

340 DETERMINATION OF SOURCES OF LEAD IN TAP WATER BY ICP-MS. G. S. Hall, Dept. of Chemistry, Rutgers University, New Brunswick; NJ, 08903; E. Murphy, Division of Science & Research, New Jersey Department of Environmental Protection and Energy, Trenton, NJ 08625.

ICP-MS was used to measure lead concentrations and its isotope ratios in concomitantly obtained tap water and plumbing materials (solder, fixtures, Cu and Pb pipe). Lead concentrations were determined by external calibration using BI as an internal standard and by summing integrated areas from PB-206, PB-207, and PB-208. Isotope ratios were determined by normalization to NIST SRM-981. Plumbing materials were dissolved in dilute ultra-pure nitric acid. Using PB isotope fingerprints, our data show that most of the PB in tap water is derived from CU pipe (PB = 0.8%). When the isotope ratios did not match any of the plumbing materials, we used a two source mixing model to apportion the PB source to different plumbing materials. Detailed sample preparation, instrument optimization, PB mixing equations, and applications to consumer tap water samples will be presented.

341 SOURCE IDENTIFICATION OF LEAD AND OTHER METALS AT MINERAL PROCESSING SITES USING INDUCTIVELY COUPLED PLASMA MASS SPECTROMETRY. Michael E. Ketterer, U.S. Environmental Protection Agency, National Enforcement Investigations Center, Box 25227, Building 53, Denver Federal Center, Denver, CO 80225.

Under the Comprehensive Environmental Response, Compensation, and Liability Act (CERCLA or "Superfund"), the EPA is obligated to prove that parties are responsible for environmental releases of "hazardous substances." These hazardous substances include metals such as lead, cadmium, arsenic, copper, zinc, nickel, chromium, and antimony. Many sites presently exist in the continental U.S. which have become contaminated as a result of mining, milling and metal processing of nonferrous ore materials. The present paper will discuss the applications of inductively coupled plasma mass spectrometry to developing the requisite evidence for such CERCLA cases. A case study will be presented where sources of lead are investigated at a mining/smelting site using a combination of lead isotope ratio measurements and elemental constituents analysis. It will be shown that ICP/MS lead isotope ratio data are well-suited for environmental source identification purposes.

342 COMPARISON OF ICP-MS WITH ZEEMAN GFAAS FOR THE ASSESSMENT OF THALLIUM EXPOSURE. D. E. Nixon, M. M. Kershisnik, T. P. Moyer and K. O. Ash, Metals Laboratory, Section of Clinical Biochemistry, Mayo Clinic, Rochester, MN 55905 and Department of Pathology, Associated and Regional University Pathologist, University of Utah Medical Center, Salt Lake City, UT 84132.

The symptoms of thallium exposure are polyneuritis and hair loss. The pathognomonic feature of exposure is excess thallium in body fluids, particularly urine. In recent years, Graphite Furnace Atomic Absorption Spectrometry has become the benchmark technique for the assessment of thallium exposure. With palladium as modifier, Zeeman GFAAS sensitivity is 1.4 μg/L with a detection limit of 1 μg/L. In contrast, the Inductively Coupled Plasma-Mass Spectrometry detection limit is 0.1 μg/L in diluted specimens. Thirteen samples (2 sera, 1 blood, and 10 urines) containing physiologic concentrations of thallium (25 to 2424 μg/L) were compared. The correlation equation is $y = 1.022x + 0.83$ with a correlation coefficient of 0.99952.

343 ANALYSIS OF MERCURY IN VACUUM PUMP OIL (U). Matthew E. Chisum and Arnie A. Duncan, Mason & Hanger, Silas Mason Co., Inc., Analytical Chem Lab, P.O. Box 30020, Amarillo, TX 79177.

The determination of trace concentrations of mercury by colorimetric methods, cold vapor atomic absorption and more recently, atomic fluorescence, has become widely accepted. All of these methods have their limitations, e.g., detection limits, matrix effects, memory effects, automation, and analysis time. A routine method for the determination of mercury in oil by inductively coupled plasma-mass spectrometry (ICP-MS) is described. Detection limits are typically less than 1.0 μg/L utilizing only a 0.25 gram sample. Alternate methods and various matrices are discussed.

344 MULTIELEMENTAL ANALYSIS OF TREE RINGS BY ICP-MS. G. S. Hall, Dept. of Chemistry, Rutgers University, New Brunswick, NJ 08903. X. Wu and E. T. Williams, Dept. of Chemistry, City University of New York, Brooklyn College, Brooklyn, NY 11210.

ICP-MS was used to determine the concentrations of multielements in tree rings. Emphasis was placed on the quantification of rare earth elements (REE). Individual tree rings (California giant sequoia) were prepared by microwave digestion. Solutions were spiked with indium as an internal standard and analyzed on a VG plasmaquad PQ+ turbo ICP-MS. The objective of the study was to determine the growth response of trees that were subjected to forest fires. When tree-ring element chronologies are plotted, our data show elemental spikes that correspond to the fire year. Data can be used to date forest fires and to investigate elemental translocation in wood. Detailed instrument optimization, sample preparation, and data handling will be discussed.

345 DETERMINATION OF RADIUM-226 IN DRINKING WATER BY ICP-MS. V. F. Hodge, University of Nevada Las Vegas, Las Vegas, NV 89154. G. A. Laing, Lockheed Engineering & Sciences Company, 980 Kelly Johnson Drive, Las Vegas, NV 89119.

This study evaluates the use of ICP-MS for the determination of radium-226 in drinking water. The detection limit as required by the U.S. EPA is 1 pCi/L or the mass equivalent of 1 pg/L. Current methodology involves concentration and separation of radium-226 from the sample, and measurement of its daughter product radon by scintillation counting. It is a labor intensive procedure involving wet chemistry to concentrate the radium-226, a long in-growth period (2–3 weeks), and a lengthy counting procedure (8 hours). An alternate method using ion exchange sample preparation and alpha counting has been proposed, but still requires a long counting time (30+ minutes). In this investigation, samples were prepared using the ion exchange sample preparation procedure followed by rapid ICP-MS detection. The ion exchange sample preparation procedure was also modified to take advantage of the ICP-MS technique. The results are compared to those obtained by alpha spectroscopy (after the ion exchange sample preparation). Both spiked drinking water samples and EPA intercomparison samples with known radium concentrations were analyzed. Excellent results were obtained. The ICP-MS method detection limit is 1 pg/L and analysis time is less than 3 minutes. Sample recoveries for ICP-MS were equivalent to those from alpha spectroscopy (71 ± 2% versus 72 ± 3%). After modifying the ion exchange sample preparation procedure, the ICP-MS analysis resulted in an average recovery of 97 ± 4%. In conclusion, this work has demonstrated that ICP-MS is an alternative analytical tool for radium-226 analysis that provides adequate sensitivity while decreasing analysis times significantly.

346 SEPARATION AND IDENTIFICATION OF THE METABOLITES OF PARA-AMINOPHENOL. Zimeng Yan and John G. Nikelly, Department of Chemistry, Philadelphia College of Pharmacy & Science, 600 South 43rd Street, Philadelphia, PA 19104.

Para-aminophenol (PAP) which induces kidney toxicity is one of the most important metabolites of acetaminophen. The separation and isolation of the PAP metabolites from the biomatrix, e.g. urine, plasma, etc, is one of the most important steps in the study of the metabolism and toxicity of this compound. Hepatocyte is a good model in drug metabolism study, which can represent the properties of the liver *in vivo*, and the isolated enzymes *in vitro*. In the study of PAP metabolism, the hepatocytes isolated from rat liver are incubated with PAP in a buffer for a ten hour period. During this time, the PAP metabolites are separated from the biomatrix by precipitating the proteins by adding an organic solvent and centrifuging. The supernatant containing the PAP metabolites is analyzed with a RP-HPLC system suing a C_{18} column and a mobile phase CH_3CN/H_2O (8/92). The proposed PAP metabolites, such as the conjugates of glutathione, sulfate, glucuronic acid, etc, are compared with synthesized compounds.

347 ANALYSIS OF LIPASE CATALYZED INTERESTERIFICATION OF TRIGLYCERIDES BY HIGH PERFORMANCE LIQUID AND GAS LIQUID CHROMATOGRAPHY. Kimberly A. Petruso, Chestnut Hill College, 600 East Mermaid Lane, Philadelphia, PA 19118. Thomas A. Foglia, Eastern Regional Research Center, USDA, ARS, NAA, Philadelphia, PA 19118.

The main component of fats and oils are triglycerides. The physical properties of any fat or oil are determined by the fatty acid composition and the triglyceride distribution, which is endowed by nature. The physical properties of a given fat or oil may be altered by the physical blending or the chemical interesterification with another selected fat or oil. More recent interests, however, have been centered on the lipase catalyzed interesterification of fat and oil mixtures. This paper will describe a number of chromatographic procedures that allow changes in such lipase catalyzed reactions to be followed. For example, both reverse phase and normal phase high performance liquid chromatography were used in determining the triglyceride distribution of interesterified fats and oils, which capillary gas liquid chromatography was used in determining the fatty acid composition of the interesterified fats and oils.

348 HPLC SEPARATION OF BIOGENIC POLYAMINES USING 2-(1-PYRENYLETHYL) CHLOROFORMATE AS A NEW FLUOROPHORIC DERIVATIZING REAGENT. Maria A. Cichy, Desirée L. Stegmeier and Hans Veening, Department of Chemistry, Bucknell University, Lewisburg, PA 17837. Hans-Dieter Becker, Department of Organic Chemistry, Chalmers University of Technology and University of Gothenburg, S-412 96 Gothenburg, Sweden.

A number of compounds have been reported previously as successful precolumn derivatizing reagents for the fluorescent labeling of primary amines separated by HPLC. These reagents include dansyl chloride, fluorescamine, o-phthalaldehyde, 9-fluorenylmethyl chloroformate (FMOC), and 2-(9-anthryl-ethyl) chloroformate (AEOC). HPLC separations of polyamines (putrescine, cadaverine, spermidine, and spermine) with fluorescence detection have been achieved using FMOC and AEOC. This presentation will describe the use of a newly synthesized fluorophoric precolumn derivatizing agent: 2-(1-pyrenylethyl) chloroformate (PEOC). The high molar absorptivity of PEOC coupled with its inherent fluorescence properties, makes PEOC an even more promising reagent than AEOC. The development of this HPLC method included the optimization of excitation and emission wavelengths, efficient gradient programming, derivatization temperature, time, and pH. Minimum detection limits were found to be 1.1, 0.9, 1.3 and 2.9 pg for putrescine, cadaverine, spermidine, and spermine, respectively. Linearity was consistent over 3 orders of magnitude subsequent to the application of corrections for nonlinear detector behavior. The procedure was applied to hydrolyzed normal and cancer serum samples as well as to cancerous breast, lymph, and colon tissues. Detection limits were more favorable than those previously reported for other chloroformate/polyamine adducts.

349 GRADIENT-HPLC SEPARATION OF PLATINUM-LABELED ADDUCTS OF CYTOCHROME C. Amy M. Bonser and Owen A. Moe, Department of Chemistry, Lebanon Valley College, Annville, PA 17003.

We are working to separate and identify labeled protein adducts resulting from the reaction of a histidine-specific protein reagent, platinum(II)-terpyridine {Pt(TRPY)$^{2+}$}, with the heme-containing protein, cytochrome C. The reaction of Pt(TRPY)$^{2+}$ with histidine residues introduces net positive charge into the protein, allowing chromatographic separation of the unreacted protein from adducts containing one, two, or more modified histidine residues. Following reaction of cytochrome C with Pt(TRPY)$^{2+}$, we remove excess labeling reagent by GPC and separate the mixture of labeled cytochrome C adducts by gradient HPLC using a preparative cation exchange column. The extent of platinum labeling in each chromatographic peak has been determined through flame and electrothermal atomic absorption spectroscopy. Molar absorptivities of the heme and platinum-terpyridine moieties in the cytochrome C-platinum adduct have been determined, allowing direct spectrophotometric determinations of the Pt/Fe ratios in the reaction products separated by HPLC. The effect of histidine labeling on the structure and function of cytochrome C is currently under study.

350 THE PRINCIPLE COMPONENT OF HUMAN BODY ODOR. THE SYNTHESIS AND CHROMATOGRAPHIC SEPARATION OF (E) AND (Z)-3-METHYL-2-HEXENOIC ACID. George Preti and Xiao-Nong Zeng, Monell Chemical Senses Center, Philadelphia, PA 19104. Norman H. Nemeroff and Stefan Mayerschoff, Philadelphia College of Textiles and Science, Department of Chemistry, School House Lane and Henry Ave., Philadelphia, PA 19144.

Recent studies carried out at the Monell Chemical Senses Center have identified the nature of the characteristic odor produced in the human underarm region. The odor bouquet consists of C6 to C11 acids with the (E)-3-methyl-2-hexenoic acid being the largest component; the (Z)-isomer is also present. The synthesis and separation by chromatographic techniques of the two isomers is being carried out to provide sufficient amounts of purified material to facilitate studies concerning the biological origin of this characteristic human odor.

351 CHROMATOGRAPHIC AND FT-IR SPECTROSCOPIC STUDIES OF A SERIES OF MONOSUBSTITUTED FERROCENES. D. Michael Byler, Jennifer F. Troy, Jeffrey M. Axten and Norman H. Nemeroff, Philadelphia College of Textiles and Sciences, Philadelphia, PA 19144-5497.

Recently a series of monosubstituted ferrocenes has been synthesized in our laboratory. The substituents include a variety of small, unsaturated organic groups in which the double and triple bonds are conjugated to the cyclopentadienyl ring. Where synthetic procedures have led to a mixture of isomers, various chromatographic techniques were used to facilitate their separation. FT-IR spectroscopy has enabled us to determine which isomer is *CIS* and which is *TRANS*. The spectra also disclose the effect of conjugation on the observed vibrational frequencies of the organic substituents.

352 THE SYNTHESIS AND CHROMATOGRAPHIC SEPARATION OF 4-(FERROCENYL)-3-SUBSTITUTED PYRROLE DERIVATIVES. Norman H. Nemeroff and Jeffrey M. Axten, Philadelphia College of Textiles and Science, Department of Chemistry, School House Lane and Henry Avenue, Philadelphia, PA 19144.

In our efforts to study the effects of various substituent groups at the three position of the pyrrole ring of 4-(ferrocenyl) pyrrole, we have carried out the synthesis of 4-(ferrocenyl)-3-methyl pyrrole, 4-(ferrocenyl)-3-acetyl pyrrole, 4-(ferrocenyl)-3-benzoyl pyrrole, 4-(ferrocenyl) 3-cyano pyrrole, and 4-(ferrocenyl) pyrrole-3-carboxylic acid. The syntheses of these compound was accomplished by building the pyrrole ring. The Michael addition reaction of tosmic (tosymethylisocyanide) to an α,β-unsaturated ferrocene derivative, having the appropriate substituent at the β-position, led to the formation of the desired 3, 4-disubstituted pyrrole derivatives. The reactions were followed chromatographically and all products were isolated and purified by flash column chromatography.

353 LIQUID-LIQUID EQUILIBRIA OF POLYMER SOLUTIONS. David J. Geveke and Ronald P. Danner, Department of Chemical Engineering, The Pennsylvania State University, University Park, PA 16802.

Phase equilibria of polymer solutions has several applications including the separation of proteins, enzymes, viruses, and nucleic acids and the solvent-casting of micro-porous separation membranes. Phase diagrams for nine ternary solvent-polymer-polymer systems have been obtained using size exclusion chromatography. The systems studied contained polystyrene with isoprene rubber and toluene, butadiene rubber and toluene, butadiene rubber and cyclohexane, poly(methyl methacrylate) and tetrahydrofuran, and poly(butyl methacrylate) and tetrahydrofuran at temperatures between 30 and 75°C. The Flory-Huggins and UNIQUAC models were used to obtain analytical expressions which accurately describe the experimental data. Additional solvent-polymer-polymer systems in the literature as well as solvent-polymer and solvent-nonsolvent-polymer systems were also correlated.

354 EFFECT OF CHAIN LENGTH OF n-ALCOHOL MODIFIERS ON THE INTERNAL VISCOSITY OF SODIUM DODECYL SULFATE MICELLES. D. A. Piasecki and M. J. Wirth, Department of Chemistry and Biochemistry, University of Delaware, Newark, DE 19716.

n-Propanol is an effective modifier in micellar liquid chromatography. The rotational diffusion behavior of tetracene was used to probe the internal viscosity of SDS micelles in the presence of several n-alcohols (C3–C8). These solutions, containing approximately the same number of alcohol molecules per micelle, were studied using frequency domain spectroscopy, where the fluorescence anisotropy of tetracene was measured. Results indicate that the addition of alcohol causes tetracene to reorient faster within the micelle; however, the chain length of the alcohol has little effect on the reorientation behavior. These findings have important ramifications regarding the choice of a mobile phase modifier in micellar liquid chromatography. Further studies explore the rotational diffusion of fluorescent probe molecules at a hexadecane/water interface, in the presence of SDS, to obtain a fundamental understanding of solute-micelle interactions.

355 PREPARATIVE HPLC OF OLIGOSACCHARIDES. Arland T. Hotchkiss, Jr. and Kevin B. Hicks. USDA-ARS, ERRC, 600 E. Mermaid Lane, Philadelphia, PA 19118.

HPLC has become an integral part of analytical carbohydrate chemistry. The advent of high-pH anion-exchange chromatography (HPAEC) with pulsed amperometric detection (PAD) has provided methodology that is selective enough to resolve underivatized monosaccharides comparable with that observed with GLC (after derivatization). HPAEC also allows for the separation of underivatized oligosaccharide positional isomers (differing only in glycosyl-linkage position), providing structural information typically obtained by methylation analysis and GC-MS or NMR. HPAEC peaks must be collected and analyzed by GC-MS or NMR in order to verify the structural information. Our lab has developed several new preparative HPLC techniques for the purification of medium to large oligosaccharide standards for HPAEC. Our group is also interested in isolating oligosaccharides that are important to the food and pharmaceutical industries as well as those oligosaccharides that play a physiological role in plants. Either polystyrene-divinylbenzene cation-exchange (H^+, Ca^{2+}, Ag^+, Pb^{2+}) or aminopropyl-silica gel preparative HPLC columns were used. Gram quantities of malto-, cello-, chito-, fructo-, and galacturono-oligosaccharides have been isolated by these means.

356 CHARACTERIZATION OF STARCHES BY HPSEC WITH VISCOSITY/REFRACTIVE INDEX DETECTION. M. L. Fishman, P. D. Hoagland and L. Rodriguez, USDA/ARS Eastern Regional Research Center, 600 E. Mermaid Ln., Philadelphia, PA 19118.

Starch granules dispersed in water with amylose: amylopectin ratios of about 0, 1:3, 1:1 and 7:3 were gelatinized by microwave heating in a high pressure container. Prior to chromatography, sufficient $NaNO_3$ was added to the aqueous starch solutions to raise the salt molarity to 0.05 m which was the concentration of $NaNO_3$ in the mobile phase. For each starch composition, non-linear least squares curve fitting of refractive index and viscosity chromatograms permitted each kind of chromatogram to be fitted with the same six Gaussian components. Calibration of the column set with pullulan and dextran standards in hydrodynamic volume and RMS radius of gyration (R_g) enabled intrinsic viscosity (IV), molecular weight (MW), and R_g to be calculated for each component and global values of these quantities for the entire distribution. Weight average MW, IV, and R_g decreased with increasing percentage of amylose in the starch. As the percentage of amylose increased, the weight fractions (w_i) of early eluting components 1 and 2 decreased whereas the w_i of components 4, 5, and 6 increased. Measurement of fractionated starches as they eluted from the column set revealed large changes in mw and R_g and rather small changes in IV. The Mark-Houwink constant (MH) for amylopectin was consistent with that of branched spherically shaped molecule whereas the MH value for amylose was anomalously low for a rod or segmented rod-like shaped molecule.

357 APPLICATIONS OF SALT-POLYMER TWO-PHASE EXTRACTION SYSTEMS TO PURIFY PROTEINS AND NUCLEIC ACIDS. Kenneth D. Cole, National Institute of Standards and Technology, Gaithersburg, MD 20899.

Partitioning of proteins and nucleic acids in two-phase systems composed of polyethylene glycol and salt offers the advantages of speed, low cost, and simplicity in operations for bioseparations. These two-phase systems can be made from aqueous solutions of a polymer such as polyethylene glycol of various molecular masses and a salt such as ammonium sulfate. We have measured the phase diagrams and physical properties of a number of these phase systems to aid in the more rational selection of extraction conditions for bioprocessing. The variables that determine the partitioning of biopolymers include polymer concentration, polymer molecular weight, salt concentration, salt type and pH. In addition other components can be added to these systems that will have a direct affect on the biopolymers and the chemical composition of the phases. These additives include such compounds such as detergents, nonphase-forming salts and chaotropes. We have examined the affect of these variables on partitioning of purified model proteins and in complex mixtures.

358 RECENT BIOMEDICAL APPLICATIONS OF FIELD-FLOW FRACTIONATION. Karin D. Caldwell, Howard Li, Jianmin Li, Birgit Langwost and Yu-Shu Gao, Center for Biopolymers at Interfaces, The University of Utah, Salt Lake City, UT 84112.

Particle size and surface composition have shown to be important criteria in the selection of vehicles for controlled intravenous release of drugs. In this selection, the particles' resistance towards adsorption of plasma proteins is a parameter of utmost concern, as low protein uptake results in extended circulation times during which release can occur. The presentation will discuss the sedimentation, flow, and electrical field-flow fractionation techniques with emphasis on their use in analyses of the size and protein resistance of pharmaceutically important fat emulsions and other colloidal systems which serve as model delivery vehicles or as immunodiagnostic tools. Examples will demonstrate the flow and sedimentation FFF techniques' ability to accurately and precisely assign surface concentrations and spatial extension of proteins and synthetic polymers adsorbed to colloidal substrates.

359 ANALYTICAL USES OF AFFINITY CHROMATOGRAPHY: PROBING MACROMOLECULAR RECOGNITION AND ASSEMBLY USING IMMOBILIZED LIGANDS.

Irwin Chaiken, David Myszka, David May and Jeffrey Culp, Biopharmaceuticals R&D, SmithKline Beecham L48, 709 Swedeland Road, King of Prussia, PA 19406.

Immobilized ligands can bind to biological macromolecules selectively and reversibly, allowing their use as analytical tools to characterize macromolecular interactions. The early development of affinity chromatography as a preparative tool, for isolation of enzymes, receptors and many other types of biomolecules, demonstrated the separatory power of this chromatographic method. Preparative affinity chromatography in turn has stimulated development of analytical affinity chromatography (AAC). The AAC method has been used to detect and quantitate biomolecular interactions over a wide range of affinity and size. Solution interactions as well as interactions directly on the affinity support can be measured simultaneously. Recent results with HIV p24 self-assembly, CD4-gp120 interactions and antisense peptide recognition of sense peptides reflect how AAC can contribute to molecular characterization and design in biotechnology. Recent results using biosensors also suggest how AAC is evolving into a more broad-based analytical solid phase science in the field of biomolecular recognition.

360 HIGH RESOLUTION SEPARATION METHODS FOR DNA POLYMERASE CHAIN REACTION PRODUCTS.

D. J. Reeder, M. Kline and K. Srinivasan, National Institute of Standards and Technology, Gaithersburg, MD 20899.

Applications for Polymerase Chain Reaction (PCR) methods which amplify DNA are being published at a very rapid rate. Optimization of protocols is often required for each laboratory's configuration of thermal cyclers and buffer systems. An example will be shown of how adjustment of cycling temperatures and magnesium content affect specificity of PCR amplification. Use of the PCR technology in such fields as human identification and genetic disease detection are requiring sensitive detection and high resolution separations. We have extended moving boundary electrophoretic separations in polyacrylamide gels to achieve reproducible resolution of as few as ten base pairs at size ranges around 900 base pairs of DNA. The system for electrophoresis employs a mini-gel format with less than two hour separations followed by silver staining of the separated PCR products. We find, however, that "standard" size ladders are not sufficiently accurate to impute correct sizes to the separated PCR fragments. Additionally, we have employed capillary electrophoretic methods to separate PCR products from Apolipoprotein B and D1S80 polymorphic allelic gene sequences. Methods for achieving high resolution of PCR products using coated capillary columns (50–100 μmeters I.D.) utilize various polymeric solutions to achieve optimal separation. Investigations of buffer type and concentration, temperature effects, capillary coating, and detection systems provide optimal conditions for separation of PCR products in selected size ranges.

361 ANALYSIS AND CHARACTERIZATION OF RECOMBINANT PROTEINS BY HIGH PERFORMANCE-CAPILLARY ELECTROPHORESIS (HPCE).

K. Tsuji, The Upjohn Company, Kalamazoo, MI 49001.

This paper reviews our efforts to analyze recombinant proteins by HPCE. Both neutral and slightly basic proteins were analyzed by the fused-silica capillary zone electrophoresis (CZE). Although standard curves were linear between the concentration of ca. 3 to 15 fmoles, adsorption of proteins on the capillary wall was noted. The relative standard deviation (RSD) of CZE methods was approximately 2 to 4%. Polymer coated columns enabled analysis of a basic glycoprotein. Due perhaps to difficulties in obtaining uniformly coated columns, RSD for the analysis of the basic glycoprotein was 2 to 3 times higher than that of the CZE methods. Use of an SDS-polyacrylamide gel-filled column indicated existence of a linear relationship between the peak migration time and the molecular weights of proteins between the range of 10,000–100,000 daltons. The RSD of peak migration time was ca. 1%. An impurity peak of ca. 3% less molecular weight than that of the parent compound of ca. 60,000 daltons may be differentiated by this column. The average molecular weights of proteins determined by the HPCE interfaced with an electrospray (ESI) mass spectrometry (MS) are nearly identical to the theoretical values. Data indicate that CZE and ESI MS cannot detect all impurities but combining the techniques enhances the analytical capabilities for characterization of recombinant proteins.

362 COUPLED MICROCOLUMN SEPARATIONS AND TIME-OF-FLIGHT MASS SPECTROMETRY FOR THE CHARACTERIZATION OF BIOMOLECULES.

Milton L. Lee, Department of Chemistry, Brigham Young University, Provo, UT 84602. Edgar D. Lee, Sensar Corporation, 1048 North Industrial Park Road, Orem, UT 84057.

The complexities of biological samples demand the highest resolution techniques for their chemical analysis. Combined capillary column gas chromatography-mass spectrometry has been extensively used for the analysis of volatile biomolecules because of its unsurpassed resolving power for small, thermally stable, uncharged molecules. Furthermore, gas chromatography is the easiest of the separation techniques to couple to mass spectrometry. Unfortunately, most of the biomolecules that one would like to analyze are not amenable to analysis by gas chromatography because they are thermally unstable, high molecular weight (nonvolatile), and often electrically charged. High performance liquid chromatography or electrophoresis have been the major analytical separation tools for the majority of biomolecules, although supercritical fluid chromatography has found some application to compounds of low to moderate polarities. Regardless of the separation methods used, there is a growing trend to utilize the microcolumn versions of the techniques for analytical purposes. In the case of mass spectrometry detection, this often requires greater sensitivity and speed than is offered by conventional scanning mass spectrometers. In this presentation, we report the design and use of an atmospheric pressure ionization (API) time-of-flight (TOF) mass spectrometer (MS) for the various microcolumn separation techniques. Selected applications using corona discharge and electrospray ionization will be presented.

363 SULFONAMIDE/CYCLODEXTRIN COMPLEXES: CONFORMATIONS AND ASSOCIATION ENERGIES FROM MOLECULAR MODELING STUDIES.

Gregory King and Robert A. Barford, Eastern Regional Research Center, Agricultural Research Service, U.S.D.A., 600 East Mermaid Lane, Philadelphia, PA 19118.

Analytical methods that reduce or eliminate the use of organic solvents are now being sought for monitoring levels of drug residues in agricultural products. It is well-known that certain carbohydrates (such as cyclodextrins and cyclic glucans) form inclusion complexes with a variety of predominantly hydrophobic solutes in water, thus increasing the effective solubilities of these solutes. Molecular modeling may provide information on the preferred conformation of a given guest/host combination, and on the increase in solubility of guest to be expected upon complexation with host. Three methods for calculating association free energies were tested on a set of sulfonamide/β-cyclodextrin complex references systems, and compared with the experimentally-determined values. Although somewhat time-consuming, the best of the three methods yields association free energies with a margin of error of about ±1.5 kcal/mol.

364 ELECTRO-MEMBRANE SAMPLE PREPARATION FOR HPLC ANALYSIS OF VETERINARY PHARMACEUTICALS IN BIOFLUIDS.

Jeffrey D. Brewster and Edwin G. Piotrowski, U.S. Department of Agriculture, ARS, Eastern Regional Research Center, 600 E. Mermaid Lane, Philadelphia, PA 19118.

Current approaches to the preparation of biological samples for HPLC typically require several manual operations and large quantities of organic solvents. Rapid, automated sample clean-up systems are needed to fully utilize the capabilities of modern HPLC equipment. Electro-membrane sample treatment (EMST) utilizes electrodialysis to rapidly isolate ionic analytes from complex matrices without the use of organic solvents. Isolation and pre-concentration of analyte can be performed simultaneously in an automated, flow-through system. Theoretical expressions for recovery, selectivity, and sample concentration in EMST will be presented and compared to experimental results. The use of a computer-controlled EMST apparatus for isolation of a variety of veterinary pharmaceuticals from milk, urine, serum, and homogenized tissue will be described. Techniques for isolation of non-ionic analytes using EMST in conjunction with selective complexing agents will be discussed.

365 SCANNING TUNNELING AND ATOMIC FORCE MICROSCOPIC STUDIES OF ORGANIC MONOLAYER FILMS.

C. A. Alves, J. Zak, E. L. Smith and M. D. Porter, Department of Chemistry and Ames Laboratory-USDOE, Iowa State University, Ames, IA 50011.

Monolayers of well ordered, functionalized interfaces are readily formed by the adsorption of alkanethiols ($X(CH_2)_nSH$) at gold surfaces. These properties provide a unique opportunity to probe the underlying chemistry and physics of reactivity at liquid-solid interfaces. This presentation describes details of these layers as probed primarily by scanning tunneling (STM) and atomic force microscopies (AFM). These techniques yield a description of the two-dimensional arrangement of the interfacial structure as well as the possible tip-induced alteration of the surface structure during imaging. These descriptions are compared with those developed from infrared reflection spectroscopy (IRS) and electrochemistry. The IRS data provide insights into the composition, spatial orientation, and reactivity of the layers. Studies of the electrode reactions that lead to the one-electron reductive and three-electron oxidative desorption of the layers provide a measure of surface coverage as well as insights into multiple modes of adsorption (e.g., terrace vs. edge).

366 SURFACE CHEMISTRY OF COMPOUND SEMICONDUCTOR ELECTRODES.

John L. Stickney, Department of Chemistry, University of Georgia, Athens, GA 30602-2556.

Studies of the surface structures resulting from the digital electrochemical processing of compound semiconductors, such as CdTe, are presented. Our group is developing electrochemical methods for digitally etching and depositing compound semiconductors. Both techniques rely on the use of underpotentials. Underpotential deposition (UPD) is a phenomena where an atomic layer of one element deposits at a potential prior to (under) that necessary to deposit the bulk element. Alternatively, similar underpotentials can be used to strip off the bulk element while leaving an atomic layer in contact with a second element. UPD results from the free energy of formation of the surface compound. We refer to our deposition process as Electrochemical Atomic Layer Epitaxy or ECALE. It consists of the alternated deposition of atomic layers of individual elements at underpotential from separate solutions. Surface studies of ECALE deposits have been performed on the low index planes of Au. LEED, STM, and Auger electron spectroscopy have been employed to follow the structures as a function of various deposition parameters. Etching experiments have also been carried out on CdTe single crystals using a square wave consisting of the stripping underpotentials for the elements of interest.

367 INFRARED SPECTROSCOPY AS A PROBE OF IONIC INTERACTIONS AT THE ELECTRODE-SOLUTION INTERFACE: ELIMINATION OF BULK INTERFERENCES.

C. Korzeniewski and V. B. Paulissen, Department of Chemistry, The University of Michigan, Ann Arbor, MI 48109.

Infrared studies of anionic adsorption have indicated the difficulty in assigning spectra of interfacial species on account of interferences from potential dependent alterations in the composition of the thin layer cavity. In this presentation, we report infrared studies of cyanide and bisulfate adsorption at platinum under aqueous electrochemical conditions using techniques which eliminate bulk interferences. For cyanide, in situ spectral analyses were performed in a cyanide free electrolyte solution following cyanide monolayer preparation according to an electrochemical procedure developed to examine this system under uhv conditions. This approach minimized spectral interferences associated with reactive cyanide species in bulk solution and simplified band assignments of surface cyanide. Two pH dependent forms of the adsorbed cyanide surface layer were identified and the frequency and potential dependence of each band shows an interesting correlation with cyanide spectral features found in recent sum-frequency generation experiments. For bisulfate, in situ analyses were performed using a thin layer spectroelectrochemical flow cell which permits dosing through a small hole in the center of the infrared transparent window. Electrolyte flow during spectral acquisition maintained the electrolyte composition in the thin layer cavity as constant, thereby eliminating the accumulation of reaction products known to obscure spectral features associated with interfacial bisulfate.

368 Abstract not received at time of printing.

369 FLUORESCENCE IMAGING OF LOCALIZED PROCESSES AT THE ELECTRODE-SOLUTION INTERFACE.

R. C. Engstrom, Qu Hongwei and D. L. Fritza, Department of Chemistry, University of South Dakota, Vermillion, SD 57069.

This work was directed at spatially-resolving the distribution of electrochemical activity at the electrode-solution interface. Processes that involve a change in interfacial pH have been studied through the use of pH-dependent fluorescent indicators. The indicator, fluorescein, exhibits fluorescence in basic solution, so that regions on a surface that generate hydroxide generate fluorescence when bathed in a solution of fluorescein and when illuminated with appropriate excitation light. A microscopic fluorescence imaging system has been used to collect and process light generated during various electrochemical events. To characterize the technique, the reduction of water at various electrodes has been conducted. Spatial resolution and potential dependence of fluorescence were characterized. Fluorescence imaging was then applied to monitoring localized corrosion processes, based on the cathodic production of hydroxide, the electrodeposition of copper onto aluminum, and the iontophoretic deposition of silver on carbon. The latter makes use of the difference in electron-transfer kinetics for the reduction of water between silver and carbon and provides a convenient way of visualizing microstructures of silver.

370 TANDEM MASS SPECTROMETRY (MS/MS) OF POLY(ETHYLENE GLYCOL) PROTON- AND DEUTERON-ATTACHMENT IONS.

Robert P. Lattimer, The BFGoodrich Research and Development Center, 9921 Brecksville Road, Brecksville, OH 44141.

A detailed study has been carried out of the FAB-MS/MS behavior of proton- and deuteron-attachment ions from several ethylene glycol polymers (PEGs). Both cyclic (crown ether) and linear (hydroxyl- and methyl-terminated) oligomers were studied. Collisional activation was carried out in the "collision octapole" of a BEoQ hybrid mass spectrometer at a translational energy of 50 eV, with collision gas air. Interestingly, it was found in several experiments that considerable H/D exchange occurs during the formation of hydroxyl-terminated carbonium product ions from $[M + D]^+$ precursors. This H/D mixing cannot be explained by simple, charge-site initiated cleavages of C—O bonds. A more complex decomposition pathway is proposed that appears to be consistent with the MS/MS data. The key intermediate is a hydroxyl-terminated (-OD) carbonium ion that can be formed from either cyclic or linear PEG $[M + D]^+$ precursors. It is proposed that reversible H/D exchange occurs between the terminal hydroxyl group (-OD) and the carbonium center ($-CH_2^+$) of this intermediate. This H/D exchange and subsequent elimination of (neutral) ethylene oxide groups is shown to be more prominent at higher collision gas pressures.

371 SECONDARY ION MASS SPECTROMETRY OF POLYMERS.

David M. Hercules, Department of Chemistry, University of Pittsburgh, Pittsburgh, PA 15260.

Time-of-flight secondary ion mass spectra (TOF-SIMS) of polymers have been obtained from thin films cast from solution and from some neat and solid polymer films in the medium-high mass range (m/z = 500–10,000). The mass of the repeat unit can be determined from the spacing between consecutive fragment or oligomer peaks, cationized with the same cation (e.g., Ag^+ or Na^+). Fragmentation patterns were unique for polymers having different repeat units but of equal mass; distinguishing between such polymers was possible. Oligomer distributions for polymer standards obtained from TOF-SIMS spectra compared well with distributions determined by other techniques (e.g., gel permeation chromatography). Principles of TOF-SIMS instrumentation will be introduced; spectra of various polymers (e.g., polystyrenes, polysiloxanes, polyurethanes, etc.) will be presented. Interpretation of spectra will focus on information they provide for structural characterization, oligomer distributions, and surface analysis of polymers.

372 CHARACTERIZATION OF ARCHITECTURED POLYMERS BY K^+IDS.

William J. Simonsick, Jr., E. I. Du Pont De Nemours & Company, Automotive Products, Marshall R&D Laboratory, Philadelphia, PA 19146.

Desorption/ionization mass spectrometric approaches that produce molecular ions on polymers are rapid, require minimal sample preparation, and characterize the composition, structure, and molecular weight distribution in a single experiment. We selected potassium ionization of desorbed species (K^+IDS) as our method of desorption/ionization because of its simplicity, wide applicability, low cost, and compatibility with our quadrupole mass spectrometer. K$^+$IDS affords a simple, but predictable mass spectrum consisting of pseudomolecular ions in the form of [M]K$^+$. K$^+$IDS has been used to characterize the oligomers synthesized from free-radical, group-transfer, condensation, and anionic polymerization techniques. The oligomers are subsequently used to produce architectured polymers.

373 POLYMER ANALYSIS BY LASER AND FIELD DESORPTION MASS SPECTROMETRY. P. Juhasz and C. E. Costello, Dept. of Chemistry, Mass. Inst. of Technology, Cambridge, MA 02139.

Recent methodological development in mass spectrometry has rekindled the interest in the utilization of mass spectrometry in polymer research. Construction of high-field instruments has extended the range of field desorption (FD) above 10 kDa, and new ionization techniques, such as matrix-assisted laser desorption (MALD) ionization and electrospray, are capable of producing intact molecular ions of few a hundred kDa molecular weight. At the MIT Mass Spectrometry Facility a JEOL HX110/HX110 mass spectrometer is available for FD studies. This instrument also offers the possibility of structure elucidation of the desorbed ions by means of MS/MS measurements. MALD ionization experiments were carried out on a VT2000 (VESTEC Corp.) time-of-flight (TOF) mass spectrometer. Three lasers were used in these studies: a frequency quadrupled Nd:YAG laser (266 nm, 9 nsec pulse), a N_2 laser (337 nm, 3 nsec pulse), and an Er:YAG laser (2.94 μm, 120 nsec pulse). Results with FD and MALD ionization methods will be presented and compared on examples including polystyrene, polyethylene glycol, polyamino acids, as well as more unusual polymers such as metallocenes and silicon dendrimers. For each method proper choice of experimental conditions (wavelength/matrix combination in MALD, solvent, sample concentration, FD emitter current) is important for optimum results. For the compounds that can be analyzed by either technique, MALD TOF offers higher mass range with limited resolution, whereas FD on the four sector instrument permits the recording of higher resolution mass spectra, and MS/MS analysis.

374 MASS SPECTROMETRIC METHODS FOR THE CHARACTERISATION OF OLIGOMERIC AND POLYMERIC SPECIES. K. Rollins, ICI Wilton Research Centre, P.O. Box 90, Wilton, Middlesbrough, Cleveland TS6 8JE, UK.

The mass spectrometric characterisation of synthetic oligomers and polymers has frequently been achieved by the use of either thermal methods (e.g. pyrolysis—GC-MS) or techniques which result in the generation of molecular weight information (e.g. field desorption (FD), LSIMS, electrospray etc.). The presentation will concentrate upon the application of thermal methods and FD-MS to polymeric applications in the Wilton laboratory. The preferred thermal approach involves the use of thermal desorption—GC-MS which permits the use of inert or oxidising desorption atmospheres and a range of temperature regimes. This combination allows the formulation of interest to be studied in terms of additives, residual monomers/oligomers, catalyst residues, polymer type etc and generates information which is often unobtainable by other means. The FD-MS technique is used in our laboratory across a wide applications base and has proved especially useful in the analysis of polymers and related formulations. The technique provides good molecular weight information as the polymerization process proceeds. Applications will be presented which illustrate the benefits of this approach in the characterisation of monomers (e.g. triphenylene esters), oligomers (e.g. calixarene resins) and polymers (e.g. polyaromatic materials). This experience with the FD technique indicates that, with current generation instrumentation, it should be regarded as a powerful tool in the mass spectroscopist's armoury.

375 THE CHARACTERIZATION OF WATER SOLUBLE POLYMERS BY FIELD AND LASER DESORPTION MASS SPECTROMETRY. Paul O. Danis and Dane E. Karr, Rohm and Haas Company, Spring House, PA 19477. Clifford H. Watson, Bruker Instruments, Inc., Manning Park, Billerica, MA 01821. Franz Mayer and Armin Holle, Bruker-Franzen Analytik GmbH, Fahrenheitstraße 4, 2800 Bremen 33, Germany.

Water soluble polymers are an important part of the coatings and surfactant industry, and the application of mass spectrometry to their analysis has distinct advantages over the conventional methods of polymer characterization. With mass spectrometry information can be obtained on polymer composition and end groups, it provides absolute molecular weight distributions without the use of polymer standards, and it is faster (min. vs hr.) and more accurate for non-linear species. For low molecular weight (<10,000 da) polymers field desorption (FD) can be applied showing the distribution of species as well as end groups. Generally, water soluble polymers must first be derivatized to decrease their polarity for FD analysis; this will be exemplified by the methylation and analysis of poly(acrylic acid). The technique of matrix-assisted laser desorption/time-of-flight mass spectrometry has proven to be very powerful for the analysis of peptides and other biopolymers into the 10^5 dalton range,[1,2] and we will show application of this technique to polymers of vinyl alcohol, acrylic acid, and styrene sulfonate ranging from 5,000 to 200,000 da.

[1] Hillenkamp, F.; Karas, M.; Beavis, R. C.; and Chait, B. T. *Anal. Chem.* **1991,** 63, 1193A.

[2] Tanaka, K.; Waki, H.; Ido, Y.; Akita, S.; Yoshida, Y.; and Yoshida, T. *Rapid Commun. Mass Spectrom.* **1988,** 2, 151.

376 MAGNETOOPTICAL ROTATION AND KERR EFFECT DETECTION IN LIQUID CHROMATOGRAPHY. E. S. Yeung, X. Xi and T. Lee, Department of Chemistry and Ames Laboratory-USDOE, Iowa State University, Ames, IA 50011.

Magnetooptical rotation (MOR) or the Faraday effect in the absence of absorption is a general physical property for all substances and can be used for universal detection in high-performance liquid chromatography. The longitudinal magnetic field with moderate field strength is provided by a cheap and compact permanent magnet assembly. A simplified equation has been derived for calculating Verdet constants of mixtures. The experimental results confirm the linear relationship between the MOR signal and weight fraction of the solute in dilute solution. The linear range is limited by the artifact signals caused by the refractive index change at high concentrations. The feasibility of this method is demonstrated in the detection of polynuclear aromatic hydrocarbons, where the limit of detection is in the submicrogram range. Electrooptical rotation or the Kerr effect can similarly be used for detection in liquid chromatography. The good sensitivity of both techniques can be attributed to the unique level of performance of the polarimeter used.

377 NEW POLARIZATION MODULATION TECHNIQUES IN RAMAN OPTICAL ACTIVITY. Laurence A. Nafie, Department of Chemistry, Syracuse University, Syracuse, NY 13244-4100.

Raman optical activity (ROA) was defined theoretically for the first time in 1971 and then successfully measured in 1973. Since that time a number of theoretical and instrumental advances have been achieved. Among those are multichannel detection, backward and forward scattering geometries and new methods of polarization modulation. Traditionally, ROA has been measured as the difference in scattering intensity between right and left *incident* circularly polarized (ICP) laser radiation. Several years ago, we measured ROA for the first time as the difference in right and left *scattered* circularly polarized (SCP) radiation for a fixed state of incident laser polarization. We have also proposed and measured two new forms of ROA based on the simultaneous use of incident and scattered (dual) circular polarization modulation, either in-phase (right-right minus left-left) (DCP_I) or out-of-phase (right-left minus left-right) (DCP_{II}). Recently, we have constructed an ROA instrument, equipped with a CCD detector, which can be configured for backscattering, forward scattering, as well as the more common right-angle scattering. In addition, we can perform all four forms of polarization modulation ROA for these different scattering geometries. We have compared the results of our ROA measurements with theoretical predictions based on the far-from-resonance approximation for Raman and ROA scattering. From these comparisons we have been able to determine the optimum form of ROA for measurements of biological samples and test the degree of non-resonance character of the ROA sample.

378 ULTRAFAST CIRCULAR DICHROISM SPECTROSCOPY. John D. Simon, Department of Chemistry, U.C.S.D., 9500 Gilman Drive, La Jolla, CA 92093-0341.

This talk will examine applications of ultrafast circular dichroism spectroscopy to the study of biological systems. In particular, the relaxation in heme proteins following photodissociation and the electronic structure of bacterial reaction centers will be examined. Future applications of this technology to the study of protein folding will be briefly discussed.

379 STUDIES OF INDUCED CHIRALITY USING LIFETIME-RESOLVED FLUORESCENCE-DETECTED CIRCULAR DICHROISM.

Linda B. McGown, Karen Wu, Lei Geng and Melissa A. Jarrell, Department of Chemistry, P.M. Gross Chemical Laboratory, Duke University, Durham, NC 27706.

Organized media, biological macromolecules and other molecular assemblies often contain helical or otherwise asymmetric structural microenvironments. Distribution of a molecular probe among different microenvironments in solutions containing such structures will produce a heterogeneous population of free and bound probe molecules with chiral characteristics determined by the intrinsic chirality (or achirality) of the probe itself as well as structural and electronic distortions that are induced by the microenvironment. Circular dichroism techniques (absorption and fluorescence-detected) are an excellent source of information about molecular chirality. These techniques are limited, however, to measurements of and *average* chirality of the total probe population. We have introduced a new technique, Lifetime-Resolved Fluorescence-Detected Circular Dichroism (LRFDCD), that combines fluorescence lifetime resolution with chiral selectivity. LRFDCD is implemented on a commercial, frequency domain fluorescence lifetime instrument that is modified for FDCD. Analysis of multifrequency lifetime data for fluorescence that is excited by right-handed and left-handed circularly polarized light enables us to resolve the lifetime and FDCD contribution for *each component*, chiral and achiral, in the sample. Thus, LRFDCD provides a direct link between the fluorescence lifetime of a component and the location and conformation of that component in a molecular structure. In this talk, we will present results for LRFDCD probe studies of cyclodextrins and nucleic acids.

380 THERMAL LENS DETECTION OF CIRCULAR DICHROISM.

Chieu D. Tran, Department of Chemistry, Marquette University, Milwaukee, WI 53233.

A new spectropolarimeter has been developed. This instrument is based on the use of the thermal lens effect to determine the circular dichroism of chiral sample. Specifically, in this instrument, the sample is sequentially excited by the left circularly polarized laser light (LCPL) and right CPL (RCPL); both of these excitation beams are derived from the same laser. The heat generated as a consequence of the sample absorption of the LCPL and RCPL is measured by the probe laser beam collinearly overlapping with the two excitation beams. Instrumentation development is described for cases where short ultraviolet wavelength (275 nm) and infrared (from 2.0 μm to 4.0 μm) laser beams were used for excitation.

381 BIASED REGRESSION FOR IDENTIFICATION OF DYNAMIC AND STATISTICAL PROCESS CONTROL MODELS.

Barry M. Wise, Battelle Pacific Northwest Laboratories, Richland, WA 99352. David J. Veltkamp, Center for Process Analytical Chemistry, Seattle, WA 98195.

The ultimate objective of on-line instrumentation is to improve the quality of the product and/or increase the process efficiency. In order to achieve this end, the process measurements must be used to control the process. This control can be one of two forms. The first is dynamic control where the measurements are used to make real-time corrections to the process inputs in order to keep the product consistent. The second is statistical process control (SPC) where the process is monitored with the objective of determining and eventually eliminating sources of unwanted process variation. Biased regression is applicable to the identification of both dynamic and SPC models. A brief overview of the use of models in dynamic control and SPC is given. The effect of using biased regression methods, such as Continuum Regression and Ridge Regression, is discussed. Use of the identification methods is illustrated with examples utilizing synthetic data along with data from actual processes.

382 ULTRASONIC INVESTIGATIONS OF POLYMERIZATION REACTIONS.

Steven D. Brown and Robert S. Bear, Jr., Department of Chemistry and Biochemistry, University of Delaware, Newark, DE 19716.

The ability to make on-line process control measurements is an important goal for the industrial polymer manufacturer. Only a narrow range of analytical techniques are appropriate for the quantitative monitoring of polymer content in a reaction mixture. Ultrasonic pulse methods provide a rapid and inexpensive analysis that can be performed with relatively simple instrumentation. Characteristics of the transient in both the time and frequency domain can be used to develop multivariate calibration schemes. Of particular interest is the nonlinear character of the time domain signals, which can be treated with nonlinear partial least squares regression.

383 Abstract not received at time of printing.

384 Abstract not received at time of printing.

385 AUTOMATIC UPDATING OF PROCESS MODELS.

D. Veltkamp, Center for Process Analytical Chemistry (CPAC), Department of Chemistry BG-10, University of Washington, Seattle, WA 98195.

Modern processes are increasingly coupled with computerized data collection systems and sophisticated chemical sensors. This leads to an increased need for systems to analyze the collected data and present the process operators with the important process information. The use of multivariate methods for the development of process models, along with the use of statistical process control charting techniques is being applied to provide simple, easily understood, tools for the monitoring of the proces status. However, changes in process operation, process disturbances, and sensor failure and/or drift can cause the process models to fail. In this talk we will discuss multivariate process modeling based on the Singular Value Decomposition (SVD) and present a method whereby the process models can be updated in response to these types of changes. The updating algorithm is rapid, flexible, and does not require one to maintain access to past process data records. The important features of the model updating scheme is that it is able identify the presence of the process changes while maintaining the ability to provide feedback to the operator as to the process status.

386 CONSTRAINED PRINCIPAL SPECTRA ANALYSIS (CPSA).

James M. Brown, Exxon Research & Engineering Company, Route 22 East, Annandale, NJ 08801.

Mathematical techniques such as Principal Components Analysis and Partial Least Squares Analysis can distinguish between sample component absorptions and spectral noise, due to the fact that the component absorptions are correlated across the spectrum, whereas the noise shows no such correlation. PCA and PLS cannot distinguish between sample component absorptions and other measurement related signals (baseline variations, purge contaminant absorptions, optical component absorptions, etc.) that are also correlated across the spectral range. Variations in these additional signals are isolated as Principal Components or latent variables, and are correlated to errors in the component concentrations and property values during the development of a predictive model. The resultant models are not robust relative to variations in these measurement related signals. The Constrained Principal Spectra Analysis algorithm allows these additional signals to be modeled and removed from the spectral data prior to the isolation of the Principal Components. The resultant CPSA model is constrained to be insensitive to variations in the modeled signals. Constraints are also developed for factors that effect the overall scaling of the spectral data, yielding models that are robust relative to variations in pathlength, and sample density. Examples comparing CPSA, PCR and PLS models will be given.

387 AN ADVANCED PROCESS COMPOSITION MONITORING ENVIRONMENT.

J. Mc Guire, B. McIntosh and E. Barnes, KVB/ANALECT, 17819 Gillette Ave., Irvine, CA 92714. J. M. Brown and B. N. Perry, Exxon Research and Engineering Company, Clinton Township, Route 22 East, Annandale, NJ 08801.

This paper will describe a software environment which integrates a Constrained Principal Spectral Analysis (CPSA) calibration method, "Smart" Sample System, and a master process monitoring program into a complete composition monitoring system. CPSA is a new multivariate calibration method described in a companion paper. CPSA builds an optimum calibration model, while ignoring instrumental, environmental and sampling artifacts. Spectrometer quality control of a reference solution using CPSA and Partial Least Squares calibration models will be presented. A variety of instrumental, environmental and sampling conditions will be compared. The "Smart" Sample System captures samples which are not accurately represented in the currently running CPSA model into bombs. Property analysis of saved sample in the bomb, along with the spectrum, can be used for updating the model or identification of an extreme process condition. The decision to save a sample is based on the sample's Mahalanobis distance, nearest neighbor distance, and mean squared residual. Finally the master process monitoring program provides all the functions required of a totally automated process instrument.

388 CHEMOMETRIC ESTIMATE OF GASOLINE PROPERTIES: GLOBAL OR LOCAL MODELS. Jon S. Gethner, Adaptive Analyzer Technologies, Inc., 614 River St., Hoboken, NJ 07030-5915.

Recently NIR is increasingly being used for real-time control of gasoline blending operations. For inter-laboratory standardization, standard samples sets must be available. We examine questions of appropriate chemometric sample sets by a detailed evaluation of a large set of gasolines collected throughout the U.S. Regional and local subset modeling will be compared to the global model. Particular emphasis will be placed on examining the bias which results when subsets are selected. The identification of multivariate outliers as distinguished from small (biased) subsets will be discussed. The *art* of examining such data sets in order to develop robust models will be discussed using these data as illustrative.

389 MODEL SELECTION AND VALIDATION FOR ON-LINE PROCESSES. David A. Russell, DuPont Engineering; P.O. Box 6090; Newark, DE 19714-6090.

In-numerable papers have been given extolling the virtues of Chemometrics in general and the Partial Least Squares Algorithm in particular. Too little attention has been given, in my view, to understanding why a particular model is successful in characterizing the target measurement. This can often lead to failed applications which hurt the credibility of both the Spectroscopist and the technology. I will present methods typically used to develop and compare candidate models both in the laboratory and on-line. I will then discuss what I like best about the offerings from the various Near Infrared vendors. I will then close with a discussion of what else is needed for the successful transfer of calibrations to on-line applications and how diagnostics can be used as an on-line validation tool.

390 HIGH PURITY SUPERCRITICAL FLUIDS—STANDARDS AND MODIFIERS. Stephen B. Miller, Ph.D. and Richard G. Heckert, Scott Specialty Gases, Inc., 6141 Easton Road, P.O. Box 310, Plumsteadville, PA 18949-0310.

In many SFE/SFC applications, modifiers and/or additives are needed in the supercritical fluid to effect complete and selective extraction of the analytes of interest. CO_2 containing modifiers has been commercially available for SFC for some time, but not in the high purity grades required for trace SFE applications. Scott Specialty Gases is now able to produce methanol-modified CO_2 in both SFE grade purities, in which both ECD- and FID-responsive contaminants are no greater than the parent pure fluid. In this paper, blending techniques for modified SFE grade CO_2 will be outlined and the key precautions required to maintain the extremely high fluid purity level will be highlighted. Analysis and calibration methods for both pure and modified SFE grade CO_2 will be discussed, including key differences between on-column and off-line analyte collection techniques. If accurately blended, modified SFE grade CO_2 can also serve as a useful internal standard in SFE. Liquid CO_2 standards can be used to measure response factors for key analytes or to determine the collection efficiency of an SFE operation. The preparation and validation of liquid CO_2 standards will also be discussed in this paper.

391 A COMPARISON OF SUPERCRITICAL FLUIDS AND FLUIDITY-ENHANCED LIQUIDS FOR EXTRACTION CHEMISTRY. Yi Cui and Susan V. Olesik, Department of Chemistry, The Ohio State University, 120 West 18th, Columbus, OH 43210.

Enhanced-fluidity solvents are prepared by dissolving large proportions of high fluidity, or low viscosity, liquids in common solvents. In previous studies we have shown that using these solvents as mobile phase in HPLC can be highly advantageous. This talk will present work that compares the relative advantages of extraction techniques using fluidity-enhanced liquids and supercritical fluids as the solvent.

392 THE SEPARATION AND IDENTIFICATION OF PICOGRAM LEVELS OF PCBs BY GC/CRYOGENIC TRAPPING FT-IR. David J. Johnson, Brian Smith and William McCarthy, Bio-Rad, Digilab Division, 237 Putnam Avenue, Cambridge, MA 02139.

Capillary Gas Chromatography/Mass Spectrometry (GC/MS) has routinely been utilized by the analytical chemist to separate and identify environmentally harmful compounds. Although a popular tool for the environmental chemist, the GC/MS is limited when required to differentiate between various isomers. A GC/Cryogenic Trapping Fourier Transform Infrared Spectrometer (Tracer GC/FT-IR) provides the sensitivity of a GC/MS with improved selectivity. The Tracer GC/FT-IR was used in this research to separate and identify picogram levels of PCBs. The ability to differentiate between various PCB isomers will be demonstrated. PCB cogeners which were analyzed for sensitivity and selectivity include 2,2′,5-trichlorobiphenyl; 2,3,6-trichlorobiphenyl; 2,2′,3-trichlorobiphenyl; 2,3,5,6-tetrachlorobiphenyl; 2,2′,4,4′-tetrachlorobiphenyl and 3,3′,4,5′-tetrachlorobiphenyl. Spectra of these compounds were collected on the fly (1 spectrum per second) and later "remapped" coadding a higher number of scans to increase the signal-to-noise of each spectrum. Once spectra of known PCBs have been collected, they may be added to a user generated library. Unknown compounds may then be searched against this database for identification. PCB spectra illustrating sensitivity will be presented. Search results demonstrating the use of the Tracer system to identify unknowns will also be shown.

393 CAPILLARY COLUMN GAS CHROMATOGRAPHY FOR MERCURY SPECIATION. Chunliang Bi and Joseph A. Caruso, University of Cincinnati, Department of Chemistry, ML 0172, Cincinnati, OH 45221.

Gas Chromatography (GC) has been used as the technique for the separation of Organomercurials in many environmental and biological sample matrices. However, problems remain in the separation process due to the poor chromatographic characteristic of these organomercury halides. In this study, Inductively Coupled Plasma Mass Spectrometry is utilized as detection system for GC, and the results will be presented.

394 THE MAXIMUM INJECTION VOLUME ONTO A CAPILLARY COLUMN WITH A RETENTION GAP. R. E. Murphy, Rohm and Haas Company, 727 Norristown Road, Box 904, Spring House, PA 19477-0904.

Retention gaps have many analytical uses in gas chromatography. They allow larger volumes of solvent to be injected onto an open tubular column, reduce the effect of non-volatile solutes and make on-column injections easier with a minimum loss in efficiency or peak distortion. The maximum injection volume for a column with a retention gap is dependent on the column temperature, deactivation material, column and retention gap dimensions (length, internal diameter, and film thickness), and injection solvent. Data on how maximum injection volume varies as a function of these parameters is used to make a predictive model which should eliminate the need for trial and error determinations and make the routine use of retention gaps more widely accepted.

395 CAPILLARY GC COLUMNS FOR THE RESOLUTION OF CO-PLANAR PCB ISOMERS. Dean Rood and Mitch Hastings, J&W Scientific, 91 Blue Ravine, Folsom, CA 95630.

Out of the 209 possible isomers of polychlorobiphenyls (PCB's), there are 20 with a hydrogen in the ortho position. These non-ortho chlorine substituted PCB's can assume a planar configuration which is a concern for toxicological reasons. High resolution capillary GC columns with selective stationary phases are required to provide the best resolution of the isomers from each other. The resolution of the co-planar PCB's with a variety of capillary columns will be investigated. Capillary columns with conventional stationary phases and one especially designed for the resolution of polychlorodibenzodioxins and furans will be examined. The best primary and confirmation columns to achieve the best resolution of the co-planar isomers from each other and from the other PCB isomers will be determined. Different column dimensions, and temperature and flow conditions will be explored to determine if a dual column system can be assembled to achieve the dual analysis with a single injection.

396 CAPILLARY CHROMATOGRAPHY USING POROUS GLASSY CARBON. L. D. Giddings, T. M. Engel and S. V. Olesik, Dept. of Chemistry, Ohio State University, Columbus, OH 43210.

Carbon adsorbents have often been used in various types of packed-column chromatography. Open tubular chromatography using carbon stationary phase was also highly desired. However, these columns were impossible to make until recently. We will described work in this talk that demonstrates the capabilities of open tubular column chromatography using films of porous glassy carbon as the stationary phase. The capabilities of these columns will be described for applications in gas, supercritical fluid, and liquid chromatography.

397 NEW APPLICATIONS OF METAL CAPILLARY COLUMNS FOR HIGH TEMPERATURE GC.

Jan Buyten, Jaap De Zeeuw, Nico Vonk and Judy Sparks, Chrompack Inc., 1130 Highway 202 South Raritan, NJ 08869.

The separation of high molecular weight materials like triglycerides, polyaromatic hydrocarbons or hydrocarbons-oils is possible by using chromatographic techniques. With the development of high temperature stable stationary phases and stable capillary surface deactivation techniques, the practical applicability of gas chromatography for analyzing these types of compounds has widely increased. The presently available fused silica columns show a very good performance but have a practical limitation caused by the polyimide protective outside coating. The use of aluminum outside coating resulted in a temperature stable column, however, the difference in expansion coefficient of the fused silica and the aluminum coating caused column fragility if used with temperature-programmed applications. The ultimate solution was found by chrompack's research organization who managed to deactivate a stainless steel metal capillary column in such a way that the inertness was directly comparable to fused silica. On these deactivated surfaces many types of stationary phases could be coated and chemically bonded metal columns showed unique temperature stability which was much higher than any fused silica capillary column coated with the same stationary phase. The ultimate practical operation resulted in an almost zero bleed level up to temperatures of 400°C. Stainless steel capillary columns of 0.25 mm and 0.50 mm internal diameter were coated with different stationary phases developed for high temperature application (CP-SIL PAH CB / SIMDIST CB / TAP CB). All these phases showed excellent stability and performance. A number of specific applications are shown.

398 MICROCOLUMN SEPARATION SYSTEMS: PAST, PRESENT, AND FUTURE.

Milos V. Novotny, Department of Chemistry, Indiana University, Bloomington, IN 47405.

Capillary gas chromatography (GC), developed in the late 1950's, was the first effectively miniaturized separation technique. As it began to enjoy wide acceptance during the last decade, capillary GC-based technologies were employed in the development of additional microcolumn techniques such as capillary supercritical fluid chromatography (SFC), microcolumn liquid chromatography (LC), and capillary electrophoresis (CE). Although various microcolumn separation methods may employ very different sample types and operating conditions, analytical separation science will continue to benefit from generalizations and cross-fertilization of ideas between GC, SFC, micro-LC, and CE in the future. Examples from the years of research with very small columns and their related instrumentation have been chosen to demonstrate the benefits of removing the artificial barriers between the different methodologies.

399 TWO DIMENSIONAL SEPARATIONS BY LC-CE.

J. W. Jorgenson, J. P. Larmann, A. W. Moore and A. V. Lemmo, Department of Chemistry, University of North Carolina, Chapel Hill, NC 27599-3290.

Resolution of sample components can be enhanced by increasing the dimensionality of the analytical technique. This is well illustrated by a method such as GC/MS. In fully orthogonal two-dimensional separation systems, the peak capacity of the system is equal to the product of the peak capacities of the two individual separation dimensions. Thus two columns, each capable of providing peak capacities of 100, yield a combined peak capacity of 10,000. The requirement of orthogonality, that the sample is spread over the entire available two dimensional space, must be met for this multiplication effect to be realized. The combination of LC with CZE has been accomplished in an automated manner under computer control and provides effective separations of proteins and peptides obtained from protein digests. These separations are done in a comprehensive manner; i.e. in a manner such that all the components of the sample are separated first by LC and subsequently by CZE. In a comprehensive two-dimensional system, the speed of analysis of the second dimension is crucial in permitting effective and yet reasonably fast analyses to be achieved. The great potential for generating separation in a short amount of time, as well as the fact that the electrophoretic separation mechanism is very different from that of most chromatographic methods, makes CZE an exceptionally good choice as the second dimension in a two dimensional system.

400 IMPACT OF SEPARATION SCIENCE ON THE QUALITY OF PHARMACEUTICALS UNDER DEVELOPMENT.

J. Vessman, O. Gyllenhaal, K-E Karlsson, S-O Jansson and J. Snopek, Astra Hässle AB, S-431 83 Mölndal, Sweden.

Compounds under investigation as candidate drugs (CD) and later on presented in applications to the authorities need through characterization. In all these phases of development the methods of choice are based on separations. Examples from substance analysis as well as formulation studies of several drugs will be given. The role of liquid chromatography (LC) in particular will be shown. Comparisons with supercritical fluid chromatography (SFC) and capillary zone electrophoresis (CZE) will be demonstrated. Structure elucidation of unknowns is a common theme and some examples where mass spectrometry (MS) in combination with LC has been valuable will prove that. An area still virgin for the analytical chemists in the pharmaceutical industry is the excipients of macromolecular type. Many of those are oligomeric mixtures and their use in high tech products do require more characterization than is really possible today. Separation methods are lacking in most cases. MS can alone do a lot but at present the combination with separation seems to be far away.

401 ANALYTICAL APPLICATIONS OF MICROELECTRODES.

R. M. Wightman, University of North Carolina at Chapel Hill, Department of Chemistry, CB# 3290, Chapel Hill, NC 27599-3290.

Because of the small size of microelectrodes, they are uniquely suited to probe chemical concentrations in microenvironments. In this talk various examples of these types of measurements will be described. These include characterization of dispersion in liquid chromatography and flow injection analysis, as well as local measurements of secretion from biological cells.

402 FLUORESCENCE QUENCHING AS A DETECTION METHOD FOR LIQUID CHROMATOGRAPHY.

Victoria L. McGuffin, Shu-Hul Chen, Faye K. Ogasawara and Ylwen Wang, Department of Chemistry, Michigan State University, East Lansing, MI 48824-1322.

Although quenching of fluorescence emission by concomitant species is generally considered to be detrimental, this phenomenon may be used to advantage for chromatographic detection. Because the interactions between the fluorophore and the quencher are highly specific, fluorescence quenching can provide sensitive and selective discrimination of individual solutes or classes of solutes in complex sample matrices. In this study, a variety of electron donor and acceptor species were examined as quenching agents for the discrimination of polynuclear aromatic hydrocarbons (PAH). The Stern-Volmer quenching constants, corrected for both primary and secondary absorption effects, were compared for both alternant and nonalternant classes of PAH. The quenching constants appeared to correlate well with a predictive model based on semi-empirical molecular orbital calculations and molecular dynamics. From this predictive model, appropriate experimental conditions were chosen for the class-selective determination of PAH in complex coal-derived samples by microcolumn liquid chromatography with laser-induced fluorescence detection.

403 SEPARATION OF CHIRAL PHARMACEUTICALS BY CAPILLARY ELECTROMIGRATION TECHNIQUES.

Helena Soini and Milos V. Novotny, Department of Chemistry, Indiana University, Bloomington, IN 47405.

The separation of optical isomers in pharmaceutical research has become a significant issue due to the increasing emphasis on regulation. The major separation techniques, such as capillary gas chromatography and high-performance liquid chromatography, have faced substantial challenges in the enantiomeric resolution of both the bulk drug substances and the acquisition of pharmacokinetic data for each enantiomer in the human body. Capillary electrophoresis (CE) is a relatively new, highly efficient technique that has been applied to a number of chiral separation problems in pharmaceutical research. From a variety of chiral selectors investigated, certain cyclodextrin derivatives have been particularly successful. This presentation will address recent developments in the area, illustrated by analyses of basic drugs in synthetic mixtures and serum samples.

404 HIGH SPEED CHROMATOGRAPHY MASS SPECTROMETRY. Milton L. Lee and Zaiyou Liu, Department of Chemistry, Brigham Young University, Provo, UT 84602. Edgar D. Lee, Sensar Corporation, 1048 North Industrial Park Road, Orem, UT 84057.

There continues to be a growing interest in high speed, high efficiency separation methods. Small diameter (<50 μm) capillary columns have been shown to significantly increase the speed of analysis in gas and supercritical fluid chromatography. Furthermore, the narrow peaks obtained with these small diameter columns lead to greater sensitivity, although this advantage can be compromised by the lower sample capacities normally associated with such columns. Small diameter columns can now be prepared using improved static coating methods which demonstrate near theoretical efficiencies in chromatographic evaluations. The limitations in speed are now primarily defined by the instrumentation used, detection being one of the major concerns. Spectrometric detectors, such as mass spectrometry, are often used for high sensitivity detection because they can be specifically tuned to compounds of interest, and they are less effected by background chemical noise. Typical scanning mass spectrometers, however, are not fast enough to handle the narrow peaks generated by high speed chromatography. Recently, an atmospheric pressure ionization (API) time-of-flight (TOF) mass spectrometer (MS) has been developed in our laboratory which meets the speed and sensitivity requirements of the microcolumn chromatographic methods. Complete spectra can be obtained every 200 μs at fg per spectra or pg s^{-1} average detection limits. In this presentation, the unique aspects of this API TOFMS system will described, and selected high speed GC and SFC applications will be shown.

405 UNBREAKABLE METAL CAPILLARY COLUMNS WITH CHEMICALLY BONDED PHASES FOR PROCESS GC. Jan Buyten, Nico Vonk, Jaap De Zeeuw and Judy Sparks, Chrompack Inc., 1130 Highway 202 South, Raritan, NJ 08869.

The application of capillary columns in process analysis is relatively small due to the straightforward and conservative approach in this analytical field. Although several types of fused silica columns have found their way in the process field the majority of the applications are still done with packed columns. One of the main demands of a separation column in process chromatography is its reliability because the column has to work 24 hours each day. Fused silica is known to be very strong but it is not guaranteed unbreakable. Besides this, the practical handling of fused silica requires a special attention which is often not appreciated in process applications. Metal capillaries of 0.5 mm I.D. By using new technology it was possible to prepare metal capillary columns with a high degree of inertness. These metal capillary columns were coated with polydimethylsiloxanes (OV-1) and polyethylene glycol (carbowax 20 M) type of phases which were chemically bonded to the metal surface. The resulting columns show a high degree of inertness and show efficiencies comparable to fused silica columns. The thermal breakdown of the stationary phase on the metal columns was lower than on fused silica which resulted in a higher reproducibility during practical application. The development of a series of metal capillary columns coated with chemically bonded stationary phases will be very welcome on the field of process applications. The metal columns will provide the reliability which is necessary for on-line process control. The applicability of these types of columns will be discussed and several applications will be shown.

406 Abstract not received at time of printing.

407 IDENTIFICATION OF PHARMACEUTICAL AND FOOD CONTAMINANT USING FT-IR/MICROSCOPY. S. C. Yasui, National Forensic Chemistry Center, U.S. Food and Drug Administration, 1141 Central Parkway, Cincinnati, OH 45202.

Food and drug samples contaminated by foreign substances can be rapidly analyzed using FT-IR/microscope. Chemical functional group information for IR spectral frequencies combined with non-destructive sample preparation, make this technique a valuable tool for contaminant analysis. Several commercially available IR library packages and search software facilitate identification of an unknown. A variety of polymers from food and drug packagings were found as product contaminants. Identification of ingredients in pharmaceutical products with or without chromatographic separation prior to IR analysis will be presented.

408 DETERMINATION OF PROTEIN SECONDARY STRUCTURE VIA FTIR SPECTROSCOPY AND INFRARED MICROSCOPY. Ming-Hsing Huang and Navid Asgari, Bristol-Myers Squibb Pharmaceutical Research Institute, P.O. Box 4000, Princeton, NJ 08543-4000.

Infrared spectroscopy has been widely used to study the secondary structures of proteins in both H_2O and D_2O solutions. The results from X-ray crystallography are generally used to correlate the infrared data with protein secondary structure. However, the crystallographic information cannot be easily extrapolate to the dynamic properties of proteins in solution. A more straightforward correlation can be established between the solid state infrared spectra and X-ray crystallography data. The differences between the solution and solid state spectra can then be used to study structural changes accompanying protein dissolution and other changes in the environment. Infrared microscopy is chosen as the preferred method of obtaining the solid state infrared spectra of proteins because of its simplicity in sample preparation and its sensitivity. The simplicity in sample preparation protects the protein samples because no mixing with KBr or high pressure is involved to denature the sample. Furthermore, infrared microscopy requires less than 1 μg of sample as compared to 10 mg of sample typically used to acquire spectra in H_2O solution; thus it makes it possible to study those synthetic peptides that are available only in microgram quantities. Selected proteins, ranging from predominantly α-helix to predominantly β-sheet and turn, will be used in this study. Their infrared spectra obtained from both H_2O solution and infrared microscopy will be presented. Their secondary structures obtained from second derivatives of these spectra will be discussed.

409 MERCURY CATALYZED DISSOLUTION OF ALUMINUM. R. P. Paradkar and R. R. Williams, Clemson University, Department of Chemistry, Clemson, SC 29634.

The acidic dissolution of aluminum is the first step in the reprocessing of spent nuclear fuels. Mercury (II) nitrate is used as a catalyst in this process to overcome the surface passivation of the aluminum by nitric acid. The kinetics and mechanism of this mercury catalyzed reaction is largely unknown. We have attempted to study the same using various techniques like Raman spectroscopy, x-ray fluorescence, auger electron spectroscopy and solvent extraction since any single technique is not adequate in establishing the mechanism conclusively. Aluminum samples were suspended in a glass reactor containing nitric acid and mercury (II) nitrate to simulate actual dissolution conditions as closely as possible. The dissolution was quenched at various time intervals and the remaining aluminum metal was analyzed along with the liquid samples for mercury. Liquid samples were analyzed for mercury using Raman spectroscopy and solvent extraction. The solid samples were studied by auger electron spectroscopy and x-ray fluorescence to determine possible distribution of mercury on the surface of aluminum. Results and findings of these studies will be presented.

410 ORGANIC ACID ANALYSIS BY ION CHROMATOGRAPHY/PARTICLE BEAM MASS SPECTROMETRY. James N. Alexander IV and Chad J. Quinn, Rohm and Haas Company, Research Laboratories, Spring House, PA 19477.

Ion chromatography/mass spectrometry (IC/MS) has been investigated, using the particle beam interface, as an analytical technique for the analysis of small organic acids. Although there are a variety of chromatographic techniques for the analysis of organic acids, ion exclusion chromatography (IEC) with UV and conductivity detection is the most commonly used technique. Normally these detectors are coupled to assist in the identification of acids because with this technique both nonionic compounds and protonated acids elute in the same time domain while inorganic anions such as sulfate and nitrate, which are dissociated, are excluded from the column. The mass spectrometer being a more universal detector can produce mass spectra that contain structural and molecular weight information on acids, thus IC/MS makes identification of organic acids an easier process. Mono- and di-carboxylic acids were separated using a Waters fast fruit juice ion exclusion column with 1 mm HCL as the mobile phase. Analyses were performed using both electron (EI) and chemical ionization (CI). Methane and ammonia CI readily produced protonated molecular ions of organic acids, and combined with structural information obtained from EI analyses, identification of organic acids is possible.

411 CHARACTERIZATION OF CHAIN ORIENTATION IN ROLL-DRAWN POLYPROPYLENE BY POLARIZED RAMAN AND BIREFRINGENCE.

P. M. Killough, D. W. Mead and C. K. Harris, Shell Development Company, P.O. Box 1380, Houston, TX 778251-1380.

Polarized Raman, employing both 90° and 180° scattering geometries, and birefringence measurements have been used to study chain orientation in roll-drawn commercially available polypropylene. Draw ratios from 0.5 to 15 were investigated. Comparisons between the second moments of the orientation distribution obtained from each technique are made for the samples. An analytical solution is proposed for the five nonlinear equations required to solve for the second and fourth moments of the orientation distribution from the Raman data.

412 APPLICATION OF LASER SPECTROSCOPY TO DECONTAMINATE METALS.

Y. M. Hamrick, R. J. Lipert and M. C. Edelson, Ames Laboratory, Iowa State University, 26 Spedding Hall, Ames, IA 50011-3020.

Neutron activation of reactor components generates massive quantities of bulk or volumetrically contaminated metal. Lasers are currently employed in highly selective isotope-enrichment schemes. This same methodology can be applied to remove radioactive constituents and reclaim the remainder of the metal. Initial proof-of-concept experiments demonstrating selective ionization of iron in an atomic beam will be discussed. Iron is photoioninized in a one-color two-photon resonant process using the output of a KrF (248 nm) excimer laser. The resulting ions are extracted from the beam. Methods to enhance efficiency will be addressed.

413 RAMAN VERSUS INFRARED SPECTRAL LIBRARIES AND LIBRARY MATCHING ALGORITHMS.

M. P. Fuller and T. R. Peterson, Nicolet Instrument Corporation, Spectroscopy Research Center, 5225 Verona Road, Madison, WI 53711.

During the last three years, a number of commercial FT-Raman spectrometers have appeared in the analytical instrument marketplace. These instruments typically use a near infrared laser which allows the analysis of many samples that are difficult, if not impossible, to analyze using visible lasers. With these systems, the infrared and Raman spectra of a sample can both be obtained typically in less than 20 minutes. The resulting vibrational spectra can then be processed using spectroscopic analysis software capable of sophisticated library searching. We will discuss the important sample preparation and data analysis procedures involved in creating FT-Raman libraries, and compare the Raman results with those obtained using infrared measurements. The topics covered include the quantitative and qualitative analysis of a set of polyethylene/vinyl acetate copolymers samples. The inherent sensitivity of the two approaches is demonstrated through the analysis of additives in polypropylene films. The effect of sample heating on Raman spectra and the impact on library search results will also be discussed.

414 EVALUATION OF REMOTE ATR METHODS FOR NONDISTRUCTIVE FT-IR ANALYSIS.

F. J. Weesner and T. E. May, Nicolet Instrument Corporation, Spectroscopy Research Center, 5225 Verona Road, Madison, WI 53711.

Technologies for sampling materials remotely from an FT-IR spectrometer are developing rapidly. This poster will present the current options commercially available and compare the major features of each. The performance of several commercial ATR probes which use fiber optic and other spectrometer coupling schemes will be shown. Applications to both liquid and solid sampling will be used for the comparisons. Attenuated Total Reflectance (ATR) sampling is the most widely used sampling method and will be the focus of the experimental results. Transmission sampling will also be included.

415 CHARACTERIZATION OF COATED INTERFACES USING FOURIER TRANSFORM INFRARED MICROSPECTROSCOPY.

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Fourier transform infrared microspectroscopy was applied for analyzing an interaction of the coated interface between two different polymers. The samples investigated were prepared by coating the urethane paint on an ethylene-acrylic acid copolymer (EAA) and on an ethylene-ethyl acrylate copolymer whose ethylester group had been partially hydrolyzed (EAA/EEA). It was demonstrated that a mixed phase was formed along the coated interface between the urethane paint and the EAA and between the paint and the EAA/EEA. The interaction between molecules of the polyurethane and the EAA was observed.

416 NMR STUDY OF GNRH ANTAGONIST ANALOG PEPTIDES IN SOLUTION.

Mark I. Liff, Philadelphia College of Textiles and Science, Philadelphia, PA 19144.

The conformations of α-methyl substituted analogs of GnRH antagonists peptides of basic sequence Ac-D-Nal-D-4-Cl-Phe-D-Pal-Ser-Tyr-D-Arg-Leu-Arg-Pro-D-Ala-NH_2 were studied by two dimensional ^1H NMR at 500 MHz in methanol-d_3. Assignments were made by conventional procedures based on TOCSY and NOESY experiments. For some residues. α_i-N_i, α_i-N_{i+1} and N_i-N_{i+1} backbone NOEs were observed with similar intensities, indicating conformational averaging. The conformational distribution, as inferred from the NOESY spectra, is not shifted significantly on lowering the temperature from 278 K to 248 K. Below 248 K, uniform broadening of all signals occurs, suggesting the onset of aggregation. Measurements in DMSO-d_6 suggested conformational distributions similar to those observed in methanol, since the same NOE patterns with similar intensities are present. The analogs examined were α-methyl substituted at residue 2 and at residues 2, 5 and 8. The NOE patterns, given the absence of certain α-protons in the second case, were similar, suggesting that the distribution is not importantly affected by the α-methylation at residues 5 and 8. I thank Professor Roger Roeske, University of Indiana, and Dr. Kenneth Kopple, SmithKline Beecham, for the opportunity to examine these peptides.

417 HPLC DETERMINATION OF DIASTEREOMERIC PURITY IN LOMETREXOL SODIUM USING BETA-CYCLODEXTRIN AS A MOVILE PHASE ADDITIVE.

L. M. Osborne and G. M. Wilson, Eli Lilly and Company, Lilly Corporate Center, Indianapolis, IN 46285.

Lometrexol sodium is a folate analog that is of pharmaceutical interest as an anti-tumor agent. The compound has two chiral centers with one of the centers fixed throughout most of the synthesis. The resulting diastereomers cannot be separated using typical reverse phase HPLC. However, when a chiral environment is employed these diastereomers can be separated. This work describes the development and optimization of an assay in which beta-cyclodextrin is added to the mobile phase. The assay has been validated and has proven to be a rugged procedure for routine analysis.

418 THE INTERACTION OF ALUMINIUM AND OSTEOCALCIN USING ALUMINIUM-26 TRACER AND CHROMATOGRAPHIC STUDIES.

L. J. A. Evans and J. P. Day, Department of Chemistry, Manchester University, Oxford Road, M13 9PL.

The toxicity of aluminium is well established, one of its major sites of action being bone. Although the pathenogenisis of aluminium related bone disease is unknown, aluminium has been found to accumulate in the mineralised section, most acutely between the osteoid and the mineralisation front. Osteocalcin, an abundant, calcium binding protein of bone, which is produced by the osteoblasts, appears at the onset of mineralisation. It binds strongly to the hydroxyapatite surface in normal bone, however, its precise function remains unknown. The interaction of aluminium and osteocalcin in solution has been investigated *in vitro* by High Performance Liquid Chromatography using gel filtration, anion exchange and reverse phase techniques. The nature of binding has been studied by dialysis techniques. Metal analysis was carried out initially by Graphite Furnace Atomic Absorption Spectrophotometry for aluminium. Contamination problems arise with this ubiquitous metal and later studies employed the radioisotopic tracer, aluminium-26, coupled with Low Level Liquid Scintillation Counting. A positive association of the metal and the protein has been found using anion exchange and reverse phase chromatography. Equilibrium dialysis measurements proved the interaction of osteocalcin, and aluminium and a provisional dissociation constant, $K_a = 3.4 \times 10^{-3}$, has been determined with one aluminium binding site per protein molecule.

419 DETERMINATION OF RADIOSTRONTIUM IN ENVIRONMENTAL AND BIOLOGICAL SAMPLES USING A STRONTIUM-SPECIFIC ION CHROMATOGRAPHY COLUMN.

Tom L. Brand and J. P. Day, Department of Chemistry, Manchester University, M13 9PL, U.K.

Traditional methods for the determination of Sr-90 are chemically laborious, involving a large number of sequential chemical separations designed to isolate the element in a form suitable for radiometric counting. We report the use of a crown ether, cis-dicyclohexano-18-crown-6, (Sr spec, *EIChrom Industries*, Chicago) which binds strontium specifically and so reduces this separation to a single step. The chelator is adsorbed onto an acrylic ester resin allowing convenient separation of strontium by column chromatography. In this laboratory we have incorporated this separation into our standard procedure for the analysis of other environmental radionuclides. Stable strontium, added as a carrier for radio-strontium, also acts here as a chemical yield monitor after determination by ICP—atomic emission spectrometry. Sr-90 is determined by low level liquid scintillation counting *(Canberra-Packard 2250CA)* on aliquots of the eluant from the column.

420 HIGH PRESSURE LIQUID CHROMATOGRAPHIC METHOD FOR THE DETERMINATION OF SCH 39304 IN PLASMA.

H. Kim and C. Lin, Schering-Plough Research Institute, 60 Orange St., Bloomfield, NJ 07003.

SCH 39304 is a novel, potent, triazole antifungal agent which has shown activity both orally and topically. It is active in vitro and in vivo against a broad range of fungal pathogens, including Aspergillus, Candida, Cryptococcus, Histoplasma and Trichophyton. SCH 39304 is a racemic mixture which contains 50% active RR isomer (SCH 42427) and 50% inactive SS isomer (SCH42426). Stereoisomers (RR and SS) of SCH 39304 were quantitated using a chiral HPLC method with UV detection at 205 nm. This method produces a good linearity ($r^2 \geq 0.99$), accuracy (Bias $\leq 6\%$) and precision (CV $\leq 5\%$). The lower limit of quantitation was 0.2 μg per ml plasma. The availability of this sensitive chiral HPLC method makes it possible to evaluate the pharmacokinetics of the active RR and the inactive SS isomers of SCH 39304 in animals and man.

421 CARBON-13 NMR SEQUENCE ANALYSIS OF ETHYLENE/α-METHYLSTYRENE COPOLYMERS.

Takashi Kanezaki, Masato Kijima, Kazuo Kume and Kazuo Sato, Polymer Research Laboratory, Idemitsu Petrochemical Co., Ltd., 1-1 Anesaki-Kaigan, Ichihara, Chiba 299-01, Japan. Tetsuo Asakura, Tokyo University of Agriculture and Technology, koganei, Tokyo 184, Japan.

Ethylene/α-methylstyrene, EMS, copolymers were prepared by anionic polymerization using buthyl lithium and N,N,N',N'-tetramethylethylenediamine (TMEDA) as initiators. The glass transition temperatures of these EMS copolymers are lower than 40°C and these copolymers are rubberlike at room temperature. Since the mechanical properties of EMS copolymer are affected by comonomer composition and sequence distribution, it is very important to investigate the microstructures of these copolymers using ^{13}CNMR methods. The ^{13}CNMR spectra of EMS copolymers were assigned using ^{13}C DEPT and 2D-INADEQUATE NMR techniques. The 2D-INADEQUATE NMR technique is very useful to assign the peaks to the comonomer sequence. The comonomer sequence, distribution in triad level, monomer composition and number average sequence length were determined from the ^{13}CNMR spectra.

422 ENHANCEMENT IN LARGE ION DETECTION EFFICIENCY FOR A DUAL MICROCHANNEL PLATE TIME-OF-FLIGHT MASS SPECTROMETER.

Richard C. King and Kevin G. Owens, Department of Chemistry, Drexel University, Philadelphia, PA 19104.

Matrix-assisted laser desorption/ionization has recently increased the interest in the use of time-of-flight mass spectrometry for the analysis of biomolecules. One of the difficulties with the method is the relatively small ion signals observed for the large analyte ions. It is difficult to maintain good time resolution and enhance the detection efficiency of large molecules. This paper discusses the results of two methods of enhancing the large ion detection efficiency of a dual microchannel plate (MCP) detector. The presentation will include experimental results from matrix-assisted laser desorption/ionization on a linear time-of-flight mass spectrometer system. The ion peak width and intensity will be studied for grid mesh sizes of 70 lines per inch (LPI), 300 LPI and 1500 LPI at several different voltages to determine the effect of grid mesh size and post-acceleration voltage on the detection of large molecules by an MCP detector.

423 CHARACTERIZATION OF PROPERTIES OF PHENOLIC TRIAZINE RESIN.

Melanie A. Kimble, Allied Signal Aerospace, Bendix Engine Controls Division, 717 N. Bendix Drive, South Bend, IN 46620.

Experimental composite parts are being constructed using a matrix of phenolic triazine resin (PT) on a carbon fiber. An attempt was made to monitor state of cure and the effect of post aging on the parts using the FT-IR. By monitoring the changing ratio of the triazine peak to the -OCN peak, state of cure and post-cure effects were evaluated. It was determined that due to unknown differences in the initial molecular weight distributions, no correlations could be made. It was also determined that using the method in an industrial environment was precluded by the absorbance of the infrared energy by the carbon fibers in a finished part.

424 SEPARATION OF MN(II)DPDP AND POSSIBLE *IN VIVO* METABOLITES IN PLASMA BY HPLC.

Jan-Ji Lai, Gene Jamieson and C. Allen Chang, Salutar Imaging Inc., 428 Oakmead Parkway, Sunnyvale, CA 94086

Manganese(II) N,N'-dipyridoxylethylenediamine-N,N'-diacetate-5,5'-bis(phosphate), Mn(II)DPDP, is a liver-specific magnetic resonance imaging (MRI) contrast agent. Phosphate hydrolysis, manganese oxidation and transmetallation with endogenous metals, such as zinc and iron, are potential *in vivo* metabolic pathways. Using a reversed phase C-8 column, Mn(II)DPDP and eight selected possible metabolites resulting from the above-mentioned reactions were separated by HPLC. The metabolite produced by phosphate hydrolysis, manganese(II) N,N'-dipyridoxylethylenediamine-N,N'-diacetate, Mn(II)PLED, was found to coelute with the plasma front, so an HPLC method using mixed bed ion exchange chromatography (Dionex PAX-500 column, UV detection at 310 nm) was developed. The PAX-500 column has both ion exchange and reversed phase functions. Separation optimization was attempted by varying the mobile phase composition, i.e. concentrations of acetonitrile and tetrabutylammonium phosphate (TBAP), and sodium phosphate buffer pH. Unlike other metabolites, the relative retention time (t') of Mn(II)DPDP was found to change dramatically with small pH variations. Increasing the amount of acetonitrile decreased t' values of manganese complexes. The optimal concentration of the ion pairing agent, TBAP, was found to be between 1.5 and 2.0 mM. Two HPLC mobile phase conditions were ultimately chosen to determine the *in vivo* Mn(II)DPDP metabolites in rat plasma. The first mobile phase contained 4.5% acetonitrile, 2.0 mM TBAP and 0.2 M sodium phosphate buffer at pH 9.12. Under these conditions, Mn(II)DPMP (manganese(II) N,N'-dipyridoxylethylenediamine-N,N'-diacetate 5-phosphate), ZnPLED, and ZnDPMP coeluted. The coeluting peaks were successfully resolved using the second HPLC mobile phase containing 3% acetonitrile, 1.5 mM TBAP, and 0.2M sodium phosphate buffer at pH 9.12.

425 VARIOUS CO-IMMOBILIZATION PARAMETERS OF ENZYME, MEDIATOR, POLY-ELECTROLYTE DURING THE ANODIC ELECTROPOLYMERIZATION OF PYRROLE FOR USE IN GLUCOSE BIOSENSOR.

P. Caglar* and G. E. Wnek, Department of Chemistry, Rensselaer Polytechnic Institute, Troy, NY 12180-3590.

It has been demonstrated that polycations are able to bind electrostatically to electroactive polypyrrole (PPy), polystyrene sulfonate (PSS), composite films. Along with anodic electropolymerization of the films—which was carried out at +0.8V vs. SCE-using Glucose oxidase (GOx) as enzyme, PSS as polyelectrolyte and (Ferrocenylmethyl) trimethylammonium bromide (FcBr) as mediator, different parameters affecting the electropolymerization of pyrrole were studied previously. The effect of polymer film thickness and amounts of Py, PSS, GOx and FcBr incorporated in the electrosynthesis bath have been investigated by using the previously determined parameters. Different concentration combinations and electrode surface areas were tried, and these experiments led us to routinely employ an electropolymerization bath containing 50 mM Py/1 mM PSS/1mM FcBr/1mg cm^{-3} GOx. Film thicknesses were initially estimated based upon the amount of charge passed during electrosynthesis. The thicknesses of several composite films were determined experimentally by scanning electron microscopy (SEM). It has been shown that these enzyme-mediator derivatized electroactive polymer films coated on platinum electrodes had various sensitivities to glucose. The responses of resulting electrodes to glucose were measured amperometrically at a constant potential (+0.5 V vs. SCE) by using a Pt coil as a counter electrode.

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426 UV LIDAR DETECTION OF BIOLOGICAL AEROSOLS.

Steven D. Christesen, M. Scott Desha and Anna Wong, U.S. Army CRDEC, Attn: SMCCR-RSL, Aberdeen Proving Ground, MD 21010-5423. Clifton N. Merrow, Mark Wilson and John Butler, Science and Technology Corporation, 101 Research Drive, Hampton, VA 23666.

A UV lidar system for detection of biological aerosols has been van mounted and tested. Using the fourth harmonic of a Nd:YAG laser, the lidar detects 266 nm elastic backscattered radiation, total 300–400 nm fluorescence, and produces a dispersed fluorescence spectrum using a spectrograph and gated intensified CCD array detector. Gating of the 300–400 nm backscatter channel and the CCD array detector, and the use of a solar blind photomultiplier tube for detection of the 266 nm backscatter enabled the detection of bacillus subtillis SSP. Globigii (BG) at ranges up to 2000 meters during the day and 3000 meters at night.

427 FTIR ANALYSES OF PLANT GERMPLASM VIABILITY.

Sharon Sowa, USDA-ARS National Seed Storage Laboratory, Fort Collins, CO 80523.

FTIR spectroscopy was used to examine biochemical parameters of plant germplasm viability. In suspension cultured cells, viability was directly correlated to respiration, measured by dissolved CO_2 (absorbance at 2343 cm^{-1}) in the CIRCLE-collected spectrum. Pollen viability was similarly detected by CO_2 production during germination. Membrane lipid phase (frequency of the symmetric CH_2 stretch) and protein secondary structure (amide I and II vibrations) of pollen at different temperature/moisture contents were monitored using transmission spectroscopy and studied in terms of imbibitional chilling injury. Changes in excised seed embryo protein and lipid spectra, the development of secondary structure and phase change from gel to liquid crystalline, were observed during hydration using transmission sampling. Protein denaturation was the first sign of embryo viability loss. Photoacoustic detection of gaseous CO_2 production (double absorbance peak centered at 2350 cm^{-1}) by intact seed was evident after 15 minutes of inhibition and holds promise as a new technique for noninvasive seed viability assessment.

428 MULTIPLE MATRIX DEPOSITION SPEEDS FOR GC-MATRIX ISOLATION FTIR-MS.

Christoph Klawun, N. Ragunathan and Charles L. Wilkins, Department of Chemistry, University of California, Riverside, Riverside, CA 92521.

Separation of complex mixtures with gas chromatography and subsequent identification of the eluents by using matrix isolation infrared spectroscopy employing a Mattson Instruments Cryolect 4800 GC-IR system is limited by the fixed rotation speed of the cryodisk, where the eluents are deposited in an argon matrix. When flame ionization detector (FID) traces and reconstructed chromatograms are compared, a tenfold decrease in chromatographic resolution in the MI-FTIR chromatogram is usually observed. In this paper, we report a straightforward solution to this problem. Specifically, a computer program has been written to allow arbitrary choice of cryodisk rotation speeds during a chromatographic run. In this way, it is possible to optimize chromatographic resolution in the MI sample collection run, sacrificing none of the fundamental resolution obtained during the original chromatographic separation. Results of application of this programmed speed approach to a variety of representative separations will be presented. Those results will be compared with results obtained in the absence of speed programming. It will be shown that substantial advantages accrue when the new algorithm is used.

429 DETERMINATION OF ESTER COMPOSITION OF SUCROSE FATTY ACID POLYESTERS IN CHOCOLATE BY LIQUID ADSORPTION CHROMATOGRAPHY.

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Sucrose fatty acid polyesters (SPE) are an emulsifier which are added to chocolate or low fat spread. We established the separation method of ester composition of SPE in chocolate. The chocolate is composed of sugar (50%), fat (30%), cacao powder (15%) and SPE (0.5%). The SPE and fat were extracted with chloroform from chocolate. The each component of SPE and fat were found to be separable by gradient elution using silica gel as the stationary phase and detected with evaporative mass detector using light-scattering monitoring techniques. We used the liquid adsorption chromatography because reversed phase HPLC could separate each component of the SPE but not separate the SPE and fat. The types of SPE in chocolate were determined from ester distribution.

430 TRAPPING EFFICIENCIES OF CAPILLARY COLD TRAPS FOR C_2–C_{10} HYDROCARBONS.

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In thermal desorption, the desorbed analytes require reconcentrating in a capillary cold trap before being injected onto the GC capillary column for analysis. Though the commonly used cooling medium, liquid nitrogen, is inexpensive, some capillary traps may not trap some hydrocarbons at all even at the lowest temperature. This may lead to errors in the sampling and analysis of VOCs in ambient air, or reduce the sensitivity of analysis. Thus, trapping efficiency should be studied as a function of trapping temperature and flow rate for different capillary traps in order to select suitable capillary traps for particular applications. Here, the trapping performance of four different capillary cold traps (deactivated, coated, Tenax-TA and Chromosorb 101 packed traps) for the C_2–C_{10} hydrocarbons (C_2–C_5 *n*-alkenes, isoprene, benzene, toluene, *p*-xylene, *o*-xylene, mesitylene, α-pinene, β-pinene, 1,2,3-trimethylbenzene and 1,2,4-trimethylbenzene) have been determined over the temperature range −20°C to −180°C. All the hydrocarbons except ethylene were found to be retained by all the traps at different temperatures, but only the Chromosorb 101 capillary trap retained ethylene, and then not completely. The coatings were found to increase the trapping efficiency for the higher hydrocarbons ($\geq C_6$), while the packings increased the trapping efficiency for all compounds (C_2–C_{10}). A linear relationship was found between the boiling point of the compound and its maximum trapping temperature. It was found that the flow rate of the carrier gas (10–60 ml/min) has no effect on the trapping efficiency of the capillary traps for the hydrocarbons C_5 and above, but breakthrough does occur for the C_2–C_4 hydrocarbons at higher flow rates. Although the coated and packed capillary cold traps may have improved trapping efficiency compared with the uncoated, their blank levels are usually very high due to leakage from the coating or bleeding from the adsorbents, which will adversely affect the detection limits.

431 DETERMINATION OF TRACE METALS IN SOLID SAMPLES VIA ON-LINE DIGESTION FLAME ATOMIC ABSORPTION SPECTROMETRY.

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A double flow injection manifold incorporating a resistively heated oven has been developed for the on-line digestion of solid samples followed by direct introduction to the spectrometer [1]. The determination of trace metals in cocoa powder by flame atomic absorption spectrometry (FAAS) was selected as a model analytical system. The cocoa powder was slurried in 10% nitric acid, injected into the manifold, merged with a stream of concentrated acid and digested under stopped-flow conditions. Gas-liquid separation was effected via a two-stage depressurization system. Copper (50 ± 2 mg kg^{-1}) and iron (188 ± 10 mg kg^{-1}) were determined by flow injection flame atomic absorption spectrometry against acid matched standards and found to be in agreement with results obtained by an open-vessel, hot-plate method and a closed-vessel, microwave digestion method. More efficient destruction of the sample matrix may be achieved through the application of microwave heating and the use of power programming. A single line flow injection manifold has been developed in which digestion of the injected slurry occurs within a glass column mounted vertically within the cavity of a microwave oven. In this design, the column acts both as a mixing chamber and a digestion vessel, greatly simplifying the manifold by eliminating the need for merging acid streams. Internal pressure is monitored by a chemically inert, high pressure flow-through pressure transducer developed in-house. A network of teflon valves are employed for slurry/digest manipulation and controlled depressurization. Operation of the manifold and its application to a variety of sample materials will be discussed.

1. Gluodenis, T. J. Jr., and Tyson, J. F., *J. Anal. At. Spec.*, accepted for publication.

432 A QUANTITATIVE METHOD TO DETECT EXPLOSIVES AND SELECTED CONTAMINANTS IN SOIL SAMPLES BY FOURIER TRANSFORM INFRARED SPECTROSCOPY.

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The current methods for hazardous waste site characterization have the notoriety of being time consuming, cumbersome, and expensive processes. For these reasons, new methods of site assessment and characterization are continually being researched. This paper describes a Fourier Transform Infrared Spectroscopy (FTIR) method that allows for the rapid screening of soil samples from potentially hazardous waste sites. Analysis of a soil sample by FTIR takes approximately 10 minutes. The method, which has been developed to identify and quantify explosives, is directly applicable to selected volatile organics, semivolatile organics, and pesticides. Consideration of field sampling was kept in mind during method development so that the technique may be adopted for use with field instrumentation in a mobile lab setting. Using a CDS 122 thermal desorption unit, the soil samples are desorbed under vacuum into a variable path-length, long-path cell heated to 180C. The spectral data, 128 co-added scans at 1 cm^{-1} resolution, are collected and stored using a Nicolet 60SX FTIR spectrometer. Classical least squares analysis has been used to obtain quantitative results.

433 SURFACE ENHANCED RAMAN (SER) OPTICAL FIBER PROBES.

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The SER substrate is fabricated on optical fibers by abrasively roughening the fiber tip with optical polishing paper and vacuum depositing 30 nm of Ag. These fibers give enhancements nearly equivalent to island films. Ion detection is accomplished by attaching indicators to the SER substrate by synthesizing a disulfide form of the indicator. The disulfide forms a monolayer of the silver thiolate anchoring the indicator to the SER surface. When the indicator complexes with an analyte or changes with pH new peaks characteristic of the indicator/analyte complexes are observed. Analyte concentrations are determined by comparing the relative intensities of peaks associated with the complexed and uncomplexed indicator. The comparison of two spectral peaks provides an internal standard to compensate for varying laser powers and degradation of the indicator or SER surface. A calibration curve for the disulfide derivative of the pH indicator cresol red was generated over a pH range of 2 to 8. The effects of surface charge were described using Gouy-Chapman-Stern theory. Attaching this indicator to an optical fiber allowed us to remotely monitor a flowing pH gradient, in real time, spectroscopically. We have tested octadecylthiol (ODT) as a potential partitioning layer for detection of organics. ODT self-assembles on the silver providing a hydrophobic region near the SER surface which partitions organics from an aqueous solution. Organics intercalated into the hydrophobic region are observed directly with SER.

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434 NEW ANALYTICAL CAPABILITIES FOR FOURIER TRANSFORM ION CYCLOTRON RESONANCE MASS SPECTROMETRY (FT/ICR/MS).

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Several qualitative advances in the analytical capabilities of FT/ICR/MS have been investigated in this lab. To perform analytical analysis with the FT/ICR mass spectrometer, a new ion trap was constructed which eliminates unnecessary sidebands and harmonics. The experimental protocol to quantitate the number of ions that are detected by this instrument was then developed. We have studied two different mechanisms for generating ions from analytically interesting samples. A fast neutral beam ionization source now permits SIMS type analysis of both conducting and insulating samples. We have also designed, constructed, and obtained experimental results with a new external ion injection device which allows ions produced by high-pressure ionization sources to be analyzed at very low pressure (and thus very high mass resolving power and mass accuracy). Compared to prior methods, this ion injection device offers the unique ability to inject ions of low energy (~2 eV) into the magnetic field, thereby avoiding the difficulties of such prior methods as cooling of translationally hot ions and/or ion acceleration with its attendant time-of-flight dispersion. Results with the electrostatic particle guide using an rf glow discharge ionization source to obtain high resolution mass spectra will be presented.

435 RANDOM WALK TREATMENT OF BAND BROADENING FOR CHARGED SOLUTES IN MICELLAR ELECTROKINETIC CAPILLARY CHROMATOGRAPHY.

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Random walk theory has been used by Terabe et. al., and Davis to derive equations that describe the origins of band broadening in micellar electrokinetic capillary chromatography (MECC) for neutral solutes. New equations applicable to charged solutes have been derived. Our main focus has been on plate height contributions from intra-column processes like longitudinal diffusion and resistance to mass transfer both in the mobile phase and the micellar phase. The relative contributions of the individual plate height terms to the total plate height are examined for a variety of experimental conditions. In order to investigate the influence that solute charge has on band broadening theoretical Van Deemter plots for solutes with different t_o/t_{ep} values are compared for one set of experimental conditions where retention time, t_r, is the same for all values of t_o/t_{ep} and another set of experimental conditions where capacity factor, k^1, is the same for all values of t_o/t_{ep}. The term t_o/t_{ep} is the time it take an unretained solute to traverse the capillary divided by the time it takes a solute to traverse the column with the surfactant concentration just below the cmc (i.e. no micelles). A brief discussion of how secondary chemical equilibria can be incorporated into the band broadening equations to account for ion-pairing will also be presented.

436 ELECTROOSMOTIC FLOW CONTROL VIA AN APPLIED RADIAL VOLTAGE FIELD FOR CAPILLARY ELECTROPHORESIS.

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Capillary zone electrophoresis is a rapidly emerging analytical technique. Within this technique electroosmotic flow is one of the most important factors in reproducibility and it allows the detection of cations and anions in a single analysis. An applied radial voltage field across the wall of the capillary has been shown to control this flow. In fact, the flow may be increased, decreased and even reversed. In this work, the effect from an applied radial voltage is examined both theoretically and experimentally. Fundamental theory has been developed by assuming the capillary acts as a cylindrical capacitor for the transfer of charge across the capillary wall. In addition, this model includes the surface conductance within the double layer and the surface potential generated by the ionization of silanol groups. This model leads to a fundamental theory which is in good agreement with experiment evidence. The applied radial voltage is applied by two separate methods; a resistive ionomer and a conductive silver sheath. Experimental data will be shown for the variation of buffer pH and concentration, and the capillary inner radius. Examples of improved separations for peptides will be presented. The effect of surface conductance in these experiments will also be discussed.

437 RETENTION INDEX FOR MICELLAR ELECTROKINETIC CAPILLARY CHROMATOGRAPHY (MECC).

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The goal of this research is to establish a Retention Index (RI) system for MECC using pure and modified micellar systems. The RI system proposed for MECC is similar to the Kováts' retention index scale used widely for qualitative analysis of samples in gas chromatography (GC). However, the homologous series of n-alkane standards that are used in GC cannot be used in MECC due to their insolubility in the electrophoretic medium and the lack of suitable detection, since the detector used in MECC is primarily a UV detector. We have examined three homologous series, n-alkyl aryl ketones; 1-nitroalkanes; and n-alkylbenzenes, that are sufficiently soluble in aqueous micellar media and meet the detection requirements for our MECC detection system. In our original study only one micellar system, sodium dodecyl sulfate (SDS), was examined. The research presented here investigates using our proposed RI system when employing a mixed micellar system, Brij® 35, polyoxyethylene(23)dodecanol/SDS. The advantages and disadvantages of the homologous series, studied previously as RI standards, will be discussed with the Brij® 35/SDS micellar system. A comparison of retention indices calculated with the both the pure and mixed micellar systems for a variety of neutral and charged solutes will be presented. The ability to reproducibly generate a (psuedo)stationary phase in MECC by preparing a relatively simple buffered solution makes the establishment of an RI system more straightforward in MECC than in high performance liquid chromatography (HPLC), where efforts have been thwarted somewhat by the inconsistency among stationary phases.

438 THE RESPONSES OF THE MICROWAVE-INDUCED PLASMA REFLECTED POWER DETECTOR TO PERMANENT GASES, ALKANES AND ALCOHOLS.

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When a sample is injected into a low power, highly efficient microwave plasma, the microwave power reflected by the cavity and plasma increases. This reflected microwave power has been used as a sensitive detector for gas chromatography. The mode of action of the reflected power detector can be thought of as a change in conductivity of the plasma as sample enters the plasma, since the elements in a hydrocarbon are much more easily ionized than the Ar plasma gas. The increase in conductivity causes the high Q cavity to become less well coupled, reflecting more power back toward the generator. Since this mode of operation does not require the formation of easily ionizable molecules, many analytes that are not sensitively detected by an FID do give sensitive responses to the reflected power detector. An attempt to characterize the response of this detector will be presented.

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439 PERFORMANCE OF AN ECHELLE BASED HE-MIP-AES DETECTOR FOR SFC.

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Recently, element specific detection for supercritical fluid chromatography has been demonstrated with a helium based microwave plasma system using atomic emission spectrometry.[1] Although the MIP-AES system is capable of monitoring metal and non-metal emissions in the UV-VIS region, the overall sensitivity was found to be limited by the low resolution of the monochromator that was employed in this work. In this paper, we will discuss the figures of merit for an Echelle based system as compared with a standard-grating monochromator using a helium MIP for non-metal and metal detection in SFC. We will present minimum detectable quantities for metal and non-metal species obtained with each of the systems and discuss the application of SFC-MIP-AES to the separation and identification of metal porphyrins.

[1] C. B. Motley and G. L. Long, *J. of Anal. At. Spectrom.*, **5**, 447 (1990).

440 IMPROVED ANALYTE TRANSPORT EFFICIENCY WITH A MOVING BAND INTERFACE FOR LC/MIP.

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Due to the unique advantages of helium microwave-induced plasmas (He-MIP) as a non-metal atomic emission source, the development and application of a He-MIP system for high performance liquid chromatography detection is the subject of this study. A modified Finnigan MAT HPLC-MS moving band interface was employed to couple the HPLC system to the plasma emission source. At the heart of this transport-type interface is a thin polyimide band which acts to carry mobile phase through the interface and to the plasma source. Solvent removal is accomplished through an IR heater coupled with a vacuum chamber, leaving dry analyte on the moving band. The analyte is then transported to a vaporization chamber where desorption is accompanied by flash vaporization. The sample vapor is carried into the plasma by helium flow. Modifications to the interface, introduced at the Pittsburgh Conference in 1991 (paper #069), were made in order to increase analyte transport efficiency into the plasma. Calibration plots and detection limits were obtained for various organic samples.

441 DIAGNOSTICS AND CHEMICAL REACTIONS IN AN ATOMIC EMISSION DETECTOR FOR GC.

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In GC-AED, chromatographic performance is described by sensitivity, selectivity and minimum detectable level. These are determined not only by plasma parameters, such as electron density and excitation temperatures, but also by chemical mechanisms in the discharge, such as oxidation, reduction, adsorption and buffering. Modern microwave plasmas, as used in the AED, are remarkably constant in helium excitation temperature (3400 to 3600 k) and in electron density (about $0.5 \times 10-^{15}$ per ml) as the reagent gases are changed. This is probably because the power to the plasma is buffered by the surrounding cooling water which absorbs some of the microwave power and stabilizes the microwave system. The rotational temperature changes slightly with the concentration of analyte. This shows up in variation of background interferences caused by interfering molecular bands. However, elemental detection algorithms ("recipes") can be optimized to reject both low- and high- temperature molecular bands. A nonlinearity in hydrogen response has been widely reported. This is shown to result from reaction with the oxygen reagent gas. New measures correct for this nonlinearity.

442 EXPLORING THE PERIODIC TABLE WITH GC-AED.

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Element selective atomic emission spectroscopic detection for gas chromatography is well established, utilizing various plasma sources for excitation and emission. The majority of developments and applications have been for element selective detection of non-metals such as halogens, sulfur, oxygen and carbon, although in general, greater sensitivity is obtainable for metallic elemental emission. Atomic spectral emission permits any element to be selectively monitored, and this paper considers some less explored areas of high resolution element-specific GC with examples of selectivities produced by chemical derivatization and reaction, chromatographic resolution and spectral method development. Volatilizable compounds of approximately 40 elements have been documented by GC-AED and figures of merit and optimal operational parameters are presented for a number of these on commercial and laboratory constructed instruments. Applications discussed include high temperature GC studies of metalloporphyrins in fuel oils, arsenic, phosphorus and selenium speciation in pyrolyzates of coals and kerogens, organotin speciation from aqueous samples, and a range of metal specific investigations for normal and transition metal complexes and organometallics. Elements discussed include titanium, chromium, cobalt, nickel, copper, iron, vanadium, palladium and platinum.

443 ATOMIC EMISSION DETECTION IN GAS CHROMATOGRAPHY.

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Gas chromatography interfaced to atomic emission spectroscopy (GC/AES) has received increasing attention in recent years. The technique provides chromatographers with selective detection capabilities for any element, and has recently been extended to several isotopes as well. This information can be used to detect compounds containing the element of interest, as is traditionally done with selective detectors. However, since the response factors for most elements are compound independent, other types of applications can be pursued. Compound independent calibration and empirical formula determination are examples. Used in conjunction with GC/Mass spectrometry and GC/Infrared spectroscopy, unknown compounds in complex matrices can be identified more rapidly and accurately. This paper will give an overview of the many types of applications GC/AES is currently being used for. Examples from areas including chemicals, flavors, petroleum, agriculture, and environmental will be discussed.

444 APPLICATION OF GC-AED IN THE PETROLEUM INDUSTRY.

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As an analysis technique, GC-AED has a number of advantages for analyzing petroleum related samples. First, the response obtained is proportional to the number of atoms in the plasma irregardless of the starting molecule. This vastly simplifies calibration and subsequent analysis of complex samples. Second, the detector can be tuned to any element other than helium, and third, it allows for simultaneous multielement analysis. This presentation will show examples of the use of GC-AED for the analysis of samples commonly analyzed in the petroleum industry. Examples of how GC-AED has been used in this laboratory include verification of the concentration of components in purchased gas calibration standards, analysis of non-radioactive tracers in natural gas, multielement high temperature simulated distillation, analysis of oxygenates in reformulated fuels, and multielement chromatographic analysis of environmental samples including the use of pattern recognition techniques for spill sourcing. Since the detector can be used to monitor hydrogen, it provides a convenient means to measure the variation in the average H/C molar ratio with boiling point. It will be shown that the use of this and other elemental data is quite useful for sample comparison problems. The multielement simulated distillation technique provides information about heteroatoms in a form that is useful to process engineers for studying catalyst effectiveness, modelling, process changes, new formulations, and heavy oil upgrading.

445 PARAMETRIC EVALUATION OF SPUTTERING IN AN RF ATOMIZER FOR ATOMIC ABSORPTION SPECTROMETRY.

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Parametric evaluation of sputtering in a radio-frequency glow discharge atomizer constructed in the laboratory of one of the co-authors of this paper (R. K. Marcus) has shown that the control of flow rate and pressure of the sputtering gas (argon) is critical in determining the amount of sputtering. Both the flow rate and the pressure of argon gas affect the rate of atom removal from the analysis volume. Results obtained for sputtering of oxygen-free hard copper indicate that glow discharge plume is constricted by an increase in the Ar gas pressure and most of the sputtered copper atoms are localized at the cathode surface. Higher pressures increase redeposition of the sputtered atoms on the cathode surface. In a low-pressure glow discharge Ar ions have a smaller energy distribution because of the longer mean free path. For sputtering to occur, the Ar ions must have an energy greater than the threshold energy of the analyte in the target cathode. Interferences with the sputter-atomization of residues of aqueous solutions of Au, Fe and Mg salts in a six-jet-assisted, direct-current cathodic sputtering atomizer (ATOMSOURCE), have been studied. Effect of change in applied dc power, discharge gas pressure and flow rate on both peak-height and peak-area absorbances has been investigated. It has been found that less than 500ng sodium chloride causes no interference with gold. However, even a small amount of sodium chloride interferes with the signals of iron and magnesium.

446 ANALYTICAL FIGURES OF MERIT FOR RF GLOW DISCHARGE ATOMIC EMISSION SPECTROMETRY.

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Radio frequency glow discharge devices appear to have a promising future for the analysis of bulk solids. The types of samples amenable to this type of sputter atomization can be either conductive or nonconductive in nature, including metals, ceramics, and glasses. The development of analytical methods for this type of radio frequency device has brought into question the criteria for analyte line selection. The glow discharge environment is unique in that the spectral background shows little or no structure, with the spectra dominated by very narrow atomic transitions. These characteristics, along with the novelty of the devices, require that a methodical, rigorous approach to line selection be evaluated which will also be used to determine figures of merit such as limits of detection based on S/B and S/N values. The methodical approach to line selection will be discussed, beginning with selection of lines using pure elements through the final selection of lines of trace elements found in various matrices such as copper, aluminum, and steel. Analytical figures of merit such as S/B and S/N values will be presented, along with calibration curves of the selected lines. It has been shown that elemental limits of detection are possible on the ppb level with the glow discharge technique. These limits of detection along with measures of precision will be discussed.

447 ANALYSIS OF NON CONDUCTIVE COATINGS USED IN VARIOUS INDUSTRIAL APPLICATIONS.

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Coated flat steel, or aluminum sheets are used in several industries such as the automotive and building industries. A large variety of coatings, conductive and non conductive, corresponding to specific applications can be used. The quality of the coating and the production processes need to be checked and verified with a lot of attention. Glow discharge optical emission spectrometry now permits the analysis of both conductive and non conductive materials, and gives a continuous depth profile analysis of several elements (simultaneously) from the surface (few nm) to several hundreds of microns. We will discuss—automotive applications: analysis of painted steel sheets (lacquer, sealer, cataphoresis, phosphatation, Zn coating, steel); building applications: analysis of flat steel sheets coated with several types of organic coating (acrylic, polyester, . . .). In both cases, it will be interesting to see the phenomena observed at the interfaces between the layers, and to see the different techniques used to improve the adherence of the coatings on the matrices. We will discuss also the semiconductor applications with analysis of SIO_2/SI samples, on which we'll see that the GD-OES technique can be helpful to detect the presence of pollution at interfaces. Some examples of ceramics and glasses will be also discussed: pollution on ceramics, and coatings on glasses, both applications used in the automotive field. A brief description of the technique, and the instrumentation will be made to give a complete view of the GD-OES technique.

448 COMPARISON OF SEVERAL MAGNETICALLY ENHANCED RF GLOW DISCHARGE SOURCE CONFIGURATIONS.

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A simple method for enhancing the performance of a glow discharge source (GDS) is the application of a magnetic field to the discharge volume. The magnetic field reduces electron loss by altering the paths of electrons. Several source configurations have been developed in the past which magnetically enhance the glow discharge performance. The widely used Grimm lamp has been modified by placing a donut-shaped Co-Sm magnet around the discharge cell.[1] Sacks and coworkers have also published extensively on magnetron-assisted dc glow discharges.[2] In our laboratory we have recently begun work on a magnetically assisted rf glow discharge source. The Macor spacer between the sample and the discharge cell in our source was modified in order to place a donut-shaped ceramic magnet around the discharge volume nearest the sample surface. Also, a magnetron-assisted discharge was constructed by placing magnets in the water-cooled rf connector which presses the sample against an o-ring vacuum seal on the ceramic spacer. The performance of the two different magnetically enhanced GDS configurations and the basic source with no applied magnetic field will be compared. The different systems were each separately optimized for atomic emission spectrometry and the optimization procedure will be discussed.

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2. L. McCaig, R. Sacks and D. Lubman, *Appl. Spectrosc.* **43.** 912 (1989).

449 INVESTIGATIONS OF PLASMA EXCITATION/IONIZATION MECHANISMS IN LOW PRESSURE GLOW DISCHARGE DEVICES.

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Glow discharge devices are finding widespread application as versatile atom sources for a variety of atomic spectroscopic methods including atomic fluorescence, atomic absorption and emission, and mass spectrometry. With the increased utility of the devices, information on the fundamental mechanisms of excitation/ionization is of importance. In particular, recent studies of pulsed glow discharge devices have shown a significant pulse of ions and excited atoms to appear after the termination of the discharge pulse, believed to be caused by the creation of a large metastable population as the discharge plasma collapses, resulting in enhanced excitation/ionization of the sputtered material via energy exchange with the metastable atoms in the afterpulse region. We will report on a variety of experiments designed to investigate the ionization/excitation processes in both dc and pulsed discharges. These investigations include optogalvanic effect and laser depopulation studies of the system, metastable quenching investigations, and studies of the effect of discharge gas identity on the emission signals produced in the discharge plasma. These studies will contribute to the understanding of the complex discharge processes that result in the analytical utility of the glow discharge source.

450 THE EFFECTS OF ALTERNATIVE DISCHARGE GASES ON ION SIGNAL PROFILES IN PULSED GLOW DISCHARGE MASS SPECTROMETRY.

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Pulsed GDMS is a recently developed technique that produces higher sputter yields and ion signals than equivalent dc discharges, in addition to exhibiting time-dependent anomalies for individual ion signals. It is these signal anomalies that are of particular interest, since it is believed that different ionization mechanisms are responsible for their formation. During the "on" portion of the duty cycle (plateau), the ion signals resemble those observed in the dc discharge and are probably produced from a combination of electron and Penning ionizations (EI and PI). Upon termination of the pulse, a sharp increase in ion signal (afterpeak) is observed for species with ionization potentials below the metastable levels of the discharge gas (PI). By the judicious placement of a data acquisition gate over the different regions of the pulse period, the effect of these different ionization modes or a different mix of ionization efficiencies was investigated using helium, neon, argon and xenon discharge gases. It is difficult to make direct comparisons among the gases since they require different operating parameters to form stable discharges. Therefore, in addition to using the pure gases, mixtures of the gases in argon were used for comparison purposes. In the case of a gas mixture, the afterpeak was observed to decease in size compared to the pure gas. Also, afterpeaks were formed or eliminated for certain species depending on the discharge gas and its concentration. In addition, the formation of metal-gas dimer species was observed in the gas mixtures. Possible reasons for these observations will be discussed.

451 EVALUATION OF ALTERNATIVE GASES FOR RF GLOW DISCHARGE. Jeffrey J. Giglio and Joseph A. Caruso, University of Cincinnati, Department of Chemistry, Cincinnati, OH 45221-0172.

Experimental work in the glow discharge field has received much attention in the literature over the past few years. In most of this work one common theme is present, the use of ultra-pure argon as the gas for sustaining the plasma, sputtering the solid sample and ionizing the analyte (Penning Ionization). Due to the nature of the sputtering process, one would expect the choice of this gas to be a significant factor in all of these processes. In this work, a range of gases from noble gases to molecular gases will be evaluated. In addition, the feasibility of utilizing a mixed gas plasma will also be addressed.

452 SAMPLING RADIO FREQUENCY POWERED GLOW DISCHARGES WITH A QUADRUPOLE ION TRAP. D. C. Duckworth, C. M. Barshick, S. A. McLuckey and G. L. Glish, Oak Ridge National Laboratory, Oak Ridge, TN 37831-6375.

Radio frequency powered glow discharge ion sources have been successfully interfaced with several mass analyzers; these include beam instruments such as linear quadrupole and double focusing mass spectrometers, and ion traps including Fourier transform ion cyclotron and quadrupole ion traps. We are investigating the use of quadrupole ion traps for the analysis of rf glow discharge generated species for several reasons. Because we are able to generate ions directly from solid nonconductors, we are interested in analyzing materials such as glasses and soils directly. Such matrices are likely to have many isobaric interferences from oxides, nitrides, and carbides in addition to common glow discharge isobars such as argides and dimers. We have found that collisions in the trap generate a "high temperature" trapping environment were species such as argides and dimers are readily dissociated. More strongly bound molecular ions such as oxides can be efficiently dissociated as they are kinetically excited with an applied resonance potential on the endcap electrodes. The ion trap is also a good environment for ion-molecule reactions. Such reactions are beneficial in reducing interferences from argon-related ions. Multiple scan functions are currently being used to optimize the dynamic range of the trap. As such, quantification is not as straightforward as on beam instruments. We hope to utilize trap parameters such as injection time to aid in quantification. Qualitative and quantitative aspects of the quadrupole ion trap as a mass analyzer for glow discharge generated ions will be presented.

453 ELEMENTAL ANALYSIS BY RF-GDMS: INSTRUMENTATION AND ANALYTICAL CAPABILITIES. J. A. Olivares, A. K. Huff, E. M. Garcia and N. C. Schroeder, Los Alamos National Laboratory, Inorganic and Nuclear Chemistry Division, P.O. Box 1663, Los Alamos, NM 87545.

The conversion of a commercial quadrupole based DC-GDMS system for RF operation will be described. The analytical features of this instrument in applications to elemental analysis of glasses, soils, and geological materials have been studied. The results of these experiments will be discussed within the context of accuracy, precision, detection limits, interferences, and standardization. The effect of some instrument parameters on the analytical performance will also be discussed, along with modifications that enhance the quality of the results.

454 CHARACTERISTICS OF A NEW RF-GDMS SYSTEM. R. K. Marcus and C. R. Shick, Jr., Dept. of Chemistry, Howard L. Hunter Laboratory, Clemson, SC 29634-1905.

Radio frequency glow discharge devices have proven useful in the analysis of both conductive and nonconductive solids. In this laboratory, we have developed a direct insertion probe (DIP) sample introduction assembly for use with mass spectrometers. Previous studies performed with the DIP on an Extrel double quadrupole system revealed a set of plasma parameters which yielded optimum system performance, particularly in terms of increased analyte intensities. A novel DIP has recently been developed for conducting rf-glow discharge studies utilizing a VG GloQuad for ion sampling. The optimized operating conditions for the new rf-GDMS will be presented in terms of the applied power, discharge gas pressure, and the sample position relative to the sampling cone. The performance of this system will be gauged by relative sensitivity factors and preliminary limits of detection for a variety of standard reference materials.

455 RECENT DEVELOPMENTS IN FLOW INJECTION ICP-MASS SPECTROMETRY. E. R. Denoyer, Q. Lu and A. Stroh, The Perkin Elmer Corporation, 761 Main Avenue, Norwalk, CT 06859-0215.

Flow Injection (FI) is becoming an important means for preparing and introducing samples into an ICP-Mass Spectrometer. Already, microsampling, vapor generation and preconcentration techniques can be used to improve sample throughput, reduce interferences, increase sensitivity and improve stability. Recent advances in FI technology have made otherwise difficult ICP-MS determinations even more practical and easy. In this paper, we will describe recent advances in FI methods and applications and new designs for on-line sample preparation components to illustrate the direction we are taking FI-ICP-MS both in our research and our applications laboratories.

456 MULTIELEMENTAL ANALYSIS OF SOILS BY FLOW INJECTION WITH SLURRY NEBULIZATION AND ICP-MS". Diane Beauchemin, Queen's University, Departments of Chemistry Science, Kingston, Ontario, Canada K7L 3N6. Maria J. Payer, Queen's University, Departments of Chemistry Science, Kingston, Ontario, Canada K7L 3N6. Heather E. Jamieson, Queen's University, Departments of Geological Science, Kingston, Ontario, Canada K7L 3N6.

The demand for techniques to achieve quick and accurate analysis of environmental samples is constantly growing. Although the analysis of many types of aqueous samples (potable water, rain, etc.) is direct and straightforward using inductively coupled plasma mass spectrometry (ICP-MS), that is not the case of solids such as soils, sediments, etc. A lengthy dissolution procedure is required, which involves many reagents and steps, increasing potential sources of contamination. Slurry nebulization in combination with ICP-MS may be an alternative and quick way of analyzing these samples (requiring only a grinding step). The technique has already been successfully applied to the direct analysis of ground coil. However, its application to soils has, so far, been hindered by the inhomogeneous nature of this type of sample. During this presentation, we will describe the various steps that were taken towards the goal of accurate analysis of soils slurries. For instance, flow injection was used to introduce the slurries since it allows a continuous rinsing of the sample introduction system between slurry injections. Requirements in terms of particle size of the ground material and type of dispersing agent will also be addressed, as well as optimization of the operating conditions of the ICP-MS instrument for this type of application.

457 INVESTIGATIONS INTO THE USE OF METHANE ADDITION TO ICP-MS TO REDUCE POLYATOMIC INTERFERENCES. M. Ford and S. Hill, Polytechnic SW, Plymouth, UK. R. C. Hutton, Fisons Instruments, VG Elemental, Ion Path, Road Three, Winsford, Cheshire, CW7 3BX.

The use of mixed gas plasmas in ICP-MS has been shown to be advantageous for the reduction of certain polyatomic ions. To date mainly N_2 has been used as the additive gas. In the work reported in the presentation, additions of CH_4 will be shown to be particularly effective in reducing those polyatomic ions based on chloride or oxide species. Simplex optimized parameters yield results where the ARCl$^+$ is completely removed and ARO and CLO$^+$ species are reduced by an order of magnitude.

458 ENHANCEMENT OF SOME ANALYTE SIGNALS BY CARBON COMPOUNDS IN ICP-MS. Gordon F. Wallace, Perkin-Elmer Corporation, 3206 Tower Oaks Boulevard, Rockville, MD 20852.

Several elements, including arsenic and selenium have been reported to show enhancements effects in samples containing carbon compounds.[1] Samples of lake water containing humic acids and biological materials such as blood and urine have exhibited similar effects in the author's laboratory. The enhancement effect appears to be quite element-selective. This affects the choice(s) of internal standard elements. The validity of spike recovery tests is also impacted. Several examples of enhancement effects in acetic acid, glycerol, blood and urine will be presented.

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459 RECENT STUDIES ON HELIUM INDUCTIVELY COUPLED PLASMA MASS SPECTROMETRY.

Sang-Ho Nam, Wellington Masamba, Hao Zhang, Chuming Hsiech and Akbar Montaser, Department of Chemistry, George Washington University, Washington, D.C. 20052.

Our previous studies have indicated presence of an intense secondary discharge when helium inductively coupled plasma is coupled to an ICP-MS. The previous techniques used to reduce this discharge for Ar ICP-MS were not found effective for He ICP-MS. In this study, a non-conductive sampler has been used for reducing the secondary discharge. A 40-MHz, crystal-controlled generator and a 34-MHz, free running generator (generator for ELAN 5000 ICP-MS by Perkin Elmer Sciex) were coupled to a quadrupole mass spectrometer. The extents of secondary discharge with these generators are compared to those of other approaches for minimizing plasma potential. The analytical performance of helium ICP-MS for detection of halogens and other nonmetals is tested.

460 EVALUATION OF A HIGH EFFICIENCY NEBULIZATION SYSTEM COUPLED TO A HIGH RESOLUTION ICP-MS INSTRUMENT.

N. M. Reed, R. C. Hutton, A. Kingston and P. Brown, Fisons Instruments, VG Elemental, Ion Path, Road Three, Winsford, Cheshire, CW7 3BX. G. Gibson, Fisons Instruments Inc., 32 Commerce Center, Cherry Hill Drive, Danvers, MA 01923.

The technique of ICP-MS using a high resolution mass analyzer offers the capability of detection limits at PPQ levels using conventional liquid sample introduction systems. Further improvements can be obtained when the efficiency of nebulization is increased possibly using an ultrasonic nebulizer. However such devices have some short comings especially with respect to memory and carryover. A new ultra high efficiency nebulization system has been developed which combines enhanced aerosol production with desolvation. The mechanism, aerosol production also minimises memory effects when combined with a HR ICP-MS, detection limits below PPQ can be achieved. Another advantage of such a system is the reduction in molecular species, allowing better detection limits when operating the instrument in high resolution mode. The system will be discussed and data on ultra pure reagents of the type used in semiconductor processing will be shown.

461 PERFORMANCE EVALUATION OF ICP-MS WITH SAMPLE INTRODUCTION BY ULTRASONIC NEBULIZATION.

Uwe Voellkopf, Willi H. Barger and A. Blum, Bodenseewerk, Perkin-Elmer GMBH, Postfach 101164, D-7770 Ueberlingen, Germany.

During the last couple of years a number of alternative sample introduction devices for ICP-MS became popular, one of those being ultrasonic nebulization. Among the potential advantages of this technique are sensitivity enhancement, lower detection limits and lower oxide ratios due to the desolvation process involved in this nebulization technique. This paper shall discuss the experience that has been made in our laboratory with this technique. Data on sensitivity, detection limits, oxide and doubly charged ion ratios and instrument stability using a commercially available USN will be discussed. Further, preliminary results shall be presented using the USN coupled with a dryer tube for further reduction of oxides.

462 EXPERIMENTAL STUDIES OF ION KINETIC ENERGIES IN ICP-MS.

Scott D. Tanner, SCIEX®, 55 Glencameron Road, Thornhill, Ontario, Canada L3T 1P2.

The development of ion optics for mass spectrometric instruments benefits from an understanding of the distribution of the kinetic energies of the ions to be analyzed. In this paper we will present ion kinetic energy distributions measured using a standard ELAN® 5000 ICP-MS vacuum interface. The distributions were measured using a triple grid energy analyzer. The impact on the measurements of the ion optics downstream of the energy analyzer will be presented and discussed. Ion energies obtained by using the mass-analyzing quadrupole as a retarding energy analyzer have been commonly reported in the literature. A comparison is made here of the two approaches, and shows that ion energies derived from quadrupole stopping curves can be severely skewed by focusing effects within the quadrupole. The cooling of the plasma central channel by increasing the nebulizer flow rate is evidenced by a decrease in the slope of the ion energy *vs* ion mass plot, which can be used to infer the plasma temperature at the sampler orifice. The oxide ions of refractory elements (e.g. CeO^+) reproducibly demonstrate lower ion kinetic energies than isobaric elemental ions. These measurements provide important insight into the source of the isobaric polyatomic interferents. The impact of changes affecting the gas dynamic expansion within the interface will be discussed.

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464 ELECTROCHEMICAL INVESTIGATIONS OF ENVIRONMENTAL REDOX COMPONENTS.

James L. Anderson, Christopher E. Todd, Mark C. Delgado and N. Lee Wolfe, Department of Chemistry, University of Georgia, Athens, GA 30602 and U.S. Environmental Protection Agency, Environmental Research Laboratory, Athens, GA 30613.

Anaerobic environmental soil sediments are capable of reducing a wide range of pollutants with time constants ranging from hours to months. Evidence suggests that these reactions are catalyzed by proteinaceous species (presumably enzymes) adsorbed at low concentrations on sediment particles. We will discuss methods for characterizing these catalytic species and the reactions that they catalyze, based on both kinetic measurements for the reduction of nitroaromatic and halogenated aliphatic compounds, and indirect coulometric titrations supplemented by spectroscopic probes for sediment slurries and extracts. We will discuss mechanisms by which these very low concentrations can effectively drive reactions whose initiation step is either kinetically unfavorable or thermodynamically uphill.

465 ELECTRODEPOSITION OF COPPER ON POLYPYRROLE FILMS.

Maria Hepel and Susan Perkins, Department of Chemistry, Potsdam College of SUNY, Potsdam, NY 13676. Tadeusz Hepel, ELCHEMA, Potsdam, NY 13676.

Recent advances in science and technology of conductive organic polymers indicate on a variety of potential applications of these materials, including microcircuit transistor devices, electrochromic devices, capacitors, batteries, controllable ion gates, ion exchangers, drug release systems and electrocatalysts. We have undertaken systematic studies of the electropolymerization of conductive organic polymers and subsequent electrodeposition of metals on these materials with special emphasis paid to the morphological developments and possible procedures for nanostructure engineering and possible applications for the metallization of PPy precoat for printed circuit boards. Electrodeposition of copper at polypyrrole (PPy) coated Pt electrodes have been investigated using the Electrochemical techniques and Scanning Electron Microscopy (SEM). Several factors influencing the micromorphology of the deposits have been investigated. The effect of pH, deposition potential, type of anions, and the morphology and thickness of the polypyrrole substrate on the electrodeposition of Cu have been studied. The effect of organic and inorganic additives such as boric acid, thiourea, benzotriazole, 1,5-naphthalene disulfonic acid, chloral hydrate, hydroquinone, EDTA, etc. and their mixtures have also been investigated. The optimal potential for the copper electrodeposition has been selected taking into account variable conductivity of the polypyrrole substrate with potential.

466 POTENTIOMETRIC SOLID-STATE ION/BIOSENSORS BASED ON ASYMMETRIC POLYURETHANE MEMBRANES.

Dong Liu, H. D. Goldberg, R. B. Brown and M. E. Meyerhoff, Department of Chemistry, University of Michigan, Ann Arbor, MI 48109.

The potentiometric response of ammonium- and proton-selective electrodes prepared by incorporating appropriate neutral carriers within novel asymmetric polyurethane membranes will be reported. The membranes are formed by first casting a plasticized polyurethane/terpoly(vinyl chloride/vinyl acetate/vinyl alcohol) based ion-selective membrane and then applying a thin second layer of hydrophilic polyurethane containing 9 wt% of polylysine (approximately 9 μm in thickness). The resulting asymmetric membranes function equivalently to normal polyurethane membranes and conventional poly(vinyl chloride) type membranes, in terms of potentiometric ion selectivity and dynamic response properties (typically 56 mV/decade in the range of 10^{-5} to 10^{-1} M of NH_4^+). The large amount of amine functional groups from the polylysine on the surface of the membrane can be further activated by glutaraldehyde (2.5 wt%) for direct enzyme immobilization. As examples, adenosine deaminase and urease are covalently immobilized on the ammonium- and proton-selective membranes, respectively. The resulting enzyme electrodes last for at least one month, with little loss in response slope or detection limits. The performance of solid-state potentiometric ion/biosensors prepared by casting (or screen printing) the polyurethane based membranes on silicon wafers will also be described.

467 SIMULATION METHODS AND EXTENDED KALMAN FILTERING FOR KINETIC DETERMINATIONS IN STEP VOLTAMMETRY.

Robert S. Bear, Jr. and Steven D. Brown, Department of Chemistry and Biochemistry, University of Delaware, Newark, DE 19716.

Simulation methods are commonly employed for modeling kinetics in electrochemistry. The estimation of charge transfer parameters from voltammetric data is usually performed by matching simulated working curves to experimental data. These manual attempts to optimize simulations for experimental data are both time consuming and lack statistical validity. Additionally, manual matching of experimental results to synthetic curves is specific to the type of voltammetric experiment used. A better method of optimizing the simulation to obtain kinetic parameter estimates is required. By incorporating a generic simulation model function into an extended Kalman filter, maximum likelihood estimates of the kinetic parameters can be obtained in a single pass through the data.

468 ELECTROCHEMICALLY GENERATED RU(BPY)$_3^{3+}$ FOR THE DIRECT CHEMILUMINESCENT DETECTION OF AMINO ACIDS.

Donald R. Bobbitt and Warren A. Jackson, Department of Chemistry and Biochemistry, University of Arkansas, Fayetteville, AR 72701.

Recently it has been shown that amino acids will react with Ru(bpy)$_3^{3+}$ producing chemiluminescent emission. This reaction sequence has been used in a detection system for amino acids which were separated in a variety of different chromatographic modes. Excellent sensitivity was demonstrated by introducing the ruthenium reagent post-column, however, for system miniaturization, this approach is problematic. Solid electrode materials can be used to electrochemically modulate the Ru(bpy)$_3^{3+/2+}$ couple. Ru(bpy)$_3^{2+}$ can then be added to the chromatographic mobile phase and electrochemically cycled to the reactive Ru(bpy)$_3^{3+}$ species within a flow-through, thin layer detection cell which contains the working electrode. Amino acids passing through the flow cell will react with the Ru(bpy)$_3^{3+}$ reagent and generate luminescence which can be observed through a transparent window on the flow cell. The light generated from the reaction is proportional to the amino acid concentration in the cell. Conditions necessary to achieve sub-picomole detection limits for underivatized amino acids with this scheme will be discussed.

469 DUAL POTENTIAL-PULSED AMPEROMETRIC DETECTION AT A SINGLE ELECTRODE FOLLOWING HIGH PERFORMANCE LIQUID CHROMATOGRAPHY.

William R. LaCourse, Department of Chemistry and Biochemistry, University of Maryland Baltimore County, Baltimore, MD 21228.

Pulsed Amperometric Detection (PAD) following High Performance Liquid Chromatography has gained popularity for the sensitive and direct detection of polar aliphatic organic compounds. Since PAD is based upon surface-catalyzed oxidations of various functional groups (e.g., alcohols, amines, and sulfur-containing moieties), selectivity is limited. Dual potential-PAD at a single electrode allows for the selective detection and/or characterization of analyte species in a chromatographic experiment. The general principles of dual potential-PAD are reviewed on the basis of the voltammetric response of various model compounds. Aspects of functional group selectivity and compound characterization are discussed and emphasized with chromatographic examples.

470 RECENT ADVANCES IN TIME-OF-FLIGHT SIMS FOR ORGANIC SURFACE CHARACTERIZATION.

Richard William Linton, Department of Chemistry, University of North Carolina, Chapel Hill, NC 27599-3290.

Secondary ion mass spectrometry (SIMS), when practiced in the static mode using time-of-flight (TOF) instrumentation, has become a powerful technique for the molecular characterization of organic surfaces, especially those involving polymeric materials. The solution deposition of polymers as monolayers on silver substrates provides TOF-SIMS data about polymer characteristics such as repeat units, end groups, and oligomer distributions. The emphasis in our research, however, is on *in situ* characterization: surface analysis, imaging, and molecular trace analysis. This presentation will highlight various recent examples from my research group, in collaboration with Alfred Benninghoven at the University of Münster, illustrating the capabilities for high transmission, spatial resolution, mass resolution, and mass range. These will include the TOF-SIMS characterization of novel block copolymers used as compatibilizing agents and surface modifiers, quantitative studies of biomimetic surfaces containing phospholipid/protein mixtures, and the molecular trace analysis of organic polymer additives such as anti-oxidants. Lateral imaging of molecular species using microprobe TOF-SIMS instrumentation also will be discussed, including our use of patterned silver overlayers, as a unique approach to enhance secondary ion yields from bulk organic materials. Ion images also provide insight into the mechanisms of silver cationization of sputtered molecules, as well as the diffusion of analyte molecules, such as polymer additives, through the silver-containing islands.

471 SURFACE CHEMISTRY OF LANGMUIR-BLODGETT AND SELF-ASSEMBLED MOLECULAR AND MACROMOLECULAR LAYERS.

Patrick C. Schamberger and Joseph A. Gardella, Jr., Department of Chemistry, 113 Acheson Hall, Suny-Buffalo, Buffalo, NY 14214.

Langmuir-Blodgett and Self-Assembled films of molecules and polymers can serve as a hierarchical series of model systems to study polymer and biomaterial surface chemistry. Our research over the past ten years has endeavored to explore this approach for modeling such surface chemistry and simultaneously developing new methods of analysis. The work presented in this paper will include electron (XPS/ESCA and high resolution electron {vibrational} energy loss {HREELS}) and mass (static SIMS) spectrometric studies of a series of films. Structural model systems will illustrate the ability of HREELS to explore the topmost molecular bonding of a complex molecular surface. New advances in data handling and well constructed model systems have pushed this development. Static SIMS and XPS studies of monolayer and multilayer films of molecular systems can explore acid-base and reactive surface chemistry at metal interfaces. Building to more complex systems, the polymerization chemistry of monolayers can be studied quantitatively to determine reaction kinetics. Langmuir-Blodgett films of models biopolymers have been studied as a means to determine composition and structure in mixed films. This models the situation when biomaterials are present in complex cellular environments. Simple biopolymer conformational variations can be induced in the model system and studied with static SIMS and vibrational spectroscopy. The understanding of effects of substratum surface chemistry on the dynamics of change of conformation in biopolymers at surfaces would be a great advance in the field of biomaterials. This series of studies working through the hierarchy of possible model structures will emphasize both the chemical results and the development of static SIMS and HREELS for quantitative analysis.

472 QUANTITATIVE SURFACE ANALYSIS OF MISCIBLE AND IMMISCIBLE POLYMER BLENDS BY STATIC-SIMS AND XPS.

P. M. Thompson, Eastman Kodak Company, Rochester, NY 14650-2132.

X-ray photoelectron spectroscopy (XPS) has been used for a number of years to gain a quantitative understanding of surface segregation in polymer blends. XPS, however, requires a unique element or functional group to be present in the repeat unit of each blend component. Static secondary-ion mass spectrometry (Static-SIMS) does not suffer from the above constraint, but is normally considered to be a non quantitative technique. Using a time-of-flight mass analyzer the "stand alone" potential for quantitative Static-SIMS has been demonstrated by determining the surface composition for both miscible {bis (phenol)—a polycarbonate and polystyrene} and immiscible {tetramethylbis (phenol)—a polycarbonate and polystyrene} polymer blend concentration series which had their surface compositions independently determined using XPS.

473 APPLICATIONS OF AN IMAGING SIMS-MS/MS MICROPROBE TO COMPLEX ORGANIC SYSTEMS.

Peter J. Todd and R. Timothy Short, Analytical Chemistry Division, Oak Ridge National Laboratory, Oak Ridge, TN 37831-6365.

We combined a secondary ION microprobe and a triple quadrupole tandem mass spectrometer in a single instrument. With this device, the distribution of organic compounds in complex organic systems can be determined. Tandem mass spectrometry (MS/MS) is necessary because organic compounds in a mixture cannot be identified solely on the basis of mass-to-charge ratio. We have used simple heterogeneous mixtures and grids to establish the veracity of SIMS-MS/MS images. The utility of the instrument can be demonstrated by a number of methods, including imaging droplets of glycerol solution. The importance of MS/MS is demonstrated by showing the distribution of isobaric secondary IONS based on different IONS from their respective MS/MS spectra. The distribution of targeted compounds in biological tissue samples can also be determined. For example, we can map the distribution of epinephrin in adrenal tissue.

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476 STATIC SIMS DETERMINATION OF THE SURFACE COMPOSITION OF POLYOLEFIN BLENDS.

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Positive and negative static sims spectra were recorded of spin cast uniform thin films of blends of polyolefins. Film thicknesses, measured by ellipsometry, ranged from 300–3000Å. In each blend, one of the components was deuterium labeled. Consequently, the fragmentation pattern for each component was readily discernable from the other. The polyolefins used to make each blend were selected from the following: D^4-high density polyethylene (D-HDPE), H^4-HDPE (H-HDPE), poly (ethylenepropylene) (H-PEP), perdeuterated poly (ethylenepropylene) (D-PEP), poly (ethylethylene) (H-PEE), perdeuterated poly (ethylethylene) (D-PEE), poly (ethylene-co-undecene) (A-PE), and hydrogenated (D^6-1,4 polybutadiene) (D^6-LLDPE). The polymer pairs used in the blends were selected to give a wide range of potential crystallinity—from amorphous (PEP, PEE, A-PE) to 40% (D^6-LLDPE) to 70% (HDPE)—in each blend. The spectra show that blends of amorphous with semicrystalline polymers generally yield surfaces heavily enriched with amorphous component (85–100%) even when the bulk concentration of amorphous component is 20% or less. Results are discussed in terms of basic surface energy arguments. Factors affecting interpretation and quantitation of the data will also be discussed.

477 MULTIPHOTON POST-IONIZATIN SNMS FOR QUANTITATIVE ANALYSIS.

S. R. Bryan, M. Nicholas and G. J. Havrilla, BP Research, 4440 Warrensville Ctr. Rd., Cleveland, OH 44128.

In recent years, post-ionization of sputtered neutrals has received increasing attention as a means of reducing the ion yield matrix effects and element-to-element variations in sensitivity that plague quantitative SIMS analysis. It has become well established that decoupling the sputtering and ionization steps greatly reduces matrix effects. However, matrix effects have not been completely eliminated because of several factors. Some of these factors are inherent to the sputtering process while others are related to the laser intensity profile. The relative importance of these factors and examples of quantitative measurements using 248 nm, 193 nm and 118 nm light will be discussed.

478 INVESTIGATIONS INTO DEPTH PROFILING USING GD-MS.

Robert Hutton, Fisons Instruments, VG Elemental, Ion Path, Road Three, Winsford, Cheshire, CW7 3BX. Angelika Raith, Charles Evans and Associates, Redwood City, CA 94061.

Accurate characterization of coatings is a key factor in materials performance. The homogeneity of layers and the composition of the interface can influence the mechanical properties of coated materials. Currently SIMS and ESCA techniques offer adequate performance for depth profiling for thickness of 0.5–200 microns, however, these techniques are not quantitative. Glow discharge devices offer considerable potential for such applications since a) the sputter rate is controllable b) quantitation of both elemental content and depth should be possible. The criteria for good depth profiling is that the measured profile should reflect accurately the interlayer composition and should not be obscured by sampling artifacts. To obtain this with GD-MS, flat bottomed craters are necessary. In this investigation the relationship between such crater shapes and discharge conditions will be presented. Quantitation using GD-MS relies also on knowledge of sputter rate from which the ion yields can be calculated. Preliminary investigations into the variations of sputter rate with different matrices will also be presented.

479 CHIROPTICAL LUMINESCENCE STUDIES OF INTERMOLECULAR CHIRAL DISCRIMINATORY INTERACTIONS.

F. S. Richardson and D. H. Metcalf, Department of Chemistry, McCormick Road, University of Virginia, Charlottesville, VA 22901.

Time-resolved chiroptical luminescence (TR-CL) spectroscopy is used to study enantioselective excited-state quenching processes between chiral luminophores (L*) and quenchers (Q) in solution. The rate parameters derived from TR-CL measurements of enantio-differential quenching kinetics reflect both the degree and sense of chiral discriminatory interactions between the luminophore and quencher molecules. In the systems of interest here, quenching occurs via short-range electronic energy-transfer processes in which both the stereochemical and electronic (donor-acceptor state) chirality of interacting L*-Q pairs may contribute to chiral recognition/discrimination. TR-CL measurements of enantio-differential quenching kinetics may also be used to determine enantiomeric excess in a quencher concentration of unknown optical purity.

480 EXTENDING LINEAR DICHROISM MEASUREMENTS INTO THE VACUUM ULTRAVIOLET FOR IMPROVED INFORMATION CONTENT.

W. Curtis Johnson, Jr., Department of Biochemistry and Biophysics, Oregon State University, Corvallis, OR 97331.

In a flow linear dichroism (LD) experiment on helical nucleic acids with one type of base, there are at least three unknowns: (1) the inclination of the bases with respect to the helix axis, (2) the orientation of the axis around which the bases are inclined, and (3) the coefficient for alignment of the polymer in the flow. If there is more than one kind of base in the nucleic acid, then each type of base may have a different inclination and axis. In an effort to obtain enough information to solve for all of the unknowns, our laboratory has developed a flow LD instrument that will make measurements into the vacuum ultraviolet region. With these extended measurements we can use the shape of the LD and normal absorption to solve for all of the unknowns. The beauty of this method is that we need not model the flow nor extrapolate the LD data to perfect alignment of the polymer. Thus any tertiary structure formed by the polymer does not affect our analysis. We have applied our method to various natural and synthetic nucleic acids to reach definite conclusions about these inclinations. We find that the bases are quite inclined, even for B-form DNA.

481 PROTEIN SECONDARY STRUCTURE DETERMINATION USING AMIDE I' AND II VIBRATIONAL CIRCULAR DICHROISM BANDS.

Timothy A. Keiderling and Petr Pancoska, Department of Chemistry, University of Illinois at Chicago, Box 4348, Chicago, IL 60680 and Faculty of Mathematics and Physics, Charles University, 12116 Prague 2, CSFR.

Vibrational circular dichroism (VCD) of the amide I' band of proteins dissolved in D_2O yields enhanced sensitivity to the conformational differences between globular proteins as compared to the more traditional IR and UV CD techniques.[1-3] We have used a statistical analysis of such data for 20 proteins to predict their fractional secondary structures.[1,2] Expansion of the data base to include the VCD of the amide II band for these proteins in H_2O leads to improved precision of the fit to selected secondary structural elements. In addition to helix, sheet, bends and "other," turns can be fit at a statistically reliable level by adding the amide II spectra to the data set. Addition of new proteins to the previously employed training set show that the analysis is stable resulting in consistent fits. Predictive capabilities of the method are being tested. Initial studies of α-lactalbumin structural dependence on solvent and species[4] and of peptide hormone structures will be described. The results to date suggest that while as a method of secondary structure prediction, VCD is more accurate than previously proposed methods using UVCD or FTIR data[3] for known crystallizable proteins. However, combination of several techniques leads to more reliable prediction of unknown structures.

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482 POLARIZATION-SELECTIVE SPECTROSCOPY: NEW TECHNIQUES FOR STUDYING COMPLEX BIOMOLECULAR STRUCTURE. Donald R. Bobbitt and Karno Ng, Department of Chemistry and Biochemistry, University of Arkansas, Fayetteville, AR 72701.

Complex biological systems present significant challenges to those attempting to understand them. The three dimensional structure of the different components comprising the system, and the interplay of these components with respect to each other are critical for optimum function. Optical activity is a very selective property which is extremely sensitive to the arrangement of atoms at, or near a chiral center. As such, optical activity measurements can provide information on the subtle aspects of the system which contribute to its' function. Laser-based polarimetry and circular dichroism are two techniques used to gain information about these different interplays and characteristics. In this presentation, new approaches to the measurement of both specific rotation and circular dichroism will be described and evaluated with respect to their ability to provide unique information on complex biological systems.

483 VIBRATIONAL CIRCULAR DICHROISM STUDIES OF AZIDE LIGAND BINDING IN HEME PROTEINS: A NOVEL APPROACH FOR STUDYING NON-COVALENT LIGAND PROTEIN INTERACTIONS. Sanford A. Asher, R. Bormett, L. Nafie and T. Freedman *et al.*, Department of Chemistry, University of Pittsburgh, Pittsburgh, PA 15260, Syracuse University, Syracuse, NY 13244.

We demonstrate the use of vibrational circular dichroism (VCD) for studying myoglobin (Mb) and hemoglobin (Hb) interactions with an azide ligand bound to the heme iron. The work here follows the pioneering observation of Marcott and Moscowitz in 1979 of an anomalously large VCD signal for the antisymmetric azide stretch of azidomethemoglobin (HBN_3). We examine this phenomenon for the first time in detail by using evolutionarily diverse and site-directed mutants of Hb and Mb. We correlate the magnitude of the VCD anisotropy ratio with interactions between the azide ligand, the heme iron and the distal E7 and E11 residues. It appears that VCD may be of incisive utility for studying certain types of ligation of metalloenzymes.

484 A TEMPERATURE CONTROLLED MULTI-SAW RESONATOR SYSTEM. William D. Bowers and R. L. Chuan, Femtometrics 1001 W. 17th St., Ste. R, Costa Mesa, CA 92627. Jay W. Grate, Naval Research Laboratory, Code 6175, Washington, D.C. 20375.

Surface Acoustic wave (SAW) piezoelectric sensors are small, rugged devices that are capable of detecting trace levels of chemical vapors when a selective polymer coating is applied to its surface. Due to the lack of highly specific sensor coatings, a common approach to detecting targeted chemical vapors in a complex matrix has been to use several individual SAW sensors each coated with a unique coating. Target vapors are identified from interferents using trained pattern recognition algorithms. When a number of individual sensors are used in this fashion the size of the instrument increases which complicates the ability to provide a stable uniform environment for the sensors. We have developed a small SAW resonator array module that uses a single sensing package that has up to 6 individual 200 MHz SAW resonators on a single 24 pin DIP. The multi-SAW array package inserts into a circuit board (5 inches/side) which provides beat frequency signal outputs for each resonator. To reduce signal drift the module is temperature controlled using a thermal electric refrigerator.

485 APPLICATION OF A TEMPERATURE CONTROLLED SAW ARRAY DETECTOR. Edward B. Overton, Institute for Environmental Studies, Room 42 Atkinson Hall, Louisiana State University, Baton Rouge, LA 70818.

Depending upon the interactions and phase of the sorbent, temperature can play a significant role in determining the magnitude of response of SAW array detectors. Using liquid crystal absorbents and precise temperature control via a Peltier thermoelectric heat pump the response-temperature characteristics of a 52 MHz SAW array detector were examined for selected volatile organic analytes.

486 MODELS OF POLYMER-COATED SAW SENSOR RESPONSES TO ORGANIC VAPORS. S. J. Patrash, E. T. Zellers and M. Han, University of Michigan, School of Public Health, Box 2029, Ann Arbor, MI 48109-2029.

Responses of four polymer-coated saw sensors to organic vapors from 11 different chemical classes were used to construct predictive models based on vapor boiling points, Hildebrand solubility parameters, and solvation parameters in conjunction with linear solvation energy relationships. Best results were obtained with the most complex model based on solvation parameters where all predicted values were within a factor of two of experimental value and 85% of the values were within +/− 25%. Even the simplest model based on boiling point predicted the majority of the responses to within a factor of two. These models should prove useful for estimating the responses of polymer-coated saw sensors to previously untested vapors and provide performance criteria such as projected limits of detection and levels at which potential interferences become significant.

487 THEORY AND APPLICATION OF ACOUSTIC PLATE MODE DEVICES FOR SENSING IN A FLUID MEDIA. J. F. Vetelino and J. C. Andle, Laboratory for Surface Science and Technology, University of Maine, Orono, ME 04469. F. Josse and Z. Shana, EE/CE Dept., Marquette University, 1515 W. Wisconsin Ave., Milwaukee, WI 53233.

The theory and application of acoustic plate mode (APM) devices for sensing subtle changes in a fluid of arbitrary viscosity and conductivity is presented. Computer software has been developed to simulate the propagation of APMS in a fluid loaded piezoelectric plate. APM properties such as the phase and group velocities, the piezoelectric coupling, the propagation loss and the acoustic amplitudes at the interface are obtained for each allowed APM. These quantities are then used in the design and modeling of an APM sensing device. The design parameters are varied to optimize the device's electrical properties for sensor applications. In particular, the generation of a single acoustic mode with low adjacent mode interference, low losses and high electromechanical efficiency is desired. This has been accomplished by using ZX lithium niobate substrates with a thickness of .5mm and an IDT period of 88 μ. The resulting APM at 50.8 MHZ has predominantly shear horizontal displacements, low losses and high coupling. The APM sensors are currently being investigated for their ability to monitor biochemical reactions, such as antibody-antigen reactions and DNA hybridization, as well as to monitor fluid and polymer properties, such as conductivity (ionic concentration) and viscoelastic properties. Preliminary results have indicated that the APM device can measure ionic concentration less than 100 μm and biochemical concentration less than 1 ng/ml.

488 PIEZOELECTRIC AND OPTICAL ANALYSIS OF POLYMERIC THIN FILMS. E. M. Bowman and L. W. Burgess, Center for Process Analytical Chemistry, Univ. of Washington BG-10, Seattle, WA 98195. S. W. Wenzel and R. M. White, Berkeley Sensors and Actuators Center, Univ. of California, Berkeley, CA 94720.

The responses of a polymer coated Lamb wave sensor and a polymeric optical waveguide sensor are used to characterize the chemical interaction of an analyte or solvent with the polymer layer. Information in the sensor response about polymer swelling, pore filling, mass loading, and changes in viscoelastic properties can be used to elucidate the interaction mechanism. Additionally, using two types of sensors in a mixed array increases selectivity by providing different information about the same sample. The complementary nature of these two sensors and they response mechanisms are explored.

489 ACOUSTIC WAVE SENSORS FOR REAL-TIME MONITORING OF VOLATILE ORGANICS. Gregory C. Frye, Richard W. Cernosek and Stephen J. Martin, Microsensor Department 1315, Sandia National Laboratories, Albuquerque, NM 87185-5800.

Polymer-coated surface acoustic wave (SAW) sensors can be used to obtain rapid and sensitive detection of volatile organics. By monitoring both wave velocity and attenuation (i.e., loss of acoustic power), we have demonstrated that the identity and concentration of an isolated species can be determined using a single sensor. Sensor sensitivity and selectivity can be optimized by understanding the dynamic interactions between the acoustic wave and the viscoelastic polymer film. A sensor system using this unique capability is being evaluated for real-time, on-line chemical monitoring of industrial processes. This system includes a PC board containing: (1) a test case with a coated SAW device, (2) RF amplifiers for operating the SAW device in an oscillator circuit, (3) a coupler attached to a frequency counter card (to monitor velocity), (4) couplers and power detectors at the SAW device input and output ports with output voltages going to an A/D card (to monitor attenuation), and (5) a circuit for controlling test case temperature. Environmental sampling consists of a pump to draw in a gas sample and a computer-activated, three-way valve for directing the gas through a carbon-based adsorbent to reestablish sensor baseline. A portable computer containing the data acquisition cards runs a menu-driven program that acquires and analyzes the data, providing real-time concentration information for an isolated chemical species. Field tests of this system demonstrated rapid, reversible, and quantitative detection of volatile organics in exhaust stacks in spray cleaning operations. The results were used to modify the process *obtaining a 25-fold decrease* in emissions. This work was performed at Sandia National Laboratories, supported by the U.S. Department of Energy under contract number DE-AC04-76DP00789.

490 PC-BASED DIGITAL SIGNAL PROCESSING: FAST FOURIER TRANSFORMS ON THE MILLISECOND TIMESCALE.

L. E. Bowman and A. P. Wade*, Department of Chemistry, University of British Columbia, 2036 Main Mall, Vancouver, B.C., Canada V6T 1Z1.

Time-to-frequency domain conversions are the rate limiting step for data analysis for many instrumental methods. Digital signal processors (DSPs) are microprocessors designed specifically for complex mathematical manipulation at very high speeds. They provide an inexpensive means for near real-time analysis of signals from many analytical instruments. We have developed a means of computing Fast Fourier Transforms (FFTs) on the millisecond timescale using a commercially available DSP card situated in a PC/AT compatible microcomputer. Modified commercial software allows the computation of complex FFTs of 1024 point data sets in a small fraction of the time that would be taken by the Intel 80286 host processor. Downloading the data to the DSP card, calculating the FFT, determining its magnitude, and uploading the resulting power spectrum to the PC can be accomplished in 63.5 milliseconds. This approach is being incorporated into software written for acoustic emission analysis to facilitate near real-time process control and speed laboratory examination of acoustic emission signals. An overview of DSP will be presented and the development of the software used in this work will be discussed.

491 THE INFLUENCE OF TEMPERATURE ON THE ORIENTATION AND ORDER IN MOLECULAR MONOLAYERS.

Christine E. Evans and Paul W. Bohn, Department of Chemistry, University of Illinois, 1209 W. California St., Urbana, IL 61801.

The formation and structure of organic monolayer systems is of considerable interest in purely fundamental studies, in direct analogy to biological systems, and in the possible fabrication of chemical sensors and switches. Spectroscopic methods have been used to advantage in probing the molecular-scale order of these interesting systems. In this study, absorbance and fluorescence spectroscopy are utilized to evaluate the aggregation state of a hemicyanine dye during monolayer formation and upon temperature perturbation. The Langmuir-Blodgett technique is successful in the fabrication of a monolayer film containing a high fraction of molecules in the aggregated state. Preliminary results indicate that the aggregate: monomer ratio is relatively constant under modest temperature conditions, but the coherence length of the aggregate may vary appreciably. This apparent change in coherence length is initially irreversible, but becomes reversible after several heating/cooling cycles. These results have interesting implications for the fabrication of molecular barriers as well as for the flow of energy within monolayer films.

492 LANGMUIR-BLODGETT MONOLAYER FILMS STUDIED BY IR SPECTROSCOPY: SUBSTRATE-MEDIATED STRUCTURAL REORGANIZATION.

Fazale R. Rana, Suci Widayati and Richard A. Dluhy, Department of Chemistry, University of Georgia, Athens, GA 30602.

The rate at which a monomolecular film is transferred from the air-water interface to a solid substrate influences the final structure of the deposited film in the Langmuir-Blodgett process of preparing supported monolayer films. ATR-IR spectroscopy of transferred monolayers on germanium shows that the substrate withdrawal speed influences the conformation of the hydrocarbon chains in film molecules transferred from an expanded monolayer at low surface pressures, but has limited influence on the hydrocarbon chain conformation of a condensed film transferred at high surface pressures. This phenomenon occurs for both a fatty acid and a phospholipid, which suggests that this phenomenon may be general for hydrocarbon amphiphiles at the A/W interface. This ordering is likely due to a kinetically limited phase transition taking place in the meniscus formed between the solid substrate and aqueous subphase, a conclusion which is supported by previous epifluorescence microscopy studies. In addition, the structure of the amphiphile may modulate the extent and nature of the transfer-induced structural changes taking place in the monomolecular L-B film. These results suggest that in order to use monomolecular L-B films on solid supports to accurately characterize the structure, orientation, and phase properties of monolayers at the A/W interface, the L-B deposition must be performed at rates which minimize this structural phase transition.

493 COMBINED IR SPECTROSCOPY AND SCANNING TUNNELING MICROSCOPY OF LANGMUIR-BLODGETT AND SELF-ASSEMBLED MONOMOLECULAR FILMS.

Brian W. Gregory and Richard A. Dluhy, Department of Chemistry, University of Georgia, Athens, GA 30602.

Work in this laboratory is presently being directed towards studies of the structure of well-ordered molecular monolayers, including both Langmuir-Blodgett (L-B) and self-assembled (SA) films. We are currently pursuing an integrated spectroscopic/imaging approach to studying these monomolecular films using infrared spectroscopy in combination with scanning tunneling and atomic force microscopies (STM/AFM) in order to obtain compositional, conformational, and topographical information about these films. We have studied SA monolayers of alkanethiols (particularly $C_{18}H_{37}SH$) on Au substrates. Our STM results indicate that under certain well-defined scanning conditions, the STM tip may play a large role in inducing chemical rearrangements within the monolayer film. In particular, the tip may induce chemical oxidation of the C-S bond of the alkanethiol, resulting in the formation of elemental sulfur (S_8). The evidence for S_8 formation includes the observation of eight-membered, square arrays of atoms as well as longer chains of atoms composed of these square arrays attached end-to-end. Additional studies involve L-B monolayers of phospholipids (*e.g.* DPPC) either alone or in binary lipid/peptide mixtures at the air-water interface. Our initial investigations have centered on mixtures of DPPC with the peptide alamethicin, which is known to act as a voltage-gated ion channel upon incorporation into lipid bilayers. Structural information obtained from both IR and STM/AFM studies will be presented.

494 HYDROCARBON CHAIN CONFORMATIONS OF SURFACTANTS ADSORBED AT MINERAL OXIDES SURFACES.

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In-situ Fourier transform infrared/internal-reflection spectroscopy (FT-IR/IRS) has been used to examine the hydrocarbon chain conformations of sodium dodecylsulfate adsorbed at the surface of a sapphire internal-reflection element (IRE) and dodecylamine adsorbed at a silica IRE. The conformation of the surfactant chains was monitored by observing the frequency of the asymmetric -CH_2 stretching band as a function of adsorption density and temperature. Shifts of 2–5 cm^{-1} in the position of the asymmetric -CH_2 stretching band were correlated with surfactant phase changes at the surface and with changes in the adsorption density.

495 USE OF EXTERNAL REFLECTION INFRARED SPECTROSCOPY TO STUDY THE SURFACE STRUCTURE AND ORIENTATION OF POLYMER FILMS.

Dennis J. Walls, The Du Pont Company, Corporate Center for Analytical Sciences, P. O. Box 80326, Wilmington, DE 19880-0326.

External reflectance measurements are a seemingly attractive option for the infrared absorption analysis of free-standing polymer films, especially when they are too thick to allow conventional transmission measurements. However, the severe distortion of these spectra due to refractive index dispersion effects and the difficulty in separating front and back surface reflections have made rigorous interpretation difficult. Recently, it has been reported that external reflection analyses made with parallel polarized radiation incident at Brewster's angle minimize the distortion of absorption bands due to optical effects.[1] In this paper, I will discuss the application of this technique to the analysis of orientation and structure in drawn polymer films. The surface specificity of orientation measurements in this sampling geometry as well as the inherent 'selection rules' of this technique as related to the presence of anisotropy in the three-dimensional absorbances of the polymer film samples employed will be compared to that available from polarized ATR-IR measurements. Specific applications to the analysis of the surface orientation of drawn polyester and polyimide films will be presented.

[1] Ishino, Y.; Ishida, H. *Appl. Spect.*, 1992, **46,** 504.

496 FTIR AS A PROBE FOR STRUCTURAL GRADIENTS AT POLYMER SURFACES.

Gangchi Chen and Leslie J. Fina, Rutgers University, College of Engineering, Department of Materials Science and Engineering, P.O. Box 909, Piscataway, NJ 08855-0909.

An FTIR-ATR depth profiling technique has been used to examine orientation gradients at polymer surfaces. An inverse Laplace treatment is used to convert variable-angle ATR data in angular space to absorption coefficients (*k*) in distance space. Two approaches have been established: one is the use of Flournoy & Schaffers' equations to model the ATR intensities from orientation gradient systems. This demonstrates that the inverse Laplace formalism can be adapted to the orientation gradient problem as predicted by Hirschfeld (1977). The second approach is an experimental one involving the use of uniaxially drawn polypropylene to obtain an orientation coefficient gradient ($P_2 \mathrm{Cos}\theta$) as a function of distance. It has been determined that the gradient in the crystallinity must be incorporated into the orientation gradient problem for meaningful data analysis. Variable-angle ATR spectra have been also analyzed for both single and bilaminate films of poly (vinylidene fluoride) and nylon 11 in both poled and unpoled films.

497 THE INFRARED SPECTROSCOPIC EVALUATION OF SLIP ADDITIVE MIGRATION IN POLYPROPYLENE FILM.

D. E. Pivonka, Hercules Incorporated, Wilmington, DE 19808.

Attenuated total reflection (ATR) infrared spectroscopy has become an extremely popular tool for the examination of polymer film surfaces, coatings, and additives. At Hercules, ATR experiments have proven useful for film applications which incorporate amide as a migratory slip additive. The relative surface amide level (RSAL) calculated from the amide to polypropylene absorbance ratio within an ATR spectrum has become a routine test used for the understanding of slip film surface properties. RSAL data are an internally consistent measure of surface amide concentration and correlate with the coefficient of friction (COF) between film surfaces. Addition of temperature control capabilities to the ATR experiment has permitted a wide range of additive migration parameters to be defined throughout the range of processing temperatures commonly encountered in lab scale production. Elevated isothermal experiments for the determination of RSAL as a function of time permit definition of the amide diffusion constant and equilibrium surface to bulk amide distribution. Non-isothermal experiments in which temperature is linearly ramped from 30°C to 120°C and from 120°C to 30°C in consecutive 4-hour segments have been used to define parameters relating to additive solubility vs. temperature, amide diffusion vs. temperature, and the effect of polymer morphology on amide migration kinetics. Amide migration kinetics have been shown to correlate with induced polymer orientation.

498 APPLICATION OF A SINGLE BOUNCE ATR-IR GEOMETRY TO THE STUDY OF ORIENTATION AND CONFORMATION IN POLYESTER AND POLIMIDE FILMS.

Dennis J. Walls and R. Scott Peacock, The Du Pont Company, Corporate Center for Analytical Sciences, P.O. Box 80326, Wilmington, DE 19880-0326.

Attenuated total reflectance infrared spectroscopy (ATR-IR) has been used extensively for the analysis of structure and orientation in polymeric materials. An important advance in the ability to quantitatively study polymer orientation with ATR-IR measurements came with the development of rotatable non-contact breaking geometries, first discussed by Sung.[1] In This paper, I will discuss the application of a modified non-contact breaking ATR-IR sampling geometry based on the use of a hemispherical internal reflection element designed around a commercially available sampling accessory. A single reflection at the sample/IRE interface is used to make absorption measurements in this geometry, better insuring that the same portion of the sample is analyzed in each sample orientation, thus further minimizing potential systematic errors from contact variation over existing non-contact breaking sampling geometries. The sample orientation can presently be adjusted continuously over a 90° range. The angle of incidence of the probe infrared beam is also easily adjustable in this sampling geometry. Polarized measurements with TM and TE polarized fields can also be made, which allow for probing the spatial anisotropy of the absorbance of the film between two orthoganol in-plane directions and the thickness direction of the film. The specific effects of uniaxial stretching on the polymer backbone orientation and conformational changes of aromatic functionalities in the polymer backbone of polyester and polyimide materials will be presented.

1. Sung, C. S. P. *Macromolecules* 1981, **14,** 591.

499 LANGMUIR-BLODGETT FILMS OF PHOSPHOLIPID BINARY MIXTURES: IR STUDIES OF MONOLAYER FILM COMPOSITION.

Fazale R. Rana and Richard A. Dluhy, Department of Chemistry, University of Georgia, Athens, GA 30602.

A method has been developed to determine the exact fractional composition of binary mixtures of phospholipids at the air-water interface by IR spectroscopy in combination with ^{31}P NMR spectroscopy and Langmuir-Blodgett film balance methods. This method utilizes classical Langmuir-Blodgett film balance techniques to transfer the binary lipid mixture from the air-water interface onto Ge crystals, thereby obtaining the monolayer ATR-IR spectra. This technique takes advantage of the frequency shift observed upon hydrocarbon chain deuteration to separate the vibrational frequencies due to each component in mixtures of deuterated and normally proteated components. Using this method, we measured the fractional composition in binary mixtures of acyl chain perdeuterated DPPC (DPPC-[d_{62}]) with DPPG. The relative ratios of the integrated areas for the C-H and C-D stretching modes in the binary mixture monolayer IR spectrum can be related to exact mole fraction by comparison with the integrated intensity ratios of the PC and PG peaks obtained from high resolution, solution phase ^{31}P NMR spectroscopy in the presence of a suitable line-narrowing reagent. The combination of IR with ^{31}P NMR spectroscopy of the binary mixtures provides the necessary calibrations for the multicomponent quantitative analysis in the absence of absolute IR absorption constants for the individual monolayer components.

500 PHASE TRANSITION BEHAVIOR OF SURFACTANTS AT SURFACES.

Yei-Shin Tung and Leslie J. Fina, Department of Materials Science and Engineering, Rutgers University, Piscataway, NJ 08855.

In situ reflection-absorption infrared spectroscopy and surface tension measurements have been used to characterize soluble monolayers adsorbed at the air-water interface. Based on the optical model proposed by Schopper, the relationship between the reflection-absorption intensities, the average chain orientation and the surface excess concentration of the monolayer has been established. The optimum incident angle for both *P*- and *S*-polarizations are determined. Based on the model calculations, the peak intensities of the CH_2 stretching bands are analyzed to give information about the chain orientation and surface excess concentration. The peak positions are related to chain conformation. The difference in chain conformation and orientation between monolayers formed by different bulk concentrations indicates the presence of a phase transition in the monolayer. The phase transitions from the infrared analysis are in the same range with the break points from surface tension isotherms in all the monolayer systems. A molecular model of the monolayers is proposed to correlate the microscopic and macroscopic behavior.

501 TIME OF FLIGHT MASS SPECTROMETRY WITH ATMOSPHERIC-PRESSURE PLASMA ION SOURCES.

Paul B. Farnsworth, Mingin Wu, Milton Lee, Edgar Lee and Jeff Prince, Department of Chemistry, Brigham Young University, Provo, UT 84602.

Time-of-flight mass spectrometers with atmospheric-pressure inlets and right-angle pulsing geometries offer potential advantages over quadrupole instruments for use in elemental analysis with plasma ion sources. Time-of-flight mass analysis provides simultaneous detection of all elemental ions, in contrast to sequential detection by quadrupole instruments. Right-angle sampling of a supersonic jet expanding from atmospheric pressure allows for high duty cycles, because the pulsing period can be set equal to the time required for the jet to fill the sampling region. Mass spectrometers of this type promise to be highly sensitive tools for elemental analysis that are particularly well suited for the detection of transient signals. The potential of time-of-flight mass spectrometers for elemental analysis has yet to be realized, however, and the development of useful combinations of such instruments with atmospheric-pressure plasmas is in its infant stages. In this paper we will describe an ICP-TOFMS instrument that is being developed at Brigham Young University and will present an initial characterization of its analytical performance.

502 PRELIMINARY CHARACTERISTICS OF A PLASMA-SOURCE TIME-OF-FLIGHT MASS SPECTROMETER.

D. P. Myers and G. M. Hieftje, Chemistry Department, Indiana University, Bloomington, IN 47405.

A recent area of innovative research activity is the development and investigation of alternative mass analyzers for plasma source mass spectrometry (PSMS). The novel combination of a time-of-flight mass spectrometer (TOFMS) and an inductively coupled plasma (ICP) is being investigated in our laboratory as an analytical tool for performing elemental analysis of solutions. The mass spectrometer employs a right-angle extraction/acceleration scheme to improve the duty cycle of the TOFMS. In addition, the continuous ion beam formed in the supersonic beam interface with the ICP can be pulsed into the flight tube easily in this configuration. The instrument has the capability of being operated in a linear or reflecting flight mode. Preliminary instrumental development has focused on building an efficient interface for transport of the ions from the ICP to the orthogonal extraction region of the TOFMS. The TOFMS is assessed in terms of its preliminary optimization, resolution, and initial sensitivity. Improvements to the current design and methods for spectral processing will be suggested. Preliminary figures of merit will be directly compared to those of existing quadrupole mass analyzers used in ICP-MS. The development of this novel mass spectrometer is aimed at providing a faster, more sensitive, and more precise instrument than current quadrupole mass analyzers for PSMS.

503 FUNDAMENTAL STUDIES OF ETV-ICP-MS.

Christopher M. Sparks, Thomas L. Pinkston and James A. Holcombe, Department of Chemistry and Biochemistry, The University of Texas, Austin, TX 78712.

ETV-ICP-MS combines the low detection limits and simultaneous multielement capabilities of ICP-MS with the microliter sample size of an electrothermal vaporizer. This allows for small sample size, increased sensitivity, and reduced matrix interferences. While ETV-ICP-MS is potentially a very powerful analytical tool, the system has not been completely characterized. The transport of the analyte from the graphite vaporizer to the plasma is one such area. Often "carriers" such as NaCl are used to enhance the transport phenomena. It is thought that the analyte condenses onto the "carrier" which is then swept into the plasma as an aerosol. As a first step in understanding this transport process, measurements have been made on the time dependent distribution of particles formed from the analyte and carrier. A particle counter is used to size classify the resultant aerosol. Discussion of transport and loss of analyte between the ETV and ICP will be presented.

504 HELIUM MIP QUARDRUPOLE MS—SOME FUNDAMENTALS.

M. Liezers, F. Godwin and D. Gregson, Fisons Instruments, VG Elemental, Ion Path, Road Three, Winsford, Cheshire, CW7 3BX. P. Brown, Fisons Instruments Inc., 32 Commerce Center, Cherry Hill Drive, Danvers, MA 01923.

The high ionization potential of helium (24.5ev) combined with other factors should allow helium microwave induced plasma-MS for certain elements below 85 amu. Unfortunately, the development of helium plasma source mass spectrometry has proved difficult. Problems experienced have ranged from the inability of helium plasmas to effectively handle aqueous aerosols, a limited linear dynamic range, complex matrix effects and complex mass spectra resulting from poor molecular dissociation attributed to low plasma temperature. Recent work indicates that most of these problems can be overcome. Preliminary results obtained from a low flow, moderate power helium MIP-quadrupole MS system using pneumatic aqueous sample introduction will be presented. Initial analytical studies have concentrated on the high first ionization potential elements arsenic, selenium and bromine. Low PPT detection limits have been achieved. Linear dynamic range appears good over five orders of magnitude and no ion suppression effects have been observed in a variety of complex media to concentrations of at least 1000ppm.

505 THE APPLICATION OF SPARK SAMPLING ICP-MS TO THE QUANTITATIVE ANALYSIS OF SOLIDS.

K. A. Ivanovic and D. M. Coleman, Wayne State University, 171 Chemistry Bldg., Detroit, MI 48202. F. W. Kunz and D. Schuetzle, Ford Motor Co., Scientific Research Laboratory, Dearborn, MI 48121.

ICP techniques have been limited, in part, by the need for solution nebulization. Solids must therefore be subjected to dissolution procedures which can result in sample loss or contamination. However, direct solid sampling eliminates this need for lengthy sample preparation. Our laboratory has developed a direct solid sampling apparatus which utilizes a high voltage spark with subsequent analysis by ICP-MS. Qualitative analysis has been successfully performed with this system and a linear response for dilute copper alloys has been demonstrated. Current research in this area is directed towards characterization of the sampling process and enhancement of performance to make possible the quantitative analysis of conductive solids.

506 TRACE DETECTION OF ORGANIC SPECIES USING AN ATMOSPHERIC PRESSURE RF GLOW DISCHARGE IONIZATION SOURCE.

J. Zhao and D. M. Lubman, Department of Chemistry, University of Michigan, Ann Arbor, MI 48109.

An atmospheric pressure radio frequency glow discharge in helium and other gases has been developed as an ionization source for organic samples introduced by liquid injection into atmospheric pressure ionization mass spectrometry (API/MS). The glow source operates typically at few watts of RF power and at a frequency of 165 kilohertz. The protonated molecule, MH^+, is generally observed with little or no fragmentation for many of the samples studied in positive mode in helium. The compounds studied include drugs, pesticides, PTH-amino acids, small peptides, antibiotics, steroids, catecholamines, vitamins and explosives. Detection limits achieved for the API RF glow discharge detection are typically in the low femtomole regime. Collision induced dissociation (CID) is used by varying the acceleration voltage across the skimmers to obtain useful structural information. RF glow discharge can also be operated in nitrogen, carbon dioxide/helium, argon, and air. Comparing with the DC glow discharge ionization source, the RF glow discharge provides more stable glow, higher ionization efficiency and the capability of operating not only in helium but also in other gases.

507 SOLUTION RESIDUE ANALYSIS USING GLOW DISCHARGE MASS SPECTROMETRY.

C. M. Barshick, D. C. Duckworth and D. H. Smith, Analytical Chemistry Division, Oak Ridge National Laboratory, Oak Ridge, TN 37831-6375.

A technique for the analysis of microliter volumes of solution by glow discharge mass spectrometry has been successfully demonstrated. Cathode preparation involves mixing an aliquot of the sample solution with a pure conducting powder, followed by drying and pressing prior to conventional GDMS analysis. The analyte signal at the 100 ppm level was observed to be stable to better than 5% for the duration of the analysis (30–45 minutes). Internal and external reproducibility was better than 5%, and the ion signal intensity was linear with concentration over at least 4 orders of magnitude. Quantification was demonstrated using user defined relative sensitivity factors. Relative standard deviations were better than 15% for several elements with no preconcentration of the analyte.

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508 PLATINUM IMPURITY ANALYSIS BY GDMS.

Duencheng Fang, R. Madan, T. Altasas and R. Mathews, Materials Research Corporation, Analytical Laboratory, 560 Route 303, Orangeburg, NY 10962.

GDMS has been proved to be an outstanding technique in surface analyses. The employment of GDMS in quantifying the trace impurity contents in sputtering targets is especially important in semiconductor industry since the atomization mechanism in GDMS is exactly the same as in sputtering system. The most unique features of GDMS superior to other atomic spectroscopies are matrix effect free and large linear dynamic range. These features provide GDMS capability in quantifying impurities leveled from percentage to ppb range by use just one set of relative sensitivity factors (RSF) for all matrices with 30 to 50% accuracy. However, as the semiconductor device keeps shrinking its size, the allowance of impurity content is further reduced and thus increase the importance of analysis accuracy. The best way to generate the RSF values for one matrix is to measure the ion beam ratios of each analyte in a standard. A good standard of GDMS shall contain most, if no all, of the elements across the periodic table ranged from several ppm to hundreds ppm. However, such kind of standard is not available at this moment, especially for precious metals. This study will use GDMS and ICP-AES to analyze at least 20 platinum samples with impurity contents ranged from several to hundreds ppm in order to generate one set of RSF values for GDMS to quantify the impurity contents in the platinum material.

509 EVALUATION OF SAMPLE PREPARATION PROCEDURES FOR W/TI SPUTTERING TARGET MATERIALS FOR THE DETERMINATION OF ALKALI ELEMENTS BY GDMS. Duencheng Fang and Purnesh Seegopaul, Materials Research Corporation, Analytical Laboratory, 560 Route 303, Orangeburg, NY 10962.

W/Ti materials are widely used in the semiconductor industry as a barrier layer in semiconductor devices. As device size continues to be reduced, material purity becomes a critical parameter. Specific individual impurity must be controlled and reduced. The alkali elements (Li, Na, K) are of particular important due to the fact that they affect the C-V relationship of semiconductor devices. High level causes greater C-V shift which results in device failures. Levels in the ppb range are now required. In order to certify such low levels of alkalis, glow discharge mass spectrometry (GDMS) has become the method of choice. In this GDMS technique, sample preparation is a critical step in determining alkalis in ppb levels because of the low sputtering rate of alkali elements, an environment filled with alkalis in the air, and the physical properties of W/Ti materials. Our studies show that the cutting wheel materials, the lubricant used in cutting, the etchants, baking temperature, and the pre-sputtering times are critical parameters in eliminating sample contamination. This presentation will address the effects of sample preparation methods. The surface morphology profile by scanning electron microscopy (SEM) and comparative analytical data will also be presented.

510 A SIMPLE INSTRUMENT FOR USE IN EXCITATION-EMISSION FLUORESCENCE POLARIZATION MEASUREMENTS. Kevin A. Destrampe and Gary M. Hieftje, Department of Chemistry, Indiana University, Bloomington, IN 47405.

A fluorescence excitation-emission matrix is an excellent way to determine a specific substance in a multi-component system. In the present investigation, a novel, rapid scanning spectrofluorometer has been developed utilizing a 0.35-meter monochromator for choosing the excitation wavelength and a continuously variable interference filter for selecting the emission wavelength. Further, fluorescence polarization measurements in the plane parallel and perpendicular to the polarized excitation light adds another dimension for characterizing the sample. The instrument is controlled by an IBM XT computer. A series of two-dimensional color-contour plots and three-dimensional excitation-emission spectral plots can be rapidly generated. Detection limits and multicomponent fluorescence-polarization excitation-emission spectra obtained with this instrumentation will be presented.

511 CORRECTION OF FLUORESCENCE EMISSION AND EXCITATION SPECTRA. J. W. Hofstraat, Akzo Research Laboratories Arnhem, Corporate Research, P.O. Box 9300, NL-6800 SB Arnhem, The Netherlands. M. J. Latuhihin, Tidal Waters Division, Laboratory Department, Rijswijk, The Netherlands.

Different approaches to obtain fluorescence spectra that have been corrected for wavelength dependent variations in response factors will be discussed. For fluorescence emission spectra calibrated light sources and reference materials can be used to obtain instrument specific correction files. For fluorescence excitation spectra quantum counters in combination with a polarization dependent correction have to be applied. The latter correction has been done using a relative photodiode measurement and a relative reflection measurement. Corrected spectra have been checked with available certified standards. Corrected spectra are required to be able to compare spectral data that have been measured on different instruments. Also, if instrumental response functions are known, spectral data can be calculated. The application of fluorescence correction files will be demonstrated with a number of examples taken from the field of marine biology, in particular using spectra of phytoplankton, and from the field of polymer analysis.

512 A COMPARISON OF STROBOSCOPIC AND STEP SCAN TIME RESOLVED SPECTROSCOPY. B. Lerner and M. Daun, Nicolet Instrument Corporation, Spectroscopy Research Center, 5225 Verona Road, Madison, WI 53711.

It is often desirable to measure mid-IR spectra as a function of time. Experiments where this ability is needed include gas chromatography/FT-IR, thermogravimetric analysis/FT-IR and kinetic experiments. In these cases the required spectral and time resolutions are such that the spectrometer is able to acquire a spectrum and be ready to take the next spectrum within the required time interval using conventional and rapid scan techniques. If the time resolution is such that this is not possible, then specialized techniques are required. These techniques are generally variations of continuous scan and step scan interferometry and are collectively known as Time Resolved Spectroscopy (TRS) techniques. The application of either of these methods is not, however, trivial. Both the continuous scan and step scan methods demand that the experiment be repeated for each point in the interferogram, which places extreme reproducibility requirements on the experiment being studied. The continuous scan and step scan methods both have their advantages and disadvantages which are discussed using some simple applications.

513 FLUORESCENCE ANALYSIS OF BIOLOGICAL SAMPLES IN THE NEAR INFRARED: NATURE OF BACKGROUND SIGNALS AND LIMITATIONS ON SENSITIVITY. John W. Silzel and Robert J. Obremski, Beckman Instruments, Inc., 200 South Kraemer Boulevard, Brea, CA 92621.

The sensitivity of fluorescence analyses of biological samples in the visible region is often limited by background signals originating from scattering of the incident beam by macromolecules and/or endogenous fluorescence of trace species present in the sample. Using instrumentation and materials for fluorometry in the near infrared (NIR) region (700–1000 nanometers), these background signals may be reduced in magnitude, and gains in sensitivity realized. Fluorescence data and backgrounds obtained with a diode laser source and charge-coupled device (CCD) detector are used for quantitation of NIR-emitting fluorophores in the presence of serum albumins. The sources of low level limitations will be examined and discussed, and compared with results in the visible region.

514 COMPARISON BETWEEN COVALENT ATTACHMENT AND PHYSISORPTION OF FLUORESCENT PROBE-PROTEIN ADDUCTS AND COMPLEXES. Run Wang and Frank V. Bright, Department of Chemistry, Acheson Hall, State University of New York at Buffalo, Buffalo, NY 14214.

We studied the complexation of 2-(p-toluidinyl) naphthalene-6-sulfonate (TNS) to the hydrophobic site of bovine serum albumin (BSA), bovine β-lactoglobulin (β-Lg), immunoglobin (IgG), and physisorbed and covalently-attached TNS. These results show that the hydrophobic sites of different proteins can be probed by TNS using steady-state and time-resolved fluorescence techniques. The TNS binding site in β-Lg is the most hydrophobic compared to BSA and IgG. The excited-state decay kinetics for the TNS-protein complexes is always best described by a distribution (Gaussian) lifetime decay model. TNS-protein adducts (covalent attachment of TNS) indicate that the conversion of TNS sulfonate to sulfonamido group strongly affects the probe photophysics. Acrylamide quenches the fluorescence intensity of TNS-protein complexes, but does not quench TNS-protein adducts. Furthermore, the fluorescence decay kinetics of the TNS-protein adducts is always best described by a discrete lifetime model. In all cases studied, added urea does not affect the recovered lifetime values but does decrease the pre-exponential factor for the longer lifetime component. This result suggests a single step urea denaturation mechanism involving two states of the protein: native and denatured.

515 COMPARISON OF INTER- AND INTRAMOLECULAR CYCLODEXTRIN COMPLEXES. Richard A. Dunbar and Frank V. Bright, Department of Chemistry, Acheson Hall, State University of New York at Buffalo, Buffalo, NY 14214.

Previous studies have shown that cyclodextrins (CDs) can include a variety of free solutes (guest) within their cavity. For example, we have reported on the thermodynamics and dynamics of these complexes and shown that they actually exist as a distribution of sub-complexes. Recently, we have been working with a fluorescent probe (Dansyl-glycine) which is covalently attached to the cyclodextrin. This system is unique because it forms an intramolecular complex which can be used to quantify non-fluorescent analytes. The unique photophysics of this system will be reported. This presentation will also describe the use of this appended cyclodextrin for construction of a fiber-optic sensor.

516 ULTRAFAST EVOLUTION OF EMISSION FROM A POLYCYCLIC AROMATIC HYDROCARBON. G. J. Blanchard, Department of Chemistry, Michigan State University, East Lansing, MI 48824.

Several polycyclic aromatic hydrocarbons (PAH) exhibit solvent polarity dependent emission. The ratio of vibronic band emission intensities has been correlated to the polarity of the medium surrounding the PAH. The fundamental reasons for this relationship are not well understood. In an effort to understand this effect we undertook a series of experiments, using perylene as a typical PAH. We found that the static emission spectrum of perylene changes very little as a function of solvent, but the way in which its emission spectrum to the measured static profile is very solvent-dependent. First, there is vibronic substructure in the perylene emission spectrum which persists for hundreds of picoseconds. We believe that this persistent substructure is due to solvent-dependent coupling between ground state vibrational modes in perylene and the solvent. In addition, there is a fast, solvent and mode dependent buildup in the emission profile. This build-up is related to the equilibration time of excited perylene with its immediate environment and can be understood in terms of an anisotropic solvation environment being sensed directionally by the vibrational structure of the perylene solute.

517 ROLE OF BARIUM AS A MATRIX MODIFIER IN THE FORMATION OF MAGNESIUM MONOFLUORIDE AS DETERMINED BY LASER EXCITED MOLECULAR FLUORESCENCE SPECTROMETRY IN A GRAPHITE TUBE FURNACE.

Alexander. I. Yuzefovsky and Robert. G. Michel, Department of Chemistry, University of Connecticut, Box U-60, Storrs, CT 06269.

The mechanism of formation of magnesium monofluoride molecules from sodium fluoride and magnesium nitrate solutions in the gas phase of atomic absorption graphite furnaces was investigated. A mechanism of formation of reacting species during the char step was proposed. It was shown that the formation of magnesium fluoride, in the gas phase, is based on the interaction between free atoms during vaporization of magnesium from oxide and fluorine from magnesium difluoride. It was shown, that due to the difference in the vaporization temperatures of the reacting species, a relatively small fluorescence signal of magnesium monofluoride was observed. The role of the barium modifier in this process was refined. When the modifier was used the mechanism of formation of reacting species during the char step was changed, and vaporization of fluoride and magnesium occurred at the same temperature, which produced significantly large amounts of magnesium monofluoride in the gas phase. The low atomization temperature for magnesium oxide was explained through the mechanism of carbothermal reduction of oxides.

518 UO_2^{2+} LUMINESCENCE AS A PROBE OF NONRADIATIVE ENERGY TRANSFER IN SOLID UO_2^{2+}-*DATURA*.

Gary D. Rayson and Huei-Yang D. Ke, Chemistry Department, Box 30001, New Mexico State University, Las Cruces, NM 88003.

When placed at liquid nitrogen temperature, the linewidth of uranyl ion fluorescence bound to a biomass material, *Datura innoxia*, has been observed to decrease with the UO_2^{2+} concentration. This line-broadening phenomenon can be explained by the existence of resonance interactions between adjacent UO_2^{2+}-*Datura* species. The analysis of the emission peak position of the bound ions has been used to provide a measure of the electronic structure factors contributing to the interaction between the uranyl ion and phosphoryl and dicarboxyl moieties on the cell wall material. An inter- and intra-molecular nonradiative energy transfer model has been successfully used to interpret the measured lifetime data of UO_2^{2+}-*Datura*. An observed blue shift of the uranyl fluorescence spectrum as a function of solution pH has been ascribed to a distortion of the normally linear O-U-O bond. The experimental basis for this conclusion will be described and the implications of this conclusion will be discussed.

519 SOLID-STATE LUMINESCENCE STUDIES OF METAL BINDING TO *DATURA INNOXIA*.

Huei-Yang D. Ke, Gary D. Rayson and Paul J. Jackson, Chemistry Department, Box 30001, New Mexico State University, Las Cruces, NM 88003 and Los Alamos National Laboratory, Los Alamos, NM 87544.

A pulsed tunable dye laser has been used to obtain fluorescence decay curves, excitation and emission spectra of solid Eu(III)-*Datura* and UO_2^{2+}-*Datura innoxia* from a series of the corresponding metal-containing complexes. Carboxyl and sulfate groups have been demonstrated to be the dominant functional groups responsible for the binding of Eu(III) on the cell wall of *Datura innoxia* at high (≥4) and low (≤3) pH conditions, respectively. A pK of 4.5 was determined for the binding of Eu(III) to the cell wall at pH ≥4. Phosphoryl and dicarboxyl functionalities are responsible for the binding of UO_2^{2+}. The excitation spectra associated with the $^7F_0 \rightarrow {}^5D_0$ electronic transition of Eu(III) luminescence and the emission spectra obtained from the bound UO_2^{2+} have been used to provide a measure of the electronic structure factors contributing to the interaction between the metal ions and the cell wall material. The experimental basis for the work will be described and the implications of the work will be discussed.

520 ENHANCEMENT OF ATOMIC SPECTROSCOPIES BY FLOW INJECTION ANALYSIS.

Jarda Ruzicka, Department of Chemistry BG-10, University of Washington, Seattle, WA 98195.

Flow injection technique,[1] has found a wide range of applications as a tool of enhancement instrumental methods, of which molecular and atomic spectroscopies have gained widespread acceptance. The strength of flow injection, which is an automated solution handling technique, is its ability to precisely manipulate sample/reagent interactions which, in the context of atomic spectroscopies, allows automated preconcentration of traces of analytes, speciation and matrix removal. This development[2] has recently been successfully commercialized by Perkin-Elmer for atomic absorption as well as for ICP-MS. In the meantime, development of FI methodology has advanced further, resulting in mechanically simpler and fully computer compatible sequential injection (SI) technique, which allows sample volumes, reagent volumes and standard dilutions to be adjusted from a computer keyboard without need for physical reconfiguration of the flow system.[3,4] The lecture will focus on principles, benefits and drawbacks of SI methodology and its compatibility with atomic spectroscopies.

1. J. Ruzicka and E. H. Hansen *"Flow Injection Analysis"* 2nd edition, Wiley N.Y. 1988.
2. J. L. Burguera *"Flow Injection Atomic Spectroscopy"* Marcel Dekker N.Y. 1989.
3. J. Ruzicka, *Anal. Chim. Acta* **261**, (1992) 3.
4. G. D. Christian and J. Ruzicka *Anal. Chim. Acta* **261**, (1992) 11.

521 OVERCOMING KINETIC LIMITATIONS OF THE FLOW INJECTION ATOMIC SPECTROMETRY COMBINATION.

Julian F. Tyson, Department of Chemistry, University of Massachusetts, Amherst, MA 01003.

In 1990, just over fifty publications appeared concerned with aspects of the combination of flow injection (FI) techniques with all types of analytical atomic spectrometry. A considerable number of these papers described the development of procedures for sample pretreatment, including separation of the analyte and matrix species and preconcentration. In many of the manifold designs reported, the injection valve could be viewed as an interface between two flow systems. Consequently, these could be independently optimized with respect to flow characteristics. However, there are still some kinetic limitations for the FI atomic spectrometry combination to overcome. Although these are mainly concerned with the adaptation of slow chemical reactions to an FI format, some spectrometers (notably those with electrothermal atomizers) have operation kinetics which make continuous flow sample presentation difficult. Also, an FI sample introduction system typically produces transient peaks, which makes multi-element determinations difficult. Controlled timing, stopped flow and the closed loop recirculating manifold have potential for overcoming these difficulties. The on-line reduction of arsenic (V) to arsenic (III) by iodide may be effected by the simple expedient of stopping the flow for about 20 s. As part of a microwave assisted flow digestion procedure slurry samples are transported into a glass column reactor and heated under sealed stopped flow conditions to allow the pressure to increase to 400 psi. After a heating program lasting 6 min, the reactor is vented and the resulting solution pumped out. The potential of precipitation reactions for the removal of matrix components has been evaluated for silver plating solutions with the aid of continuous recirculation through a column filter. A similar loop manifold has been used for sample leaching and for interfacing a flow injection system with a graphite furnace.

522 Abstract not received at time of printing.

523 ON-LINE PRECONCENTRATION OF TRACE ELEMENTS IN BIOLOGICAL MATERIALS FOR DETERMINATION BY ATOMIC ABSORPTION SPECTROMETRY.

B. Welz, M. Sperling and X. Sun, Department of Applied Research, Bodenseewerk Perkin-Elmer GmbH, W-7770 Ueberlingen, Germany.

On-line preconcentration of trace elements and their separation from the bulk of the matrix using complexation with diethyl dithiocarbamate (DDTC) and solid sorbent extraction was found to be fairly straightforward for surface water and seawater samples. The main constituents do not form DDTC complexes and are hence not retained on the column. Biological materials often contain high concentrations of copper or iron which form strong complexes with DDTC and compete for the active sites at the sorbent. Various methods have been investigated to overcome these problems and to arrive at a reliable trace element determination. Cadmium in urine and lead in wine were determined successfully using flame atomic absorption spectrometric detection. The extraction of lead from wine was only possible after an acid digestion. Preliminary experiments have shown that on-line microwave digestion using flow injection techniques might be feasible.

524 EVALUATION OF ON-LINE PRECONCENTRATION TECHNIQUES FOR ICP-MS. Diane Beauchemin and Zengbiao Li, Queen's University, Department of Chemistry, Kingston, Ontario, Canada K7L 3N6. Eric R. Denoyer, The Perkin-Elmer Corporation, 761 Main Avenue, Norwalk, CT 06859-0001.

Two different on-line preconcentration techniques were characterized for ICP-MS in view of the analysis of saline samples (such as seawater and biological fluids). The first approach involves silica-immobilized 8-hydroxyquinoline (I-8-HOQ) as the packing material for the on-line preconcentration column. This material selectively binds certain metals (such as many of the transition elements) while not retaining the alkalis, and retaining alkaline earths only partly. Selected metals can therefore be separated from the alkalis and, to some extent, the alkaline earths (which are discarded), and can then be released from the column by an acidic eluent. If the sample volume is larger than that of the eluent, a preconcentration is achieved in the same process. The second approach can also carry out a separation and/or preconcentration of selected analytes. It is based on sorbent extraction where a complex between the analyte and a chelating agent is selectively adsorbed onto a column of C-18 bonded silica (a reversed-phase adsorbent). Methanol is then used for the elution. The efficiency of the separation relies on the selectivity of the chelating agent chosen. Each approach has advantages and shortcomings which will be compared, particularly with regard to efficiency, ease of implementation and operation, and range of application.

525 DETERMINATION OF BARIUM IN SEA WATER BY FLOW INJECTION SAMPLE-TO-STANDARD ADDITION METHOD AND INDUCTIVELY COUPLED PLASMA-MASS SPECTROMETRY. Chitra J. Amarasiriwardena, Steven F. Durrant, Elzbieta G. Bakowska, Yecheskel Israel, and Ramon M. Barnes, Department of Chemistry, Lederle Graduate Research Center, University of Massachusetts, Amherst, MA 01003-0035.

The use of inductively coupled plasma-mass spectrometry (ICP-MS) permits the continuous monitoring of the responses of isotopes of analyte and internal reference elements introduced by flow injection. A sample or blank solution injected into a continuously flowing standard solution produces transient peaks and troughs the heights of which are related to the concentration of the elements sought. The usefulness of this sample-to-standard addition method is illustrated by the determination of barium in fresh and sea waters. The application of an internal reference is beneficial to compensate for matrix suppression resulting from the presence of high salt concentrations in the sample. By applying Cs and Pr as internal reference elements, an accuracy of about 95% and 90% was obtained for the determination barium in the range of 5 to 200 ng/ml in fresh and saline waters, respectively.

526 IMPROVING DETECTION LIMITS BY AN ORDER OF MAGNITUDE BY COUPLING HYDRIDE GENERATION FLOW INJECTION TECHNIQUES WITH ELECTROTHERMAL ATOMIZATION. Michaela Feuerstein and Gerhard Schlemmer, Bodenseewerk Perkin-Elmer GmbH, P.O. Box 101164, D-7770 Uberlingen, Germany.

Hydride generation AAS coupled with flow injection offers absolute detection limits in the lower pg range for hydride forming elements. Relative detection limits depend upon the matrix concentration in the samples. Assuming a sample volume of 500 μL, average relative detection limits of 0.05–0.1 $\mu g/L$ are obtained. While this is sufficient to reach the required limits of determination in e.g. drinking water and waste waters, it is not sufficient to measure the levels of these elements in lakes and oceans. The coupling of hydride generation with graphite furnace AAS is an attractive way to generate hydrides from larger sample volumes, decompose the analyte, trap the decomposed analyte species on the graphite tube surface and improve the relative detection limits for these elements. There is some confusion about the graphite surfaces best suited for trapping the analyte, temperatures required to decompose the hydrides and modifiers required. A Perkin-Elmer Model 4100ZL AA spectrometer in combination with a FIAS 200 system was used in this study. For most of the experiments, uncoated graphite tubes with integrated L'vov platforms and, for comparison, pyrolytically coated tubes with integrated platforms were used. The efficiency of trapping and atomization is similar with coated and uncoated tubes if small sample volumes were used. However, with higher volumes, the trapping efficiency on the different surfaces was found to depend strongly on the sample volumes, but not on the analyte concentration. Recoveries close to 100% were found for the elements under investigation. Depending on the sample volume preconcentrated, the relative detection limit could be lowered by about one order of magnitude. As, Bi, Sb and Se were determined in drinking waters collected from a large water supply. The results were in good agreement with the expected values.

527 DISPERSION OF DISCRETE SAMPLES IN AEROSOL FORM: FUNDAMENTAL STUDIES. John A. Koropchak, L. B. Allen and J. M. Davis, Department of Chemistry and Biochemistry, Southern Illinois University, Carbondale, IL 62901.

Aerosol techniques are commonly employed to interface discrete sampling techniques (flow injection analysis and liquid chromatography) with various detectors, such as atomic and mass spectrometers. Aerosol interfaces consist of an aerosol generator (nebulizer), a spray chamber operating in the turbulent flow regime, and any ancillary transfer or aerosol modification apparatus which generally operates in the laminar flow regime. These components invariably have large gas-phase volumes (100's of *mL*). However, transport of discrete samples through μL level liquid-phase volumes causes peak dispersion, which will lead to loss of resolution in chromatographic analysis, increased analysis time, and loss of signal magnitude/poorer limits-of-detection (LOD's) in both flow-injection analysis (FIA) and chromatography. As new aerosol interfacing techniques employ more efficient and larger volume processing techniques, an understanding of dispersion phenomena in the aerosol phase is required for adequate understanding of the effects of these systems on discrete sample signals. Recently, we reported that dispersion of discrete aerosol samples could be described by a convective model.[1] In this report, we will extend our description of aerosol interfacing effects on discrete sample introduction, particularly within the laminar flow regions of the aerosol interface, to include description of the influence of aerosol particle size on discrete sampling. Specific examples of where these effects are important, with comparison to liquid-phase dispersion, will also be included.

1. J. A. Koropchak, L. Allen and Joe M. Davis, *Applied Spectroscopy*, **46**, 682 (1992).

528 CLOSED LOOP RECIRCULATING MANIFOLD FOR MATRIX ISOLATION IN FLOW INJECTION FLAME ATOMIC ABSORPTION SPECTROMETRY. E. Debrah and J. F. Tyson, Chemistry Department, Lederle Graduate Research Center, University of Massachusetts, Amherst, MA 01003. M. W. Hinds, Royal Canadian Mint, Ottawa, Ontario, Canada.

The determination of trace metals in silver solutions by flame atomic absorption spectrometry using air/acetylene can be problematical due to the formation of unstable silver acetylide in the spray chamber. This leads to blockage of both the nebulizer and the burner. The insertion of a filter in-line does not cause a problem when the amount of precipitate is small, but for large amounts of solid the use of precipitation with direct coupling to an atomic spectrometer presents some difficulties due to the changes in flow rate which occur as the precipitate collects on the filter medium. This is particularly true if a high concentration of a matrix is to be removed by precipitation. To overcome this problem, a flow injection recirculating, closed loop manifold containing two valves was used to remove the silver by on-line precipitation as the chloride. A 163 μL sample was injected into the circulating stream (660 μL) of 2 M HCl. The precipitate formed was collected on filter column consisting of nylon fibers packed in a 50 × 3 mm glass column. A 237 μL sub-sample was injected into a single line manifold for transport to the spectrometer. Good recoveries of copper, iron, zinc and nickel from solution containing up to 100 $g\ L^{-1}$ silver were obtained with over 95% of the silver retained on the filter. The filter was regenerated by flushing ammonia solution (1 + 1). Calibration plots for all four elements were linear.

529 ELEMENTAL SPECIATION BY INDUCTIVELY COUPLED PLASMA MASS SPECTROMETRY WITH DIRECT INJECTION NEBULIZATION. Sam C. K. Shum, Ho-Ming Pang and R. S. Houk, Iowa State University, Ames Lab USDOE, Ames, IA 50011.

New results on measuring elemental speciation by liquid chromatography with ICP-MS detection are presented. Various Hg species (Hg^{+2}, CH_3Hg^+, $CH_3CH_2Hg^+$ and $C_6H_5Hg^+$) and Pb species ($((CH_3)_3Pb^+$ and $(C_2H_5)_3Pb^+$)

can be separated as ion pairs by reverse phase LC with detection limits of 20 pg Hg and 0.5 pg Pb. Application of this method to measurements of elemental species in difficult real samples such as urine will be described. The feasibility of the direct injection nebulizer for interfacing open tubular micro LC and capillary electrophoresis to ICP-MS will also be described.

530 FAST TRANSIENT ICP-MS: HOW MANY IONS ARE ENOUGH? Eric R. Denoyer and Steven A. Beres, The Perkin-Elmer Corporation, 761 Main Avenue, Norwalk, CT 06859-0215.

With the emergence of transient sample introduction techniques, data acquisition parameters in ICP-MS become much more critical. The restriction placed on the time domain by the transient signal event means that a careful choice must be made between sampling, measurement, and data acquisition parameters. In this presentation, a critical evaluation of the interaction between discrete sampling and transient signal analysis and the effect on data quality will be made. This will provide a basis for defining operating boundary conditions for flow injection, electrothermal vaporization and laser sampling sample introduction techniques for ICP-MS.

531 SPECIATION OF ARSENIC COMPOUNDS BY SUPERCRITICAL FLUID CHROMATOGRAPHY WITH INDUCTIVELY COUPLED PLASMA MASS SPECTROMETRIC DETECTION. Uma T. Kumar, Nohora P. Vela, John G. Dorsey and Joseph A. Caruso, University of Cincinnati, Department of Chemistry, Cincinnati, OH 45221-0172.

Arsenic compounds are used for a variety of industrial and agricultural purposes, including herbicides, pesticides and wood preservatives. This widespread use results in a need for methods that can accurately assess environmental and occupational exposure to toxic arsenic compounds. Supercritical fluid chromatography (SFC) when coupled with a suitable element-selective detector like Inductively coupled plasma mass spectrometry (ICP-MS) can provide a sensitive method for speciation. Results will be presented showing the separation of arsenic compounds detected by ICP-MS.

532 LOW PRESSURE INDUCTIVELY COUPLED PLASMA MASS SPECTROMETRY AS A DETECTOR FOR GAS CHROMATOGRAPHY. Theresa M. Castillano, Jeffrey J. Giglio, and Joseph A. Caruso, University of Cincinnati, Department of Chemistry, Cincinnati, OH 45221-0172. E. Hywel Evans, Elemental Research Inc., 309-267 West Esplanade, N. Vancouver, B.C. Canada V7M 1A5.

Inductively coupled plasmas (ICPs) have been widely used as an efficient ion source for mass spectrometry. However, ICPs at atmospheric pressure suffers from spectral interferences due to the entrainment of atmospheric gases. In addition, ICPs formed from argon are not energetically sufficient for the ionization of halogens. Results from the study of the use of a low pressure helium plasma (ICP-MS) as a detector for gaseous samples in comparison to an argon atmospheric and an argon low pressure ICP will be presented. Optimization of parameters such as rf power, gas flows, and ion lens tuning will also be discussed. In addition, the design of the torch and interface will be shown for the low pressure ICP and figures of merit presented.

533 CATION EXCHANGE PATTERNS FOR 50 ELEMENTS IN HYDROCHLORIC ACID MEDIA BY ICP-MS. V. Hodge, M. Amano, K. Zarrabi and K. Stetzenbach, University of Nevada, Las Vegas, Las Vegas, NV 89154.

Cation exchange resins have been used to concentrate many elements, mainly metals, from environmental waters prior to analysis by spectroscopic methods, including AAS, ICP, and ICP-MS. In general, reported methods are often optimized for a single metal or a small number of metals. In the present study, one or two liters of ground water were passed through exchange resins and the absorbed ions removed, often concentrated by 100, by graded elution with hydrochloric acid or nitric acid. A semiquantitative-multielement ICP-MS application program was used to determine the concentration of about 50 elements in 10 mL elution volumes. Studies indicate that the ICP-MS coupled with ion exchange may become a valuable tool in the investigation of metal speciation because multiple peaks were observed in the elution procedure for some elements. Data was also obtained for some nonmetals. Information on the elution pattern of the alkaline earth elements was used to improve a radiochemistry procedure for the determination of radium in water.

534 INDUCTIVELY COUPLED PLASMA MASS SPECTROMETRIC DETECTION OF CHROMIUM CONTAINING COMPOUNDS USING HIGH-PERFORMANCE LIQUID CHROMATOGRAPHY. Francine A. Byrdy, Uma T. Kumar and Joseph A. Caruso, University of Cincinnati, Department of Chemistry, Cincinnati, OH 45221-0172.

Since chromium is used in many industrial processes such as steel alloying and textile production, much interest has been placed on the toxicity of chromium compounds. The oxidation state of the metal ion in these compounds is one factor in determining their toxicity. Chromium (VI) is considered more toxic than chromium (III), since the former can cross cellular membranes by way of nonspecific anion carriers. High-performance liquid chromatography inductively coupled plasma mass spectrometry (HPLC-ICP-MS) will be used for the detection of chromium containing compounds. Interfacing HPLC with plasma MS provides specific elemental detection with low detectability and high sensitivity. ICP-MS has become the method of choice for the analysis and speciation of trace elements. The ability to obtain low detection limits is just one advantage of this increasingly popular detector.

535 SUPERCRITICAL FLUID EXTRACTION FOLLOWED BY INDUCTIVELY COUPLED PLASMA MASS SPECTROMETRY FOR THE ANALYSIS OF ORGANOMETALLICS. Nohora P. Vela and Joseph A. Caruso, Department of Chemistry, University of Cincinnati, Cincinnati, OH 45221-0172.

Supercritical fluid extraction (SFE) has gained interest as a sample preparation technique. SFE gives advantages of a fast, safe, and efficient extraction method, compared to the traditional Soxhlet procedure. The extractant obtained is analyzed by inductively coupled plasma-mass spectrometry (ICP-MS). Carbon dioxide is used as a solvent for the extraction of organometallic species present in a real sample. The effect of the addition of a co-solvent (methanol) for the extraction is evaluated. Parameters such as temperature, pressure and duration of extraction are also considered. Efficiency of the extraction is measured by comparing the results obtained with a regular procedure and with the SFE method. Advantages of using ICP-MS as a detector after SFE are excellent sensitivity and selectivity, giving additional information about several metal containing species co-extracted with the analyte of interest.

536 NICKEL AND VANADIUM SEPARATION VIA LIQUID CHROMATOGRAPHY WITH ICP-MS DETECTION. Medha J. Tomlinson, Uma T. Kumar and Joseph A. Caruso, University of Cincinnati, Department of Chemistry, Cincinnati, OH 45221.

Vanadium is used in the metallurgical, paint and ceramic industries. Environmental concerns about vanadium arise primarily from air pollution problems since it can be released from fly ash and oil combustion products. Nickel is present in mineral oils and is known to be a carcinogen. Since differences in the oxidation state for inorganic compounds can produce markedly different toxicities, speciation information is essential. Using a chromatographic sample introduction system and an inductively coupled plasma mass spectrometer (ICP-MS), ultra trace levels of nickel and vanadium can be detected and the results of the separation will be presented.

537 LASER EXCITED ATOMIC FLUORESCENCE IN GRAPHITE FURNACES FOR METALS AND NON-METALS. Robert G. Michel, Department of Chemistry, University of Connecticut, 215 Glenbrook Road, Storrs, CT 06269-3060.

Laser excited atomic fluorescence in a graphite furnace, ETA-LEAFS, is capable of detection limits at the femtogram level in 20 μL of sample, which are comparable or better, in concentration terms, than detection limits in Inductively Coupled Mass Spectrometry. Research in recent times has shown that the technique is remarkably free of interference effects, and apart from the complexity of the lasers that are used, the technique is as easy, or easier, to use than graphite furnace atomic absorption, which is less sensitive by about three orders of magnitude. The ease of use of ETA-LEAFS stems from its long linear dynamic range of calibration curves and excellent detection limits. Its freedom from interference effects stems directly from technological developments in the atomic absorption graphite furnaces that are used for ETA-LEAFS, plus the lack of background signals compared to atomic absorption spectrometry. The technique of laser excited fluorescence is capable of extraordinary detection limits for non-metals as well as the metals. For example, the elements Te, Sb, P give detection limits in the femtogram region. In addition, by molecular fluorescence of the MgF molecule it is possible to determine fluorine with excellent detection limits. The potential of ETA-LEAFS will be evaluated with respect to the above considerations, and the new types of lasers that could be used for this technique. In particular, pulsed Ti:sapphire lasers show great potential as continuously tunable sources of radiation throughout the UV-VIS.

538 RESONANCE DETECTION OF PHOTONS. Giuseppe A. Petrucci, Raul G. Badini, Denise Imbroisi, Ben W. Smith and James D. Winefordner, University of Florida, Department of Chemistry, Gainesville, FL 32611-2046.

Resonance detection of photos in three different atom reservoirs and based on three different detection processes is described. A resonance ionization detector (RID) based on the two-step laser-enhanced ionization of magnesium in a miniature acetylene/AIR flame is described. The detector utilizes the 285.21 nm resonance absorption of MG as the signal transition. The minimum detectable number of photons, obtained for the excitation scheme $3s^2\ {}^1S(285.21\ \text{nm}) \rightarrow 3p\ {}^1P \cdot (435.19\ \text{nm}) \rightarrow 6d\ {}^1D$, was determined to be 1000 (7×10^{-16} J). The quantum efficiency of this excitation scheme, defined as the number of charge pairs created per incident signal photon, was found to be 0.75. The detector had a stray light rejection ratio (SLR) of approximately 10^{-5} at 100 cm^{-1} displacement from the absorption maximum of the RID at 285.21 nm. The SLR was limited by the collisionally broadened absorption profile of the MG in the atmospheric pressure flame. Preliminary results are also given for a low pressure-magnesium based resonance detector, operating on the double-resonance photoionization of dense magnesium vapor in an optical heat pipe and a resonance detector based on the double-resonance optogalvanic effect of neon in a hollow cathode lamp.

539 COLLISIONAL COUPLING RATES OF COPPER AND SILVER IN AN ICP AND AN AIR ACETYLENE FLAME USING FLUORESCENCE DIP SPECTROSCOPY. Donna J. Robie, J. B. Simeonsson, B. W. Smith and J. D. Winefordner.

The fact that laser induced fluorescence (LIF) is a technique with excellent selectivity and high sensitivity is well documented in the literature. Stepwise excitation techniques using two or more lasers to sequentially excite atoms, ions, or small molecules to high levels demonstrate both high spatial and high spectral resolution. Fluorescence dip spectroscopy is a technique that uses stepwise excitation to study the excited states of an atom, ion, or small molecule by monitoring the decrease, or dip, in the LIF emission from an excited state when a second laser is used to probe excited state transitions from the fluorescent level. Fluorescence dip spectroscopy in the ICP has been used to study many elements, including copper and silver, to demonstrate the high sensitivity and unprecedented selectivity of the method. One of the conclusions that was reached in these studies is that collisions play a large role in the dynamics of atomic species in the ICP. This collisional coupling and mixing of excited states was previously viewed as a disadvantage in ICP-LIF studies. It is now, however, being used as a way to determine the collisional rates of exchange between excited levels in both an ICP and in an air acetylene flame. A model of the fluorescence dip, based on steady state considerations, has been shown to be in good agreement with experimental results for both copper and silver. The previously mentioned steady state theory is now being replaced with more modern theories using a density matrix approach for estimation of collisional coupling constants in these atoms.

540 RESONANCE LINE LASERS AS EXCITATION SOURCES FOR ATOMIC SPECTROMETRY. Norma L. Ayala, United States Department of Agriculture, Agricultural Research Service, North Atlantic Area, Eastern Regional Research Center, 600 E. Mermaid Lane, Philadelphia, PA 19118. Tye Ed Barber, Oak Ridge National Laboratory, P.O. Box 2008, Oak Ridge, TN 37831-6113. James D. Winefordner, Department of Chemistry, University of Florida, Gainesville, FL 32611-2046.

Resonance line lasers (RLLs) were evaluated as excitation sources for atomic spectrometry. RLLs produce stimulated emission by a photodissociation mechanism. When RLLs are constructed using metal halide salts as the active media, the wavelengths which are obtained correspond to atomic transitions of the metal. RLLs have peak powers on the order of kW and irradiances of several hundreds of kW cm^{-2}. The uniqueness of RLLs as excitation sources can be attributed to the combination of narrow linewidth radiation, naturally locked to an atomic transition, with the irradiance and coherence of a laser. The added convenience of their simplicity in design and operation makes the RLL an almost ideal source for analytical atomic spectrometry. Three RLLs, employing GaI_3, InI, and TlI, were constructed and characterized. The analytical figures of merit (AFOM) of the RLLs such as spectral output, source irradiance, temporal behavior, and source lifetime were determined. The applicability of RLLs to spectrochemical methods of analysis such as laser enhanced ionization (LEI) and laser induced fluorescence (LIF) in flames was demonstrated. The limits of detection obtained for both techniques using RLLs as excitation sources were in the parts-per-billion (ppb, ng mL^{-1}) range.

541 HIGH-RESOLUTION SPECTROSCOPY OF ATOMIC VAPORS USING DIODE LASERS. R. J. Lipert, S. C. Lee and M. C. Edelson, Ames Laboratory-USDOE, Iowa State University, Ames, IA 50011.

The low cost and narrow bandwidth of diode lasers make them attractive light sources for high-resolution spectroscopy. This is especially true if one can obtain satisfactory performance without the need for additional optical or electronic feedback equipment to stabilitize the laser frequency. We have been exploring the usefulness of commercial diode lasers for the analytical atomic spectroscopy of high-temperature vapors of rare earth metals and yttrium. Progress in using diode lasers for measuring isotope and hyperfine splittings and isotope ratios will be discussed.

542 FIRST OBSERVATION OF ACTINIDE ELEMENTS BY OPTOGALVANIC SPECTROSCOPY USING A DIODE LASER SOURCE. S. C. Lee, R. J. Lipert and M. C. Edelson, Ames Lab.-USDOE/Iowa State University, Ames, IA 50011.

Semiconductor diode lasers are used for the first time to investigate the optogalvanic spectroscopy of actinides. Diode lasers we used showed 10–20 MHz line width and relatively stable beam intensity that are significant factors for monitoring the actinides and their isotopes. Excited uranium atoms were produced in the commercially sealed hollow cathode lamp by electric sputtering. The optogalvanic signals were detected when the diode laser excited the sputtered uranium atoms resonantly. The diode laser was scanned upto 3–5 GHz without mode hopping by current modulation. The results showed Doppler limited optogalvanic spectra (about 450 MHz band width). In addition, optogalvanic spectra of thorium were measured same way. Detection of several electronic transitions was successfully made. We couldn't detect uranium-235 because the commercial hollow cathode lamps are made of depleted uranium for safety reason. Currently, a modified hollow cathode lamp is being designed for the detection of the actinides and their radioactive isotopes. Practical view of monitoring the actinides using diode lasers will be discussed.

543 ULTRATRACE DETERMINATION OF URANIUM BY TIME-RESOLVED LASER-INDUCED FLUORESCENCE. C. Moulin, P. Decambox and P. Mauchien, CEA/DCC/DPE/SPEA/SPS, Analytical Laser Spectroscopy Group, 92265 Fontenay Aux Roses, BP 6, France.

Uranium determination at ultra low level is required in several fields such as in the nuclear, in the medical and more recently in the environment and for waste storage assessment. In the nuclear for process control at various stages, in the medical to estimate the body burden and in the environment for control near nuclear sites. Time-resolved laser-induced fluorescence (TRLIF) is a very selective and sensitive technique for such determinations that has been used. The principle of this technique is based on a pulsed laser excitation, followed by time resolution of the fluorescence signal which leads to the elimination of unwanted short lifetime fluorescence. In complex matrices, the triple selectivity (excitation wavelength, specific emission and fluorescence lifetime) is mandatory and allows uranium determination down to 1 ng/l (5.10^{-12} m). The present limit of detection being 0.1 ng/l in pure solution. Furthermore, this determination is fast (15 min) and requires no chemical preparation but only dilution. Last results obtained on various type of samples (ground waters, vegetals, urines, . . .) will be presented.

544 LEAFS DEVELOPMENT FOR DIRECT ANALYSIS OF ENVIRONMENTAL SAMPLES. V. Cheam, J. Lechner, I. Sekerka and R. Desrosiers, National Water Research Institute, Research and Applications Branch, P.O. Box 5050, Burlington, Ontario, Canada L7R 4A6.

A copper vapor laser-based LEAFS has been developed and used in the development of a method for direct determination of Pb in water samples. The preconcentration steps required by the conventional methods are no longer necessary. The generation of analytical data is simple. The method was successfully applied to analysis of Great Lakes waters. Pb profiles will be discussed. The LEAFS design and development as well as the method's figure of merits will be presented with some preliminary results on analysis of seawater and estuary inter-tidal samples.

545 Abstract not received at time of printing.

546 IDENTIFICATION OF ORGANIC FUNCTIONAL GROUPS USING VAPOR PHASE INFRARED SPECTRA AND ARTIFICIAL NEURAL NETWORKS.

Barry J. Wythoff and Stephen E. Stein, Chemical Science and Technology Laboratory, National Institute of Standards and Technology, Gaithersburg, MD 20899.

Organic functional group identification is a fundamental step in the process of generating proposed candidate structures for an unknown compound. Due to this importance, there have been manifold attempts over the past twenty five years to perform automated functional group identification, using a computer program of some sort to process spectroscopic data. Systems written to use infrared spectra have included both knowledge based systems, as well as abstract pattern recognition approaches. Artificial neural networks have received a great deal of attention in recent years for their ability to approximate arbitrary mathematical functions. Work is being done at NIST to develop a system for identifying functional groups in unknown molecules, using infrared spectral data from the NIST/EPA Gas Phase Infrared Database. Optimal reduction of the spectral data is being sought. The system will be composed of functional group specific subsystems which are heuristically connected to form the overall functional group classification program. The system architecture will be presented along with results on actual training and test data sets.

547 SPECTROSCOPIC CALIBRATION WITH ARTIFICIAL NEURAL NETWORKS: SOME COMMENTS ON OPTIMAL CONFIGURATIONS.

P. J. Gemperline and S. Li, Department of Chemistry, East Carolina University, Greenville, NC 27858.

In our studies using neural networks for spectroscopic calibration several problems have emerged that indicate overfitting is a significant problem. A typical spectroscopic calibration problem in the NIR region might require a neural network with 700 input nodes, 5 hidden layer nodes, and one output node, giving a total of $700 \times 5 + 5 = 3505$ weights that must be adjusted during the training process. Optimization of this many adjustable parameters is a formidable problem. Solutions tend to be highly dependent on the choice of the random starting point and spectroscopic signatures do not tend to evolve in weight vectors during the training process. Principal component transformation of the input variables is a popular solution to the above problems; however, the practitioner may forfeit some of the inherent nonlinear fitting capabilities of neural networks when this strategy is employed. We have been investigating alternate approaches to the problem, including weight smoothing during training and automatic pruning of redundant nodes identified by newly defined figures of merit like "variance propagated forward by a node." In this presentation we will describe these alternate strategies in detail and present some results obtained using them.

548 THE USE OF ARTIFICIAL NEURAL NETWORKS FOR FUNCTIONAL GROUP ANALYSIS IN VAPOR PHASE SPECTRA.

Rosa McMillan, Robert C. Morrison, David Lunney and Paul J. Gemperline, Department of Chemistry, East Carolina University, Greenville, NC 27858-4353.

Infrared spectra of polyatomic molecules are complex and contain much structural information: functional groups in an organic molecule can be correlated with absorptions at specific frequencies in the infrared spectrum of the molecule. It is our goal to make this information more accessible to visually impaired users. That is, we want to map functional group information into auditory patterns. To achieve this goal, we needed a method that would extract functional group information from a variety of input types. The method that we developed uses artificial neural networks. Artificial neural networks consisting of three layers of nodes were trained to recognize the alcohol, amine and carboxylic acid functional groups and subgroups. Inputs to the networks contained spectroscopic information and the response vectors were used to classify compounds according to organic functional groups. Sigmoid functions were used in the internal, and output layer to facilitate nonlinear fitting of the data. The networks were trained using the generalized delta training rule. Several network cases were studied. In this presentation, the construction and the results of these network cases will be discussed.

549 PITFALLS OF APPLYING NEURAL NETWORKS FOR MULTIVARIATE CALIBRATION.

A. Lorber, Nuclear Research Centre Negev, P.O. Box 9001 Beer-Sheva 84190, Israel.

The appetite grows with success. The success of multivariate calibration methods to solve various analytical problems leads to the current endeavor to develop and apply techniques which overcome the limitations of the traditional methods. Traditional methods such as MLR, PCR and PLS all rely on the linear additive model. Although, PCR and PLS have the capability of modeling non-linearities in certain cases, the generated model uses more principal components and therefore grabs more noise and is less robust. Recent publication have successfully demonstrated the advantage of using non-linear methods such as, non-linear modeling of the principal components, non-linear PLS and neural-networks to relax the linear additive model. On the other hand, the increased number of parameters to be estimated for non-linear modeling, raise concern about the robustness of such models. A variant of a neural-network model, which is especially suited to tackle calibration problems, will be presented. It will be demonstrated that, under certain condition, it might result in poor prediction compared to PLS/PCR. Reasons to such phenomena and diagnostic tools to detect their occurrence will be discussed.

550 SORTING OF WASTE PLASTICS USING NEAR INFRARED SPECTROSCOPY AND NEURAL NETWORKS.

M. K. Alam and S. L. Stanton, Sandia National Laboratories, P.O. Box 5800 Albuquerque, NM 87185.

Nine percent of the municipal solid waste stream is plastic. Yet only 1–2% of this stream is recycled, compared with a 25% recycling rate for the paper waste stream. The major impedance to plastic recycling is cost. In order for plastic recycling to be economically feasible, the recovered material must be less costly than the virgin feedstock and it must have virtually the same properties (tensile strength, resistance to cracking, moldability, etc.) as the original product. Although gains have been made in commingled recycling, the most value arises from the recovery of plastics as a high-grade, high-purity polymer. However, sorting of plastics into separate polymer streams, is, at present, labor intensive and error prone. A system for sorting waste plastics has been developed at Sandia National Laboratory. We have developed a training set using post-consumer plastics that have been marked as recyclable. Near infrared spectra and neural networks have been explored for sorting the plastic waste into six groups. Each group is composed of one type of plastic that has been identified by the Society of Plastics as recyclable. Initial work has examined the use of backpropagation neural networks for sorting the near infrared spectra. Several architectures were investigated, and effects of various network parameters were studied. When HDPE and LDPE categories are combined (five categories), a 98% classification rate is achieved. The classification rate drops to 95% when the network trains using six categories.

551 OPTIMIZATION OF PREPARATIVE CHROMATOGRAPHY WITHOUT EQUATIONS.

Georges Guiochon, Attila Felinger, Sadroddin Golshan-Shirazi and Stephen Jacobson, The University of Tennessee, Department of Chemistry, 300 South College, Knoxville, TN 37996-1501.

The results of several years of theoretical investigations of the optimization of preparative chromatography for maximum production rate of fractions of a given degree of purity are presented in simple language and compared to experimental results. One of our most salient and unexpected conclusions is that the production rate experiences a sharp maximum for values of the retention factor of the first component often lower than 1. The maximum production rate increases in proportion to the square root of the allowed pressure drop, but the optimum experimental conditions vary also with this pressure. There is an optimum value of d_p^2/L (d_p, particle size, L column length), which decreases with increasing allowed pressure drop.

552 BULK CHIRAL SEPARATIONS FOR PHARMACEUTICAL STUDIES.

Alfred J. Mical, Dupont-Merck Pharmaceutical Co., Wilmington, DE 19880-0353.

With the availability of preparative columns, new studies are being done on first-time isolations of enantiomers. A range of drugs in cardiovascular, central nervous system, anti-cancer, inflammatory and anti-viral research are being studied as separate drugs in pharmacokinetics and toxicology.

553 SELECTION AND OPTIMISATION OF PREPARATIVE LIQUID CHROMATOGRAPHIC METHODOLOGIES.

Geoffrey B. Cox, Prochrom Inc., 5622 West 73rd Street, Indianapolis, IN 46278.

The technique of preparative liquid chromatography has undergone a dramatic transition over the past five years. Developments in theory have led to a new understanding of the optimisation of both the separations and the technologies required to operate them. The major influences upon the technique have been the upsurge of computer modelling of chromatography and the improved understanding of solute—solute displacements which occur under appropriate chromatographic conditions. The influence of these developments upon batch and continuous chromatographic separations are discussed, particularly with reference to optimal particle and column dimensions. Factors influencing the choice of methodology based upon a knowledge of the chromatographic parameter set and the goals of the optimisation are considered, and the relevant technologies for the large-scale operation of such separations are discussed.

554 STRATEGIES FOR SUCCESSFUL PREPARATIVE LC.

Brian A. Bidlingmeyer, AC Enterprises, P.O. Box 99, Hopkinton, MA 01748.

Analytical and preparative separations differ significantly in goals, and the attitude of the chromatographer must be matched to the task at hand to insure the best possible outcome. Preparative LC is used to isolate, enrich or purify one or more components in a mixture. To accomplish this task five independent elements must be addressed—purity, quantity, time, difficulty and cost. In many practical ways, preparative LC is simpler than analytical LC. However, before any separation is attempted, careful planning must be done to insure success. This paper will give an overview of strategy for preparative LC with supporting examples.

555 PERFUSION CHROMATOGRAPHY WITH 50 μM MEDIA.

Fred E. Regnier, Department of Chemistry, Purdue University, Lafayette, IN 47907. Noubar Afeyan, PerSeptive Biosystems, 38 Sydney Street, Cambridge, MA 02139.

The ideal preparative chromatography packing material for macromolecular separations would i) be of high loading capacity, ii) operate at low pressure, and iii) show little loss of resolution at high mobile phase velocity. The only known way to achieve high capacity with low operating pressure has been to use large, porous particles of high surface area. Unfortunately, intraparticle mass transfer is very poor in large, porous particles. This paper will report a solution to this problem that involves two new types of technology, i) large throughpores which allow intraparticle convective transport and ii) fimbriated stationary phases to increase loading capacity. It will be shown that 50 um particles of these kinetically enhanced sorbents can be used in five min preparative separations. The paper will conclude with a discussion of rapid cycling preparative chromatography with small columns as an alternative to single cycle separations with large columns.

556 PREPARATIVE CHIRAL SEPARATIONS USING THE SAMPLE SELF-DISPLACEMENT TECHNIQUE.

J. Newburger, Robert Wood Johnson Pharmaceutical Research Institute, Welsh and McKean Roads, Spring House, PA 19477. S. Taylor, Bristol-Myers Squibb Pharmaceutical Research Institute, P.O. Box 4000, Princeton, NJ 08543. G. Guiochon, Department of Chemistry, University of Tennessee, Knoxville, TN 37996.

The sample self-displacement effect, a column overload phenomenon, is a special case of displacement chromatography where consecutively eluting mixture components display competitive adsorption behavior so an external displacing agent is not required. In a binary mixture, for example, the second component can act to displace the first, pushing the first ahead of itself down the column. The practical outcome of this phenomenon is an overall increase in the recovery of pure material. Furthermore, the first eluting component is recovered in ≥99% purity because the self-displacement effect induces a sharp boundary between the two components. The sample self-displacement technique is well-characterized for binary mixtures. Parameters such as loading, mixture ratio, column efficiency, alpha, k' and flowrate have been studied.[1,2] As a logical extension of this research, the technique has been applied successfully to the separation of enantiomers. In this presentation, features of the technique relevant to racemate separations are discussed and laboratory examples of enantiomer purification are provided. The development of a self-displacement separation and a strategy for individual enantiomer production are described.

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557 RECENT ADVANCES IN DYNAMIC 2D IR SPECTROSCOPY.

Curtis Marcott, A. E. Dowrey and Isao Noda, The Procter & Gamble Company, Miami Valley Laboratories, P.O. Box 398707, Cincinnati, OH 45239-8707.

Two-dimensional infrared (2D IR) spectroscopy is a useful tool for studying the submolecular-level dynamics of polymer systems undergoing dynamic deformation as a function of temperature. In 2D IR spectroscopy, a polymer sample is perturbed by a small-amplitude oscillatory strain. The dynamic fluctuation in the IR spectral response is then represented in the form of a set of two-dimensional correlation maps. Such 2D maps are useful for obtaining detailed information about the local dynamics of submolecular constituents of the system. For example, 2D IR spectra of glassy atactic polystyrene reveal that, while the main-chain backbone reorients in the direction of the applied strain, there also exist highly localized reorientational motions of phenyl side groups occurring independently of the main-chain realignment. Such localized submolecular distortion is not as dramatic at temperatures well above the glass-to-rubber transition temperature (T_g). Nevertheless, the spectroscopic observations suggest that above T_g, the phenyl side groups tend to reorient perpendicular to the main-chain backbone. Below T_g, however, the phenyl side groups tend to fan back more along the main-chain backbone when the sample is dynamically strained. This difference in the local reorientability of the phenyl side groups is likely due to the change in free volume which occurs around the T_g of polystyrene.

558 FT-IR TIME RESOLVED SPECTROSCOPY USING A DYNAMICALLY-ALIGNED STEP-SCAN FT-IR SPECTROMETER.

Richard A. Crocombe, Senja V. Compton and John C. Leonardi, Bio-Rad Digilab Division, 237 Putnam Avenue, Cambridge, MA 02139.

At this conference last year we presented preliminary data for applications of a dynamically-aligned step-scan Fourier transform spectrometer.[1] In this paper, time dependent applications of this spectrometer are described, with presentation of some novel data. If a sample is changing slower than the interferometer scan rate, then normal rapid-scanning techniques can be used to monitor the change. For instance, it is routine to obtain data at 50+ scans per second, for studies such as flame emission and UV-induced curing of adhesives. However, if the sample is changing at a rate that is the same, or faster than, the spectrometer scan rate, it is even possible to track the changes provided that the experiment is reproducible. Rapid-scanning TRS (time resolved spectroscopy) is a stroboscopic-type technique, and it can easily produce spurious data, the discovery of which,[2] more than ten years ago, diminished interest in the method. Recent developments in step-scan interferometry[3,4] and the advent of a high performance commercial step-scan FT-IR[1] have rekindled interest in TRS. Data illustrating this latter application on chemical systems of interest are shown.

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559 INVESTIGATION OF SUB-MOLECULAR LIQUID CRYSTAL DYNAMICS BY USE OF STEP-SCAN AND STROBOSCOPIC CONTINUOUS-SCAN FT-IR.

Vasilis G. Gregoriou and Richard A. Palmer, Department of Chemistry, Duke University, Durham, NC 27707. Hirokazu Toriumi, Department of Chemistry, University of Tokyo, Komaba Meguro, Tokyo 153, Japan. James L. Chao, IBM Corporation, Research Triangle Park, NC 27009.

The information that can be acquired by the implementation of vibrational spectroscopy in the study of reorientations of uniaxially aligned liquid crystals is of fundamental importance to the design and development of new types of liquid crystals for advanced display devices. We have used polarized, time-resolved step-scan FT-IR spectroscopy to observe the dynamic response of nematic and smectic liquid crystals to AC and pulsed DC electric field perturbations. Impulse-response time-resolved step-scan FT-IR experiments are used to analyze the rise dynamics of reorientation resulting from pulsed DC perturbations, whereas synchronous modulation time-resolved step-scan FT-IR experiments are used to monitor both rise and decay processes in response to AC electric fields. In the pulsed experiments the change in infrared transmission as an explicit function of time is used to extract the dynamic information, while in the synchronously modulated measurements the phase of the response signal and/or its in-phase and quadrature components, is determined. In both types of experiments the absolute and relative rates of reorientation of the separate functional groups of the liquid crystal molecules in response to the perturbation are observable in terms of intensity changes in their characteristic absorption bands. In the synchronous modulation measurements, the sub-molecular view of the dynamics of liquid crystal director reorientation is enhanced by frequency correlation analysis, to yield 2D FT-IR spectra. In preliminary studies (Chem. Phys. Lett. **179,** 491 (1991)) we have shown how these techniques can be used to distinguish the reorientation behavior of the rigid and flexible parts of nematic LC molecules. In this paper we will present new and expanded studies of related nematic LC's as well as smectic *C (ferroelectric) LC phases studied both by step-scan and stroboscopic continuous scan IR techniques.

560 SPECTROSCOPY AND KINETICS OF TRANSIENT MOLECULES BY TIME-RESOLVED FOURIER TRANSFORM EMISSION SPECTROSCOPY WITH 50 ns AND 0.25 cm^{-1} RESOLUTION.

G. V. Hartland, D. Qin, and H. L. Dai, Department of Chemistry, University of Pennsylvania, Philadelphia, PA 19104.

Time-resolved fourier transform emission spectroscopy (TR-FTES) has been used to study the kinetics and spectroscopy of the $CH_2 b^1B_1$—a^1A_1 band. CH_2 was produced in the a^1A_1 state by pulsed photolysis of ketene and excited to a single rotational level in the b^1B_1 state by a pulsed dye laser. Spectral and temporal analysis of the subsequent fluorescence by TR-FTES yields information about the RO-vibrational energy level spacing in the a^1A_1 state and the kinetics of the b^1B_1 state. The results to be presented include the observation of several new, highly excited vibrational levels in the $CH_2 a^1A_1$ state, and cross-sections and propensity rules for state-to-state rotational energy transfer in the $CH_2 b^1B_1$ state induced by collisions with ketene. The rotational energy transfer cross-sections are up to five times the hard sphere gas-kinetic rate.

561 USING STROBOSCOPIC FTIR SPECTROSCOPY TO TRACK IONS AS THEY ARE TRANSPORTED ACROSS MEMBRANES.

Mark S. Braiman and Timothy J. Walter, Department of Biochemistry, University of Virginia Health Sciences Center, Charlottesville, VA 22908.

We have analyzed the mechanism of the light-driven chloride pump, halorhodopsin (hR), with strobscopic time-resolved FTIR spectroscopy. This technique is ideal for observing difference spectra of hR and its hL photoproduct, for which we observe a 12-ms lifetime at 20°C. We assign a difference band near 1690 cm^{-1} in the hR → hL spectrum to a downshift in the guanidino C═N stretch vibration of an arginine. This assignment is based on its characteristic frequency, and on shifts of both positive and negative components of the difference band to ~1610 cm^{-1} in deuterated buffer. Furthermore, the frequency of the positive difference component is sensitive to external halide ion: in chloride buffer it is at 1688 cm^{-1}, while in iodide it is at 1681 cm^{-1}. This counteranion-induced shift is comparable to that observed for a phenylguanidinium model compound in CCl_4 solution. We attribute the negative component of the hR → hL arginine difference band (at 1695 cm^{-1} regardless of external anion) to the guanidino vibration of arginine complexed to an internal Asp or Glu anion in the hR starting state; its higher frequency is well modeled by phenylguanidine acetate in CCl_4. These results indicate that one of the arginines in hR transiently binds a chloride ion during the 12-ms lifetime of hL. The negative Schiff base $C{=}NH^+$ band (near 1630 cm^{-1}) in the hR → hL difference spectrum also shows a ~4 cm^{-1} Cl^-/I^- downshift. It is thus possible that the halide ion is transferred from the protonated Schiff base in the starting (hR) state to arginine during the hR → hL, photoreaction. *This work was supported by a grant from the Lucille P. Markey Charitable Trust.*

562 RAMAN SATURATION SPECTROSCOPY IS A NEW TECHNIQUE TO MEASURE EXCITED STATE RELAXATION RATES.

Sanford A. Asher, Dept. of Chemistry, University of Pittsburgh, Pittsburgh, PA 15260.

We have developed a new spectroscopy to monitor excited state relaxation back to the ground state[1-3] which can often have significant advantages over fluorescence lifetime measurements. We measure resonance Raman spectra using pulsed laser sources and monitor the dependence of the Raman intensity of the ground state analyte as a function of the incident photon flux density. Because the analyte also absorbs the incident photons, a depletion of the ground state occurs during each excitation pulse. The extent of depletion depends upon the incident photon flux, density, the analyte absorption cross section and its T_1 relaxation rate. We extract the relaxation rate with vibrational resolution. We will demonstrate the ability to examine trp and tyr lifetimes in proteins and will also demonstrate novel optical decoupling mechanisms which can be used to select, for example, different PAH bound to DNA.

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563 Abstract not received at time of printing.

564 ULTRAFAST INFRARED SPECTROSCOPY OF MOLECULAR AND PROTEIN DYNAMICS.

R. M. Hochstrasser, Department of Chemistry, University of Pennsylvania, 231 S. 34th Street, Philadelphia, PA 19104.

A survey of the various methods used to examine vibrational spectra with ultrafast time resolution will be followed by examples chosen from recent work at Penn concerning surface dynamics, solution phase chemical reactions and biological systems.

565 TIME-RESOLVED VIBRATIONAL STUDIES OF HEME PROTEINS.

R. B. Dyer, P. O. Stoutland, K. A. Peterson, T. Causgrove, K. A. Bagley and W. H. Woodruff, Los Alamos National Laboratory, Los Alamos NM 87545. M. W. Schauer, S. E. Plunkett, V. G. Gregoriou and R. A. Palmer, Department of Chemistry, Duke University, Durham NC 27706. J. L. Chao, IBM Corporation, Research Triangle Park, NC 27709.

The determination of structure-function relationships is crucial to understanding the mechanisms of protein action. Time-resolved infrared and resonance Raman spectroscopies are applied to the characterization of intermediates formed after photodissociation of CO from myoglobin and cytochrome oxidase. In cytochrome oxidase, a Cu_B^+-CO intermediate that forms in less than 1 ps is observed by picosecond time-resolved infrared (TRIR), and decays with a halflife of 1 μs as seen with real-time TRIR measurements. Transient UV-vis spectra, kinetics, infrared, and Raman evidence suggest that an endogenous ligand is transferred from Cu_B to Fe_{a3} when CO binds to Cu_B, forming a cytochrome a_3 species with axial ligation which differs from the reduced unliganded enzyme. The time-resolved magnetic circular dichroism results suggest that this transient is high spin and therefore five coordinate. Thus we infer that the ligand from Cu_B binds on the distal side of cytochrome a_3 and displaces the proximal histidine imidazole. The post-photodissociation transients of myoglobin were followed by two TRIR approaches: point-by-point single-frequency measurements and time-resolved step-scan FT-IR (TRS^2 FTIR). The latter technique allows the simultaneous observation of the entire mid-infrared region (7900-0 wavenumbers) with a time resolution of 5 μs. Conformational changes in the protein structure, as evidenced by the Amide I, II, and III bands, can be followed at specific times (5 μs to 100 ms) after CO photodissociation.

566 LIQUID CHROMATOGRAPHY/TIME-OF-FLIGHT MASS SPECTROMETRY WITH A PULSED SAMPLE INTRODUCTION INTERFACE.

Alan P. L. Wang and Liang Li, Department of Chemistry, University of Alberta, Edmonton, Alberta, Canada T6G 2G2.

Liquid chromatography combined with mass spectrometry (LC/MS) can be a very powerful analytical tool for the analysis of thermally labile and nonvolatile molecules in complex matrices. Recently, several powerful interfacing techniques have been developed to combine LC with quadrupole or sector MS. However, no suitable interfaces have yet been developed for combining conventional LC with time-of-flight mass spectrometry (TOFMS). With modern electronics and advanced computer technology, though, TOFMS has its potential to become a very important tool for LC detection with several unique features including its versatility and higher detection sensitivity with no mass limit. Our research is directed towards the development of interfacing techniques for combining LC with TOFMS. Recently, a pulsed sample introduction (PSI) interface,[1] capable of handling high flow rates ranging from 0.5 to 1.6 mL/min, has been developed. In PSI, sample molecules carried by a liquid carrier are vaporized by passing through a heated capillary tube and then through a sample vaporizer of a high temperature pulsed nozzle. The resulting sample vapors are introduced into TOFMS in a pulsed form and ionized by a UV laser beam. In this presentation, it is shown that this interface is able to introduce a variety of both volatile and nonvolatile molecules into TOFMS. The use of LC/TOFMS for the detection of biochemicals and polyaromatic hydrocarbons in mixtures is also demonstrated.

1. Wang, A. P. L.; Li, L. *Anal. Chem.* 1992, **64,** 769–775.

567 DETERMINATION OF PEPTIDE SEQUENCE AND DISULFIDE BONDS BY LC/MS AND LC/MS/MS. Mark S. Bolgar and Gerald C. DiDonato, Bristol-Myers Squibb Pharmaceutical Research Institute, P.O. Box 4000, Princeton, NJ 08543-4000.

Peptide sequence analysis and disulfide mapping often involves proteolytic or chemical cleavages prior to mass spectrometric analysis. These cleavages produce peptides with lower molecular weights making them more amenable to sequence analysis by MS/MS. Cleavages occurring between cysteine residues are useful for determining disulfide bond positions. Frequently non-specific or multiple enzymes are required due to difficulty associated with cleaving disulfide containing peptides. This introduces the potential for producing a complex mixture containing the uncleaved peptide, products from enzymatic and chemical cleavages as well as enzyme autolysis products and reagents. In our laboratory we have used two different LC/MS interfaces for the analysis of these types of mixtures. Using electrospray and frit-FAB LC/MS the disulfide bonding and amino acid sequences of endothelin-1 and analogues have been determined. Data will be presented from on-line low energy LC/MS/MS and from high energy CAD-MS used for sequence and disulfide assignments.

568 ANALYSIS OF PLATELET-ACTIVATING FACTOR AND RELATED COMPOUNDS BY LC/MS AND LC/MS/MS. Bethanne M. Warrack, Bristol-Myers Squibb Pharmaceutical Research Institute, PO Box 4000, Princeton, NJ 08543-4000.

Amphipathic compounds, such as platelet-activating factor (PAF), lyso-PAF, lysophosphatidylcholines (LPC), lysophosphatidylethanolamines (LPE), plasmenyl-LPC and -LPE, and acylcarnitines (AC), may contribute to dysfunction and electrophysiological derangements during myocardial ischemia. These compounds contain no UV chromophore and are not easily detected by conventional HPLC; however, a method for separation of these molecular species in cardiac tissue using an HPLC equipped with an evaporative laser light scattering detector has been developed. LC/MS and LC/MS/MS were used to identify LPC, LPE, plasmenyl-LPC and -LPE, AC and lyso-PAF in the ischemic region of canine myocardial tissue. Separation of eight long-chain AC and four LPC, present in the ischemic region of canine hearts, was achieved in under 30 minutes using a YMC Basic column, 250 × 4.6 mm. The mobile phase consisted of 55:25:20 methanol:acetonitrile:water (0.1% TFA), at a flow rate of 0.7 ml/min. Flow splitting was employed to deliver 35 µl/min to the ion spray interface on a Sciex API *III* mass spectrometer. LPE are readily separated from LPC using a Bond-Elut cartridge. LPE, once separated from LPC species, can also be separated using the HPLC system described above. Ion spray spectra showed intense pseudomolecular ions, providing molecular weight information for all molecular species. LC/MS/MS spectra exhibited the characteristic product ions for AC at m/z 85 and 144. Product ion spectra for LPC and plasmenyl-LPC showed characteristic ions at m/z 86, 104, 125, and 184. Plasmenyl-LPC product ion spectra show an additional ion at m/z 181, so plasmenyl-LPC are immediately distinguishable from LPC. LPE and plasmenyl-LPE product ion spectra show loss of the polar head group, but do contain a common product ion at m/z 44. Rapid screening for the presence of these compounds in extracts was achieved using flow injection analysis and utilizing precursor ion scans, monitoring m/z 85 for AC, m/z 184 for LPC, m/z 181 for plasmenyl-LPC, and m/z 44 for LPE.

569 THE UTILITY OF HPLC/MS USING THE PARTICLE BEAM INTERFACE. Paul A. Lehman, Joseph Bloom and Anna Radominska, Departments of Dermatology (PAL) and Gastroenterology (AR), University of Arkansas for Medical Sciences, Little Rock, AR 72205 and The Medical University of South Carolina (JB), Charleston, SC.

The monodisperse aerosol generation interface for liquid chromatography/mass spectrometry (MAGIC) is now better known as the particle beam (PB) interface. This interface permits electron ionization (EI) or chemical ionization (CI) spectroscopy for those compounds which are non-volatile, or not suitable to GC/MS. We have investigated the utility of this LC/MS technique for a wide variety of compounds using various approaches for example: 1) *on LC/MS interface comparison:* the PB proved as discriminating as thermospray/MS for the characterization of the antitumor and antibiotic anthracyclines: doxorubicin, daunorubicin and carminomycin; 2) *on structure identification:* for the carboxyl-linked glucuronide metabolite of the bile acid lithocholic acid, the methyl ester, and the poly-acetate methyl ester derivative assisted in its identification; 3) *on sensitivity limits:* using negative CI the PB interface facilitates the measurement of the LC separated all-trans and 13-CIS isomers of retinoic acid in the picogram range by selected ion monitoring of their pentafluorobenzyl ester derivative.

570 PHARMACEUTICAL, BIOTECHNOLOGY AND ENVIRONMENTAL APPLICATIONS OF LC/MS AND LC/MS/MS USING ATMOSPHERIC PRESSURE IONIZATION TECHNIQUES. Mark H. Allen, Bori Shushan, Tom Covey, Ron Bonner, Takeo Sakuma and George Scott, PE-SCIEX, 55 Glen Cameron Rd., Thornhill, Ontario L3T 1P2.

This Paper will describe two API techniques; IonSpray (nebulizer assisted electrospray) and Heated Nebulizer APCI, which supply effective and easy methods of analysing biologically and environmentally significant compounds in HPLC effluent streams. Applications of IonSpray LC/MS which will be presented include: the characterisation of proteins, glycoproteins, peptides, nucleotides and oligosacharrides; the characterisation of drug metabolites including hydroxides, as well as glucuronide, glutathione and sulfate conjugates; the characterisation of low level (0.01–1%) impurities in drugs under development; as well as quantitative analysis of trace levels of drugs and metabolites in support of clinical pharmacology. Applications of Heated Nebulizer APCI LC/MS to be presented include: the high throughput quantitative analysis of drugs and phase I metabolites in clinical pharmacology studies providing low picogram/mL plasma level detection; and the determination of carbamate pesticides.

571 UTILITY OF HPLC/MS/MS FOR THE ANALYSIS OF VARIOUS DRUG METABOLITES. K. J. Ng and E. C. Huang, Schering Plough Research Institute, 60 Orange Street, Bloomfield, New Jersey 07003.

Drug metabolism studies play a very important role in the development of chemical entities for therapeutic and diagnostic uses. Most drugs undergo metabolic transformation to facilitate their elimination from the body. In general the metabolic products are more polar than the parent compounds and very often thermally labile. Before the advent of interfacing high performance liquid chromatograph to mass spectrometer (LC-MS) much time and effort were spent on isolating the individual metabolites from complex matrices. Chemical derivatization were required to make the metabolites volatile and stable enough for GC or GC/MS analyses. With the recent commercial availability of the various methods of interfacing LC to MS such as thermospray, electrospray, ion spray, particle beam and continuous flow FAB, the identification and quantitation of drugs and metabolites have become much easier, especially when tandem mass spectrometers are available. Examples of various drugs and metabolites, including conjugates such as sulphates, and glucuronides, as analysed by thermospray-LC/MS/MS and ion spray-LC/MS/MS will be discussed.

572 QUANTITATIVE ANALYSIS OF LOW MOLECULAR WEIGHT PHARMACEUTICAL COMPOUNDS BY HPLC COMBINED WITH ATMOSPHERIC PRESSURE IONIZATION MASS SPECTROMETRY. David Wang-Iverson, Bristol-Myers Squibb, New Brunswick, NJ 08901.

Pneumatically-assisted electrospray or ionspray (ISP) as the interface between HPLC and an atmospheric pressure ionization mass spectrometer (API-MS) has been successfully utilized for the quantification of pharmaceutical compounds and their metabolites with molecular weights in the range of 400 to 600 amu. Assays designed to measure acidic, neutral and basic compounds have been developed and validated. Bioavailability or bioequivalence data from such applications were used to directly support registrational filings. ISP/API-MS generally provided sensitivities of approximately 1–3 ng/ml, with basic compounds appearing to be the most sensitive. Standard curves were usually best fit with quadratic functions when ranges were extended to 1000 ng/ml. Both single MS and Tandem MS techniques were employed. Typical chromatographic conditions included the use of 1mm or 2mm ID HPLC columns, flow rates of 40 µl/min or 300 µl/min and either isocratic or gradient elution. The system proved over the course of thousands of sample assays to be extremely rugged and provided reliable and rapid results when required to meet deadlines.

573 THE RAPID AND SYSTEMATIC IDENTIFICATION OF DRUG METABOLITES USING LC/MS AND LC/MS/MS TECHNIQUES. Mike S. Lee, Edward H. Kerns, Kevin J. Volk and Jinping Liu, Bristol-Myers Squibb Company, 5 Research Parkway, Wallingford, CT 06492.

Advances in soft ionization and liquid chromatography/mass spectrometry (LC/MS) techniques in combination with tandem mass spectrometry (MS/MS) have resulted in rapid and comprehensive protocols for drug metabolite identification. These protocols involve the use of MS/MS methods to rapidly screen physiological samples for metabolites which retain substructures of the parent drug. LC/MS techniques with gradient elution are used to generate metabolic profiles and observe isobaric metabolite structures. Finally, LC/MS/MS techniques are used postulate and/or confirm structures by direct spectral interpretation or by comparison with authentic standards. In this way, metabolic profiles are rapidly generated to provide an initial framework for metabolism guided structural modifications as well as preliminary insight into *in-vivo* metabolism. These approaches are illustrated with the analysis of bile and urine samples for the phase I (addition and dealkylation products) and phase II (glucuronides) metabolites of buspirone. Extensions of these methods and strategies for the analysis of biomolecules will also be discussed.

574 ON-LINE DETERMINATION OF WATER AND METHANOL IN MULTIPLE STREAMS OF AN ORGANIC SYNTHESIS PROCESS. Paul K. Aldridge, David M. Pfisterer, Christine L. Evans and Marta M. Andino, Pfizer Inc., Central Research Laboratories, Eastern Point Road, Groton, CT 06340.

A method using on-line near infrared (NIR) spectroscopy for monitoring water and/or methanol in five streams associated with the synthesis of an organic food product is described. Of the five streams, three are associated with the purification of methanol, the two remaining streams are methanol slurries of reaction intermediates. A centrally located spectrophotometer is coupled to sampling points via fiber optics. A sampling system was developed to allow measurements on the slurries to be performed without filtration. PLS calibrations with automatic outlier detection are used on each of the five streams. Predictive ability of the system is quite good. The rapid rate and increased precision of analysis allows for tighter control of the process, compared to the previous method of off-line Karl Fischer and Headspace GC Assays.

575 SEMICONDUCTOR LASERS AND DETECTORS IN ANALYTICAL SPECTROSCOPY. G. Patonay, G. Casay and D. Shealy, Department of Chemistry, Georgia State University, Atlanta, GA 30303.

Spectroscopic techniques have long been applied to the determination of chromophores. Despite numerous applications, however, relatively few studies have been reported for near-infrared (NIR) absorbing chromophores. The NIR region is advantageous due to the inherent low interference and the high molar absorptivities of NIR absorbing chromophores. When NIR absorption and fluorescence spectroscopy is coupled with the use of semiconductor lasers and detectors, an especially useful technique emerges. Semiconductor lasers have all the properties of other types of lasers with the added benefits of compactness, low power consumption and low cost. Semiconductor detectors have their spectral sensitivity maximum in the region where commercial laser diodes emit. This paper discusses the analytical application of NIR fluorophores in conjunction with semiconductor lasers and detectors. The studies presented focus on the application of NIR chromophores and their analytical utility. The NIR chromophores may be used to determine several analytical properties of the system under study, e.g., solvent hydrophobicity, pH, metal ion concentration, oxygen concentration. These probes may be used in free solution or with appropriate chemical modifications and they may be immobilized to form a convenient fiber optic probe. Several analytically interesting applications will be given with special emphasis on the use of semiconductor lasers and detectors. The use of NIR fluorophores as reporting groups will also be discussed.

576 CHARACTERIZATION OF IMMUNOCHEMICAL-BASED FIBER OPTIC SENSORS. Michael J. Sepaniak, James R. Bowyer, Melissa M. Armstrong and Tuan Vo-Dinh, The University of Tennessee, Department of Chemistry, Knoxville, TN 37996-1600.

Remote sensing is analytically desirable in situations for which conventional sample acquisition and preparation is dangerous, time consuming, or results in degradation of the sample. Quantitative and qualitative information is obtained with fiber optic chemical sensors (FOCS) based on spectroscopic signals that result from interactions between the analyte and a reagent phase immobilized at the sensing terminus of the fiber. We have shown that it is possible to perform remote flouroimmunoassays using FOCS that employ immunochemical reagent phases. Two types of immunochemical sensors, one based on passive sampling of analyte and one capable of active sampling and regeneration, will be described. The usual analytical figures of merit for these sensors in the measurement of test proteins or environmental toxins will be presented.

577 NEAR INFRARED (NIR) SPECTROSCOPY AS A PROCESS ANALYTICAL TECHNIQUE FOR MONITORING THE RESOLUTION OF ENANTIOMERS VIA THE FORMATION OF A DIASTEREOMERIC SALT. P. A. Hailey, Analytical Research and Development Pfizer Central Research, Sandwich, UK.

Near infrared (NIR) spectroscopy is beginning to receive wider acceptance within the pharmaceutical industry, mainly as a technique for the identification of raw materials and excipients. The potential of NIR spectroscopy is now being explored in other areas of pharmaceutical analysis largely as a result of the technique's ability to analyse samples rapidly without prior sample preparation. NIR therefore has considerable potential for use as a process analytical technique. One area that is of particular interest to the pharmaceutical industry is the analysis and control of chiral purity during drug manufacture. NIR has been shown recently to be a technique capable of chiral discrimination.[1,2] This presentation will describe the development of an NIR process analytical technique for monitoring the resolution of enantiomers in an organic slurry via the formation of a diastereomeric complex.

1. Honigs D, Buchanan B, Grunke A and Cuirczak E, *Spectroscopy*, 3(5), **25**, 1988.
2. Hailey P. A. Presentation L8-04, The 4th International Conference on Near Infrared Spectroscopy, Aberdeen, August 19–23, 1991.

578 PROGRESS IN ON-LINE APPLICATION OF RAMAN SPECTROMETRY FOR DISTILLATION PROCESS CONTROL. A. A. Garrison, C. F. Moore, P. D. Hall and M. J. Roberts, University of Tennessee, 119 Perkins Hall, Knoxville, TN 37996-2000.

Research at the University of Tennessee, Knoxville has led to the development of an on-line Raman spectrometer for chemical composition determination. Plans for testing the device on a distillation process at Tennessee Eastman Corporation in Kingsport, Tennessee were discussed in a presentation for FACSS 1991. The test cell, fiber optics and spectrometer are scheduled for placement on-line during summer 1992. Initial results will be presented with emphasis on reproducibility and reliability of the sensor. Static and dynamic modeling of the distillation column, necessary prior to sensor installation, will be discussed. The goal of this program is to lower energy use by providing accurate information on composition at a suitable point internal to the column. Product throughput can also be increased by improved control. Research progress on the optimal utilization of the data acquired and studies related to other potential applications for FT-Raman in industrial environments will be reviewed. This project has received funding from the Department of Energy and the Measurement and Control Engineering Center, an NSF Industry/University Cooperative Research Center.

579 A COMPACT SOLID STATE SPECTROPHOTOMETER SYSTEM FOR CONTROL APPLICATIONS. D. M. Mayes, A. G. Cavinato and D. S. Koza, D^2 Development, 1108 J Ave., LaGrande, OR 97850.

A novel spectrophotometer system for the 400–700nm (DPA-200v) and 600–1100nm (DPA-200s) regions has been developed with broad applicability. The system is modular in design allowing custom configurations to be easily accommodated while maintaining a compact system size. The unique optical system incorporated in the design measures 1.5″ × 1.5″ × 0.75″. This small optical design allows the instrument to be highly stable making it ideal for process monitoring applications. The talk will focus on the instrument's performance in terms of signal to noise, spectral resolution, stray light, dynamic range, and long term stability. Another unique feature incorporated in the system design is 'adaptive instrument integrity'. Because the DPA-200 series spectrophotometer systems utilize the latest in computer and electro-optical components, the entire system is self calibrating in terms of wavelength and absorbance accuracy thus maintaining system integrity. The brain of the system is a sophisticated

32 bit risc computer processor which enables the system to accomplish complex chemometric analyses in real-time and accept input from a wide range of additional sensors such as temperature, pressure, etc. for inclusion in the chemometric model or for diagnostic purposes. The processor also allows communication with and/or control of an almost unlimited number of external devices. A sample application for the direct control of a flow injection analysis (FIA) system is discussed.

580 CUSTOMIZED ELECTRONIC WAVELENGTH SWITCHING AND ACQUISITION FOR TRANSIENT MONITORING WITH ACOUSTO-OPTIC TFS. D. L. Wetzel and A. J. Eilert, Kansas State University, Shellenberger Hall, Manhattan, KS 66506.

Random wavelength access with electronic wavelength switching is used to maximize duty cycle in order to minimize the amount of time required to make a single analytical determination. The high wavelength switching speed of our experimental acousto-optic tunable filter spectrometer with extended range In-Ga-As detection and customized computer control permits very rapid absorbance measurements at wavelengths of interest over the entire near-infrared spectrum. Computer analysis of the data immediately after acquisition allows real-time analytical monitoring of rapidly changing processes or transient variations.

581 HIGH SPEED SORTING AND QUALITY CONTROL WITH A SOLID-STATE NIR ANALYZER. David E. Honigs and Sean Knepper, Katrina, Inc., 91 Western Maryland Parkway, Hagerstown, MD 21740.

Near infrared instruments have been used extensively as laboratory and quality control devices for the past ten to fifteen years. During the past four to six years, they are being applied to on-line process measurements. Most of the process measurements have been for the analysis of concentration in slurries or webs. However, many food and agricultural processors handle products which are solids. Furthermore, their quality depends not only on the mean concentration, but also on the ability to detect and reject extreme samples which might be unsightly, burned, raw, or otherwise undesirable. In this presentation, data will be presented from on-line process monitoring of french fries for total solids and candy for individual defects. An unusual instrument design with switching light emitting diodes which handles the process speeds and fluctuations inherent with these solid streams will be described. The effects of bed-depth variation, high optical density materials, and the difficulty of calibration will also be discussed.

582 AN ALL SOLID STATE NIR SPECTROMETER FOR REMOTE, ON-LINE APPLICATIONS. Xiaolu Wang, Jolanta Soos, Jack Crystal and John Havlik, Brimrose Corporation of America, 5020 Campbell Blvd., Baltimore, MD 21236.

A novel NIR spectrometer based upon an Acousto-Optic Tunable Filter (AOTF) will be presented. In this spectrometer, the output of a tungsten lamp is directed into a TeO_2 AOTF. The monochromatic light is generated at the output of the AOTF via acousto-optic interactions. The light from the AOTF is then coupled into a bifurcated fiber bundle. The light exits the spectrometer and terminates in a probe designed for reflection or finite-path-length absorption measurements. Light from the sample passes back along the fiber where it is focused onto a photodector. The spectrometer is an all solid state device with no moving parts. It has the characteristics of fast speed (100 microseconds switching time between random selected spectrum lines), ruggedness, and compact size. It is especially suitable for real time, on-line NIR spectroscopy in industrial environments.

583 NEAR INFRARED DETERMINATION OF BENZENE IN GASOLINE. S. J. Foulk, B. E. DeSimas and R. L. Muegge, Guided Wave, Inc., 5190 Golden Foothill Parkway, El Dorado Hills, CA 95762.

The determination of Benzene in Gasoline is becoming increasingly important for refineries due to new environmental legislation. The ability to make measurement of parameters such as Octane Number and oxygenate content using Near Infrared Spectroscopy has been demonstrated in both laboratory and on-line situations. The measurement of Benzene is more challenging given the levels in gasoline (0–2%) and the number of potential interferents. Also to be considered is the reference method that must be used for the Benzene determinations on the calibration samples. The accuracy of any secondary method developed using such reference data will be limited by the accuracy/precision of the reference method. This presentation will show data for Benzene determination in both a laboratory and an on-line environment. The Near Infrared measurements are made utilizing the wavelength region from 900 nm to 1600 nm. The sample cell (1 cm) is located 50 meters from the instrument itself using fiber optics.

584 DETECTION LIMITS IN FT-INFRARED AND FT-RAMAN MICROSPECTROSCOPY: HOW LOW CAN YOU GO? C. J. Petty, J. M. Casper and J. A. Reffner, Nicolet Instrument Corporation, 5225 Verona Road, Madison, WI 53711.

A major consideration in selecting an analytical technique can be the detection limit for an analyte by that particular technique. For microspectroscopy, the detection limit can be thought of in various ways, such as, spatial resolution, minimal particle size, or minimum quantity of material. In this paper, the detection limits of FT-infrared and FT-Raman microspectroscopy will be explored. Factors that influence detection limits such as instrument design, instrumentation practice, and sample preparation will be discussed.

585 A UNIT MAGNIFICATION FT-IR MICROSCOPE: PERFORMANCE ADVANTAGES FOR BOTH OPTICAL AND INFRARED MICROSCOPY. Robert G. Messerschmidt, Connecticut Instrument Corporation, 22 Elizabeth Street, S. Norwalk, CT 06854. Dean E. Roberts, Mattson Instruments, Inc., 101 Fourier Drive, Madison, WI 53717.

A unit magnification FT-IR microscope offers several performance advantages over traditional designs, both for infrared sampling and visual viewing. The unit magnification system described here replaces the Cassegrainian optics of a conventional FT-IR microscope. It avoids several objectionable features of Cassegrainian systems, such as field curvature, central obscuration, and difficult alignment. The unit magnification system is more likely to be optimally aligned and therefore more likely to achieve diffraction limited performance. A shared aperture is another advantage of a unit magnification system. A portion of the aperture stop of the objective lens is reserved for viewing, and the rest is dedicated to infrared sampling. For viewing, an optimized multiple-element achromatic lens system is used. In reflection mode, the aperture is utilized differently. The input beam is moved off-axis, allowing the output beam from the sample to pass by unvignetted. This allows extremely high sensitivity in reflection mode.

586 SURFACE CHARACTERIZATION BY FT-IR MICROSCOPY. William T. Wihlborg, Spectra-Tech Inc., 652 Glenbrook Road, Stamford, CT 06906.

Surface characteristics often determine whether a component or product is acceptable. For example, in the electronics industry foreign material on an integrated circuit connector can alter the electrical properties of the connector significantly and cause the circuit to fail. For paper producers an off color or spotted appearance is disastrous. Detection and characterization of the materials which cause product failures is an imperative and difficult task. FT-IR microscopy is useful for characterizing both reflective and non-reflective surfaces. Characterization of submicron films on metallic substrates by grazing incidence microscopy will be presented. Non-reflective surfaces will be examined by attenuated total reflectance microscopy.

587 REFLECTANCE MAPPING OF MINERAL SURFACES WITH AN INFRARED MICROSCOPE. Philip J. Stout, Stephen L. Hill and K. Krishnan, Bio-Rad, Digilab Division 237 Putnam Avenue, Cambridge, MA 02139.

Mineral specimens may contain a variety of pure, segregated compounds including hydrated forms and localized trace organic impurities. Infrared measurements of minerals reveal compositional information about oxides, hydrates, and trace organic substances. An infrared microscope in reflection mode used in conjunction with a computer-controlled x-y mapping stage can be used to characterize the spatial specificity of mineral surface composition. The absorbances for a given functionality may be expressed in terms of the x-y sample location in the form of contour and three dimensional fishnet plots. In this way, a mineral may be mapped for specific spatial composition. Infrared microscope mapping data for several minerals, including serpentine, will be presented.

588 STUDY OF POTENTIAL INTRUSION FROM PACKAGING OF FOOD PRODUCTS WITH FT-IR MICROSPECTROSCOPY. D. L. Wetzel, Kansas State University, Shellenberger Hall, Manhattan, KS 66506. R. L. Wehling, University of Nebraska—Lincoln, Dept. of Food Science & Technology, 235 Food Industry Complex, Lincoln, NE 68583.

Modern packaging of foods leads to concerns about the chemical integrity of the food. This is of interest in this study with regard to foods intended to be microwave cooked in the package. The modern technique of FT-IR microspectroscopy is used to determine if a localized intrusion may occur. A model for the study was established by topical adulteration and subsequent use of localized microspectroscopy to detect the intrusion in comparison with background characteristics.

589 IN SITU ANALYSIS OF BRAIN WHITE MATTER IN TWITCHER AND NORMAL MICE BY FT-IR MICROSPECTROSCOPY. D. L. Wetzel, Kansas State University, Shellenberger Hall, Manhattan, KS 66506. S. M. Le Vine, University of Kansas Medical Center, Dept. of Physiology, 3901 Rainbow Blvd., Kansas City, KS 66160.

FT-IR microspectroscopy enables the collection of good quality spectra from small, discrete regions of a specimen. In an earlier study we used FT-IR microspectroscopy to compare the *in situ* distribution of functional groups in two different regions of the mouse brain—white matter and grey matter. Significant differences, at many wavenumbers, were reproducibly observed between these two regions. In the present study we used FT-IR microspectroscopy to compare white matter in normal mice with white matter in mice that carry genetic mutations which affect the deposition of biological material in white matter. Significant differences were observed between normal and mutant animals. These differences help elucidate chemical alterations that result from these pathological states.

590 SCANNING INFRARED MICROPROBE ANALYSIS OF BIOLOGICAL TISSUES. John A. Reffner and Pamela A. Martoglio, Spectra-Tech Inc., 652-Tech Inc., P.O. Box 2190-G, Stamford, CT 06906.

With thin tissue sections, the infrared microprobe can analyze a nanogram of tissue at any single point. With automatic scanning techniques, it is possible to produce molecular composition maps of tissue sections. These maps are then analyzed to correlate the molecular chemistry with tissue morphology. The techniques, methodology, and results of tissue studies will be presented.

591 QUANTITATIVE ANALYSIS OF POLYMERS WITH THE INFRARED MICROPROBE. John A. Reffner and Kenneth J. Ward, Spectra-Tech Inc., 652-Tech Inc., P.O. Box 2190-G, Stamford, CT 06906.

The use of the infrared microprobe for quantitative spectral analysis has been evaluated for transmission, specular reflection, diffuse reflection, and ATR operating modes. Specific applications will include the analysis of polymer systems: block co-polymers, polymer blends, and chemically-modified polymers. The sample-preparation methods required to produce good quantitative analysis will also be presented.

592 AUTOMATED FT-IR GRAZING ANGLE MICROSCOPY FOR MICRO SPATIAL CHEMICAL MAPPING. Frederick P. Eng and Charlene D. Shebib, International Business Machines Corporation, 5600 Cottle Road, E35/028 San Jose, CA 95193.

With the recent emergence of microscopes combined with FT-IR spectrometers, a new approach to micro-analyze polymer, organic, and inorganic materials has evolved. Samples with size and thickness less than 100 micrometers and 5 nanometers, respectively, can be analyzed. There are basically two types of infrared microscopes—near normal and grazing angle of incidence. The former provides both transmission and reflectance (near normal angle of incidence) sampling modes whereas the latter focuses only on reflectance using a grazing angle of incidence. The grazing angle microscope, which is relatively more sensitive, is a better approach in analyzing or characterizing micro thin films, smears, or spots on reflective surfaces. Automation of the grazing angle microscope expands its capability further to study micro spatial chemical mapping of polymer, organic, and even inorganic thin films on reflective surfaces. The results yield the thickness map of the thin film in a microscopic scale that could not possibly or easily be achieved in the past by any analytical technique. A program with different mapping patterns such as straight lines, squares, rectangles, circles, spirals, sectors, and circular bands has been developed using an IBM PC/AT that controls both the FT-IR spectrometer and the motorized X-Y-Z and theta positioning stage of the microscope.

593 FORENSIC ANALYSIS OF ACRYLIC FIBERS BY INFRARED MICROSCOPY. Mary W. Tungol, Edward G. Bartick and Akbar Montaser, FBI Academy, Forensic Science Research Unit, Quantico, VA 22135 (E.G.B.) and Department of Chemistry, The George Washington University, Washington, DC 20052 (M.W.T. and A.M.).

The potential application for using comonomer ratios in the forensic examination of copolymer fibers was explored. Carbonyl/nitrile peak area ratios ($A_{C=O}/A_{C\equiv N}$) of single acrylic copolymer fibers were obtained by IR microscopy. The precision and accuracy of the technique were evaluated. Results indicate that certain types of acrylic fibers may differ by manufacturer as indicated by $A_{C=O}/A_{C\equiv N}$. Acrylic fibers encountered as evidence in criminal cases were also examined.

594 A NEW APPROACH TO STUDIES OF SIZE AND SIZE DISTRIBUTION OF SMALL MOLECULAR AGGREGATES USING FLUORESCENCE ANISOTROPY DECAY. Guang Li and Linda B. McGown,* Department of Chemistry, P.M. Gross Chemical Laboratory, Duke University, Durham, NC 27706.

Dynamic fluorescence anisotropy is an important technique for studying the processes that contribute to the reorientation of the transition moment of a fluorescent probe in a host system. In addition to the size and shape of the probe and the characteristics of its binding microenvironment, the size of the host carries an overall rotation to the reorientation relaxation. In general, for large host assemblies such as conventional micelles and biological membranes, the size of the host has only minor effects on the reorientation of the transition moment of the probe. Bile salt aggregates, in contrast, are much smaller and provide a much more viscous and rigid binding microenvironment for the probe; in this case, the rotation rate of the probe is tremendously reduced and the rotation of the micelle could be the fastest of the reorientation processes. In this talk, we will present the theoretical treatment for the small aggregate system and show experimental results for perylene in the bile salts sodium taurocholate (NaTC) and sodium taurodeoxycholate (NaTDC). Effects of temperature and ion strength will be shown. The polydispersity of bile salt micellar solutions will be discussed and a perylene-bile salt aggregate model will be presented.

595 A MULTIDISTRIBUTIONAL APPROACH TO FLUORESCENCE PROBE STUDIES OF MICROHETEROGENEOUS SYSTEMS. Lei Geng and Linda B. McGown, Department of Chemistry, P.M. Gross Chemical Laboratory, Duke University, Durham, NC 27706.

Despite the complexity of probe-host interactions in microheterogeneous systems, the fluorescence characteristics of the probe fluorophore have been described by small numbers of discrete components, such as a single vibronic band intensity ratio, or one or more discrete rotational correlation times. In this talk, we present a multidistributional dynamic fluorescence approach that is based on distributions of lifetime, rotational correlation time and vibronic band intensity ratio to describe gradients in microenvironmental polarity and microviscosity experienced by the probe and size distributions of the host. This multidistributional approach provides a more detailed and accurate picture of microheterogeneous systems. We will discuss the limitations of recovering lifetime distributions with *a priori* distribution functions, such as Gaussian, Lorentzian and uniform distributions. The recoverability of lifetime, rotational correlation time and vibronic band intensity ratio distributions with the maximum entropy method (MEM) will be shown with studies of micellar systems.

596 EFFECTS OF ANTILIPIDEMIC PHARMACEUTICALS ON THE FLUORESCENCE CHARACTERISTICS OF HUMAN SERUM. Robert D. Stevens and Linda B. McGown, Department of Chemistry, P.M. Gross Chemical Laboratory, Duke University, Durham, NC 27706.

Our previous studies of the intrinsic and extrinsic fluorescence of human serum indicate that fluorescence measurements can be used to better characterize and discriminate between sera that have been stripped of or enriched with certain components. In this talk, we will describe the use of fluorescence probe techniques, including measurements of fluorescence spectra, spectral band ratios, lifetime and anisotropy to study the effects of several drugs on the photophysical properties of human serum. Measurements of the intrinsic serum luminescence in the visible region, which contains contributions from lipids and lipoproteins, will be compared for normal and pathological sera in the presence and absence of therapeutically-significant concentrations of the drugs. In addition, measurements of extrinsic fluorescence probes will be used to study the effects of the drugs on lipid-related binding microenvironments in the sera.

597 IMPROVED CHARACTERIZATION OF COMPLEX COAL LIQUID SAMPLES USING PHASE-RESOLVED-FLUORESCENCE SPECTROSCOPY.

Jeremy M. Shaver and Linda B. McGown, Department of Chemistry, P.M. Gross Chemical Laboratory, Duke University, Durham, NC 27706.

Phase-Resolved-Fluorescence Spectroscopy (PRFS) combines fluorescence spectral and lifetime information in the measurement of Phase-Resolved-Fluorescence Intensity (PRFI):

$$\mathrm{PRFI} = A'\, m_{ex}\left[\frac{\cos(\phi_D - \arctan(\omega\tau))}{\sqrt{1+(\omega\tau)^2}}\right]$$

where A' is the steady state (time-independent) component of the emission; m_{ex} is the modulation depth of the excitation beam; ω is the angular modulation frequency of the excitation beam intensity; τ is the fluorescence lifetime; and ϕ_D is the detector phase angle, which can be set at any angle from 0° to 360°. Both ϕ_D and ω can be used alone or in combination to selectively enhance or suppress components as a function of their fluorescence lifetime. In recent work, PRFS has been used to study complex samples containing multiple fluorescent compounds. Most of this work has utilized variation of the modulation frequency, ω, to achieve lifetime selectivity. However, the detector phase angle, ϕ_D, may provide improved selectivity for analysis of samples or discrimination between samples. In this talk, we will discuss the role of detector phase angle in the PRFS characterization of coal samples.

598 CHARACTERIZATION OF HUMIC SUBSTANCES IN AQUATIC SAMPLES BY PHASE-RESOLVED FLUORESCENCE SPECTROSCOPY.

Sherry L. Hemmingsen and Linda B. McGown, Department of Chemistry, P.M. Gross Chemical Laboratory, Duke University, Durham, NC 27706.

Phase-Resolved Fluorescence Spectroscopy (PRFS) is a powerful tool for chemical analysis which combines spectral and lifetime information in a single, time-independent measurement of phase-resolved fluorescence intensity. This multidimensional fluorescence technique allows selective enhancement or suppression of spectral contributions from individual components in mixtures. In complex samples, these capabilities of PRFS can be used to improve discrimination and classification. In this talk, the application of PRFS for characterization of humic substances in aquatic samples will be discussed. Humic substances are highly complex mixtures that contain components comprising a wide distribution of molecular weights. The complex, heterogeneous nature of these materials makes studying the naturally occurring humic matrix more desirable than employing prior separation of the sample components. Humic matter is known to neutralize hazardous chemicals by complexation with toxic metals or by association with toxic organic chemicals, while also acting detrimentally as a precursor to other toxic chemicals. Characterization of humic substances is essential in order to understand their impact on the fate of potentially hazardous pollutants and for the development of predictive models. Fluorescence is an excellent method for studying such complex samples; because the samples can be observed with minimal perturbation and the uniqueness of these systems in their native matrices can then be exploited for characterization, classification, and fingerprinting. We will present results for commercial humic substances and discuss applications to environmental water samples.

599 STUDIES OF NUCLEIC ACID BINDING USING LIFETIME-RESOLVED FLUORESCENCE-DETECTED CIRCULAR DICHROISM.

Melissa A. Jarrell, Karen Wu and Linda B. McGown, Department of Chemistry, P. M. Gross Chemistry Laboratory, Duke University, Durham, NC 27706.

Lifetime-Resolved Fluorescence-Detected Circular Dichroism (LRFDCD) is a new technique that links the structural information of CD and the resolving power of fluorescence lifetime measurements. One important use of this technique is the study of induced chirality in probes that are bound to helical or otherwise asymmetric microenvironments in biological macromolecules. Analysis of multifrequency fluorescence lifetime data for both orientations of circularly polarized excitation yields the chirality of each lifetime component. This information is used to determine the distribution of a probe among different binding sites in macromolecules. In this talk, we will show results for LRFDCD studies of the binding interactions between fluorescent probes such as ethidium bromide and nucleic acids.

600 ENZYME BEHAVIOR IN MICROAQUEOUS ENVIRONMENTS UNDER SUPERCRITICAL CONDITIONS.

JoAnn Zagrobelny and Frank V. Bright, Department of Chemistry, Acheson Hall, State University of New York at Buffalo, Buffalo, NY 14214.

Recent studies have shown that certain enzymes retain their activity in non-aqueous media and under supercritical conditions. This information should prove useful in various chemical processes, (e.g., pharmaceutical and agrochemicals) and analytical immunoassays, which could combine the selectivity of enzyme reactions with increased mass transfer in supercritical fluids. In an effort to understand the behavior of enzymes in microaqueous environments under supercritical conditions, we have investigated the activity of β-galactosidase in-situ using fluorescence spectroscopy. This presentation will focus on changes in the β-galactosidase activity as a function of fluid pressure and temperature.

601 PRESSURE-DEPENDENT SOLVENT RELAXATION WITHIN REVERSE MICELLES FORMED IN SUPERCRITICAL FLUIDS.

Jing Zhang and Frank V. Bright, Department of Chemistry, Acheson Hall, State University of New York at Buffalo, Buffalo, NY 14214.

In normal liquids, the rate of water reorganization within the interior of AOT (sodium bis(2-ethylhexyl) sulfosuccinate, or Aerosol-OT) reverse micelles is a strong function of water loading and temperature. In this report, we discuss our most recent efforts to understand the internal dynamics of reverse micelles maintained in highly compressible solvents (near-critical propane). By using steady-state and time-resolved fluorescence spectroscopy, we report the first evidence for pressure-assisted control of the rate of solvent relaxation within the core region of a reverse micelle maintained in a highly compressible fluid. Three factors are taken into account in this study; amount of water loading, temperature, and bulk fluid density. The key conclusion is that the continuous phase density can influence the rate of solvent reorientation within the interior of AOT micelles formed in near-critical propane. These results demonstrate that modest changes in continuous phase can be used to control the rate of chemical reactions within the core region of reverse micelles.

602 PROBING THE LOCAL SOLUTE ENVIRONMENT IN SUPERCRITICAL FLUIDS.

Jeanette K. Rice, Thomas A. Betts and Frank V. Bright, Department of Chemistry, Acheson Hall, State University of New York at Buffalo, Buffalo, NY 14214.

Supercritical fluids (SFs), substances above their critical temperature and pressure, are used extensively in areas ranging from extraction to enzyme catalyzed reactions. However, in spite their use, we still lack a complete molecular understanding of the interactions between solutes and SFs. For example, in the critical region, spectroscopic studies have shown that the local density about the solute can exceed the bulk density, a phenomena termed clustering. Recent work from our group has shown that these solute-fluid clusters may actually exist as a distribution of domains. Additionally, excited state reactions, specifically twisted intramolecular charge transfer (TICT) state emission, may be occurring. This presentation will focus on our most recent efforts to understand solute-fluid interaction in SFs.

603 FOOD ANALYSIS BY INDUCTIVELY COUPLED PLASMA-ATOMIC EMISSION SPECTROMETRY WITH A LOW-COST ULTRASONIC NEBULIZER.

Huiying Liu and A. Montaser, Department of Chemistry, The George Washington University, Washington, DC 20052.

Previous studies have shown that the detection limits obtained with a low-cost, humidifier-based ultrasonic nebulizer were superior to those measured with a pneumatic nebulizer by a factor of 8–50 and equivalent to the commercial ultrasonic nebulizers for multielement analysis. The applicability of this ultrasonic nebulizer for food analysis by inductively coupled plasma-atomic emission spectrometry will be investigated.

604 DETERMINATION OF TOTAL IODINE IN FOODS BY ON-LINE VOLATILIZATION ICP-AES. Scott P. Dolan, Division of Contaminants Chemistry, Food and Drug Administration, Washington, DC 20204. Akbar Montaser, Department of Chemistry, George Washington University, Washington, DC 20052.

The detection limit of argon inductively coupled plasma-atomic emission spectrometry (Ar ICP-AES) is not sufficient for determining total iodine in most foods when conventional means are used to introduce test solution. Iodine detection limits were improved by on-line volatilization of iodine in test solutions prior to nebulization into an Ar ICP-AES. Foods were solubilized by a microwave hydrolysis (sodium hydroxide) procedure. Samples analyzed include National Institute of Standards and Technology Standard Reference Material 1549 (Non-Fat Milk Powder), FD&C RED #3 and a variety of food products.

605 DETERMINATION OF TOTAL MERCURY IN ENVIRONMENTAL, CLINICAL AND WASTE EFFLUENT SAMPLES BY FLOW INJECTION COLD VAPOR ATOMIC ABSORPTION SPECTROMETRY. C. P. Hanna and J. F. Tyson, Department of Chemistry, University of Massachusetts, Amherst, MA 01003. S. McIntosh, Perkin Elmer Corporation, 50 Danbury Road, Wilton, CT 06897.

A flow injection procedure has been devised for the determination of total mercury in a variety of water samples and in urine. For the water samples, a simple on-line oxidative pretreatment with concentrated sulfuric acid and potassium persulfate proved sufficient to release all the organically bound mercury prior to reduction with tin(II) chloride and phase separation. It was found that a rise in temperature due to the heat of dilution of the concentrated acid produced increased efficiency of release of mercury into the vapor phase. Quantitative recoveries of a number of organomercury compounds added to various water matrices were obtained. For the urine samples, a rapid off-line procedure involving oxidation with solid potassium permanganate and sulfuric acid and a direct analysis procedure were compared. A simple trap in the gas transfer line allowed operation for extended periods of time without the need for shut down to remove accumulated water. An amalgam trapping apparatus for refocussing the liberated mercury vapor was also examined for its effect on sensitivity.

606 USE OF YEAST METALLOTHIONEIN IN TRACE METAL ANALYSIS. Brian R. Anderson and James A. Holcombe, Department of Chemistry and Biochemistry, University of Texas at Austin, Austin, TX 78712.

Metallothioneins are metal-binding proteins found in almost all living organisms. Yeast metallothionein, which binds Cu^+ in vivo, shows a lesser affinity for Cd^{2+} and Zn^{2+} in vitro. This talk will cover the binding characteristics of the yeast metallothionein-cadmium system and efforts to construct a metal chelating column using yeast metallothionein for use in separating and preconcentrating cadmium for analysis by atomic absorption spectroscopy.

607 DETERMINATION OF TRACE METALS BY PLASMA SPECTROMETRIC DETECTION WITH SUPERCRITICAL FLUID EXTRACTION. Sandra L. Cleland, Nohora P. Vela and Joseph A. Caruso, University of Cincinnati, Department of Chemistry, Mail Location 172, Cincinnati, OH 45221.

Supercritical Fluid Extraction (SFE) has received considerable attention in the past few years, and appears to be gaining support over the more conventional liquid solvent extraction methods. Some advantages of SFE include; speed of extraction, the non-toxic nature of the more common supercritical fluids (i.e., CO_2), and the ability to extract thermally labile compounds. Standard reference samples will be extracted both by the traditional Soxhlet method and by SFE. A comparison of these methods will result in optimized parameters for the extraction of various metals. Plasma spectrometric methods will be utilized for the detection of metals in the reference samples.

608 TRACE METAL ANALYSIS OF MIXED PHASE (WATER-SEDIMENT) SAMPLES. Stacy Wells-Sendler and Richard D. Foust, Jr., Chemistry Department, Northern Arizona University, Flagstaff, AZ 86011.

The analysis of water/sediment samples is a necessary component of environmental sampling, and large variances are often observed for total metal and total-recoverable metals because of problems associated with analyzing mixed phase samples. Synthetic water samples prepared from well characterized materials have been sampled with an ultrasonic cell homogenizer to improve the sample reproducibility, digested in closed teflon vessels, and cleaned with ion chromatography prior to inductively coupled plasma emission spectroscopy analysis. This process improves the reproducibility of the trace metal data, and increases the percent recovery over traditional open beaker wet chemical digestions. The greatest improvements are observed for elements known to be lost in wet chemical digestions through the formation of volatile halides (e.g., antimony, lead and selenium).

609 AN IMPROVED METHOD FOR THE DETERMINATION OF MERCURY SPECIATION BY AQUEOUS PHASE ETHYLATION AND CARBOTRAP PRECONCENTRATION, FOLLOWED BY ISOTHERMAL GAS CHROMATOGRAPHY WITH COLD VAPOUR ATOMIC FLUORESCENCE SPECTROMETRIC (CVAFS) DETECTION. Liang Lian, Brooks Rand, Ltd., 3950 Sixth Avenue Northwest, Seattle, WA 98107. Milena Horvat, "J Stephan" Institute, Nuclear Chemistry, Jamova 39, 61111 Ljubljana, Slovenia. Nicolas S Bloom, Brooks Rand, Ltd., 3950 Sixth Avenue Northwest, Seattle, WA 98107.

Bloom (1989) presented a technique for the determination of picogram levels of methyl and ionic mercury. The CH_3Hg^+ and Hg^{++} were first ethylated and collected by purging onto a column filled with carbotrap™. The ethylmercury derivatives were then thermally desorbed and transferred to a GC column cooled in liquid nitrogen. The species were chromatographically separated by heating the column from $-196°C$ to 180°C in a single ramped step. The organo Hg compounds were decomposed at 800°C to Hg°, which was quantified by CVAFS. In this work, a problem of the method, the thermal decomposition of the ethyl derivatives on the carbotrap, was overcome by improved trap design. This results in significant improvements in precision and accuracy, as well as allowing the simultaneous determination of $(CH_3)_2Hg$, CH_3Hg^+ and Hg^{++} in water, sediment, and biological samples. Moreover, the optimal conditions for the determination of CH_3Hg^+ were confirmed, and they were investigated and supplemented for $(CH_3)_2Hg$ and Hg^{++}. Isothermal GC conditions were developed, making the use of liquid nitrogen unnecessary, but yet maintaining the same levels of precision and accuracy. This results in a three-fold improvement in analytical speed. The detection limits (as Hg) of the method are 0.6 pg, 0.6 pg, and 1.3 pg for $(CH_3)_2Hg$, CH_3Hg^+, and Hg^{++} respectively.

610 SAMPLE PRETREATMENT AND MICROWAVE DIGESTION OF BIOLOGICAL SAMPLES FOR ANALYSIS BY INDUCTIVELY COUPLED PLASMA SPECTROMETRY. B. S. Barnes, L. A. Kaine, B. S. Sheppard, M. P. Votel and K. A. Wolnik, U.S. Food and Drug Administration, National Forensic Chemistry Center, 1141 Central Parkway, Cincinnati, OH 45202.

The analysis of certain foods and other biological samples by plasma spectrometry can be especially difficult in the presence of hard to decompose materials, such as fats. Total destruction of the matrix is possible using conventional "wet" digestion; however, conventional digestions are not always practical. Conventional digestion is time consuming, and there are safety considerations when using acids such as perchloric. In addition, it is desirable to avoid using perchloric and sulfuric acids for ICP-MS determinations. Closed vessel microwave digestion of samples gives more complete digestion than conventional digestion using only nitric acid; however, all of the matrix is not destroyed by nitric only digestion. Supercritical fluid extraction (SFE) is a relatively new technique which can rapidly and selectively extract fats from a sample. By extracting a sample with SFE prior to microwave digestion, it may be possible to reduce or eliminate many of the problems associated with the presence of residual organic materials, thus enabling microwave digestion for analysis by plasma mass spectrometry. This presentation will summarize the results of the investigation of the effects of prior extraction with SFE on the determination of toxic and nutritional elements in troublesome food matrices.

611 OPTIMIZATION OF MICROWAVE ACID DIGESTION PROCEDURES FOR ORGANIC SAMPLE MATRICES USING A DUAL PRESSURE AND MICROWAVE IMMUNE FIBER OPTIC TEMPERATURE CONTROL SYSTEM. W. Gary Engelhart, CEM Corporation, 3100 Smith Farm Road, Matthews, NC 28105.

Analysts frequently receive samples of unknown organic content and composition for trace metal analysis. Developing safe and effective microwave digestion procedures for such samples requires the use of specific acid temperatures. Direct measurement and control of temperature and pressure conditions inside sealed sample vessels located in a microwave field using conventional sensors, such as metallic thermocouples, poses significant performance and safety problems. New design solutions overcoming these difficulties have recently been developed. Fiber Optic thermometry probes are microwave immune (thermally and electrically non-conductive) allowing precise in-situ measurement and control of microwave sample preparation reactions. This capability allows analysts to determine the vapor/liquid equilibrium conditions resulting from microwave heating of acid mixtures before commencing method development with samples. Trial and error techniques are eliminated because specific acid temperature conditions can be selected to optimize microwave assisted acid decomposition procedures. Results obtained utilizing dual pressure and temperature feedback control to optimize microwave assisted acid digestion procedures will be presented.

612 AN INTERFACE FOR ACRIDINIUM CHEMILUMINESCENCE DETECTION WITH CAPILLARY ELECTROPHORESIS. Michael A. Ruberto and Mary Lynn Grayeski, Department of Chemistry, Seton Hall University, South Orange, NJ 07079.

An interface has been designed to couple the sensitivity of acridinium chemiluminescence detection with the separation efficiency of capillary electrophoresis. The reagents are introduced into the electrophoretic system post column in a sheathing flow profile. The chemiluminescence reaction of the oxidation of an acridinium ester by hydrogen peroxide occurs in the coaxial reactor of the interface. The reaction conditions including pH, concentration, and flow rates of the reagents for acridinium chemiluminescence have been studied to evaluate the effect on the detector response. The detection limit for a trichloro-phenyl substituted acridinium ester is estimated to be in the attomole range. The interface was evaluated as a potential source of zone dispersion by investigating its effects on band width. "Chemical band narrowing" was observed due to the fast rate of the chemiluminescence reaction.

613 A NOVEL INTERFACE FOR CAPILLARY ZONE ELECTROPHORESIS AND A REFLECTRON TIME-OF-FLIGHT MASS SPECTROMETER. A. P. D'Silva and S. J. Bajic, Ames Laboratory, 9 Spedding Hall, Ames, IA 50011.

The coupling of capillary zone electrophoresis (CZE) and mass spectroscopy (MS) has been successfully performed via a new and unique interface. This interface provides a low-cost alternative to electrospray, thermospray, and fast atom bombardment approaches currently utilized in interfacing CZE and MS. The interface allows direct coupling of CZE to a conventional mass spectrometer with minimal modification to the mass spectrometer. The interface employs an ionized gas to provide a conductive medium to terminate the CZE circuit at the stainless steel tip which is held at ground potential. Nebulization of the CZE eluent is controlled by the flow of the ionized gas. The nebulized eluent is introduced directly into the ionization region of a home-built reflectron time-of-flight mass spectrometer. The design of this novel interface is described and the performance of the CZE-reflectron time-of-flight MS technique discussed.

614 A PRELIMINARY INVESTIGATION OF CAPILLARY ELECTROPHORESIS WITH ICP-MS FOR TRACE ELEMENT DETERMINATION. Jiansheng Wang, Lisa K. Olson and Joseph A. Caruso, Department of Chemistry, University of Cincinnati, ML 172, Cincinnati, OH 45221-0172.

The investigation of suspected element deficiency or toxicity in biological samples such as blood serum, plasma and urine etc. has become more and more important. However, the toxicological and biological importance of many elements depend to great extent upon not only their total concentration but also their chemical forms. Therefore, the identification of the chemical forms, or speciation is necessary as well. The number of applications of capillary electrophoresis (CE) has greatly increased recently. Capillary electrophoresis (CE) combined with mass spectrometry (MS) has high potential for high-resolution separations, with excellent specificity and sensitivity for very small samples. In this work, inductively coupled plasma mass spectrometry (ICP-MS) will be used as a detector for capillary electrophoresis (CE). The interface between CE and ICP-MS will be discussed, and preliminary figures of merit for CE with ICP-MS will also be presented.

615 STRUCTURE AND DYNAMICS OF GELS IN ELECTROPHORESIS CAPILLARY COLUMNS STUDIED BY RAMAN MICROPROBE SPECTROSCOPY. Tracey L. Rapp, Will K. Kowalchyk, Kevin L. Davis, Elizabeth A. Todd, Kei-Lee Liu and Michael D. Morris, Department of Chemistry, University of Michigan, Ann Arbor, MI 48109-1055.

We will describe the application of time-resolved Raman microprobe spectroscopy to monitoring formation and chemistry of polyacrylamide gels in electrophoresis capillaries. Strong Raman spectra of starting materials and products at typical CGE concentrations are easily obtained by this technique. The formation of cross-linked polyacrylamide is followed in 75 μm i.d. electrophoresis capillaries using a locally-constructed Raman microprobe, employing a low-power solid state laser. The reaction progress is monitored via disappearance of the acrylamide 1292 cm^{-1} vinylic C-H bending mode. Polymer kinetics for this system will be compared to polymerization of the same starting composition in a bulk reactor. The Raman spectrum is also monitored over the working lifetime of a capillary. We will discuss the instrumentation requirements for these measurements, as well as the criteria for selection of probe bands. The underlying Raman spectrum of polyacrylamide will be described, and discrepancies in literature assignments will be resolved. The use of and prospects for intracapillary Raman spectroscopy as a gel diagnostic will be discussed.

616 CAPILLARY ARRAY ELECTROPHORESIS USING CONFOCAL FLUORESCENCE DETECTION: AN APPROACH TO HIGH-SPEED, HIGH-THROUGHPUT DNA SEQUENCING. Xiaohua C. Huang, Mark A. Quesada and Richard A. Mathies, Department of Chemistry, University of California, Berkeley, CA 94720.

A laser-excited, confocal-fluorescence scanner is used for high-sensitivity, on-column detection of electrophoresis performed using an array of capillaries. A linear array or ribbon of capillaries is assembled on a scan stage and then translated past a laser excitation and confocal-fluorescence detection system. The small depth of focus of the excitation coupled with confocal detection through a spatial filter reduces the background due to scattering, stray fluorescence, and reflections from the capillary walls, while the high numerical aperture objective provides efficient collection of the fluorescence. Because we can run hundreds of capillaries in parallel, capillary array electrophoresis (CAE) is an important new high-throughput analytical technique. To illustrate the power of CAE we have applied this method to the development of high-speed, high-throughput DNA sequencing. First, electromigration data are presented for fluorescently-labeled T-fragments separated on an array of gel-filled capillaries and detected with a one-color system. Data will be presented using 24 capillaries run in parallel, demonstrating the feasibility of CAE. To sequence DNA with capillary electrophoresis it is desirable to detect all four sets of DNA sequencing fragments on the same capillary. Thus, we have developed a sequencing method that utilizes capillary arrays, two-color fluorescence detection, and a two-dye labeling protocol. Sanger DNA sequencing fragments are separated on an array of capillaries and then distinguished by using a binary coding scheme that employs only two different fluorescently-labeled dye primers to identify four sets of fragments. DNA sequencing results will be presented using a 25 capillary array. This apparatus has the capability of sequencing DNA at a rate of 20,000 bases/hour.

617 A LASER-EXCITED FLUORESCENCE EEM DETECTOR FOR HPLC. T. A. Taylor, S. Mathew and J. E. Kenny, Tufts University, Medford, MA 02155.

We have developed a laser-excited fluorescence HPLC detector that obtains excitation-emission matrices (EEMs) on a 1 S time scale. Laser excitation radiation between 230–400 nm is generated by pumping a Raman shifter with 18 mj/pulse of fourth harmonic Nd:Yag laser radiation at 10 hz. The Raman shifter contains a mixture of hydrogen and methane gas, and 10 of the laser beams produced in the Raman shifter are simultaneously launched into optical fibers for transport to the HPLC detection cell. The detection cell allows all beams to excite separate regions of the HPLC eluent simultaneously using a total cell volume of 30 μL. Laser-excited fluorescence is collected by a second set of optical fibers, dispersed with an imaging spectrograph, and detected with a liquid nitrogen cooled CCD detector. Sub-ppm level detection limits of pollutants have been detected with this instrument using 1 nm emission spectral resolution, and a 1 S exposure time. The cross-talk between adjacent detection channels was less than 0.0001. Advantages of our instrument over previously described HPLC EEM detectors include high-intensity laser excitation throughout the deep and near UV regions of the spectrum, simultaneous eluent excitation at all wavelengths when interfaced with a low-volume detection cell, all excitation wavelengths are known exactly and can not change over time, and low interchannel cross-talk over all 13 detection channels. Our instrument also has no moving parts when collecting data.

618 CAPILLARY ZONE ELECTROPHORESIS WITH INDIRECT FLUOROMETRIC DETECTION OF INORGANIC ANIONS.

MaryAnn Gunshefski, A. M. Pless and J. D. Winefordner, Department of Chemistry, University of Florida, Gainesville, FL 32611.

Capillary Zone Electrophoresis (CZE) is quickly becoming a viable method of separation for many different types of compounds, from large biomolecules to small inorganic ions. This method of separation uses an electric field to effect a separation of charged molecules. Indirect fluorometric detection (IFD) methods are being utilized more and more due to their high sensitivity and their ability to act as a universal detector. Indirect fluorometric detection works by displacement of a highly fluorescent probe molecule by the analyte of interest. This displacement can be based on a charge displacement, a volume displacement, or a combination of both. The sensitivity of fluorescence measurements can be enhanced by the use of a laser as the excitation source, known as laser induced fluorescence (LIF). A combination of the separating power of CZE, the universal detection of IFD and the sensitivity of LIF can bring about excellent results. In this work this combination is utilized. A homemade CZE system is coupled with a commercial SPEX Fluorolog spectrofluorimeter which is equipped with a HeCd laser as an alternate excitation source. The ability to adapt a commercial fluorimeter to be used as a detector for CZE is studied. Various fluorescent dyes are used as probe molecules for the indirect detection of inorganic anions.

619 ENHANCED EVAPORATIVE LIGHT SCATTERING DETECTION FOR LIQUID CHROMATOGRAPHY.

Lori B. Allen and J. A. Koropchak, Department of Chemistry and Biochemistry, Southern Illinois University, Carbondale, IL 62901.

We have previously reported our efforts at developing a condensation nucleation light scattering detector (CNLSD) for liquid chromatography.[1,2] In a stepwise fashion, an aerosol is generated; the solvent is removed by sequentially passing the aerosol through a heated drift tube and then a series of condensers; the dry particles are then saturated with the vapors of a condensible fluid; the vapor-saturated particle mixture is passed through a cooled condenser where the particles act as condensation nuclei; and finally, the particles are detected by light scattering. Compared to normal evaporative light scattering detection (ELSD), the detection limit for sodium nitrate in an FIA mode approached the part-per-trillion level, approximately two orders of magnitude lower than the best current ELSD limits. Further, the linearity of response improved with respect to ELSD. In this report, we will focus on a detailed characterization of the condensation nucleation process. This will include the importance of the initial aerosol particle size distribution, the influence of the desolvation system and design factors that influence the final particle size. Ideally, this report will also include efforts at extending the process to other solvents and analyte systems as well as efforts at real world applications and comparisons to other common HPLC detection methods.

1. Koropchak, J. A.; Allen, L., FACSS XVIII, Anaheim, CA., 547, 1991.
2. Koropchak, J. A.; Allen, L., PITTCON '92, New Orleans, LA, 917, 1992.

620 NETWORKING FOR IMPROVED PRODUCTIVITY AND ELECTRONIC ARCHIVAL OF MASS SPECTROMETRIC DATA.

*Mark J. Hayward, Paul V. Robandt, Jon T. Meek, Dale H. Chidester, Richard S. Wayne and Michael L. Thomson, American Cyanamid Company—Agricultural Research Division, P.O. Box 400 Princeton, NJ 08543.

Several mass spectrometer data systems have been networked together in order to achieve the following two primary objectives: (i) to allow access to mass spectrometric data and data processing functions from remote locations without affecting simultaneous data acquisition at the instruments and (ii) to electronically archive mass spectrometric data at a central location on a high capacity, fast access device that allows rapid retrieval of archived data for all data processing operations at all locations. UNIX workstations, IBM PC/AT compatible computers and Data General Nova mini-computers have been connected via Ethernet interfaces in order allow rapid data transfer between all systems and X-Windows access to UNIX based systems. Bridging techniques have been employed to isolate possible high traffic areas of the network and to enable security measures for adequate protection of files. Additionally, serial connections have been made through a Northern Telecom phone system in order to provide multiplexed remote terminal access to the Data General Nova based systems. Use of these connectivity techniques has significantly improved productivity by allowing retrieval, processing and printing of data from remote locations such as office areas without affecting the usual data acquisition, processing and printing performed simultaneously at the instruments. For archival purposes, data files are electronically stored on high capacity magneto-optical disks for rapid retrieval. A high capacity fixed disk is also available for centralized temporary data file storage. A Digital DECstation 2100 UNIX workstation has been used as the file server for centralized data storage while being simultaneously utilized as the data system computer for one of the mass spectrometers. Utilization of this UNIX based file server system in conjunction with Ethernet connectivity techniques provides a centralized, rapid access, high capacity, cost and space efficient method for electronic archival of mass spectrometric raw data recorded at all of the instruments.

621 NICKEL OXIDE ELECTRODE AMPEROMETRY AND POTENTIOMETRY.

Y. Arikawa, B. Hui, C. Strommen and C. Huber, Department of Chemistry, University of Wisconsin-Milwaukee, P.O. Box 413, Milwaukee, WI 53201.

A series of thiols and other polar organics in water solution have been determined in the micro- to milli- molar levels using nickel electrodes in alkaline solutions. The amperometric FIA approach allows samples of low pH and samples requiring pre-detection reaction to be accommodated. Potentiometric operation involves pretreatment to form an oxidized surface followed by potentiometric monitoring of its reduction. With proper procedure, chloride and alkaline earth cations do not interfere.

622 A SOLID INORGANIC GEL MEMBRANE SENSOR FOR MERCURY.

S. K. Srivastava,* Vandana Sahgal and Harsh Vardhan, Department of Chemistry, University of Roorkee, Roorkee-247667, India.

A heterogeneous solid membrane sensor of polytungstoantimonate with polystyrene as binder has been developed for the estimation of mercury ions. Water content, porosity and other similar membrane characteristics are negligibly small. This membrane electrode exhibits a nernstian response to mercury ions in the range 5×10^{-5} to 10^{-1}M at pH 4–6 with a slope of 25mV/decade of concentration. The response time is less than one minute and the potentials stay constant for more than ten minutes. This assembly can also be used in partially non-aqueous medium. Monovalent cations do cause some interference, but bivalent and polyvalent cations exhibit absolutely no interferences. Precipitation titrations involving mercury chloride have also been monitored by using this membrane sensor. Besides this the sensor could also be used for assessing the concentration of mercury ions in contaminated water.

623 ELECTRO-OXIDATION BEHAVIOR OF SULFAPHENAZOLE AT A PYROLYTIC GRAPHITE ELECTRODE.

Alok Mittal and Rajendra N. Goyal, Department of Chemistry, University of Roorkee, Roorkee-247667, U.P. India.

Electrochemical oxidation of antibacterial drug sulfaphenazole has been studied using cyclic voltammetry, coulometry and related techniques at a pyrolytic graphite electrode in phosphate buffer of pH range 2.0–11.0 (ionic strength 0.1 m). The oxidation of this drug occurred in a single well defined 2e, $2H^+$ step at aromatic amino group. The peak potential was dependent on pH and shifted toward less positive potential with increase in pH. The E_p versus pH plot was linear and the dependence of E_p versus pH can be represented by the equations, $E_p = -0.067\text{pH} + 0.933$ and $E_p = -0.022\text{pH} + 0.669$ between pH 2.7–5.6 and 5.7–11.0 respectively. The change in peak current function with variation of sweep rate indicated the process to be diffusion controlled. Spectral studies during electrolysis indicated the formation of more extensive π-conjugation in the product by shifting of λ_{max} to longer wavelength. The product of oxidation was separated using column chromatography and identified as azo-sulfaphenazole on the basis of M.P., IR and ^{1}HNMR spectra. A tentative redox mechanism for the formation of AZO product is also suggested. The paper will present the advantage of electrochemical studies coupled with spectral studies to probe the redox mechanism of biologically important molecules.

624 THE DETERMINATION OF EMULSION IONIC STRENGTH BY AC IMPEDANCE.

Carleton J. Barbour and R. S. Beckley, Analytical and Polymer Synthesis Research, Rohm & Haas Co., 727 Norristown Rd., Spring House, PA 19477.

Electrochemical Impedance Spectroscopy determined the ionic strength (IS) of an anionic acrylic latex partially neutralized by added aqueous KCl. Potassium ions adsorbed to latex particles and decreased the concentration of "freely diffusing" ions. The decrease in concentration changed the impedance spectra and the "effective" IS of the solution. Comparing the impedance spectra of aqueous KCl solutions and KCl doped emulsions made these differences clearer. Emulsion and aqueous solutions of the same potassium ion concentration did not give similar impedance spectra. The emulsion's impedance was always greater than the aqueous solution with the same potassium concentration. The concentration of "freely diffusing" ions (K_{soln}) can be determined from the simple ratio $((I_{app}/I_o) = (K_{soln}/K_{con}))$, where I_{app} is the emulsion's ionic strength, I_o is the aqueous electrolyte's ionic strength and K_{con} is the aqueous electrolyte's potassium ion concentration. Adsorption is specific for cations since similar results were obtained when either KCl or KOH was used as the control. This talk will discuss the potential applications of this technique to polymer systems.

625 THE APPLICATION OF MULTIVARIATE INSTRUMENT STANDARDIZATION IN GAMMA RAY SPECTROMETRY.

Clarke X. Xu and Ron R. Williams, Department of Chemistry, Clemson University, Clemson, SC 29634.

Three gamma ray spectrometers with CsI detector, integrated PIN diode and microcontroller have been developed in our laboratory for operater-unattended in field monitoring. It is designed for automatically collecting spectrum daily for up to one week. Calibration was performed with linear regression by transporting samples among three instruments. The standard gamma ray radiation samples like ^{137}Cs, ^{60}Co and ^{22}Na have been used. Results have shown that the calibration models differ apparently between instruments due to different size of crystals and other effects in instrumental response. It's also not linear within one instrument under various gains which is caused by stepping the different EEPOTs. A shift of energy scale versus time is also observed. These variations caused not by sample concentrations and experimental condition changes which is contained in the calibration model results in an inaccuracy in peak determination while apply the calibration model built on one instrument to the spectrum took from other instrument. It seems not adequate to use a single energy scale correction for the entire spectrum region. Attempts to correct for spectral variation among different instruments has been reported recently by using the full multivariate nature of the differences and has been applied to NIR successfully. The method also simplifies the calibration between multiple instruments. In this presentation, the detail in applying the multivariate instrument standardization method for multiple gamma ray spectrometers will be given.

626 CORRECTION OF COTTON STRENGTH MEASUREMENTS FOR MOISTURE CHANGES USING GENETIC ALGORITHMS.

E. W. Setzer and R. R. Williams, Chemistry Department, Clemson University, Clemson, SC 29631. R. A. Taylor, USDA, ARS, CQRS, P.O. Box 792, Clemson, SC 29633.

Genetic algorithms (GA) have been recently developed to perform system optimizations. GA were used to predict the strength correction factors for cotton fibers. The strength of cotton fibers is used to grade the cotton. Small changes in the moisture content of the fibers can result in large changes in the measured strength of the fibers. The change in moisture content is easily monitored by NIR spectroscopy. Using GA, random pairs of wavelengths were combined with random algebraic operators (+, −, /, *) to make a regression equation. The equations which predicted the best corrections were allowed to "breed" and mutate thus producing different regression equations. The process was repeated until an optimal regression equation was reached. Preliminary results show that GA give results comparable to PLS while using only eight to ten wavelengths. A comparison of the results obtained for predicting a correction to the strength measurement using PLS with the full spectra and a limited number of wavelengths and genetic algorithms will be presented. Factorial design was used to determine the parameters that effect the predictability of both methods.

627 SUBMICRON OPTICAL FIBER CHEMICAL AND BIOLOGICAL SENSORS.

Weihong Tan, Zhong-You Shi and Raoul Kopelman, Department of Chemistry, The University of Michigan, Ann Arbor, MI 48109.

Nanometer sized fiber optic sensors have been prepared by a near field optical technique based on nanofabrication of optical fiber probes and photoinitiated polymerization. These nanometer sized pH sensors have excellent sensitivity (zeptomole), good reversibility, reproducibility and stability. They have very short response times, less than 100 milliseconds, due to their extremely small sizes and covalent bonding of pH sensitive dyes. These sensors have been tested successfully on both chemical unknown samples and biological cells and embryos. Newly developed internal calibration methods have been used for pH measurements, making use of the differences not only in absorption, but also in fluorescence of the pH sensitive dye at different wavelengths. Tests have demonstrated the high spatial resolving abilities of the pH sensor and their potential application in producing concentration profiles inside cytoplasm and in monitoring fast chemical and biological reactions as well as other microscopic operations related to biology, physiology, toxicology, medicine and materials science.

628 A COMPUTER PROGRAM FOR PROCESSING LASER-EXCITED FLUORESCENCE EEMS.

S. Mathew, T. A. Taylor and J. E. Kenny, Tufts University, Medford, MA 02155.

A computer program is developed for the processing of raw fluorescence excitation-emission matrix (EEM) data from our laser array fluorescence instrument. This software package automatically accomplishes photodiode dark current subtraction, wavelength calibration, Rayleigh scattering intensity integration, excitation power normalization, blank subtraction and quantum normalization for all spectra of an EEM. Accurate subtraction of scattered excitation signal from all the emission spectra of an EEM is a critical step in the determination of the concentrations of its components. Least-squares and polynomial fitting procedures have been used to accomplish this subtraction. Least-square analysis and rank annihilation factor analysis of the corrected EEM data is done to determine the concentrations of the components from the EEM of mixtures and compared with results from the analysis of uncorrected spectra. This program is written in turbo pascal and to be used with IBM PC or compatible.

629 APPLICATION OF AN AUTOMATIC STANDARD PREPARATION UNIT IN THE CONTEMPORARY ANALYTICAL LAB.

Peter Grandsard and Robert Megargle, Cleveland State University, Chemistry Department, Cleveland, OH 44115. Michael Markelov, BP America Warrensville Research and Environmental Center, 4440 Warrensville Center Road, Cleveland, OH 44128.

The preparation of standard solutions is the most quality determining activity in an analytical lab with good QC/QA practices. It is however an error-prone manual procedure requiring careful manipulation and a clean lab environment. It is not uncommon that an 'analytically bad' result can be traced back to a wrongly or imprecisely made standard. The time constraint and repetitive character of preparing standards by hand can make people run a minimum number of standard solutions, spikes and blanks. This again compromises the quality of the analytical data. The development of an automated multi-component standard solution preparation system is finished. It has eliminated the sacrifices mentioned above. Concentrations are in the ppm-range, or with the serial dilution feature, in the ppb-range. These concentrations are prepared using pure and/or prediluted chemicals. The prototype was built using chemically inert valves and liquid delivering systems and uses a PC to control these components. The valves and chemicals are put in a table-top refrigerator to improve chemical stability and to minimize exposure to chemicals. Users can edit and save standard specifications through the menu-driven software and can call for a series of standards to be prepared in designated containers. The system is also capable of automatic sample spiking and dilution, all according to loaded specifications. The system was tested as a standalone unit and in conjunction with a laboratory robot. Both systems were found repeatable within the requirements of IC, ICP and GC and showed cross-contamination less than the detection limits.

630 ANALYTICAL METHODS FOR CYANIDE: A COMPARATIVE STUDY FOR GROUNDWATERS.

Kathleen M. Cirillo-Penn and Sandra K. Deiseroth, Aluminum Company of America, Alcoa Technical Center, 100 Technical Drive, Alcoa Center, PA 15069.

Several analytical methods exist for the determination of cyanide in ground and drinking waters. These methods include total cyanide distillation, weak acid dissociable cyanide distillation, chlorination amenable determination, microdiffusion, and ion chromatography. The study presented compares the various techniques and their minimum detection limits as they relate to groundwater samples.

631 INVESTIGATION OF THE EFFECT OF PH, IONIC STRENGTH AND SOLVENT POLARITY ON THE CHEMILUMINESCENT REACTION OF ALDEHYDIC PHEROMONES WITH REDUCED FMN.

Donald R. Bobbitt, Stephen N. Brune, Diane B. Frazier and Jacob R. Phillips, Department of Chemistry and Biochemistry, University of Arkansas, Fayetteville, AR 72701.

A flow injection analysis/bioluminescence scheme for the detection of long chain (C12-C18) aldehydes has been developed. These long chain aldehydes are essential components of the chemical communication systems of a variety of pest insect species. In the presence of the biological catalyst luciferase, the pheromone and reduced FMN are simultaneously oxidized producing excited state FMN. The FMN species subsequently decays to the ground state with the emission of light. The FIA system provides reproducible introduction of microliter quantities of aldehyde into the detection region where the bioluminescent reaction occurs producing light emission centered at 490 nm. The effect of pH, ionic strength and various organic solvents on the reaction has been investigated. Properly optimized, a detection limit of 1 femtomole of tetradecanal has been demonstrated at a SNR of 3. The key experimental variables which control sensitive detection of pheromones at the fmol level will be discussed.

632 BRINGING RESEARCH REFLECTANCE FT-IR SPECTROMETRY INTO THE QUALITY CONTROL LABORATORY.

Cindy Friedman-Baulsir and Jeffrey D'Agostino, Spectra-Tech, Inc., 652 Glenbrook Road, Stamford, CT 06906.

A number of applications can be made easier with the development of new Reflectance Fourier transform infrared accessories for the Quality Control laboratory. There are very strict requirements placed on the scientist when applying techniques used only in the research lab and need to be transferred to the QC laboratory, such as; the technique must not require detailed installation assistance, it must be easy to use, easy to clean, and it must be robust enough to last throughout non-ideal sampling conditions. This paper will illustrate a variety of applications that could not previously be performed by FT-IR spectrometry.

633 GASTROINTESTINAL UPTAKE IN HUMANS USING ALUMINIUM-26 MASS SPECTROMETRY.

J. Templar and J. P. Day, Department of Chemistry, Oxford Road, University of Manchester, Manchester, M13 9PL. England.

Aluminium is now regarded as a toxic element, particularly in people with reduced renal function. There is also suspected involvement in the aetiology of Alzheimer's Disease. Previous aluminium *in vivo* studies have been hampered by the lack of a suitable isotopic tracer. The long lived isotope Al-26, with negligible natural abundance and low radiological hazard, is ideal for such work. However its low specific activity (0.71 Bq/ng) means that detection in biological samples, after dosing with physiological concentrations, is difficult by standard counting techniques. Aluminium-26 Accelerator Mass Spectrometry (AMS), co-developed in our laboratory and at the Nuclear Structure Facility Daresbury UK, gives a detection limit of ca. 7×10^{-18}g (5nBq), about one million times lower than could be achieved by conventional radiochemical methods. From toxicity studies with fish, it has been suggested that silicon may reduce the bioavailability of aluminium and consequently absorption as a result of hydroxyalumininosilicate formation. We have investigated the effect of silicic acid on gastrointestinal absorption in humans. Dosing experiments were conducted on five healthy males, who drank orange juice containing Al-26 (50 Bq in 200ml). Serial blood samples were taken and Al-26 levels were determined by AMS. After 6 weeks, the experiment was repeated with additional sodium silicate (100μM, pH5, effectively silicic acid). The average uptake for the first experiment was 0.012% (1 hour plasma sample) and was reduced by over a factor of six when silicon was added. These results have clear implications for epidemiological studies concerning the bioavailability of aluminium in water supplies.

634 SPECTRA MANAGEMENT™—A SPECTROSCOPIC IMAGING DATABASE MANAGEMENT SYSTEM.

Kenneth N. Davis, Spectral Intelligence Corporation, 30 East Swedesford Road, Malvern, PA 19355.

A full page optical scanner will be utilized to input existing hardcopy spectroscopic or chromatographic data from any analytical instrument into a personal computer. These spectra can then be scaled, rotated, cropped, zoomed and compressed. A spectra database management system will be developed which allows: input of lab notebook numbers, spectra conditions, user definable data fields and spectral parameters. The data and image can be stored, retrieved, correlated and compared according to both pictorial and text content. Special features will include: A natural language interface such that the user can retrieve, in narrative form, all data and the related spectra images; An "Electronic Lightbox" that will allow several spectra to be visualized and compared on the screen. To achieve automaticity in the chemical instrumentation laboratory, a convenient computerized method of spectra input must be realized. It is true that modern instruments have analog and digital output that can be interfaced to computers. However, there exist a large of compendia of existing spectra in hard copy binders. These spectra need to be databased and retrieved according to application specific interpretation requirements. Commercial databases of spectra are available. However, often they are not obtained under desired experimental conditions. They may not contain the exact impurities and reaction intermediates that are necessary for spectra comparison. The proposed SPECTRA MANAGEMENT™ system will facilitate the scanning of spectra from Gas Chromatography, Nuclear Magnetic Resonance, Infrared Spectroscopy, HPLC, Mass Spectroscopy, Atomic Absorption, X-ray etc. into an IBM compatible, MS-DOS computer. Any instrumentation modality can be scanned and databased. Optionally, the user can "crop" and digitize into xy data pairs any portion of the scanned image. Spectral analysis, scaling to a common axis dimension, multiple comparisons (e.g. electronic lightbox), storage, pictorial and text retrieval can then be performed.

635 SOME FUNDAMENTAL PROBLEMS IN THE HYDROGEN-ION CONCEPT.

Carl E. Moore, Bruno Jaselskis and Alfred von Smolinski.

In the early development of the hydrogen-ion concept, the naked proton was thought to exist in aqueous solution. This original notion of the nature and behavior of the proton led to the development of extensive—but what was to become fundamentally questionable—definitions of the concentration of the proton. In solution the naked proton was first treated as a real thing, thus allowing it to fit nicely into the moles per liter concept. Later, authors—notably R. P. Bell and I. M. Kolthoff—showed that it was impossible for a naked proton to exist in an aqueous solution, but because solutions of the proton acids behaved in ordinary chemical reactions like solutions of naked protons, the moles per liter definition, *molarity*, of hydrogen-ion concentration continued in use. The hydrogen-ion, no longer amenable to a real-thing definition, fell into the nominal definition category. From an entirely different philosophical perspective, another definition, *normality*, was developed to represent the concentration of the proton acids. The definition was based on the operational standards—one gram atom of hydrogen and the Faraday. *Normality* could be expressed without reference to the naked proton. These two definitions relating to the treatment of the solvated proton are complementary, and each has been used widely, particularly in aqueous solution chemistry. The current and questionable trend in elementary chemistry is to minimize or even eliminate the use of normality. These complications pose interesting philosophical and practical problems having relevance in today's science, particularly fast-reaction chemistry.

636 BONE LEAD ANALYSIS: DEVELOPMENT OF SAMPLING AND ANALYTICAL METHODOLOGY FOR MILLIGRAM SAMPLES.

K. S. Subramanian, M. J. Inskip and J. W. Connor, Environmental Health Centre, Health and Welfare Canada, Tunney's Pasture, Ottawa, Ontario, Canada K1A 0L2.

This presentation will describe the development of a contamination-free sampling technique for obtaining milligram amounts of cortical and trabecular bones from biopsies of cynomolgus monkeys, and the development of a platform-in-furnace atomic absorption spectrometric method for the determination of lead in these small samples of monkey bone. The contamination control measures adopted during sampling and sample preparation will be emphasized. The sampling sites for the adult female monkeys involved the iliac crest and for the fetus involved the femur. Sample preparation consisted of room temperature digestion with nitric acid and palladium matrix modification. Lead was measured using stabilized temperature platform furnace AAS. Data on sensitivity, detection limit, precision and accuracy will be presented. Accuracy was assessed using the IAEA animal bone reference material and by intercomparison with isotope dilution mass spectrometry. Application of the method to the investigation of maternal-fetal transfer of lead in primates will be discussed. Preliminary lead concentration data in adult and fetal cortical and trabecular bones subsequent to the dosing regimen of lead during pregnancy suggest significant differences between the two compartments examined.

637 DETERMINATION OF NITROGEN IN TITANIUM ALLOYS: A RAPID QUANTITATIVE DISSOLUTION PROCEDURE.

N. A. Marotta and E. M. Skelly Frame, GE Corporate Research and Development, P.O. Box 8, Bldg. K-1, Room 2A32, Schenectady, NY 12301.

Determination of nitrogen in titanium alloys can be accomplished by a variety of techniques, but titrimetric and photometric methods require the dissolution of the sample prior to analysis. Complex titanium alloys, especially those with high levels of TiN, will not dissolve readily using standard procedures. A rapid, quantitative dissolution procedure for Ti alloys containing 1–5% N will be described.

638 A PRECISE, COMPUTER-CONTROLLED MICROTITRATOR.

D. A. Lee, C. C. Hanzelka and W. W. Johnson, Martin Marietta Energy Systems, Inc., Oak Ridge Y-12 Plant,* Plant Laboratory, Building 9995, MS-8189, Oak Ridge, TN 37831-8189.

An automatic microtitrator has been developed to titrate, with good precision, micro-quantities of samples. A step-motor, controlled by a personal computer (PC), drives the piston of the microburet. The computer program determines the volume of increments of the titrant. The titration data are recorded. From these data, the inflection points on the curves are calculated and the answer for the component analyzed is printed. The program is also used to fill the buret exactly to zero. A complete titration curve can be printed. The titrator has been used for the titration of free acids in hydrolyzable metal ion solutions, the determination of boron in various compounds, the determination of alkali metal carbonates in alkaline solutions, and routine acid-based titrations.

*Managed for the U.S. Department of Energy by Martin Marietta Energy Systems, Inc., under contract DE-AC05-84OR21400.

639 DEVELOPMENT OF RECOGNITION COATINGS FOR CHEMICAL SENSORS.

E. J. Poziomek and Jun Li, Harry Reid Center for Environmental Studies, Las Vegas, NV 89154. H. Wohltjen, J. R. Lint and N. L. Jarvis, Microsensor Systems, Inc., Bowling Green, KY 42103.

Most chemical sensors rely either on changes in mass, optical characteristics, electrical properties, or heat to signal that a particular analyte is present. Such changes are usually associated with a specific chemical reaction or molecular association event between the analyte and a recognition coating which is coupled with some physical transducer, such coatings must be stable to allow sensor operation for sustained periods of time. Results of a long-term stability study of specific coatings on surface acoustic wave microsensors will be presented. Effect of temperature and vapor flow rate will also be discussed. Although the information in this paper has been funded in part by the U.S. Environmental Protection Agency under cooperative agreement no. CR818353 with the University of Nevada-Las Vegas, it has not been subject to agency review and, therefore, does not necessarily reflect the views of the agency, and no official endorsement should be inferred.

640 THE NET WEIGHT DISPENSER: A DEVICE FOR RAPID AND VERY PRECISE SAMPLE AND STANDARD PREPARATION.

John O. Beyer and Q. Gordon von Nehring, Dow Chemical USA, Analytical Sciences, 1897A Bldg., Midland, MI 48667.

Traditional sample and standard preparation methods have been based upon dilution by an added volume or to a final volume. It is commonly recognized that this approach is limited by both volumetric equipment and personal technique. However, there has been little attention paid to the fact that volumetric sample preparation is also limited by temperature-related changes in the density of the diluent. Since the coefficient of expansion is typically 0.14%/°C for common organic solvents, the actual concentration of solutions prepared at different times may vary by as much as 0.5 to .1% relative. Finally, precise sample and standard preparation is time-consuming and, therefore, expensive. The Net Weight Dispenser (NWD, patent pending) rapidly prepares sample solutions or mixtures on a weight/weight basis with high accuracy and precision, independent of laboratory temperature and operator technique, and produces a GLP-compliant record. The need for careful target weighing with related time costs and the potential for non-representative sampling is completely eliminated, as are the limitations of the volumetric approach. The NWD is capable of preparing samples and standards at a pre-determined weight/weight ratio within the accuracy and precision limitations of the analytical balance (RSD $\leq$ 0.02% for current applications). For analysis of routine samples, the need for transferring weight data to the device used for calculation of final results is eliminated, along with the associated errors and cost.

641 GENERIC JCAMP-DX/BDX.

Robert S. McDonald, JCAMP, 9 Woodside Dr., Burnt Hills, NY 12027. Charles Anderson, JCAMP, N11W 31812 Phyllis Pkwy, Delafield, WI 53018.

JCAMP BDX is a binary version of the JCAMP-DX[1] protocol for exchanging computer readable lab data. Both are self-documenting forms in which major items are identified via labels. DX/BDX is a *dual* protocol combining major features of JCAMP-DX, NetCDF/CDL, and Star. DX is the *print-form* of BDX, much like NetCDL is the *print-form* of NetCDF. The main differences between DX and BDX are: 1) binary representation of major data blocks, like spectra, 2) a binary byte count preceding each label, and 3) freedom to combine related data blocks simply by appending to an existing BDX file without modifying previous contents. Items 1 and 2 provide random access to data elements and attributes without parsing a complete file. Item 3 allows information acquired at different times and by different means to be combined for Good Laboratory Practice (GLP) without compromising integrity of existing data. BDX has promise as a standard form for native data acquisition which can be used for data exchange without need of an intermediate form like either JCAMP-DX or NetCDF. The flexibility of such self-defining data can free vendors from the rigidity of existing data acquisition formats which specify the address and size of each data item.

[2] "JCAMP-DX: A Standard Form for Exchange of Infrared Spectra in Computer Readable Form", R. S. McDonald and P. A. Wilks, Applied Spectroscopy 1988, 42(1), 151–162.

642 THERMOSONIMETRY OF POLYMERS.

K. A. Soulsbury and A. P. Wade,* Department of Chemistry, University of British Columbia, 2036 Main Mall, Vancouver, BC, Canada V6T 1Z1.

Thermosonimetry is the measurement of sound emitted from a substance as a function of temperature, while the substance is heated in a controlled manner. Previously, it has been applied mainly to inorganic materials, with few applications in polymer science. In this work the thermal degradation of polymers including poly(vinyl chloride), poly(ethylene), poly(ethylene terephthalate) and poly(propylene) has been studied using thermosonimetry. An apparatus has been developed that permits simultaneous thermogravimetric analysis (TG) and thermosonimetry (TS). This apparatus was used to investigate the sources of the sound emitted and to evaluate the suitability of thermosonimetry as a mechanistic probe for these thermal degradation reactions. The isothermal and non-isothermal crystallization of polymers was also investigated to see if thermosonimetry could be used as a complementary technique to other standard thermal methods of analysis such as Differential Scanning Calorimetry (DSC) and Differential Thermal Analysis (DTA).

643 INDUSTRIAL APPLICATIONS OF AN HPLC-FTIR INTERFACE.

J. L. Dwyer and J. N. Willis, Lab Connections, 5 Mount Royal, Marlborough, MA 01752.

Liquid chromatography has no ability to provide chemical identification of eluted species. Coupling of infrared spectroscopy to HPLC has heretofore proved difficult, due to the chromatography solvents interference with spectroscopy of eluants. The LC-Transform● instrument uniquely eliminates the solvents and presents eluted peaks as pure compounds that are amenable to infrared spectroscopy. This paper demonstrates application of this technology in providing identification of materials in polymers, foods, pharmaceuticals, and environmental applications. In polymer analysis applications the methodology is useful in providing composition drift (structural change as a function of molecular weight) of backbone composition of polymers, analysis of polymer blends, and identification of additives in polymers. Food and beverage samples typically are very complex mixtures of constituents (sugars, acids, esters, lipids), and the identification of species is of great interest to the food chemist. The combination of HPLC and IR spectroscopy offers a cost effective approach to this problem. In pharmaceutical applications, the technique is used to identify trace components of a known product. This paper describes sample preparation techniques that enable such identification of minor components.

644 QUANTITATIVE BROMATE ANALYSIS VIA REDUCTION WITH SODIUM NITRITE. Robert C. Duty and Jesse S. Ward, Baylor University, P.O. Box 97348, Chemistry Dept., Waco, TX 76798.

Sodium bromate has been previously titrated with standardized solutions of sodium nitrite. [Guyani, B. P. and Prasad, R. K., *J. Indian Chem. Soc.*, 1969, 41(6), 449] This procedure required several minutes to reach equilibrium at each increment of titrant. Consequently, we elected to shorten the analysis time by titrating the reduced product of sodium bromate, the bromide ion, with a standard solution of silver nitrate with a laboratory constructed silver/silver bromide electrode verses a glass electrode. Quantitative results with known solutions of sodium bromate produced results with greater than 95% accuracy. The bromide ion was also precipitated with silver nitrate from known solutions of bromate solutions reduced with sodium nitrite, and results were better than 95% accurate. In these titration reactions it was found that an excess of sodium nitrite in the solutions would interfere with the titrations by eliminating the potential jump in the titration curves. This problem was overcome by adding sodium peroxide to oxidize the sodium nitrite by heating the solution. The potential jump in the titration was restored and accuracy was restored to the titration curves. We accomplished the same results when we reduced potassium chlorate with sodium nitrite and titrated the chloride ion with silver nitrate with a laboratory constructed silver/silver chloride electrode with accuracy comparable to the bromide ion titrations.

645 THE INVESTIGATION OF "ZINC FINGERS" BY ELECTROSPRAY MASS SPECTROMETRY. Mark H. Allen, PE-SCIEX 55 Glen Cameron Rd, Thornhill, Ontario, Canada L3T 1P2. Chee Ming Li, Tai-Tung Yip and T. William Hutchens, USDA/ARS Children's Nutrition Research Centre, Department of Pediatrics, Baylor College of Medicine, Houston, TX 77030.

We have used electrospray ionization mass spectrometry (ESI) to evaluate the relative metal-binding specificity and stoichiometry of the two different C_2-C_2 type "zinc-finger" metal-binding sites within the DNA-binding domain (ERDBD) of the human estrogen receptor protein. The 71 residue ERDBD was analyzed by ESI in up to 100uM Zn (II), Cu(II), or different molar ratios of both metal ions. Peptides with multiple bound metal ions were fully resolved: ERDBD was observed with up to 2 bound Zn but preferred 4 bound Cu. Mass accuracies allowed the verification of different coordinate covalent reaction mechanisms for Cu and Zn binding.

646 USE OF CAPILLARY ELECTROPHORESIS-ELECTROSPRAY IONIZATION MASS SPECTROMETRY TO CHARACTERIZE BIOMOLECULES. D. R. Goodlett, J. H. Wahl, H. R. Udseth and R. D. Smith, Battelle PNL, P.O. Box 999, P8-19, Richland, WA 99352.

The combination of capillary electrophoresis (CE) with electrospray ionization mass spectrometry (ESI-MS) creates a powerful on-line technique for separation and characterization of biological molecules. Typically, characterization of a covalently modified protein requires off-line purification from unmodified proteins before digestion with a proteolytic enzyme. The mixture of peptides produced by proteolysis can then be analyzed or may require further fractionation to enrich the peptides of interest. Alternatively, on-line analysis of a mixture of covalently modified proteins without prior purification can be advantageous. We are exploring CE/ESI-MS methods for the on-line separation and characterization of mixtures of structurally similar proteins.

647 FUNDAMENTALS OF ELECTROSPRAY IONIZATION FOR LIQUID CHROMATOGRAPHY/ MASS SPECTROMETRY APPLICATIONS. Craig M. Whitehouse, Shida Shen and Fred Banks, Analytica of Branford, Inc., 29 Business Park Drive, Branford, CT 06405.

Performance of an Electrospray Ion Source with and without ultrasonic nebulization assist will be presented. The coupling of Electrospray with ultrasonic nebulization expands the range of solution chemistries and liquid flow rates that can be used with this technique for Liquid Chromatography/Mass Spectrometry applications. The effects of solution chemistry on the Electrospray ion signal will be discussed form some classes of compounds. Sample and solution parameters such as solubility, Pka, Ph, and concentration play a role in the efficiency of ion evaporation from liquid droplets with Electrospray ionization. Rules of thumb will be given for maximizing the Electrospray signal response for isocratic and gradient Liquid Chromatography separations.

648 CONTINUOUS-FLOW FAB AS A LC/MS INTERFACE-PAST!!! PRESENT . . . FUTURE??? John Coutant, Bradley Ackermann, Brian Regg and Teng-Man Chen, Marion Merrell Dow Research Institute, 2110 E. Galbraith, Cincinnati, OH 45215.

In the decade of the '80s, fast atom bombardment (FAB) mass spectrometry rapidly grew and allowed the analysis of thermally labile and high molecular weigh compounds which could not be done by other ionization techniques. The development of continuous-flow FAB (CF-FAB) allowed the continuous introduction of liquid samples and the monitoring of LC effluents. The resulting use of CF-FAB as a LC/MS technique has allowed the LC/MS analysis of complex samples such as drug metabolites and peptides. Examples of LC/MS using CF-FAB for these classes of compounds will be presented for the analysis of glycopeptide antibiotics, urinary profiling of drug biotransformation products, and analysis of tryptic maps for protein structure by LC/MS and LC/MS/MS. CF-FAb will be compared with the current rival interfacing technique, electrospray, in regards to the relative strengths and weaknesses of each as a LC/MS technique.

649 DEVELOPMENT OF AN HPLC/MS METHOD FOR THE QUANTITATIVE DETERMINATION OF A BIOLOGIC. P. E. Farrow and J. N. Kyranos, Arthur D. Little, Inc., 20 Acorn Park, Cambridge, MA 02140-2390.

A mass spectrometry method for the determination of a biologic at the femto-mole level in plasma samples has been completed. The test article was administered at doses no greater than 150 ng/kg. Blood samples were collected at pre-determined time intervals. After subsequent extraction, cleanup and concentration, the samples were analyzed for the determination of residual test article and its metabolites. The metabolites predicted to be formed were analyzed by the same method. It was estimated that the maximum dose 150 ng/kg, would result in a final extracted sample volume of 10 μl, containing approximately 8 ng of test article. The method was designed to detect at this level and to one or two orders of magnitude below. The expected metabolite concentrations were of the same magnitude.

650 THERMOSPRAY LC/MS FOR THE MEASUREMENT OF ENDOGENOUS PRODUCTION RATES OF CORTISOL AND 25-OH VITAMIN D. Al Yergey, D. Vicchio, K. O'Brien, N. V. Esteban and D. J. Liberato, National Institutes of Health, 9000 Rockville Pike, Building 10, Room 6O101, Bethesda, MD 20892.

A brief introduction to the technique of thermospray LC/MS is given and its applicability to quantitative measurements discussed. Results from studies of the production rates of the endogenous molecules cortisol and 25-OH vitamin D in human subjects are presented.

651 UTILITY OF THERMOSPRAY HPLC/MS FOR THE ANALYSIS OF PHARMACEUTICALS AND METABOLITES. W. A. Korfmacher,* J. Abian, J. Bloom and M. I. Churchwell, National Center for Toxicological Research, Jefferson, AR 72079. C. C. Lin, Schering-Plough Research Institute, 60 Orange St., Bloomfield, NJ 07003.

Thermospray HPLC/MS has been shown to be a very useful technique for the analysis of various compounds and sample types. This report will describe the utility of this technique for the analysis of several pharmaceuticals and some of their metabolites. Examples will include the analysis of ten sulfonamides as well as the analysis of three anthracycline antibiotics and metabolites.

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volatilization, atomization, and excitation processes. For many samples, the CRA volatilizes and only partially atomizes the sample, while the laser plasma completes the atomization and excites the analyte. This combination should lead to nearly complete atomization of many samples. Although the plasma background is substantial immediately after breakdown, it decays rapidly with time. Time resolution with observation a few microseconds after breakdown allows the analyte emission to be observed with little background from the plasma. Also, we have observed a decrease in background emission from the inert gas (argon) used for the CRA during the atomization stage as a result of gas expansion. This enables high signal-to-background (S/B) ratios to be achieved for analyte emission. The design, characterization, and performance of the instrument are described. Data are presented that demonstrate the high S/B ratios that are achieved during the atomization cycle. Analytical performance data are discussed for several elements.

671 LASER PLASMA EXCITATION OF ELECTROTHERMALLY ATOMIZED SPECIES. Martha R. Joseph and Vahid Majidi, Department of Chemistry, University of Kentucky, Lexington, KY 40506.

Trace and ultratrace quantities of metals are detected using electrothermal atomization with laser plasma excitation. The sample solutions were deposited inside a graphite furnace and then dried. The 10 Hz frequency doubled output of a Nd-YAG laser is focused to form a plasma inside the graphite furnace, directly above the dried sample. As the graphite furnace is electrothermally heated the sample vaporizes and begins to atomize. While in the gas phase, but before diffusing out of the graphite furnace, the analytes undergo further atomization as well as thermal excitation from the laser induced plasma. The multichannel detection system is triggered to begin collecting the emissions from the end of the furnace tube at 100 ms intervals beginning at the onset of the 4 second atomization cycle. The resulting emission spectra provide both qualitative and quantitative information concerning the species present in the sample. Solutions of known composition and concentration are examined, characterizing the emission wavelengths, relative intensities, and atomization temperatures for a range of samples.

672 GAS BREAKDOWN BEHAVIOR IN AN EXCIMER LASER-ABLATED PLASMA. Yong-Ill Lee, Joseph Sneddon, Gi-Ho Kim and Ye-Yung Teng, Department of Chemistry (J.S. and Y.L.) and Physics (G.K. and Y.T.), University of Massachusetts, Lowell, MA 01854.

In recent years there has been considerable interest both from the fundamental and pragmatic point of view in laser ablated plasma production for use in direct elemental analysis of solid samples. The recent development of powerful UV-excimer lasers has opened new possibilities in analytical atomic spectroscopy by providing efficient atomization and excitation processes. The research in this laboratory showed that the shape, size and emission spectra of an ArF-excimer laser (λ = 193 nm)-ablated plasma are largely dependent on the atmospheric surroundings, gas composition and the pressure.^{1,2} In particular, ambient gas breakdown phenomena and the reaction between the ablated metal atoms and gas species occurred in the plasma before complete mixing of the ablated plume. The atmosphere greatly affects the generation of the plasma and emission spectra. A detailed study of ambient gas breakdown in an excimer laser-ablated plasma will be presented including the effects of different metal targets, laser energy over 50–200 mJ/pulse, and different gas composition (air, nitrogen, argon, and helium) through the time- and space-resolved spectrometry. The influences of gas breakdown in laser-ablated plasma emission were also studied to obtain optimum condition for spectrochemical analysis. The efficiency of metal ablation in different ambient conditions was investigated by weighing the target materials after laser irradiation. The excitation temperature was estimated by the Boltzmann plot method using both metal atom lines and ambient gas emission lines.

1. Y. I. Lee, S. P. Sawan, T. L. Thiem, Y. Y. Teng, and J. Sneddon, *Applied Spectroscopy*, 1992, **46**, 436.
2. Y. I. Lee, T. L. Thiem, G. H. Kim, Y. Y. Teng, and J. Sneddon, *Applied Spectroscopy*, 1992, submitted.

673 RAPID ANALYSIS OF METAL PARTICLES ON FILTERS BY LASER ABLATION-INDUCTIVELY COUPLED PLASMA SPECTROSCOPY. Aaron Koskelo and David Cremers, MS-J567, Los Alamos National Laboratory, Los Alamos, NM 87545.

Hazardous metal aerosols are typically monitored by collection of the aerosol on a particle filter for a fixed time period. The filter is then digested and the resulting solution is then analyzed by an appropriate atomic spectroscopy. The wet-ash digestion process is slow, typically requiring about an hour. This is too long for applications where minutes can make a difference in worker safety. By ablating the particles from the filter with a focused laser beam, the solution processing step can be eliminated. In the apparatus described in this paper, the ablated material is entrained in a flowing stream of inert gas and transported to the sample inlet of an inductively coupled plasma atomic emission spectrometer. Complete analysis of a 37 mm diameter filter can be obtained in less than thirty seconds. In this presentation, the detection limits and precision for beryllium, lead, chromium and aluminum analyses will be described. The use of atomic carbon emission, originating from ablated filter material, as an internal standard will be discussed. In addition, optimum parameters for the title apparatus will be presented.

674 SOLID SAMPLE ANALYSIS BY OPTICAL EMISSION SPECTROSCOPY IN LASER PRODUCED PLASMA. P. Mauchien, A. Briand, J. L. Lacour, N. Andre and A. Semerok, DPE/SPEA/SPS Ce Fonenay Aux Roses, BP6, 92265 Fontenay Aux Roses Cedex, France.

Laser produced plasmas have been widely studied for several years in the field of analytical spectroscopy mainly with the ICP-MS technique. For some applications like on-line control of melting materials or routine analysis in industrial environment, the direct measurement of the plasma emission presents some advantages: the plasma can be produced in air at atmospheric pressure (simple and fast measurement); the technique is based only on optical spectroscopy (suitable for remote sensing measurements); the analysis can be localized by using a microscope device. Although a lot of work has been performed with this technique, it has never gained general acceptance due to a strong lake in reproducibility. Our results are obtained with an experimental set up specially designed to reduced irreproductibility causes. The solid sample is mounted on a precise positioning device. Ablation is produced by a 400 mJ Xecl laser. Optical emission is detected with a time gated multichannel spectrometer. Our results show that the reproducibility is mainly affected by the sample heterogeneity due to the localized character of the measurement. This is illustrated in the case of aluminum target. In the best use of the technique, the reproducibility is 1,3% at 10000 ppm level and results have been demonstrated to be free from matrix effects using different aluminum alloys.

675 THE CHALLENGE OF THE SUCCESSFUL ETV-ICP-MS ANALYSIS. Richard D. Ediger, The Perkin-Elmer Corporation; 761 Main Avenue; Norwalk, CT 06859-0215.

This paper critically examines the current state-of-the-art of electrothermal vaporization ICP-Mass Spectrometry (ETV-ICP-MS), documenting several of the challenges of the technique and offering methodology permitting these challenges to be successfully met. An initial hurdle had been the inefficient transport of picogram-quantities of analyte from the ETV vaporization surface to the ICP ion source. The addition of modifiers to act as physical carriers of the analyte eliminates this effect. ETV-ICP-MS has detection limits 100 to 1000 times better than graphite furnace atomic absorption for most elements. While this is an obvious benefit, it also results in more challenges with environmental analyte contamination. Careful control over the laboratory environment and reagent purification techniques however reduces the degree of contamination. Examples of other issues that are addressed in this paper are the number of elements that may be determined in an ETV measurement and the extent of matrix-induced space charge effects.

676 MULTIELEMENT DETERMINATION OF TRACE CONTAMINANTS IN TETRAMETHYL AMMONIUM HYDROXIDE BY INDUCTIVELY COUPLED PLASMA MASS SPECTROMETRY. T. L. Pinkston and C. Sparks, SEMATECH, 2706 Montopolis Drive, Austin, TX 78741.

Tetramethyl Ammonium Hydroxide (TMAH) is used as an advanced photoresist developer chemicals in the manufacture of semiconductors. This process chemical is now being produced with extremely low levels of trace metallic impurities. For many of these materials the levels of most contaminants is at or below 1 ng/g. These chemicals now require analysis by a more sensitive technique than emission spectroscopy and a more rapid technique than furnace atomic absorption. The use of inductively coupled plasma mass spectrometry (ICP-MS) allows for the rapid analysis of these chemicals with sensitivity similar to furnace atomic absorption and with minimal or no sample preparation. Improved sample introduction techniques such as ultrasonic nebulization allow for rapid analysis of TMAH with improved detection limits. Instrumentation and techniques will be discussed. In addition, the use of electrothermal vaporization (ETV) as a sample introduction technique will be discussed and figures of merit given for selected elements.

677 Abstract not received at time of printing.

678 DETERMINATION OF ALKALINE EARTH AND RARE EARTH ELEMENTS IN MARINE FERROMANGANESE DEPOSITS. Eric H. De Carlo, Department of Oceanography, 1000 Pope Road, University of Hawaii, Honolulu, HI 96822. Ewa Pruszkowski, The Perkin Elmer Corp., 10 Faraday, Irvine, CA 92718.

The alkaline earth and lanthanide elements within marine Fe-Mn oxide crusts were determined by LA-ICP-MS. Approximately one centimeter wide slabs were sliced from a 9-cm thick crust to yield a surface consisting of the entire oxide growth sequence and its underlying substrate. Slabs were further fragmented to fit within the sample chamber of the laser system. Use of a laser sampling time of 30 s across a 2 mm horizontal distance resulted in ablation lines of typically 100 μm in diameter. Response factors obtained by ablation of a pressed powder pellet of standard USGS Nod A-1 were employed to initially establish the response curve. Although yielding acceptable results for certain elements this approach led to errors of up to one order of magnitude for other elements depending on the area of the crust sampled. Much of this error is attributable to differences in the ablation efficiency of the samples relative to the pressed powder. Furthermore, because marine Fe-Mn oxide deposits consist of Fe and Mn oxides interspersed with other minerals and are extremely heterogeneous even on a scale of a few millimeters, it is nearly impossible to achieve uniform ablation of the untreated sample. We will discuss approaches taken to remedy the differential volatilization problems and the use of wet chemical analysis of hand-picked microsamples to update response curves. Suggestions as to pretreatment of heterogeneous samples to normalize the ablation efficiency will be provided.

679 DETERMINATION OF PT, PD, RH, AND IR IN GEOLOGICAL MATERIALS BY DIRECT SOLID SAMPLING OF FIRE ASSAY BEADS USING SPARK ABLATION ICPMS. Raymond L. Van Hoven, M. W. Doughten, S-. H. Nam, A. F. Dorrzapf and A. Montaser, The George Washington University, Department of Chemistry, Washington DC 22052.

Platinum group elements (Pt, Pd, Rh, and Ir) are preconcentrated into gold and silver beads for direct spark ablation of the bead into an ICPMS system. An evaluation of the analytical merits of the overall methodology will be presented, including application to selected geological reference materials.

680 USE OF PRINCIPAL COMPONENTS ANALYSIS WITH LASER SAMPLING ICP-MS. K. J. Fredeen and D. A. Yates, The Perkin-Elmer Corporation, 761 Main Ave., Norwalk, CT 06859-0215.

The use of laser sampling for ICP-MS provides the analyst with many benefits that result from the ability of LS-ICP-MS to analyze solid samples directly. One of the strengths of LS-ICP-MS is the wealth of data that can be obtained from a solid sample in a relatively short time: Complete mass spectra for solid samples with elemental concentrations ranging from sub-ppm to percent levels can usually be obtained in a matter of minutes. In order to take advantage of the large amount of data that can be obtained using the LS-ICP-MS technique, Principal Components Analysis (PCA) has been applied to the data sets from the LS-ICP-MS analysis of several sets of solid samples. PCA techniques provide a way of reducing a large set of data into distinct linear combinations of independent terms. Each individual component describes a source of variation in the data set, allowing the analyst to differentiate samples rapidly and without prejudice. PCA can offer additional benefits to LS-ICP-MS because the use of calibration standards, which can often be a barrier for solid sampling techniques, is not required for PCA.

681 CHARACTERIZATION AND STRUCTURAL ELUCIDATION OF PHARMACEUTICALS AND NATURAL PRODUCTS BY MASS SPECTROMETRY. Marshall M. Siegel, American Cyanamid Company, Medical Research Division, Lederle Laboratories, Pearl River, NY 10965.

Mass spectrometry is a powerful tool for rapidly characterizing and elucidating the structures of pharmaceuticals and natural products. Mass spectral techniques will be applied to solve a variety of problems related to the characterization of pharmaceuticals and natural products. Examples will include structure elucidation of antibiotics and anti-cancer agents, determination of biosynthetic pathways, deuterium exchange studies, polymeric therapeutic agents, peptide sequencing and the analysis of drugs conjugated to proteins. A variety of mass spectral ionization techniques will be applied including electron impact, fast atom bombardment, thermospray, electrospray and matrix-assisted laser desorption as well as tandem mass spectrometry methods.

682 APPLICATIONS OF FAB AND ESI TECHNIQUES TO MOLECULES OF PHARMACEUTICAL INTEREST. L. Baczynkyi, Physical and Analytical Chemistry Research, The Upjohn Company, Kalamazoo, MI 49001.

For the past ten years, we have used the fast atom bombardment (FAB) ionization technique to obtain mass spectral information on compounds isolated from fermentation beers. Usually these were antibiotics or anticancer compounds that were thermally unstable. Accurate mass measurements of the pseudo-molecular ions and some key fragment ions helped in rapid identification of known antibiotics. In addition, library searches of our mass spectral data base which contains also FAB mass spectra often identify the "unknown" sample. The use of appropriate matrices is important in obtaining good FAB mass spectra. This will be illustrated by FABMS recorded in glycerol and other matrices. Similarly some antibiotics do not yield MW information in the positive ion mode but show prominent (M-H) in the negative ion mode. Collision induced dissociation (CID) mass spectra have also been recorded for certain antibiotics. More recently, we have applied the electrospray (ES) ionization method to the determination of the molecular weights of recombinant proteins and large peptides. In some cases, this ionization technique has allowed rapid identification of impurities isolated by HPLC. Thus, the MW of impurities present in lots of recombinant bovine somatrotropin (rbST) were determined by this ionization technique. Results from interfacing the electrospray ion source to the high performance liquid chromatography (HPLC) and capillary zone electrophoresis (CZE) instruments will be illustrated using tryptic digest samples.

683 APPLICATION OF MASS SPECTROMETRY TO THE STRUCTURAL CHARACTERIZATION OF ANTIBIOTICS AND NON COVALENT PROTEIN COMPLEXES. B. N. Pramanik, P. Bartner, A. K. Ganguly, O. Sarre, V. Girijavallabhan, A. Tsarbopoulos and E. Huang, Schering-Plough Research Institute, 86 Orange St., Bloomfield, NJ 07003.

This paper will detail the application of advance mass spectral techniques to the solution of two difficult structural problems; the identification of a novel class of oligosaccharide antibiotics, everninomicin, and the study of the non covalent complex of human RAS:GDP. Everninomicins are produced by *micromonospora carbonaceae* and are highly active against gram-positive bacteria. Everninomicins possess many unusual features in their structures: an orthoester, an aliphatic methylene dioxy group, a nitro sugar and a fully substituted phenolic ester residue. Everninomicin structure elucidations involved chemical degradation, NMR and MS methods. This talk will highlight the Cs^+-LSIMS work on everninomicin with emphasis on the 13–384 component; techniques involved were positive ion LSIMS, salt addition positive LSIMS, negative ion LSIMS, high mass LSIMS peak matching and camikes. RAS proteins are guanine nucleotide binding regulatory proteins that exist in two interconvertible conformational states; one an inactive GDP-bound state and the other an active GTP-bound state. In the latter form, they serve as signal transducers controlling cell proliferation. We here describe the use of ion-spray MS for the study of the noncovalent complex of human RAS protein with GDP as well as the effect of the pH and cosolvent on the stability of the RAS:GDP complex system.

684 QUANTITATIVE AND STRUCTURAL ELUCIDATION ASPECTS OF CAPILLARY-HPLC/ELECTROSPRAY/MASS SPECTROMETRY, D. A. Garteiz, K. T. McManus and R. A. Newman, TEXms Analytical Services, 15701 West Hardy Rd, Houston, TX 77060.

Capillary HPLC/electrospray/MS has become a routine tool in our laboratories for the detection, identification and quantitation of drugs and their metabolites. Concentration levels in the picogram per ml of biological matrix can be achieved with most compounds. The technique is especially useful with those compounds in the 800 to 1500 Dalton range where conventional GC/MS methods do not work. Accuracy and precision of the quantitative methods are well within regulatory guidelines. A CAP-HPLC/ESP/MS has been developed for the determination of plasma levels of echinomycin, a potent anticancer drug with a MW of 1102 Daltons. Quantitative methods out of whole blood have also been developed for two very important immunomodulating agents, rapamycin and FK 506. Finally, the excellent chromatographic resolution of the capillary columns along with the ability to fragment compounds in the ESP source via "CAD" processes permits structural elucidation. This technique has been successfully used to develop confirmatory methods for agricultural chemicals. Results will be presented and discussed.

685 THE IMPACT OF MASS SPECTROMETRY IN PRE-CLINICAL ADME STUDIES. Steve E. Unger, M. Arthur Moseley and Kathy A. Halm, Glaxo Inc., Department Drug Metabolism, 5 Moore Drive, Research Triangle Park, NC 27709.

Mass spectrometry has many roles in determining the biological fate of new therapeutics. Its use in the early definition of the metabolic fate of new chemical entities (NCEs) is increasing, with LC/MS and MS/MS methods the premiere choice for structural analysis. For drugs designed to effect dual receptors questions regarding their metabolic fate are essential to understanding efficacy and examples of dual pharmacophores as cardiac drugs are presented. The extension of this methodology from thermospray to electrospray ionization is shown for other NCEs from biological fluids. The sensitivity and specificity of mass spectrometry is useful in determining pharmacokinetic data for ADME studies and examples comparing GC/MS with LC/MS are presented.

686 CAPILLARY ELECTROPHORESIS-ELECTROSPRAY IONIZATION MASS SPECTROMETRY. D. R. Goodlett, J. H. Wahl, H. R. Udseth and R. D. Smith, Battelle PNL, P.O. Box 999, P8-19, Richland, WA 99352.

The combination of capillary electrophoresis (CE) with electrospray ionization mass spectrometry (ESI-MS) creates a powerful on-line technique for separation and characterization of biological molecules. Typically, characterization of a covalently modified protein requires off-line purification from unmodified proteins before digestion with a proteolytic enzyme. The mixture of peptides produced by proteolysis can then be analyzed or may require further fractionation to enrich the peptides of interest. Alternatively, on-line analysis of a mixture of covalently modified proteins without prior purification can be advantageous. We are exploring CE/ESI-MS methods for the on-line separation and characterization of mixtures of structurally similar proteins.

687 OVERVIEW OF THE MECHANISMS IN SOLID PHASE EXTRACTION. Nigel Simpson, Varian Sample Preparation Products, 24201 Frampton Avenue, Harbor City, CA 90710.

Solid phase extraction has developed into a science led by applications—thousands of applications in peer-reviewed journals alone—yet there are few sources for information that pull together the accumulated wisdom on this technology. In this presentation the principles behind the retention/elution process will be defined and the implications of the various intermolecular forces that are present on a bonded silica surface will be described. This will allow us to rationalize the success or failure of an extraction method and to learn to enhance the ruggedness of an extraction procedure in a scientific manner. The parallels between SPE and HPLC will be highlighted with emphasis on how data from HPLC or TLC can be used to speed up the development of an SPE method. Differences between various sorbents will be analyzed in terms of the balance between a non-polar surface and a polar sub-surface. Conclusions will be drawn on solvent strength, the desirability of silanol interactions and the effectiveness of aqueous/organic wash solvents.

688 Abstract not received at time of printing.

689 Abstract not received at time of printing.

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691 Abstract not received at time of printing.

692 THERAPEUTIC DRUG MONITORING USING EMPORE SOLID-PHASE EXTRACTION MEMBRANE. Gary L. Lensmeyer, Clin. Labs. Univ. Wisc. Hosp. & Clinics, Dept. Path. and Lab. Med., Madison, WI 53792-2472.

Solid-phase extraction membranes (SPEM) represent a significant refinement of a widely used technology. In our clinical laboratory, we observed distinct advantages of the SPEM over conventional mainstay large-particle (40 μm) solid-phase sorbents of bonded silica or polymeric particles packed in cartridges. In appearance, the SPEM is a thin (500 μm thick), flexible membrane developed by 3M company (St. Paul, MN) under the name Empore. The membrane consists of small-particle (8 μm) bonded silica enmeshed in a matrix of teflon fibrils. Using the SPEM, we developed reliable extraction procedures for antidepressant, antiarrhythmic, and immunosuppressant drugs in blood. Companion SPEM extraction/HPLC separation comprises each method, permitting mobile-phase elution of the analyte from the SPEM and direct injection of eluate onto the HPLC column without further concentration steps. This approach is possible because of the high capacity and small elution volume of the SPEM. Method performance is equal to or better than that seen with conventional sorbents. Usually, recovery exceeds 90% precision CV is <5%, and analytical responses are linear within and beyond the therapeutic range. Minimal amounts of solvent are required and time-consuming evaporation/concentration steps that can influence analyte stability are avoided.

693 Abstract not received at time of printing.

694 DETERMINATION OF OIL AND GREASE IN WASTEWATER BY SOLID-PHASE EXTRACTION, Martha J. M. Wells, Center for the Management, Utilization and Protection of Water Resources, Tennessee Technological University, Box 5033, Cookeville, TN 38505.

Industrial and municipal wastewater dischargers rely upon periodic determination of oil and grease content to monitor permit compliance and to provide feedback for proper wastewater treatment. Current standard protocol utilize chlorofluorocarbons for liquid/liquid extraction (LLE) in the determination of oil and grease in wastewater. Environmental concern with this practice prompted investigation into alternative procedures. EnvirElut™ solid-phase extraction (SPE) columns were evaluated for this analysis. The Freon™-free SPE protocol developed is efficient, reproducible, and provides a reduction in both analysis time and solvent consumption relative to LLE.

695 SOLID PHASE EXTRACTION FOR ESTROGENS. S. U. Sheikh and J. C. Touchstone, Department of Obstetrics and Gynecology, University of Pennsylvania, Philadelphia, PA 19104.

Few biological samples are amenable to chromatography without some form of cleanup. Solid phase extraction using C_{18} spice cartridges (Analtech, Newark, DE) proved to be suitable for extraction of estrogens from amniotic fluids. After conditioning of the column with water-acetone (80:20) followed by methanol and water, the amniotic fluid was applied directly to the column. Washing with water-acetone was followed by washing with hexane. The estrogen fraction was then collected by elution with methanol. The fraction from the cartridge was evaporated and reconstituted in methanol for injection into an HPLC column. Using a mobile phase of acetonitrile-methanol (65:35) with a C_{18} column (Whatman, Clifton, NJ) and a temperature of −20°C estriol shows a retention time of 7.08 minutes. With this method, free estriol is readily detected in normal amniotic fluid. Amniotic fluids from subjects suspected of down syndrome had undetectable amounts. Estrone and estradiol are readily separated with the C_{18} column.

696 ABSOLUTE INSTRUMENT STANDARDIZATION METHOD FOR NEAR-INFRARED SPECTROMETRY. David H. Tracy, Timothy M. Davidson, Alan M. Ganz and Robert A. Hoult, The Perkin-Elmer Corporation, 761 Main Avenue, Norwalk, CT 06859-0284.

Instrument standardization is an attractive approach to the calibration transfer problem in near-infrared (NIR) spectrometry when multivariate regression methods are used to extract chemical and physical property estimates from spectra. Such methods frequently demand high spectrometric reproducibility and stability. We introduce and describe an approach, the absolute virtual instrument (AVI™) technique, by which a set of properly equipped laboratory or process spectrometers can be self-calibrated with high accuracy to a prescribed *absolute* spectroradiometric specification. The AVI specification includes absolute wavelength, instrument profile shape and width, and ordinate response. Instruments employing the AVI use a set of relatively non-critical internal physical standards to create and maintain their absolute calibration over time. The standards themselves are not transferred between instruments, nor do they need to be closely similar between instruments. Any number of AVI equipped instruments can generate sample spectra which are interchangeable to the absolute accuracy tolerance of the AVI, for use in chemometric model building, property prediction, or other purposes. There is no master instrument or calibration hierarchy. In appropriate applications, the result is simplified model building and maintenance, long term stability, and essential elimination of calibration transfer as an issue. Calibration accuracy, stability, and transferability results on the AVI equipped PIONIR diode array NIR spectrometer are presented.

697 USE OF NEAR-INFRARED SPECTROSCOPY TO IDENTIFY PHARMACEUTICAL DOSAGE FORMS.

Emil W. Ciurczak, F. A. DeThomas and S. Monfre, NIRSystems, Inc., 12101 Tech. Road, Silver Spring, MD 20904.

With the proliferation of generic drugs, there is a strong temptation to substitute one dosage form for a proprietary brand. There is also the possibility of "pirate" dosage forms being sold to retailers by foreign firms. Near-ir is shown to be a tool in the identification of "false" products. Using reflectance NIRS in combination with a Spectral Matching and PCA algorithm different brands of the same drug as well as illegal substitutes are easily identified.

698 ON-LINE ANALYSIS OF SOLIDS AND ANALYSIS OF FLOWING MATERIALS BY TRANSIENT INFRARED SPECTROSCOPY.

Roger W. Jones and John F. McClelland, Ames Laboratory-USDOE, Iowa State University, Ames, IA 50011.

The in-line, real-time infrared analysis of solid materials is usually prevented by the opacity or roughness of the materials. Transient Infrared Spectroscopy (TIRS) circumvents these problems and has been developed as a method for acquiring the infrared spectra of continuous solids as they move along process lines. TIRS uses a jet of hot or cold gas to heat or cool a surface layer of the passing material. This layer then either emits (if heated) or absorbs (if cooled) infrared radiation in a different way from the rest of the material. This layer is thin enough not to be opaque, and its spectrum is independent of the rest of the material. TIRS has undergone a series of tests and demonstrations on the pilot and production lines of several manufacturers, and the in-line TIRS measurements agree with independent, off-line analyses. Results from these tests will be presented. TIRS is now also being applied to flowing materials (e.g., pellets, polymer melts and other viscous liquids) that cannot readily be passed through a sufficiently thin transmission cell for conventional spectroscopy. TIRS can be applied to such materials if they are contained or their motion in response to the TIRS gas jet is otherwise controlled. How this is achieved and the results of tests on such materials will be discussed.

699 SIMULTANEOUS DETERMINATION OF DOPANT CONCENTRATIONS, SAMPLE THICKNESS AND SAMPLE TEMPERATURE USING INFRARED EMISSION SPECTROSCOPY.

T. M. Niemczyk, B. Wangmaneerat, C. Chen and J. E. Franke, Department of Chemistry, University of New Mexico, Albuquerque, NM 87131. D. M. Haaland, Sandia National Laboratories, Albuquerque, NM 87185.

There are a number of thin-film dielectrics that are widely used in the microelectronics industry. Monitoring the properties of these thin films during production can potentially increase the yield of successful product. Infrared emission spectroscopy is a good candidate for use as a *in-situ* processing tool for samples of thin-film dielectric materials. We will show that when combined with multivariate calibration infrared emission spectral data can be used as the basis for rapid quantitative determinations of sample content, sample thickness, and sample temperature. The temperature determination is of particular note as it is a demonstration of optical pyrometry with samples of widely varying spectral emissivities.

700 IN-SITU MONITORING OF THIN FILM DIELECTRICS USING FT-IR REFLECTION SPECTROSCOPY AND MULTIVARIATE CALIBRATION TECHNIQUES.

James E. Franke, Lizhong Zhang and Thomas M. Niemczyk, Chemistry Dept., Univ. of New Mexico, Albuquerque, NM 87131. David M. Haaland, Sandia National Laboratories, Albuquerque, NM 87185.

Specular FT-IR reflectance spectra at 15° incidence angle were obtained for phosphosilicate glass (PSG) films deposited on Si wafer substates. These spectra have been analyzed with multivariate calibration techniques to quantify the thickness and wt.%P of the films. Predictions for these variables were as good as or very near the reported reference method precision. Hence, these results show the promise of the specular FT-IR reflection method as an in-situ process monitoring technique for quality control of dielectric thin films used in the electronics industry.

701 APPLICATION OF FOURIER TRANSFORM INFRARED SPECTROSCOPY TO THE REAL TIME ANALYSIS OF AUTOMOTIVE EXHAUST EMISSIONS.

Alexander O. McArver, Mantech Environmental Technologies, Inc., 2 Triangle Drive, RTP, NC 27709.

The application of FTIR technology to the real time analysis of automotive exhaust emissions is investigated. The advantages and disadvantages of this application are discussed utilizing experimental data obtained from two commercially available systems (Nicolet's REGA and Mattson's REA). Real time data for several compounds such as CO, CO_2, NO, NO_2, N_2O, methanol, and formaldehyde are examined and related to vehicle operating parameters. Emission concentrations for these compounds are reported for several vehicles and driving cycles. Fuels used in these studies were gasoline, and gasoline blended with methanol, MTBE, or ethanol. Similarities and differences of the two FTIR systems are discussed.

702 MONITORING FOR CHLORINE IN PROCESS AND STACK APPLICATION USING ION MOBILITY SPECTROSCOPY.

Tad Bacon, Environmental Technologies Group, P.O. Box 9840, Baltimore, MD 21284.

Monitoring for chlorine in stacks and for process control has become a major concern for several industries. This paper describes instrumentation based on a relatively new technique: ion mobility spectroscopy (IMS). Laboratory and field installations have demonstrated the ability of this technique to accurately measure chlorine where other techniques have failed. Typical installations include monitoring scrubber efficiency, and process control applications such as measuring chlorine in hydrogen. IMS instrumentation has been configured to provide sensitivity down to the 1 ppb range, as well as ranges in the low percent range. Interference free operation has been demonstrated in the presence of high levels of sulfur compounds, moisture, solvents, chlorine dioxide and other compounds. Theory of operation, hardware and performance characteristics will be discussed.

703 OPTICAL HIGH ACIDITY PROCESS SENSORS-AN UPDATE.

Howard Nekimken and Betty Jorgensen, Los Alamos National Laboratory, MS E501, Los Alamos, NM 87545.

Several companies, including Los Alamos National Laboratory, have high acidity processes (e.g., metal reprocessing). Discrete sampling and titrimetric analysis is now the predominant method for quantifying molar (M) concentrations of acid. This method of analysis precludes obtaining real time data and generates additional liquid waste. We have developed an optical sensor which can make on-line real time acidity measurements while generating no waste. Our sensing material (an indicator, polymer combination) is deposited onto an optical surface which is in direct contact with the acidic solution. The indicator's absorbance is dependent on the acid concentration of the solution. We have identified various sensor materials that can sensitively and selectively determine solution acidity (0.1 M $[H^+]$ and above) while remaining stable and reversible for months. We will report results for various sensor materials in HF, HCl, HNO_3 and H_2SO_4 solutions. These results include long term stability studies, temperature dependence and sensitivity for different acid concentration regions.

704 Abstract not received at time of printing.

705 PAPER CHEMICAL APPLICATIONS OF SUPERCRITICAL FLUID CHROMATOGRAPHY.

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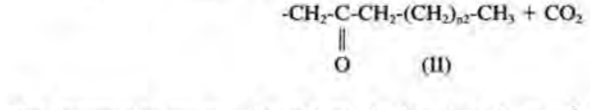
Alkylketene dimer (AKD) is a widely used sizing agent for alkaline paper. It is made from a mixture of fatty acids consisting primarily of palmitic and stearic acids. Small amounts of other homologs are also present in the fatty acid feed. Therefore, commercial AKD consists of a statistical distribution of combinations of fatty acids, generally represented below (I) where n1 and n2 = 13–15.



$$\underset{\text{(I)}}{CH_3\text{-}(CH_2)_{n1}\text{-}\underset{|}{CH} = \underset{|}{C}\text{-}CH\text{-}(CH_2)_{n2}\text{-}CH_3} \quad (\text{ring: } O\text{-}C = O) + H_2O \rightarrow CH_3\text{-}(CH_2)_{n1}\text{-}CH_2\text{-}\underset{\underset{O}{\|}}{C}\text{-}CH_2\text{-}(CH_2)_{n2}\text{-}CH_3 + CO_2 \quad \text{(II)}$$

The lactone ring reacts with cellulosic hydroxyls to form a β-keto ester bond to the cellulose fiber imparting hydrophobic character to the paper. In the presence of moisture, AKD can also hydrolyze by decarboxylation to a ketone (II). The assay and homolog distribution of AKD or ketones by HPLC, with UV or refractive index detection, and by GC has been reported. However, each technique has disadvantages. The primary disadvantage is that no published technique can simultaneously detect and assay, with acceptable sensitivity, a mixture of AKD and ketone homologs. Supercritical fluid chromatography (SFC) has successfully been applied to this problem. SFC using CO_2 and a packed C8 or C18 column with FID detection can separate and detect, with equal sensitivity, mixtures of AKD and ketone homologs. Various samples of AKD from around the world have been characterized using this SFC technique. Homolog distributions as well as the extent of hydrolysis can vary significantly.

706 SUPERCRITICAL FLUID EXTRACTION OF THERMALLY LABILE COMPOUNDS FROM AQUEOUS MATRICES.

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Supercritical fluid extraction (SFE) methodology has been developed to efficiently extract thermally labile moderately polar compounds from aqueous systems. Previous studies have demonstrated that SFE is a successful technology for the extraction of solid and semi-solid samples. Efficient direct extraction with aqueous and liquid samples has been more tedious. Experimental requirements necessitated extreme pH adjustment or the inclusion of a preliminary concentration step which makes SFE cumbersome. The experiments which will be presented will address the optimization of aqueous extractions of herbicides by supercritical fluids. Parameters which will be discussed include: mobile phase composition, matrix adjustment, pressure, temperature, density, flow rate, and analyte derivatization. Extraction results are confirmed using liquid chromatography with ultraviolet detection.

707 SYSTEMATIC OPTIMIZATION STRATEGIES IN SUPERCRITICAL FLUID CHROMATOGRAPHY.

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Although supercritical fluid chromatography (SFC) is now well established, little attention has been given to the systematic optimization of SFC separations of non-homologous or non-oligomeric analytes, a much more challenging task than separating homologues or oligomers. Basic chromatographic theory provides little direction for these separations, due to peak reversals that often occur when conditions are changed. Historically, SFC researchers have generally focused on only 2 or, at most, 3 experimental variables at a time, despite the fact that numerous variables have been identified as significant. Furthermore, they have chiefly used trial-and-error as their optimization "strategy". It is clear from chemometric principles, however, that *any procedure which does not consider all the* ***significant*** *variables simultaneously will seldom, if ever, locate the true optimum*. The objective here is to acquaint the audience with the basic principles of SFC optimization by summarizing the results of two very different approaches that we have investigated: sequential simplex optimization and the "simultaneous" window diagram approach (response surface mapping). Research on the simplex algorithm, introduced in SFC about 2 years ago,[1] is extended to more variables and more complex samples with analytes that exhibit both LC and GC-like behavior, including a 12-component synthetic mixture and a sample of Arochlor 1254 (a complex mixture of polychlorinated biphenyls). Results for the window diagram optimized separation of 5–8 component mixtures are also presented, using data obtained from a 3-level, 2-variable (density and temperature) experimental design.

1. J. A. Crow and J. P. Foley. *Anal. Chem.*, 1990, **62**, 378–387.

708 PACKED COLUMN SELECTIVITY IN SUPERCRITICAL FLUID CHROMATOGRAPHY.

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Packed chromatographic columns commonly used for HPLC are also useful for SFC. The retention behavior in SFC is analogous to normal-phase liquid chromatography, yet there are several key advantages of SFC compared to normal-phase HPLC. Because of the diversity in the characteristics of the silica packings available for chromatography and the variety of moieties bound to or coated on these silica supports, paced columns offer the chromatographer considerable leverage in optimizing chromatographic separations. Advantages of SFC over normal-phase HPLC, differences between column packings, strategies for choosing a packing, and approaches to optimizing conditions will be discussed and illustrated with relevant examples.

709 TRACE LEVEL ISOLATION OF VETERINARY ANTIBIOTICS FROM BIOLOGICAL MATRICES USING SUPERCRITICAL FLUID EXTRACTION.

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Supercritical fluid extraction (SFE) is under investigation in this laboratory to determine its potential application in isolating antibiotic drug residues at trace levels from matrices such as edible tissue. Prior to SFE, equilibrium solubilities of antibiotic classes such as the polycyclic ethers, nitrobenzamides and sulfonamides were measured in carbon dioxide at using a recirculation-type apparatus at temperatures of 60° and 80° and pressures up to 480 bar. SFE extractions studies on fortified edible tissue samples were carried out using a flow-through laboratory-assembled apparatus which could be pressurized up to 680 bar. Uniform flow rates were maintained using a micrometering value encased in an aluminum housing and fitted with a cartridge heater and a thermocouple. Recovered solutes were collected on solid phase extraction cartridges attached directly to the micrometering value. Several modifications to this system were required to optimize antibiotic recoveries. Extractions of antibiotic classes such as the nitrobenzamides, nitrofurazones and sulfonamides from muscle and liver tissue in carbon dioxide were carried out at 680 bar over a temperature range of 40 ~ 80°C. Residue recoveries from fortified tissues were compared with calculated solubilities to determine whether such measurements can predict the performance of an SFE procedure.

710 SFC APPLICATIONS IN PHARMACEUTICAL EXCIPIENT ANALYSIS.

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We used Supercritical Fluid Chromatography (SFC) to characterize pharmaceutical excipients used in the manufacture of tablets. Lubricants such as glycerol monostearate were fingerprinted with SFC. The SFC patterns showed the difference in quality of the same product obtained from different vendors from different parts of the world. This chemical analysis data from SFC corroborated with other physical studies such as solid state NMR and powder x-ray diffraction studies done on the same lots. The comparative analysis will be shown. Our SFC studies also agreed with the quality of the manufactured tablets using these different lots. Compared to other techniques, SFC can provide a relatively inexpensive and accurate way to control the quality of these excipients on a worldwide basis.

711 SFE/GC-MS DETERMINATIONS OF PAHS IN SOIL.

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Supercritical fluid extraction (SFE) has a broad range of applicability, especially with regards to environmental problems. SFE has achieved a significant amount of attention due to the benefits of eliminating, liquid solvent usage, reduction in sample preparation time and an increase in the overall analytical reliability of determinations. On-line SFE/GC-MS is a powerful technique to accurately analyze and quantitate environmental analytes. In addition, the off-line transfer of SFE effluents to collection vials adds a considerable amount of flexibility in characterizing complex matrices since a full compliment of analytical tools can be used (i.e. GC, LC, IR, NMR and UV). The discussion will include the use of on-line and off-line SFE/GC-MS methodologies for the determination of polynuclear aromatic hydrocarbons (PAH) in soil. In addition, focus on the experimental verification of optimized SFE variables to achieve efficient and quantitative extractions of these various target analytes.

712 LAGUERRE-DOMAIN REPRESENTATION OF FLOW INJECTION PEAK SHAPES.

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Our laboratories have been investigating the use of a series of discrete, orthogonal Laguerre functions for both approximation and identification of transient responses from flow injection (FI) analysis. Laguerre functions are an ideal choice since the functions are themselves transients, and thus match the responses that are to be approximated. Hermite and Chebyshev series which have been previously applied to chromatographic peaks are less appropriate due to the high skewness common to FI peaks. This paper describes a set of discrete Laguerre functions and their synthesis. Applications to data compression, simultaneous filtering and identification were investigated. A typical FI peak can be adequately represented by a linear combination of less than 10 functions, which translates to a substantial decrease in data storage. As a filter, the Laguerre method performs significantly better than polynomial, cubic spline, *and* FFT-based digital filters/smoothers when tested on simulated peaks. The Laguerre spectrum, formed from a plot of the function coefficients against coefficient number, provides a powerful means for identification. Depending on the coefficient estimation method, the shape of the Laguerre spectrum resembles that of the FI peak. The coefficients (or a subset) were used as descriptors for a pattern recognition system to separate FI peaks based on their shape. This approach is being used to qualify analyses and identify faulty operation in an automated flow injection analyzer developed in our laboratory.

713 COMPARISON OF OPTIMIZED MANIFOLD CONFIGURATIONS FOR INCREASED SENSITIVITY IN FLOW INJECTION ANALYSIS.

S. J. Chalk and J. F. Tyson, Department of Chemistry, University of Massachusetts, Amherst, MA 01003.

Three flow injection manifold configurations have been optimized for maximum sensitivity for the determination of iron(II) by reaction with 1,10-phenanthroline. This reaction was chosen because it is fast, the product is stable and the effect of pH is minimal. Thus the extent of reaction depends primarily on the dispersion coefficient and reactant concentrations with only a minor dependency on residence time. Single, double and reverse manifolds were optimized by changing flow rate, reagent concentration, injected volume, manifold length and geometry for the determination of 2 ppm Fe^{2+}. Results to test the hypothesis that the maximum sensitivity of each configuration is the same, when peak height is the parameter to be maximized, will be presented. In each case optimum conditions showed that a dispersion coefficient of less then 1.2 was needed to obtain maximum peak height, and that was mainly attainable through an increase in the reagent concentration. This indicates there is a limit to the sensitivity available in conventional flow injection manifolds and that, in contrast to some literature statements, a single line manifold can produce the same sensitivity as the other two configurations (which have been referred to as "high sensitivity" configurations). However, refractive index effects seen near the detection limit with the single line manifold show that a double line configuration is more practical.

714 A FLOW INJECTION METHOD FOR THE DETERMINATION OF Hg(II) BASED ON PERTURBATION OF THE BELOUSOV-ZHABOTINSKII OSCILLATING CHEMICAL REACTION.

Roger T. Echols and Julian F. Tyson, Chemistry Department, University of Massachusetts, Amherst, MA 01003.

Oscillating chemical reactions are complex chemical systems in which the concentration of one or more reaction intermediates vary systematically with time (oscillate). One of the popular lecture demonstrations of these reactions is the Belousov-Zhabotinskii (BZ) reaction, which typically consists of cerium, malonic acid, bromate and ferroin in sulfuric acid. This reaction system has been the focus of much research in the area of chemical kinetics for the past two decades. A flow injection (FI) system has been used as a tool for producing the BZ reaction from stable reagent solutions. Species, such as Hg(II), that will complex bromide (a reaction intermediate), are injected into reagents that form the BZ reaction when mixed and progress of the reaction is monitored in a stopped-flow mode using UV/visible absorbance spectrometry. The time to an oscillation feature on the absorbance-time profile is correlated with the concentration of Hg(II) introduced. Preliminary results for this kinetic method will be presented along with some of the difficulties that have been encountered in this work. The potential for extending the use of FI methodology for generating complex reactions such as oscillating chemical reactions and for using such reactions analytically will also be discussed.

715 SOLID-STATE DETECTORS FOR TIME-BASED MEASUREMENTS IN FLOW INJECTION ANALYSIS.

Mary K. Carroll and Julian F. Tyson, Department of Chemistry, University of Massachusetts at Amherst, Amherst, MA 01003.

The development of compact, inexpensive solid-state detectors for time-based measurements in flow injection analysis (FIA) is described. Light-emitting diodes (LEDs) or visible-emitting laser diodes are used as the source elements; PIN photodiodes are the detecting components. Basing the measurement on time, not signal intensity, obviates the need to use expensive, drift-free sources or detecting components; additionally, the detector response need not be linear with concentration. Measurement of the time between doublet peaks can be related to concentration of analyte injected into FIA system, or to other FI variables.[1] Doublet peaks occur in FI systems when the sample species is in excess in the profile center and equivalence occurs at two points, one on the leading edge and the other on the trailing edge of the profile. Initially avoided, due to their detrimental effect on peak-height-based measurements, doublet peaks can be used to advantage in FIA experiments. As in more conventional peak width measurements, the time interval measured is related to the logarithm of the sample concentration, which results in an expanded working range. Design considerations and experimental applications of the detector will be presented.

1. J. F. Tyson, *Analyst* 1987, **112,** 523–526.

716 FLOW INJECTION ANALYSIS (FIA) METHOD FOR THE DETERMINATION OF ACTIVE PEROXIDES IN CHLOROPRENE MONOMER;

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Peroxides are used as initiators in many chemical processes. Active peroxide concentration thus becomes an important operating consideration and a potential safety problem. A quick and accurate analytical technique can thus be an important tool. Active chloroprene peroxides have been monitored in a polychlorobutadiene process stream by FIA. Polychlorobutadiene is an important synthetic rubber made by polymerizing 2-chloro-1,3-butadiene (chloroprene) monomer. The method measures the active chloroprene peroxides, which correlate to their effect on polymerization reactivity. It is applicable to samples containing from 0–100 ppm peroxide, and is nominally calibrated for 0–15 ppm. The carrier consists of ferrous thiocyanate dissolved in an acetone/water mixture. The organic oxidizes the ferrous ion to ferric ion which reacts with thiocyanate ion to form a red ferric thiocyanate complex. The absorbance of the red complex (in the FIA cell) obeys the Lambert-Beer law and thus is directly proportional to the peroxide concentration. Calibration is performed using hydrogen peroxide standards dissolved in acetone/water. Reagent and sample redox stability are maintained via 1) a helium pressurized, teflon-coated, stainless steel carrier reservoir and 2) an in-line sampler under inert gas. The analysis cycle is automatic to include calibration, analysis and system flush. This maintains analysis precision and accuracy and minimizes any problems with plugging due to polymerizable monomer.

717 COLORIMETRIC FLOW INJECTION METHOD FOR DETERMINATION OF RESIDUAL CHLORINE DIOXIDE.

M. J. Wintjes, M. D. Kester and A. P. Wade, Laboratory for Automated Chemical Analysis, Department of Chemistry, University of British Columbia, 2036 Main Mall, Vancouver, BC, Canada V6T 1Z1.

Recently Cl_2 has been replaced by ClO_2 as the bleaching agent used in some British Columbia pulp mills. This has decreased production of unwanted chlorinated matter to very low levels. Lissamine Green B (LGB), a triphenylmethane dye, is rapidly decolorized (<3 s) by ClO_2 under basic conditions. This recently reported chemistry forms the basis of a sensitive, selective and very rapid inverse colorimetric flow injection method for determination of ClO_2 in basic aqueous solution. The LGB method is more sensitive than direct photometric detection of ClO_2; its extinction coefficient (in its commercial form) is 67200 ± 300 $L.mol^{-1}.cm^{-1}$ (616 nm), whereas that for ClO_2 is only 1244 ± 2 $L.mol^{-1}.cm^{-1}$ (358 nm)—its maximum absorbance at longer wavelength is a further advantage. Method development included characterization of the effects of pH and temperature, and kinetic studies. A calibration curve based on peak height yielded a linear dynamic range of 0.5–26.0 mg/L and a usable range of 0.2–35 mg/L. The precision (%RSD) for a 2 mg/L ClO_2 standard was 4% ($n = 5$), and can be improved further. Beyond 35 mg/L ClO_2 decolorization of the LGB was essentially complete at peak maximum. A curve based on peak width resulted in linear and usable ranges of 4–200 mg/L and 1–235 mg/L respectively. The precision (%RSD) for a 212 mg/L ClO_2 standard was 2% ($n = 5$). The peak width curve was used for $ClO_2 > 26$ mg/L. The maximum sample throughput rate is 200 hr^{-1} for a 70 μl sample. The FIA method developed shows strong potential for on-line and at-line monitoring of ClO_2 in process streams.

718 FIA MONITORING OF THE DEGRADATION OF ORGANIC POLLUTANTS. A. H. Oue, L. E. Bowman and A. P. Wade, Laboratory for Automated Chemical Analysis, Department of Chemistry, University of British Columbia, 2036 Main Mall, Vancouver, B.C., Canada V6T 1Z1.

There is presently high interest in methods which rapidly degrade organic impurities in water to less toxic and/or non-toxic species (ideally, CO_2, H_2O and HCl). Many chlorinated organics can be degraded by heterogeneous photocatalysis using continuously illuminated photoexcitable solid catalysts such as TiO_2. Injection of power ultrasound causes similar reactions, but without the need for additional chemical reagents. Combined irradiation by UV light and power ultrasound further improves efficiency. In this work, we have used flow injection analysis (FIA) and appropriate detectors (chloride ion selective electrode, pH, conductance, UV-visible absorption) to monitor the rate and extent of degradation reactions taking place in a laboratory reactor vessel. This has allowed us to systematically characterize the effectiveness and utility of various catalysts (*e.g.*, anatase TiO_2 powder and glass) and dechlorination/decomposition strategies. The efficiency order for dechlorination of chloroform is found to be UV/TiO_2 + sonication > UV/TiO_2 > UV or sonication. Preliminary studies show porous glassy TiO_2 to be 50% as effective as fine TiO_2 powder, and much easier to handle. Applications include environmental decontamination, drinking water purification, and detoxification of effluent and process streams.

719 A VERSATILE, INTERACTIVE, GRAPHICAL USER INTERFACE FOR SEQUENTIAL INJECTION ANALYSIS AND FLOW INJECTION ANALYSIS. M. D. Kester, I. H. Brock and A. P. Wade, Laboratory for Automated Chemical Analysis, Department of Chemistry, University of British Columbia, 2036 Main Mall, Vancouver, BC, Canada V6T 1Z1.

Microsoft's Windows environment and Intel 80386/80486-based microcomputers are changing the face of laboratory microcomputing. Writing software to take full advantage of multiple movable, resizable windows of information, multiple processes, dynamic data exchange, high-resolution color graphics, pointing devices and sound used to be a task beyond almost all analytical chemists. Now, such programs can be constructed by adventurous instrument designers using Windows-oriented languages such as Microsoft's Visual Basic. In this work we present a versatile, interactive, Graphical User Interface (GUI) for sequential and flow injection analysis. System components are displayed as icons (pump, reaction coil, waste container, reagent bottle, etc). Clicking on the appropriate icon allows the user to view the status and change settings for each component. The windows implemented include system overview (for direct control of system components), strip-chart displays for one or several detector outputs, and control programs for pump(s), stirrers and other devices. Each window has multiple pull-down menus which access linked windows. Version 1.0 of Visual Basic lacks primitive functions (INP, OUT, etc.) needed for instrument control; we have added these via a dynamic-link library of Quick-C routines. For speed and convenience the program runs under Windows 3.0/3.1 on a 33 MHz Intel 80486-based microcomputer equipped with 4 Mb RAM memory, 100 Mb hard drive, and color VGA display.

720 IMPROVED CHROMATOGRAPHIC SELECTIVITY OF STRUCTURALLY SIMILAR STEROIDS VIA LOW TEMPERATURE REVERSED PHASE LIQUID CHROMATOGRAPHY. Karen B. Sentell and Scott T. Shearer, Department of Chemistry, University of Vermont, Burlington, VT 05405-0125.

Temperature is not usually considered to be an effective parameter for maximizing resolution in reversed phase liquid chromatographic (RPLC) systems. However, for very difficult separations subambient temperatures can offer the selectivity necessary to bring about improved chromatographic resolution. The principal application for low temperature RPLC is the separation of solutes with minor structural differences which exhibit similar retention at ambient and higher temperatures. Low temperature RPLC can be utilized for these separations because lower temperatures bring about a more ordered stationary phase structure. An ongoing study in our laboratory is the application of low temperature RPLC for enhanced resolution of pharmaceutical compounds, such as steroids, which are closely related structurally. The two sets of compounds which will be discussed are norethindrone and ethinyl estradiol and cortisone, hydrocortisone and deoxycorticosterone. We will present results obtained using two monomeric C_{18} stationary phases with different alkyl bonding densities (1.5 and 4.4 $\mu mol/m^2$) in conjunction with two hydro-organic (methanol and acetonitrile) mobile phase systems. The contribution of hydrophobic versus silanophilic selectivity in these systems will be compared and discussed.

721 DETERMINATION OF POLYNUCLEO AROMATIC HYDROCARBONS IN MOTOR VEHICLE OIL AND GREASE, AND ENVIRONMENTAL MATRICES BY REVERSED PHASE CHROMATOGRAPHY WITH UV ABSORPTION PHOTOMETRY AND PARTICLE BEAM MASS SPECTROMETRY. In Suk Kim, Fassil I. Sasinos, Raimund Roehl and Robert D. Stephens, Hazardous Materials Laboratory, California Department of Health Services, 2151 Berkeley Way, Berkeley, CA 94704.

Liquid chromatography mass spectrometry (LC-MS) has been used for the analyses of polar, thermally labile and volatile compounds. This method is also useful for non-polar compounds. PAH extracts from motor vehicle oil and grease, soils and air particulate matter are separated by a Vydac C18 column, and detected by UV photometry for quantitation and mass spectrometry for confirmation. PAH sensitivity of the LC-UV is compared with the PAH sensitivity of two different LC-PB-MS instruments. Method detection limits and the spike recoveries of PAHs will be presented.

722 IMPROVED SEPARATIONS OF HETEROCYCLIC NITROGENOUS COMPOUNDS UTILIZING SURFACTANT-BASED RPLC AND CE METHODS. Matthew T. Swartz, Michael C. Danielski and Karen B. Sentell, Department of Chemistry, University of Vermont, Burlington, VT 05405-0125.

Many heterocyclic nitrogenous compounds are of vital interest in pharmacological, clinical and other biochemical studies. These compounds often exhibit ionic and/or polar characteristics that cause their analysis from physiological samples via traditional reversed phase liquid chromatographic (RPLC) methods to be difficult. We have been developing novel separation methods for the determination of heterocyclic nitrogenous compounds in *untreated* physiological fluids utilizing surfactant-containing carrier fluids. These methods include RPLC with sodium dodecyl sulfate (SDS) mobile phases (termed micellar liquid chromatography or MLC) as well as capillary electrophoresis with buffer solutions containing SDS (termed micellar electrokinetic capillary chromatography or MECC). The RPLC stationary phases examined include C_8, cyano and phenyl. Solutes of interest include purine and pyrimidine-derived compounds and also nicotine and its metabolites. The effects of pH and SDS concentration on the retention of these compounds is being investigated. We have found that pH effects solute interactions with the surfactant modified stationary phase as well as interactions with micellar assemblies in the mobile phase. We will present our results on these promising methodologies and compare and contrast MLC chromatographic retention behavior to MECC migration behavior displayed by these compounds. We will also discuss our promising results for the analysis of nicotine and cotinine via direct injection of untreated physiological fluids.

723 GPC CLEANUP OF OILY SAMPLES: REMOVAL OF ALIPHATIC INTERFERANTS DURING SEMIVOLATILE ORGANICS ANALYSIS. Nancy S. Henegar, Evelyn E. Conrad and Kevin P. Kelly, Ph.D., Oruada U. Ukoha, ABC Laboratories, Incorporated, P.O. Box 1097, Columbia, MO 65205.

Environmental samples may contain hydrocarbons derived from fuel spillage, lubricants, paint vehicles, etcetera. Aliphatic interferants reduce the quality of trace organic analysis by masking target compounds. Currently used adsorption cleanups (e.g., SW-846, method 3611) that remove aliphatic interference are tedious. This study presents separations of aliphatic hydrocarbons from semivolatile analytes using high efficiency GPC columns. Theoretically, separation of a mixture by GPC is based solely upon a size exclusion mechanism; however, affinity chromatography may also take place. This is certainly true for solutes (e.g. aromatic compounds) containing electronic structures that are capable of attractive interaction with a GPC stationary phase. The ability to adjust elution profiles using this behavior produces more effective elimination of hydrocarbon interferants. Affinity characteristics (and therefore elution profiles) of aromatic systems are manipulated primarily through the variation of mobile phase components providing differing degrees of affinity suppression/allowance. In contrast, elution of non-aromatic sample components is controlled solely through size exclusion. This principle can be employed to enhance exclusion of aliphatic interferants from sample extracts containing trace level target analytes. Using mobile phase mixtures of cyclopentane with methylene chloride or with ethyl acetate, excellent cleanup of oily waste samples were obtained, with good recoveries of spiked analytes.

724 DETERMINATION OF COCAINE AND BENZOYLECGONINE IN HUMAN SERUM USING CAPILLARY ELECTROPHORESIS.

Hong Chen, Michael P. C. Ip and Yan Xu, Department of Chemistry, Cleveland State University, Eucild Avenue at East 24th, Cleveland, OH 44115.

A capillary electrophoresis method for the determination of cocaine and its metabolite, benzoylecgonine, in human urine sample will be presented. The study includes the optimization of separation conditions (e.g., applied voltages, buffers and additives, pHs and ionic strengths, temperature, column lengths, and column diameters), the pretreatment of urine samples, and the recovery of cocaine and benzoylecgonine in urine matrix, as well as, the comparison data from the current clinically used method.

725 ENANTIOMERIC QUANTITATION WITHOUT SEPARATION OF TRAMADOL INTERMEDIATES VIA LASER-BASED POLARIMETRY.

Thomas J. Edkins, Michael Fronheiser, and Thom Rossi, Analytical Research and Development, The R. W. Johnson Pharmaceutical Research Institute, Welsh and McKean Roads, Spring House, PA 19477-0776. Donald R. Bobbitt, Dept. of Chemistry and Biochemistry, University of Arkansas, Fayetteville, AK 72701. John E. Mills, Chemical Development, The R. W. Johnson Pharmaceutical Research Institute, Welsh and McKean Roads, Spring House, PA 19477-0776.

Tramadol hydrochloride is an analgesic which is marketed as a racemic compound of a cis isomer. While the current HPLC enantiomeric separation adequately resolves the enantiomers of this isomer, it can not also resolve those of a process impurity (trans isomer). This presentation will focus on using enantiomeric quantitation without separation for solving this analytical problem. Currently a detection limit of ca. 1.5% enantiomeric enrichment (ee) for the cis isomer is achievable. Detectability improves by an order of magnitude when quantitating pure enantiomer alone (0.16% relative to the mass injected for the standard). Preliminary results indicate that a limitation in the ee case may be caused by refractive index effects in the polarimetric detection cell during quantitation. The validity of this hypothesis will be discussed by studying the relationship between mass injected and detectability for standards of low ee (0–10%). A comparison will be shown between results obtained using quantitation without separation and with the enantioselective separation. Data acquired with laser-based polarimetry and heat of fusion experiments will provide evidence that all of the intermediates in the tramadol synthesis are racemates.

726 IMPROVED HPLC/POST-COLUMN TECHNIQUES FOR RUGGED CARBAMATE AND GLYPHOSATE ANALYSIS.

Michael W. Dong and Joseph DiBussolo, The Perkin-Elmer Corporation, 761 Main Avenue, Norwalk, CT 06859-0250.

This paper provides an overview of the fundamental concepts of post-column derivatization techniques used in EPA Methods 531.1 (carbamates) and Method 547 (glyphosate). Problem areas for their practical implementation are described. Specific solutions leading to a more reliable analysis are discussed. For carbamate analysis, which utilizes a 0.05 N sodium hydroxide hydrolysis reagent, the prevention of backflow of this reagent into the silica-based analytical column is critical. For glyphosate analysis, the replacement of the calcium hypochlorite oxidant with sodium hypochlorite eliminates reactor blockage problems. Also, the regeneration of the cation exchange column after each analysis with 5 mM potassium hydroxide is necessary to maintain retention time reproducibility. The incorporation of several post-column pressure monitoring points and pressure relief valves in the system significantly enhances system reliability. The use of borate salts which contain high levels of insoluble matter, should be avoided in preparing the OPA buffer.

727 PHOTODIODE ARRAY DETECTION FOR QUALITY CONTROL IN PETROCHEMICAL ANALYSIS.

Kathleen M. Gorski, Timothy J. Stanton and George E. Barringer, Groton Technology, 45 Winthrop St., Concord, MA 01742.

Successful industrial quality control methods must provide the capability to reliably discriminate differences in complex mixtures that comprise the usual process flow stream. The differences may be subtle but the economic impact can be major. The successful method must be robust and sensitive. The petrochemical industry provides an excellent example of the need for a fast, reliable, automated system for quality control. Chromatographic analysis to resolve and identify the individual components of typical petrochemical flow streams is time consuming and error prone. On-line chromatographic methods require complex instrumentation and interfaces. On the other hand, photodiode array spectroscopy in conjunction with digital hardware and software signal processing yields a robust, simple solution for on-line, high speed measurements of flow streams typical in the petrochemical industry. When applied to flow analysis, photodiode array detection provides composite spectral data sets amenable to automated library search routines for the purpose of comparison and identification. A brief description of the data treatment will be presented along with practical application results. Pairs of complex petrochemical mixtures have been analyzed by using the diode array detector in conjunction with chromatographic separation and in "stand-alone" mode to illustrate the ability of this on-line scheme to identify and match complex samples to standard library entries under conditions typical in the process industry.

728 DETERMINATION OF COPPER SPECIATION IN A HYDROCARBON MATRIX BY HPLC.

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A method is described that allows one to distinguish and quantitate two different classes of copper compounds in the same hydrocarbon sample. This will enable the study of the affects of different copper compounds on the performance and stability of petroleum samples. Copper N,N′-disalicyliden-1,2-propylenediamine (CuDMD) and copper carboxylates (CuCarbs) were preconcentrated from a hydrocarbon matrix using a column packed with polyvinylpyrrolidone, $(C_6H_9NO)_x$, a novel polymeric stationary phase. The copper complexes were then sequentially eluted using a step gradient program beginning with hexane/isopropyl alcohol as the eluent and ending with an acetic acidic/isopropyl alcohol eluent. The copper complexes were detected by serial UV absorbance and flame atomic absorbance (FAA) detection. With on-column preconcentration and FAA detection, the limits of detection were 7 and 40 ppb copper for CuDMD and the CuCarbs, respectively. With this method, it was possible to distinguish between the two different classes of copper compounds in the same hydrocarbon sample, which will help to provide an understanding of the catalytic activity of different copper compounds, leading to a better understanding of the factors causing fuel instability. The method promises to be a valuable tool in the analysis and characterization of copper compounds in petroleum samples.

729 FUNDAMENTAL AND PRACTICAL ASPECTS OF HPLC METHODS VALIDATION.

Michael W. Dong and Joseph DiBussolo, The Perkin-Elmer Corporation, 761 Main Avenue, Norwalk, CT 06859-0250.

This paper reviews the fundamental and practical aspects for validating HPLC methods. Controlling factors for HPLC accuracy, precision, sensitivity, linearity, ruggedness and selectivity are discussed. Practical guidelines for improving LC method precision and ruggedness are described. Factors controlling retention time precision including pump flow, column temperature and mobile phase degassing are delineated. The sampling precision of the autosampler and injection volume are found to predominate over the repeatability of peak area with integration parameters becoming more important under low signal-to-noise conditions. HPLC method ruggedness is controlled by instrumental factors (pump flow and composition calibration, detector stability and wavelength resettability), column stability and batch-to-batch reproducibility, and the ruggedness/reproducibility of mobile phase composition.

730 THE DEVELOPMENT OF A UNIVERSAL SPRAY CHAMBER DESIGN FOR FLAME ATOMIC ABSORPTION SPECTROMETRY (FAAS).

Douglas E. Shrader, Christine Flajnik, J. Moffett and H. Howarth, Varian, 201 Hansen Court, Suite 108, Wood Dale, IL 60191.

The atomization system, spray chamber, nebulizer and burner is significant in determining the performance of a flame atomic absorption spectrometer and previous work has established optimized designs for these system components. Traditionally, FAAS spray chambers are manufactured from plastic. Polypropylene has been a frequently used material as it resists attack from both acid and alkali solutions as well as organic solvents. However, polypropylene can absorb organic solvents, resulting in swelling of critical spray chamber components. The aim of this work was to develop and characterize a spray chamber material which could be used for both aqueous and organic solvents while retaining the performance benefits of an optimized design. A universal spray chamber material was sought which is resistant to both acids and organic and relatively cheap and easy to manufacture. A unique polymeric material was identified and, when permanently chemically treated, resulted in a material with the required resistance properties at an acceptable cost. Results are presented proving the performance benefits of the new design applied to the analysis of organic solvents and aqueous samples. The resistance to swelling of the polymer is established with practical examples provided from the determination of wear metals in oil samples from heavy machinery.

731 MULTIELEMENT ATOMIC ABSORPTION SPECTROMETRY. Joseph Sneddon, Kim S. Farah and Peter R. Pascucci, Department of Chemistry, University of Massachusetts, Lowell, MA 01854.

The development of multielement atomic absorption spectrometry from multielement hollow cathode lamps, through continumm source, laser based systems and multichannel systems will be described. The major focus in the presentation will be a discussion on a system based on one photomultiplier tube which uses a galvanometer driven grating in its monochromator. This mechanism allows the instrument to scan several wavelengths in a short time. The full spectrum can be scanned in 20 µs. This, coupled with the galvanometer driven mirror to select lamps, allows for multielement and multiwavelength analysis when a single sample is introduced into the atomizer. The use and application of this simultaneous system will be described. In particular the optimization of parameters for flame and furnace determination of four metals simultaneously. The results of the system applied to environmental samples will be further presented.

732 MULTI-ELEMENT DETERMINATIONS BY CONTINUOUS FLOW HYDRIDE GENERATION. G. R. Dulude, S. Karpova and D. O. Pfeil, Thermo Jarrell Ash Corporation, 8E Forge Parkway, Franklin, MA 02038.

This work describes the application of a multi-element atomic absorption spectrometer to the simultaneous determination of certain metalloids using the hydride generation technique. The AA employed was a Smith-Hieftje 8000 and employs rapidly moving galvanometers to attain time-shared measurements of each of four elements. The automated AVA 880 hydride generator was used as an accessory to the AA and is a continuous flow system. It utilizes a peristaltic pump to combine sample with acid and reducing agent in line. Reduced sample is mixed in line with inert gas and emptied into a gas liquid separator where solution is allowed to drain and the hydride vapors are purged into a flame heated absorption cell. Optimum conditions where determined for arsenic by varying cell type, reducing agent strength, and pre-reducing agent concentrations. These optimized conditions were then applied to the simultaneous determination of arsenic and antimony. Best results were obtained using an open-ended quartz cell, 0.3% sodium borohydride, and 0.5 potassium iodide as the pre-reducing agent. Experimental results will be presented.

733 A STUDY OF THE CHEMISTRY OF NATURAL SURFACE WATER OF THE HOPI INDIAN RESERVATION. Matthew T. Bell, Jr. and Richard D. Foust, Jr., Chemistry Department, Northern Arizona University, Flagstaff, AZ 86011-5698.

The isolated springs on the Hopi Indian Reservation were sampled quarterly and analyzed for macrochemical (Ca, Mg, Na, K, HCO_3^-, Cl^-, SO_4^{2-}, NO^{-3} and PO_4^{3-}) and microchemical constituents (Al, As, Cu, Fe, Hg, Pb, Se and Zn). Atomic spectroscopy (FAAS, ETAAS and ICP) was used to determine metal concentrations and ion chromatography was used to measure anions. The high levels of sulfate, carbonate, calcium, magnesium and dissolved solids in these water samples required special cleanup procedures to eliminate the many interferences known to be present when complex matrix samples are analyzed spectrochemically. Ion chromatography sample pre-treatment has been shown to yield the best data with the least amount of sample preparation time. The generalization of an ion chromatography cleanup procedure to other samples with complex matrix problems will be discussed.

734 REAL TIME INTERNAL STANDARDIZATION FOR TRACE AND MAJOR ELEMENTAL DETERMINATION IN LUBRICATING OIL BY ICP-AES. Sue F. Franz and Daniel P. Anderson, Malte X. Lukas Spectro Incorporated, 160 Ayer Road, Littleton, MA 01460.

More skill and care are required for the analysis of lubricating oils by ICP-AES to obtain similar levels of precision as are routine for aqueous samples because oil samples have complex matrices, differences in viscosity from samples to standards, and high concentrations of additive elements. In this work, real time intensity ratios of analytes to an internal standard were measured to improve short and long term precision compared to measuring only the raw intensities of the analytes. Results with and without internal standards are compared. Various internal standard elements were tested to find the most suitable internal standard. Results show that Sc is the most appropriate internal standard for oil analysis because Sc is not normally present in either new or used lubricating oil samples and it is free of spectral interferences on the commonly measured elements in lubricating oil samples. Other factors for oil analysis compared to aqueous analysis are also discussed.

735 SPECTRAL INTERFERENCE CORRECTION FACTOR INSTABILITIES IN ICP-OES. Edgar F. Paski, Bondar-Clegg & Company Ltd., 130 Pemberton Ave. North Vancouver, B.C., Canada V7P 2R5.

When complex substances such as hazardous waste and geological materials are analyzed by ICP-OES, the accuracy, precision, and detection limits attainable are governed by stability of the spectral interference correction (IEC) factors applied and the concentrations of interferents present in the sample solution. The effects of minor changes in polychromator optical center position on the IEC factors for some 35 analytical lines was investigated. Results from Paschen-Runge and echelle polychromator systems will be compared and contrasted. In unfavorable situations, the IEC factor underwent up to a threefold change when the polychromator optical center position is varied within a window of +/− 0.5 spectrum shifter or aperture plate movement positions from peak center. Examples of complex IEC factor changes within this window when background correction is applied will be shown. Relationships between line separation, background correction point, instrument resolution, and spectral interference correction factor change will be presented.

736 AN INTELLIGENT SYSTEM FOR AUTOMATION OF QUALITY ASSURANCE AND CONTROL PROCEDURES IN GRAPHITE FURNACE ATOMIC ABSORPTION SPECTROMETRY (GFAAS). Fred Delles and Michael Knowles, Varian, 201 Hansen Court, Suite 108, Wood Dale, IL 60191.

Laboratories participating in the United States Environmental Protection Agency (US EPA) contract laboratory program (CLP) are required to follow stringent quality assurance and control procedures to validate analytical data. The complexity of these procedures requires the analysis of a large number of test solutions, restricts the number of sample determinations and requires close monitoring to ensure compliance. The aim of this work was to develop a system for the automation of US EPA CLP requirements for the analysis of waste waters by atomic absorption spectrometry. This requires the development of a system which can automatically analyze data and take the required corrective action in accordance with US EPA requirements. Software approaches to this problem are described which address the challenge of accommodating both random and regular (sample frequency based) tests. The development of an intelligent system for regular and automatic updating of statistical control limits is described, applied to analytical spike recoveries. Application of the system is demonstrated for the determination of target elements in waste waters.

737 EXAMINING COMPLEX THERMAL DECOMPOSITION PRODUCTS USING TG-GC-IR. Silvio C. Pattacini, Brian J. McGrattan and Gregory L. McClure, The Perkin-Elmer Corporation, 761 Main Avenue, Norwalk, CT 06859.

Thermogravimetry coupled with infrared spectroscopy allows the identification of gases evolved during a thermal decomposition, and can help deduce the decomposition mechanism. Often, the decomposition is complex and gives a mixture of gases nearly simultaneously. For example, during the decomposition of aspartame, methanol and ammonia are evolved early and can be easily identified, but the high temperature destruction of the molecule produces toluene, ethylbenzene and succinimide simultaneously, resulting in a complex infrared spectrum of the mixture. Coupling the effluents of thermal gravimetry to GC-IR enables the resolution and identification of these products. This paper will discuss the TG-GC-IR technique with this and other examples.

738 MEASUREMENT OF FERROCYANIDES AND OXYANIONS IN WASTE SLUDGES BY FOURIER TRANSFORM INFRARED REFLECTION METHODS. T. V. Rebagay, D. A. Dodd and D. W. Jeppson, Westinghouse Hanford Company, Richland, WA 99352.

Irradiated nuclear fuels were reprocessed at the Hanford Site near Richland, Washington to recover special nuclear materials for the nation's defense programs. The wastes from reprocessing are stored temporarily in carbon steel tanks. The management of these wastes has become a major concern, particularly the potential for the release of radionuclides to the environment. To aid in the resolution of tank wastes safety issues, Fourier transform infrared reflection methods were investigated to detect and quantify tank waste components. Surrogate waste sludges with compositions very similar to some of the tanks actual waste sludges were prepared. These sludges were dried, pulverized, and examined for the presence of ferrocyanides, nitrates, sulfates, and phosphates using diffuse reflectance (DR) and attenuated total reflectance (ATR) cells interfaced to a Fourier transform infrared spectrometry system. Spectra were collected in the mid-infrared region and analyzed using a sequential spectral subtraction technique. The results showed very good agreement of the DR and ATR values. The applicability of these methods to analyze actual radioactive wastes is discussed.

739 ANALYSIS OF OUTGASING IN HIGH TEMPERATURE COMPOSITE AND CERAMIC MATERIALS BY TGA-FTIR.

Dean E. Roberts, Mattson Instruments, Inc., 1001 Fourier Drive, Madison, WI 53717.

Outgasing of toxic substances from high-tech composites and ceramics poses both a health risk for employees, and liability for manufacturers. TGA-FTIR provides a means of quantitation and identification of substances which are present in the materials. Of additional interest is the ability to duplicate actual process conditions used in the factory with the TGA. This allows the analyst to determine which compounds are generated by chemical reactions with the material, in addition to those components which are present in the materials.

740 AIR-BORNE ASBESTOS ANALYSIS USING DIFFUSE REFLECTION INFRARED SPECTROSCOPY.

Patricia L. Lang and Vir-Vir Chu, Department of Chemistry, Ball State University, Muncie, IN 47306. David W. Schiering, Perkin-Elmer Corp., 761 Main Ave., Norwalk, CT 06859-0204.

An infrared spectroscopic method has been developed for quantitation of air-borne asbestos. The method involves ashing away the cellulose filters on which the asbestos is collected, recovering the asbestos with salt, and obtaining an infrared diffuse reflection spectrum of the asbestos-salt mixture. Detection limits for amosite and chrysotile for this method are about 1 μg and 5 μg, respectively. In addition, the identification and quantitation of mixtures of chrysotile and amosite have been evaluated both in the presence and absence of significant amounts of kaolin, a common silicate associated with asbestos samples.

741 APPLICATION OF FTIR FOR CERTIFICATION OF HIGH ACCURACY CALIBRATION GASES.

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High accuracy, multicomponent calibration standards are widely used in industry. The analysis and certification of these mixtures are often tedious and time-consuming requiring the use of gas chromatography and multiple individual component sensors such as chemiluminescence and NDIR. This paper discusses the use of fourier transform infrared spectroscopy, FTIR, for fast, simultaneous analysis of multiple components in gas mixtures containing EPA criteria pollutants (e.g., CO, SO_2, NO) with a targeted analytical uncertainty of ±1% relative. The accuracy and precision of FTIR are compared to the above mentioned techniques. Approaches for addressing dynamic range, calibration stability and linearity issues are discussed. An automated FTIR system implemented in a production laboratory for the analysis of EPA protocol samples is also described.

742 THE USE OF TGA-FTIR TECHNIQUES AS A DEVELOPMENT TOOL IN EVALUATIONS OF CURING OF PHENOLIC RESINS.

J. C. Bowman and F. J. Weesner, Nicolet Instrument Corporation, Spectroscopy Research Center, 5225 Verona Road, Madison, WI 53711.

It has become increasingly important for many urea—formaldehyde resin laboratories and producers/manufacturers to begin developing quantitative methods for monitoring volatile organics. TGA-FTIR is a hyphenated technique that can be used as a method development tool for the analysis of urea, formaldehyde and phenolic resins. The evolved gases from two different resins will be analyzed by TGA-FTIR. We will also study the evolved gases from cured resin decompositions.

743 INFRARED INVESTIGATION OF MATERIALS FOR EYE IMPLANTS.

N. I. Afanasieva, E. G. Brame, A. R. Koriodsky, O. V. Arinushkina and V. V. Kireev, The CECON GROUP, Inc., 242 N. James Street, Wilmington, DE 19804. Institute of Spectroscopy, Institute of Eye Microsurgery, and Moscow Chemical Technology Institute of Russia.

Results of a systematic spectral study of polymers that are used in opthalmology are presented. The spectral criteria for selection of intraocular lens (IOL) implants of long service in an organism are defined. Since non-inflammatory implantation of IOL is critical, both new siloxane-polyurethane block copolymers and poly(methylphenylsiloxane) materials show promise. Infrared analyses will be discussed in terms of these different polymers that are now finding use.

744 SPECTROSCOPY OF REACTIONS IN SUPERCRITICAL WATER.

T. B. Brill, M. Kieke and J. Schoppelrei, Department of Chemistry and Biochemistry, University of Delaware, Newark, DE 19716.

Supercritical water (SCW) is an attractive medium for destroying especially hazardous and toxic organic chemical wastes. A combination of hydrolysis-thermolysis chemistry occurs leading to stable products, such as CO_2, N_2, Cl^-, SO_4^{2-}, etc., in a closed system. However, the safety and efficiency of the process demand that details of the chemistry be known inside the reactor. This is especially true if very hazardous or toxic materials, such as explosives or chemical agents, are being destroyed. FTIR and FT-Raman spectroscopy are excellent techniques for following reactants, intermediates, and products in time in this medium. However, SCW attacks most metals and IR-transparent materials. This fact combined with the high pressures and temperatures involved makes "clean" experiments very difficult to make. The special considerations of cell design, process design, and data analysis will be presented.

745 ESTIMATION OF GLOBULAR PROTEIN SECONDARY STRUCTURE BY SOLVENT-ELIMINATION MAGIC/FT-IR SPECTROMETRY.

Vincent E. Turula Jr. and James A. de Haseth, Department of Chemistry, University of Georgia, Athens, GA 30602-2556. Richard F. Browner, School of Chemistry, Georgia Institute of Technology, Atlanta, GA 30332.

A procedure has been developed that allows the estimation of protein secondary structure composition by Fourier transform infrared (FT-IR) spectrometry without the presence of water (H_2O or D_2O) absorptions in the measured spectra. This approach has utilized the desolvating capabilities of the MAGIC/FT-IR interface to remove the *"masking"* effect of water in the conformational sensitive Amide I region. MAGIC is an aerosol particle beam apparatus originally developed as a HPLC interface for Mass Spectrometry and Infrared Spectrometry, that eliminates the solvent from the analyte molecules by evaporation. In this study several globular proteins, as well as some amino acid residues, were isolated from water by MAGIC, and analyzed by FT-IR spectrometry. Individual amino acid residues were analyzed so their contribution to the protein spectra could be estimated. During the solvent elimination process, aqueous protein particles produced by the aerosol generator cool as the water evaporates. Towards the later stages of the desolvation process, the temperature of the particles drops further eventually causing the small amount of residual water, trapped with the protein, to freeze producing a frozen protein/water *"comet"*. The frozen beam of particles then impacts onto an IR transparent substrate which is later removed from the interface and placed into an off-line FT-IR/microscope for measurement of the spectrum. The residual water, keeping the protein solvated, contributed insignificantly to the spectrum. Since there was no heat added to assist desolvation, the structural integrity of the protein was maintained during solvent removal process. Once a spectrum was obtained, several computational methods such as Fourier-self deconvolution, resolution enhancement, and curve-fitting were employed to estimate the structure. Comparisons with literature determinations were made.

746 EFFECT OF SURFACTANT IN POLYURETHANE FOAMS MONITORED BY MID-INFRARED FIBER FOURIER TRANSFORM SPECTROMETRY.

Joel A. Caughran, William M. McClarin, Melissa C. Berry, Karen Braden and James A. de Haseth, Department of Chemistry, University of Georgia, Athens, GA 30602-2556.

The role of surfactants in the production of water slab stock polyurethane foams is not well understood. In order to study the role of the surfactant, most commonly a silicone surfactant, a large number of foams of different formulation were produced. From the formulations, those suitable for the production of stable foams were determined, and the characteristics of the cured foams were recorded. Physical characteristics, such as cell size, density, and initial growth, were considered. Spectra of the cured foams were recorded by attenuated total reflectance (ATR) Fourier transform infrared spectrometry. Correlations were then performed between the spectra and the qualitative properties such as breathability, compressibility and the extent of the open cells. These results were correlated back to the actual formulations. Selected stable foams were monitored with the use of mid-infrared fiber probes. Particular attention was paid to the reaction kinetics and the morphology changes in the foams. The results of this study were used to determine the exact role of the surfactant in the production of these materials.

747 A STUDY OF SOLUTE INFLUENCE ON THE BINDING OF METALS TO *STICHOCOCCUS BACILLARIS* WITH ^{113}Cd NMR. Weixing Zhang and Vahid Majidi, Department of Chemistry, University of Kentucky, Lexington, KY 40506.

Many studies have been directed toward the application of algae for its binding properties, such as the use of algae as an analytical tool for preconcentration of trace elements for quantitative analysis, as a potential tool for the removal of toxic metals from water and for the recovery of precious elements from industrial wastewater or natural water. Despite extensive research, the interactions between the algae and metals are not fully understood. In this work, the interaction between an unialgal culture (*S. bacillaris*) and cadmium, in presence of several different solutes, was investigated by ^{113}Cd NMR. Upon addition of different solutes into the solution, either the cadmium in the Cd-algae biomass was removed or its chemical shift was changed. In acetic acid and sodium acetate buffer solutions ($pH \approx 5.3$), both the cadmium acetate and the Cd-algae biomass have similar chemical shifts, suggesting that the chemical environments are nearly the same for both types of cadmium. This chemical shift similarity indicates that the functional group on the cell wall of *S. bacillaris* is most likely carboxylic in nature.

748 AUTOMATED ANALYSIS OF POTENTIAL AGRICULTURAL CHEMICALS USING FLOW INJECTION THERMOSPRAY MASS SPECTROMETRY. *Mark J. Hayward, Joseph T. Snodgrass and Michael L. Thomson, American Cyanamid Company—Agricultural Research Division, P.O. Box 400, Princeton, NJ 08543.

Flow injection Thermospray (TSP) mass spectrometry (MS) has been developed and utilized for molecular weight and structural confirmation for thousands of potential new agricultural chemicals. Initially, it was necessary to find a set of TSP conditions which provide an optimal compromise between delivering reproducible, informative mass spectra and being sufficiently universal and rugged for a wide variety of compound types. Two sets of TSP conditions which are used to obtain both positive and negative ion spectra have been found which work extremely well. As a result, flow injection TSP-MS now provides the required information in approximately 70% of the mass spectrometric structural confirmations performed at the Agricultural Research Division of American Cyanamid. The high degree of success using flow injection TSP-MS has led to the development of instrumentation to fully automate these analyses. An IBM PC/AT compatible computer is used to control sample delivery, data acquisition and data output. The PC performs the functions of both terminal and operator for a Finnigan TSQ 46 triple quadrupole mass spectrometer and its Data General Nova 4X data system, while simultaneously controlling a Micromeritics 725 (Alcott) autosampler and its Reodyne 8126 pneumatically actuated 6 port sampling valve. Furthermore, the need to document analyses in a manner that is consistent with Good Laboratory Practices (GLP) has led to automated documentation for the instrument analysis log, as well as for the headers of the electronic data files and the printed spectra output. The new automated flow injection TSP-MS system described here has improved the efficiency of mass spectrometric operations at the Agricultural Research Division by reducing the instrument time required to record spectra and minimizing the required analyst intervention.

749 ION MOBILITY DETECTOR FOR CHROMATOGRAPHY. F. E. (Frank) Bales, Pylon Electronics Inc., 147 Colonnade Road, Ottawa, Ontario, Canada K2E 7L9.

Recent advances in ion mobility technology as applied to detection for GC applications are presented. Chromatograms and analysis of chromatographic results demonstrate the sub pico mole sensitivity and linear dynamic range of over a hundred obtained as a GC detector. The detector has been configured specifically as a GC detector. Both the hardware and software have been optimized for this purpose. Developments described include compatibility with standard GC's, improved gas integrity, increased temperature of operation and bakeout, optimized control of the accelerating voltages within the tube, and specialized software. How these improve the utility of the ion mobility detector is emphasized. Further application and operational considerations will be described, including how peaks in the ion mobility scan may be simultaneously tracked and integrated under the control of user-defined methods.

750 RESONANCE RAMAN EXCITED (200–257 nm) SPECTRA OF BACTERIA. S. Chadha, R. Manoharan, P. Moenne-Loccoz, W. H. Nelson, W. L. Peticolas and J. F. Sperry, University of Rhode Island, Chemistry Department, Kingston, RI 02881.

UV resonance Raman spectra have been excited over the range 200–257 nm. Results emphasize 200, 218 and 257 nm. Spectra excited at 200 nm reflect both protein and nucleic acid components. At 218 nm spectra consist of protein peaks primarily with evidence for ribosomal RNA. At 257 nm bacteria have been studied at low CW power by means of a micro Raman spectrograph which demonstrates single-cell sensitivity. 257 nm spectra reflect nucleic acid contributions primarily. Bacterial identification is possible from either nucleic acid or protein peaks.

751 ANALYTICAL SPECTROSCOPY AND STRUCTURE OF SMALL BIOMOLECULES USING AN *AB INITIO* COMPUTATIONAL METHOD. Y. Choi and D. M. Lubman,* Department of Chemistry, University of Michigan, Ann Arbor, MI 48109.

The derivatives of phenyl and catechol compounds are studied extensively due to their potent biological activity and pharmaceutical importance. Although these biomolecules have been studied by a variety of spectroscopic techniques, any particular spectroscopic method can provide only a limited amount of information and their experimental spectra may not be easily interpretable by themselves. Consequently, there has been a motivation toward developing computational methods that can be used to predict *a priori* a broad range of spectroscopic properties. However, it is only recently that application of *ab initio* computational methods to these biomolecules have become feasible due to easier access to fast computers and development of more efficient computational algorithms. In the present study, an *ab initio* method is applied to the study of phenethylamine and substituted phenethylamines to predict the geometries of stable conformers and their spectroscopic properties. The structure of these molecules are optimized and their stabilities are determined by performing vibrational frequency calculations on the optimized structure. Three stable conformers are found for phenethylamine of which two have an ethylamine-folded structure and the other has an ethylamine-extended structure. The *ab initio* results are compared with experiments and other theoretical studies by semiempirical methods. In addition, predictions of vibrational spectra ionization potentials and electron affinities, and the electronic charge densities of these molecules are discussed.

752 *AB INITIO* APPROACH TO UNCOVER TRYPTAMINE CONFORMERS OBSERVED IN 1C-R2PI SPECTRUM. T. Barstis, L. Grace, T. M. Dunn and D. Lubman, University of Michigan, Department of Chemistry, 930 North University, Ann Arbor, MI 48109.

The jet-cooled one color (1C) resonant two-photon ionization (R2PI) spectrum of tryptamine has been obtained. Within the first 200cm^{-1} of the excitation spectrum, several vibronic origins have been observed. These vibronic origins can be attributed to different conformers of tryptamine. A theoretical approach was employed to uncover the possible conformers. By performing ab initio calculations, four stable conformers of tryptamine were revealed. The structure of these conformers along with a tentative vibronic analysis of the 1C-R2PI spectrum will be presented. The vibronic analysis of tryptamine was based on the vibronic analysis of indole and ground state fundamental mode assignments of tryptamine. The fundamental vibrational modes of tryptamine were assigned through the aid of an ab initio frequency calculation and were based on the fundamental vibrational mode assignments of indole.

753 ELECTROCHEMICAL DETERMINATION OF TOTAL DISSOLVED ALUMINUM IN HEMODIALYSIS WATER AFTER MICROWAVE DECOMPOSITION. Jorge E. Taha´n and Romer A. Romero*, Laboratorio de Instrumentacio´n Analitica Universidad del Zulia. Venezuela.

The electrochemical evaluation of the total dissolved aluminum content in hemodialysis water samples requires the quantitative generation of electrolabile aluminum species. A microwave-based mineralization procedure was developed to eliminate the organic matter content present in the hemodialysis water to permit the subsequent electrochemical determination of total dissolved aluminum by differential pulse polarography (DPP). Hemodialysis water test portions (5 mL) were digested with 5 mL concentrated nitric acid and 2 mL of hydrogen peroxide (30% v/v), during seven 5-min microwave irradiation periods at 100% of power. The quantitative electrochemistry of aluminum was achieved by the metal complexation with the azo ligand solochrome violet RS, reducing at −0.60 V vs Ag/AgCl. Accuracy of the microwave decomposition procedure was evaluated by comparison with results provided by the graphite furnace atomic absorption spectrometric (GFAAS) technique. The correlation was excellent: DPP = 0.924 GFAAS − 1.08, $r = 0.983$, $p < 0.001$. The detection limit was 6 µg/L. It is concluded that the quantification of metals in high organic matter content samples depends upon the ability of producing, by oxidative means, a sole electrolabile species of the analyte under study.

*Conicit F-142

754 ANODIC STRIPPING VOLTAMMETRY OF BLOOD PLASMA COPPER.

Jorge E. Taha'n and Romer A. Romero*, Laboratorio de Instrumentacio'n Analitica Universidad del Zulia, Venezuela.

This work describes the application of the differential pulse anodic stripping voltammetric (DPASV) technique to the evaluation of the total copper content present in blood plasma samples from patients with chronic renal failure (CRF) and control individuals. The plasma copper electrolabile species was produced by microwave mineralization of the organic interferences. In this sense, 1 mL of blood plasma was digested with 5 mL concentrated nitric acid during seven 5-min microwave irradiation periods. A 2-mL aliquot from the first digestion was subsequently mineralized with 5 mL of perchloric acid. Plasma copper determined by DPASV was compared with data obtained by graphite furnace atomic absorption spectrometry (GFAAS). The correlation between the two methods was excellent: DPP = 0.985 GFAAS − 2.919, $r = 0.998$, $p < 0.001$. The detection limit of the electrochemical method was 0.2 µg Cu/L. Mean concentrations (± one standard deviation) of 1168 ± 119 and 760 ± 33 µg Cu/L were found for CRF patients and controls, respectively. The proposed DPASV-based method was a reliable analytical alternative for the quantification of copper in medical materials.

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755 ANALYSIS OF ELECTRIC ARC FURNACE DUST USING SPECTRASOL REAGENTS.

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Laclede Steel Company is commissioning a heat thermal metal recovery facility to process electric arc furnace dust. This requires monitoring the dust for Al, Ca, Cd, Cr, Cu, Fe, K, Mg, Na, Pb, Si and Zn levels. Dust samples are prepared using HF and closed vessel microwave digestion apparatus prior to ICP analysis. We wanted to use all glass ICP transport apparatus for the dust digests and other routine samples. We did not want to complex the HF with boric acid to avoid nebulizer clogging or having to use HF resistant transport apparatus. Therefore, we evaluated the spectrasol coal fly ash (CFA) reagents for the preparation and ICP analysis of the dust samples. The spectrasol reagents are designed to completely deactivate free fluoride using a mixture of water soluble tertiary amines which do not add solids to the digests and allows the use of all glass ICP transport apparatus with concentric nebulizers. The evaluation, using eurostandards 876-1 and 877-1, showed recoveries of greater than 95% for all elements when compared to certified values. Details on the microwave digestion conditions, analytical data and ICP programs used will be shown and discussed.

756 FORENSIC COMPARISON OF HOUSEHOLD ALUMINUM FOILS USING ICP-AES.

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Inductively coupled plasma-atomic emission spectrometry (ICP-AES) provides the precision, sensitivity, and specificity for element concentration determinations required for good discrimination among sources of household aluminum foil. The concentrations of Cu, Fe, Ga, Mg, Mn, Ti, V, and Zn were determined in aluminum foil by ICP-AES with relative precisions (r.s.d.) in the 1 to 2 percent range and Ni and Si with relative precisions of about 5 percent. For these 10 elements, the combined analytical uncertainties and variations along the length of a single roll of foil are much smaller than the variations from roll to roll, both within a single brand and across brands. The aluminum foils in this study, exhibit measurable roll-to-roll compositional variation across the different brand names as well as across those rolls produced by the same manufacturer in different production runs. In some instances, rolls of foil produced in a single production run have analytically distinguishable compositions. Thus, a high degree of discrimination capability exists among sources of household aluminum foil.

757 ANALYTE ISOFORMATION AFFECTING THE VANADIUM SPECTROSCOPIC RESPONSE IN THE GRAPHITE TUBE.

Romer A. Romero,* Janeth A. Navarro and Victor A. Granadillo, Laboratorio de Instrumentacio'n Analitica Universidad del Zulia, Venezuela.

We present several analyte isoformers, such as nitric acid, magnesium nitrate, citric acid and palladium, used for the graphite furnace atomic absorption spectrometric evaluation of vanadium in biological and clinical materials. In real samples, a deflection below the baseline before the absorbance signal of V was found, when employing either nitric acid or magnesium nitrate, indicating a possible background attenuation-type interference. Citric acid, in conjunction with 0.1 M nitric acid and 0.1% v/v triton X-100, produced neat absorbance-time V profiles and accurate data. This probably suggests that the isoformer together with a reducing environment control the V atom-forming step. It was observed that at a constant atomization temperature the appearance time (t_a) for aqueous standards and real samples were equivalent under the citric acid influence. However, aqueous V showed a higher t_a than the analytic V after adding 100 µg Pd/L to the citric acid isoformer. It is pausible that a carbon-limiting mechanism occurred and, thus, the Pd stabilization effect was decreased in real samples with a high carbon content. Relative errors < 2% were obtained for the standard reference materials analyzed and no memory effects detected.

*Research Supported by Conicit F-142

758 SPECTROMETRIC DETERMINATION OF TRACE METALS IN UREMIA.

Victor A. Granadillo, Romer A. Romero* and Janeth A. Navarro, Laboratorio de Instrumentacio'n Analitica Universidad del Zulia, Venezuela.

IWe report the graphite furnace atomic absorption spectrometric (GFAAS) determination of aluminum, copper, iron, zinc, vanadium and lead in whole blood and bone specimens from hemodialyzed patients (CRF) and control individuals, using GFAAS-based methodologies developed in our laboratory. Before GFAAS analyses, the test portions were diluted with triton X-100 (whole blood) or with nitric acid (bone specimens). The following atomization temperatures (°C) and analyte isoformers were used:

	Al	Cu	Fe	Zn	V	Pb
Atomization °C/s	2300/5	2200/5	2500/5	2100/5	2700/6	2300/6
Isoformer	$\leftarrow$--- triton X-100/HNO_3 ---$\rightarrow$				$NH_4H_2PO_4$ HNO_3 $Mg(NO_3)_2$	Pd/citric acid/HNO_3

Results showed that CRF bone Al, Fe and V were increased ($p < 0.001$) and whole blood metal concentrations were statistically different from those found in controls ($p < 0.01$). It is concluded that the GFAAS technique provides an important analytical tool to evaluate metal intoxication in humans.

*Research Supported by Conicit F-142.

759 MINERALIZATION OF BIOLOGICAL MATERIALS TO PERMIT TOTAL MERCURY EVALUATION BY THE COLD VAPOR TECHNIQUE.

Romer A. Romero,* José M. Sa'nchez, Herna'n S. Cubilla'n, Victor A. Granadillo and Jorge E. Taha'n, Laboratorio de Instrumentacio'n Analitica Universidad del Zulia, Venezuela.

Mineralization procedures need to be developed to allow the subsequent cold vapor atomic absorption spectrometric (CVAAS) determination of the total mercury content present in biological and clinical materials. We used two mineralization approaches that require high-pressure reactors heated by convection C (for 4 h at 125 ± 5°C) and by microwave irradiation MW (for 90 s at 100% of power), subsequently applied to the decomposition of lyophilized tuna muscle tissue, whole blood and urine specimens. Accuracy was tested by analyzing the reference material RM-50 (*albacore tuna*) from the National Institute of Standards and Technology (NIST) with a concentration of 0.95 ± 0.10 mg Hg/Kg (measured value = 1.10 ± 0.01 mg Hg/Kg) and by recovery studies: 95 ± 5% and 98 ± 5%, for C and MW, respectively. In real samples, the CVAAS-based Hg evaluation was interference-free and the limit of detection (2σ), for 3-mL solution undergoing analysis, was 53 ng Hg/L. The following total mercury concentrations were obtained when using the described mineralization procedures: 1.45 ± 0.09 mg/Kg and 40 ± 10 and 22 ± 5 mg/L, for commercial tuna, whole blood and urine samples, respectively. Results showed that Hg losses by volatilization were eliminated.

*Research supported by Conicit F-142.

760 ASSESSING WATER METAL QUALITY FOR DRINKING PURPOSES BY ATOMIC SPECTROMETRY.

Janeth A. Navarro, Herna'n S. Cubilla'n, José M. Sa'nchez, Jorge E. Taha'n and Romer A. Romero,* Laboratorio de Instrumentacio'n Analitica Universidad del Zulia, Venezuela.

We studied the quality of the drinking water supplied to Maracaibo City (Venezuela) through the evaluation of its aluminum, calcium, iron, magnesium, potassium and sodium contents. Aluminum was determined by graphite furnace atomic absorption spectrometry; for the other metals, flame atomic absorption (Fe, Ca, Mg) and emission spectrometries (K, Na) were employed, following methodologies developed in our laboratory. The following mean metal concentrations in the tap water were found (± SEM, mg/L): Al = 0.515 ± 0.019, Ca = 32.1 ± 0.4, Fe = 0.17 ± 0.01, Mg = 5.0 ± 0.1, K = 3.0 ± 0.3 and Na = 15.3 ± 0.2. Tap water Al was higher than the upper concentration ruled by the Venezuelan Water Administration (*ca.* 0.300 mg Al/L) and by international water standards (*ca.* < 0.100 mg Al/L). On the other hand, tap water Mg, Ca and Na were within the normal ranges established for drinking water in the USA (*ca.* 6.25 Mg, 26 Ca, 12 Na, mg/L). Contrarily, the mean levels of Fe and K in the tap water exceeded the corresponding USA upper values for these metals in drinking water (*ca.* 0.04 Fe and 1.6 K, mg/L). Spectrometric methods proved to be useful to monitor metals in the tap water in order to ascertain the safeness of the water used for drinking purposes.

*Research supported by Conicit F-142.

761 NEAR-INFRARED ACOUSTO-OPTIC IMAGING MICROSCOPY: PRINCIPLES AND APPLICATIONS.

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A novel spectroscopic imaging technique, near-infrared acousto-optic microscopy will be described including recent applications to studies of biological materials. The instrument is constructed around an acousto-optic tunable filter (AOTF) coupled to a refractive microscope optimized in the near-infrared with indium antinomide (InSb) focal plane array (FPA) detection. AOTFs are electronically addressable optical notch filters that provide extremely rapid, random wavelength access, wide spectral coverage and moderately high spectral resolution. InSb FPA detectors are state-of-the-art near-infrared imaging detectors (1.0–5.0 μm) that are only now finding applications in spectroscopic laboratories. In addition, we employ novel methods of analysis which integrate conventional digital image enhancement techniques with chemometric methods reserved for the analysis of more traditional spectroscopic data.

762 FTIR STEP-SCAN PHOTOACOUSTIC SPECTROSCOPY WITH VARIABLE SAMPLING DEPTH.

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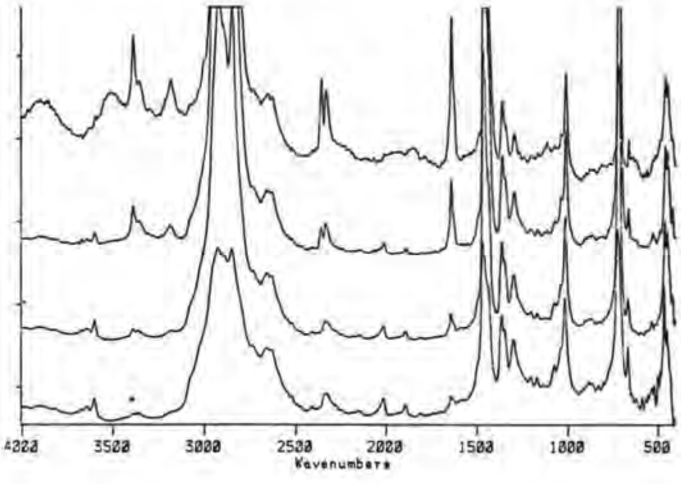
Step-scan FTIR systems significantly expand by over a factor of seven the depth profiling capability of photoacoustic spectroscopy relative to conventional FTIR systems. The sampling depth range for typical polymers is from several micrometers to over 100 micrometers for the Bio-Rad FTS 60A system. The figure shows spectra with sampling depth increasing from top to bottom, of a polymer with additives which are either concentrated near the surface (absorbance band at 1640/cm) or uniform in the bulk (band near 1000/cm). The sampling depths for the 1640/cm band are 5, 15, 50, and 150 micrometers going from top to bottom.



763 PHOTOACOUSTIC SPECTROSCOPY USING A DYNAMICALLY-ALIGNED STEP-SCAN FT-IR SPECTROMETER.

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Fourier transform photoacoustic spectroscopy (PAS) is a valuable method for detecting and identifying materials as a function of distance from the sample surface. Dynamically aligned step-scan-Fourier transform spectrometers offer significant advantages that increase the flexibility of PAS. Varying the interferometer scanning velocity probes deeper layers as the velocity is reduced. Analysis of the phase delay of the photoacoustic signal provides additional depth discrimination. The photoacoustic spectra of polymeric materials were collected with the Bio-Rad FTS 60A spectrometer utilizing the 896 interferometer, an MTEC photoacoustic cell, and the Bio-Rad two phase demodulator accessory, which was specifically designed to accommodate the wide dynamic range (up to 20 volts peak-to-peak) of the signals produced. The multichannel spectroscopy feature of the 896 allows simultaneous collection of in-phase and quadrature phase information. The results of varying the scanning velocity, controlling the phase modulation amplitude, and varying the phase modulation frequency will be discussed.

764 STRATEGIES FOR STEP-SCAN FT-IR PHOTOACOUSTIC DEPTH PROFILING.

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One of the main advantages of photoacoustic spectroscopy (PAS) is its ability to probe different depths in a sample, depending on the experimental conditions. The sampling depth (in the absence of saturation) for homogeneous materials is limited theoretically to the thermal diffusion depth, $\mu = (\kappa/\pi C_p \rho f)^{1/2}$. However, for laminar materials consisting of layers which absorb at distinctly different wavelengths, the PA probe depth may extend to several times μ. The ability of PAS to obtain depth dependent information is a result of the inverse dependence of μ on the modulation frequency and of the phase lag of the PA signal. The strategy used for depth profiling is dependent on the instrumentation available. In the area of infrared (IR) spectroscopy there are three main instrumentation options to couple with PA detection: IR laser spectroscopy, continuous-scan FT-IR, and step-scan FT-IR. (In general the low throughput of dispersive IR instruments precludes their use in PAS). IR laser spectroscopy is useful if only a small wavelength range is required. Depth profiling is possible by use of either the frequency dependence or phase of the signal. In continuous-scan FT-IR PAS, depth profiling is closely controlled by the Fourier frequencies, $F = 2v/\lambda$ where v is the mirror velocity and λ is the wavelength, which result in wavelength dependent modulation frequency and, therefore, a wavelength dependent thermal diffusion depth. Depth profiling can be performed by collecting a number of spectra, each at a different mirror velocity; however, the extraction of the phase information is difficult in continuous-scan FT-IR. Step-scan FT-IR combined with PA detection is inherently a much simpler experiment due to the single modulation frequency across the whole spectral range. As the modulation frequency is changed for each scan, the depth from which signals can be detected varies, and facile extraction of the signal phase provides additional depth discrimination. In this paper continuous-scan and step-scan FT-IR PAS will be compared and contrasted with emphasis on enhancement of depth profiling by phase analysis.

765 QUANTITATIVE DRIFTS USING AN OPTIMIZED INTEGRATING SPHERE ACCESSORY, F. J. Weesner and M. P. Fuller, Nicolet Instrument Corporation, Spectroscopy Research Center, 5225 Verona Road, Madison, WI 53711.

Sampling reproducibility is often a limiting factor in the quality of quantitative analysis results. Diffuse reflectance sampling presents special problems in this regard due to strong particle size effects and the potential for specular reflectance artifacts in the spectra. The integrating sphere is an instrument often used in other spectral regions for reflectance spectroscopy. Infrared applications have been limited due to low signal-to-noise spectra, a consequence of the inherently low optical throughput of integrating spheres has been. This talk will present mid infrared diffuse reflectance results obtained using an integrating sphere accessory designed for the Mid infrared experiment. Signal-to-noise performance is evaluated. Effects of sample composition and homogeneity on DR spectra will be compared to conventional DRIFTS accessories. Implications to quantitative analysis will be demonstrated by application to powders and extended solid samples.

766 THREE INDEPENDENTLY PURGED FTIR ATTACHMENTS FOR QC ANALYSIS. J. Lucania, S. L. Berets, N. J. Harrick and M. Milosevic, Harrick Scientific Corp., P.O. Box 1288, Ossining, NY 10562.

The designs and applications of three spectroscopic attachments, incorporating Permapurge™, are discussed. Plusone™ analyzes solids and liquids at controlled elevated temperatures by 45° single internal reflection (ATR) spectroscopy. This equipment allows flow-through liquid applications and repeatable contact solid applications. Sampling techniques which use the heated ATR element to melt powders and cast samples from volatile solvents are demonstrated. The Refractor Plus™, with its built-in brewster angle silicon polarizer, performs grazing angle reflection analyses of thin coatings on specular substrates. The fixed 75° angle of incidence is obtained through the use of wedged zinc selenide windows (rather than by conventional mirrors). A more compact configuration for the attachment results. The corrosion resistant DGC Plus™ performs short pathlength (5 or 10 cm) transmission analyses of gases. The gas cell body is constructed of borosilicate glass. Window holder terminations on either side of the cell body have electroless nickel or gold plating. Hence, the cell can withstand a wide range of chemical species. Each of the three attachments is independently purged. Therefore, purge wait times between samples are eliminated. Alignment and sample introduction have been kept straightforward without sacrificing optical performance. Both the Plusone™ and Refractor Plus™ attachments have convenient top-loading horizontal sampling surfaces. Such features are ideal for laboratories that must routinely obtain spectra on a high volume of samples.

767 THE NEW 3M DISPOSABLE IR CARD FOR QUALITATIVE MID-INFRARED ANALYSIS. James E. Gagnon, 3M Company/DPD, Bldg. 230-3F-03, 3M Center, St. Paul, MN 55144-1000. Neale Povey, Jr., 3M Company, MISD, Bldg. 230-2A-47, 3M Center, St. Paul, MN 55144-1000.

The new 3M Disposable IR Card is described for use in mid-infrared analysis or organic liquids, colloids, semi-solids, water containing solutions, and soluble solids. Three key features of the Disposable IR Card are the 1) unique sample application area, contained within; 2) cardboard frame, which; 3) universally fits standard FTIR sample compartments. A sample is quickly and easily applied to the sample application area. Any volatiles present in the sample usually quickly evaporate under ambient laboratory conditions. The cardboard frame provides a writable surface for sample identification, while permitting easy disposal after analysis thereby eliminating the sample clean-up step. Universal fitting frame easily slides into standard sample holder brackets of major FTIR's, without special adaptors, or alignment tools. Various sample application techniques successfully employed in conjunction with the new sample holder will be presented. Spectral examples of commercially available products analyzed using the 3M Disposable IR Card will be discussed. Infrared spectra obtained contain minimal spectral interference, thereby facilitating spectral manipulations such as determining ratios, baseline corrections, etc. Infrared spectra obtained can normally be searched against standard condensed phase spectral libraries prepared using conventional sample accessories.

768 ANALYSIS OF FT-IR SPECTROSCOPIC DATA. J. T. Reilly, J. M. Walsh, M. L. Greenfield and M. D. Donohue, Dept. of Chemical Engineering, The Johns Hopkins University, Baltimore, MD 21218.

A novel spectral analysis technique involving a combination of fourier analysis and profile modeling is presented for the determination of peak areas from spectra in which there are multiple overlapping peaks. Although the technique presented could be applied to many different type of problems (analysis of UV-VIS spectra of chromatographic results) it is applied here to the problem of determining, from FT-IR spectra, the peaks areas which correspond to monomeric and hydrogen bonded species. For FT-IR spectra it is found that the Voigt profile is better than either the Lorentzian or Gaussian profiles. Use of the Voigt profile leads to more accurate and more descriptive spectral peak parameters and in turn, to more accurate determinations of concentrations of monomeric and hydrogen bonded species. The technique is demonstrated using the carbonyl peaks for the mixture of the acetone\methanol\carbon tetrachloride system.

769 THE USE OF A PLUME DISPERSION MODEL WITH CONCENTRATION DATA FROM THE EPA REGION VII FTIR INTERCOMPARISON STUDY. R. H. Kagann and O. A. Simpson, MDA Scientific, Inc., 3000 Northwoods Pkwy, Suite 185, Norcross, GA 30071. R. L. Scotto and B. C. Sanders, Blasland, Bouck & Lee, Raritan Plaza III, Fieldcrest Ave., Edison, NJ 08837.

The EPA Region VII open path FTIR intercomparison study, conducted in June 1991, provided an opportunity to test the Gaussian plume dispersion model for a point source of nonbuoyant emissions. The study involved a performance comparison and evaluation of participating open-path FTIR systems based on controlled upwind releases of mixtures of gaseous chemicals, together with simultaneous measurements of atmospheric transport and dispersion conditions. We report the results of using the MDA FTIR open-path measurements with on-site meteorology to assess the accuracy of the Gaussian plume dispersion model "textbook" vertical dispersion (σ_z) estimates. Calculated values for σ_z versus the "textbook" values obtained from tables are presented for a total of 17 multicompound controlled release tests over a range of observed atmospheric stability conditions.

770 THEORETICAL ANALYSIS OF THE LENSING EFFECT OF WIRE MESH GRIDS ON ION TRANSMISSION IN TIME-OF-FLIGHT MASS SPECTROMETRY. Richard C. King and Kevin G. Owens, Department of Chemistry, Drexel University, Philadelphia, PA 19104.

In this paper we present the results of a theoretical analysis of the effect wire mesh grids have on the ion transmission in time-of-flight mass spectrometry. Wire mesh grids are used in time-of-flight mass spectrometry to define regions of different electric field. It is generally accepted that these grids reduce the ion transmission due to the collision of ions with the grid wires. In addition to these collisional losses, ion transmission may be reduced by the lensing effect of the wire mesh grids. Each hole and its associated wires that make up a grid acts as a separate ion lens. The results show that not only are ions lost due to collisions with grid wires, but they are also lost because of the off-axis acceleration given by the lensing effect of the wire mesh grids. The calculated ion transmission including the loss due to the lensing effect of the grids will be compared to the optical transmission of the grid for several different instrument conditions. The results of the calculations suggest that ion transmission may be improved by reducing the lensing effect of the grids. Several methods of reducing the lensing effect will be presented including reducing the electric field difference across the grid, using grids with lower optical transmission, and assuring ions have large on-axis velocities at the grid.

771 DESIGN OF A REFLECTION TIME-OF-FLIGHT MASS SPECTROMETER USING SIMPLEX OPTIMIZATION. Richard C. King and Kevin G. Owens, Department of Chemistry, Drexel University, Philadelphia, PA 19104.

In this paper we present the results of using a simplex optimization method to design a reflectron time-of-flight mass spectrometer. The simplex was allowed to vary the instrument electric fields by changing applied voltages and the distances between ion optic elements. The only restrictions were practical limits set on the overall instrument length and the maximum and minimum voltages applied. The simulated peak shape is calculated using a monte carlo approach to include the distributions of ion formation time, initial kinetic energy, and initial potential energy. The model also includes the effects on the flight time distribution of ions passing through wire mesh grids. The simulated peak width was used to estimate the resolving power of each new instrument configuration chosen by the simplex procedure. The results will be explained in terms of space and energy focussing and the effects of grids on the ion time-of-flight. The presentation will include the results of the simplex optimization and the experimental results using the reflectron time-of-flight mass spectrometer constructed according to the simplex optimization results.

772 A LASER ABLATION—TIME OF FLIGHT MASS SPECTROSCOPY SYSTEM FOR THE ANALYSIS OF ENVIRONMENTAL SAMPLES.

David Baldwin, Stan Bajic and A. P. D'Silva, Ames Laboratory, 8 Spedding Hall, Iowa State University, Ames, IA 50011.

This work involves the development of a laser ablation-time of flight mass spectroscopy system for the analysis of complex environmental samples. The system will employ atmospheric-pressure laser ablation and laser desorption, laser ionization, a 2 meter flight tube, and a microchannel plate detector for the analysis of environmental samples for radionuclides as well as inorganic and organic contaminants. Preliminary experiments address the problems of measurement of isotopic abundances and isobaric interferences using resonance ionization mass spectroscopy.

773 SEPARATION AND DETECTION OF THE FRAGMENTS OF A LASER ABLATED POLYMER USING REFLECTION TIME-OF-FLIGHT MASS SPECTROMETER AND CAPILLARY COLUMN GC.

Y. Choi, S. Fountain and D. M. Lubman, Department of Chemistry, University of Michigan, Ann Arbor, MI 48109.

A polymer is laser ablated with an ArF excimer laser ($\lambda = 193$ nm) and the resulting neutral fragments are analyzed using both reflection time-of-flight mass spectrometer and capillary column GC preliminary studies using reflection time-of-flight mass spectrometer give a fragment with $M/E = 44$ which, based on the structure of polymer, can be acetaldehyde, ethylene oxide, or both. In order to make a positive identification of this fragment, the fragments from laser ablated polymer are first passed through a loop on a 6-way valve and then are swept into a capillary column. The separated fragments are detected by flame ionization detector. The resulting spectra are compared with the spectra of acetaldehyde and ethylene oxide. The technique and experimental conditions for the study of laser ablation of polymer are discussed. Problems associated with interfacing capillary column GC and reflection time-of-flight mass spectrometer are also discussed in detail.

774 MS/MS PEPTIDE SEQUENCING BY LASER TIME-OF-FLIGHT MASS SPECTROMETRY.

Richard C. King and Kevin G. Owens, Department of Chemistry, Drexel University, Philadelphia, PA 19104.

Mass spectrometry/mass spectrometry has proven to be a valuable tool for the determination of primary structure of peptides and proteins. MS/MS experiments are routinely performed on sector, quadrupole, and FT mass spectrometers. In this presentation we will describe a method of performing MS/MS experiments by laser time-of-flight mass spectrometry. The experiment consists of laser desorption of neutral molecules followed by gas phase laser ionization to produce parent ions. Daughter ion formation is accomplished by a third laser pulse to fragment the parent ions. The difference between this and other similar experiments previously performed is that the instrumental configuration is such that the daughter ions from several parents can be mass analyzed in the same mass spectrum. The first experiments presented will be to demonstrate the method of mass calibration and the ability to establish parent-daughter relationships. Then results from mixtures of parent ions will be presented to investigate the ability of the method to distinguish daughters from different parents. In addition, experiments will be conducted to determine the practical mass range of the photofragmentation step and the differences in parent mass necessary to permit assignment of the parent-daughter relationships for mixtures of parents. The advantages of the method as well as the limitations will be discussed and compared to other MS/MS systems for determination of protein and peptide primary structure.

775 CHARACTERISTICS OF IONS AND NEUTRALS EJECTED DURING MATRIX-ASSISTED LASER DESORPTION.

Curtis D. Mowry and Murray V. Johnston, Department of Chemistry and Biochemistry, University of Delaware, Newark, DE 19716.

The development of Matrix-Assisted Laser Desorption Ionization (MALDI) has dramatically increased the mass range and sensitivity for laser mass spectrometric methods. Optimization of the MALDI technique requires more information regarding both ionic and neutral products of the desorption event. The desorption and ionization steps are decoupled with techniques such as electron impact, multi-photon ionization, and chemical ionization, which post-ionize the neutral desorption products. Unlike these techniques, photoionization using vacuum ultraviolet (VUV) radiation permits soft and universal ionization of desorbed neutrals. Laser Desorption/Photoionization (LD/PI) is performed in the source region of a linear Time-of-Flight mass spectrometer. To compare the yield of ions and neutrals produced under various conditions, MALDI and LD/PI mass spectra are obtained simultaneously for a single desorption event. In another experiment the MALDI ions are rejected to collect only LD/PI ions. The kinetic energy distributions of the desorbed neutrals are determined by adjusting the time delay between MALD and PI. The relative fragmentation observed in LD/PI provides information on the internal energies.

776 PHOTODISSOCIATION—PHOTOIONIZATION MASS SPECTROMETRY.

Philip L. Ross, Scott E. Van Bramer and Murray V. Johnston, Department of Chemistry and Biochemistry, University of Delaware, Newark, DE 19716.

In conventional mass spectrometry ionic fragmentation is used to obtain structural information. Study of neutral fragmentation yields information not necessarily available from ionic fragmentation. One method that probes neutral fragmentation is Photodissociation/Photoionization Mass Spectrometry (PDPI/MS). An excimer laser is used to induce neutral fragmentation in the source region of a time of flight mass spectrometer. After pulsing away any ionic products, the neutral fragments and remaining parent molecules are softly ionized with coherent VUV radiation. VUV photoionization provides the universal but soft ionization required for characterizing the neutral photodissociation products. The use of several photoionization wavelengths in the VUV makes it possible to balance the tradeoff between soft and universal ionization. The neutral unimolecular fragmentation observed in PDPI/MS provides unique structural information which makes it possible to characterize a wide variety of simple organic molecules. Most recently, PDPI/MS has been used to study cyclic alkenes, saturated thiols, and some difunctional compounds. The mass spectra show that neutral fragmentation is characteristic of the original structure. In addition, the tuneable VUV wavelength capability provides control over the relative amounts of primary and secondary fragmentation, yielding additional structural and mechanistic information.

777 GAS-PHASE CHEMISTRY OF ALKYL HALIDES WITH PHENYL IRON;

E. Garcia, Y. Li, Y. Huang and B. S. Freiser, Department of Chemistry, Purdue University, West Lafayette, IN 47907.

We report the gas-phase chemistry of Fe(phenyl)$^+$ with CH_3F and the small alkyl halides, $C_nH_{2n+1}X$ (n = 1–3; X-Cl, Br, I). Reaction mechanisms are postulated based on the product ion structures which are determined by ion-molecule reactions and collision-induced dissociation. In general, the reactions are observed to proceed by an initial C-X, C-H, or C-C insertion. If β-hydrogens are present on the alkyl moiety, subsequent β-H transfer and elimination of an alkene is observed. There are few secondary reactions; they generally involve halogen abstraction. One of the most interesting reactions is with CH_3I. Following C-I insertion, transfer of the CH_3 group to the phenyl ligand results in an Fe(I)(toluene)$^+$ intermediate and a condensation product. The former competitively eliminates predominantly C_7H_8 to generate FeI$^+$ to I to generate $FeC_7H_8^+$. Additionally, CID and ion-molecule reactions suggest that $FeC_7H_8^+$ has an Fe(toluene)$^+$. Additionally, CID and ion-molecule reactions suggest that $FeC_7H_8^+$ has an Fe(toulene)$^+$ structure. For ethyl iodide, the analogous product ion was observed. Finally, the thermochemical implications of these results are discussed.

778 COLLISION-INDUCED AND INFRARED MULTIPHOTON DISSOCIATION STUDIES ON M(ACETONE)$_2^+$ (M = Al, Fe, Co, ScO) IN THE GAS PHASE;

I. Surjasamita and B. S. Freiser, Department of Chemistry, Purdue University, West Lafayette, IN 47907.

Collision-induced dissociation (CID) on M(acetone)(acetone-d_6)$^+$ for M = Al, Fe, and Co yields primarily, if not exclusively, equal amounts of acetone and acetone-d_6. Likewise, infrared multiphoton dissociation (IRMPD) yields, exclusively, equal losses of the labeled and unlabeled acetone. These results suggest that the two acetone ligands bind in an equivalent fashion. IRMPD of ScO(acetone)$_2^+$, however, produces loss of CH_4 and not acetone. IRMPD result is explained by studying primary and higher order of Sc$^+$ with acetone which shows a rich chemistry as well as CID of ScO(acetone)$_2^+$.

779 WAVELENGTH CALIBRATION METHODS FOR DIODE-ARRAY SPECTROMETERS.

J. Thomas Brownrigg, American Holographic Inc., 521 Great Road, P.O. Box 1310, Littleton, MA 01460.

In general, the reciprocal linear dispersion of a diode-array spectrometer is not constant, and varies with wavelength. We have investigated two methods for wavelength calibration. The first requires two known wavelengths, their location on the array, and the rating groove frequency. The second method requires fitting a set of calibration wavelengths to a polynomial in the diode index. The relative merits of the two approaches will be discussed.

780 TUNING THE DIODE LASERS BY MODE HOPPING.

Ring-Ling Chien, Varian Associates, 3075 Hansen Way, Palo Alto, CA 94304.

The ability to tune the wavelength is an important feature of diode lasers for variety of applications in analytical chemistry. A diode laser's wavelength is determined primarily by the band gap of the semiconductor material and then by the junction temperature and current density. Frequently, the wavelength is coarsely tuned with temperature and finely tuned with current. Unfortunately, the gain curve in a typical Fabry-Perot diode laser shifts at different rates from the cavity length changes as temperature varies. This results in discrete steps, or mode hopping, in the tuning curve and only a small percentage of the potential range of lasing wavelengths may be accessed. Some researchers have used external cavity such as gratings mirrors, or graded index lens to select the oscillating mode and control the lasing wavelength. However, those techniques are rather complicated and have their own problems. In this report, we use the combination of mode hopping and the hysteresis characteristics, where the lasing wavelength depends upon the direction of the temperature ramp, to control the wavelength of diode lasers. We also found the shift of the gain curve is sensitive to the carrier density. Consequently, the mode hop occurs at different wavelengths and temperatures as injection current changes. By purposely hopping into the selected mode and choosing the direction of temperature ramp, the tuning gap could be minimized and the specific absorption lines could be reached. In the diode laser we tested, a 100% coverage in the lasing wavelength is achieved.

781 LIGHT SCATTERING MEASUREMENTS OF PARTICLES: VISIBLE VS. NIR LIGHT SOURCES.

Min-Lee Cheng, Nalin Shah, Robert Obremski, Donna St. Thomas and Mohsen Ordpour, Beckman Instruments, Inc., 200 S. Kraemer, Brea, CA 92621.

Latex spheres of known sizes and concentrations are used as models for simulated measurements of biological molecules by light scattering method. The wavelength of the light source extends from 300 nm to 1400 nm and the signal is collected at multiple angles. The amount of light scattered by any particles decreases with increasing wavelength of the source, but increases proportional to the size and concentration of latex particles. Smaller latex particles at a concentration of 0.0125% are indistinguishable from the background in the wavelength range above 900 nm. The study demonstrates the potential benefits of using NIR light sources in immunological quantification of molecules in biological samples in which the background due to the presence of other particulates can be minimized.

782 CHARACTERIZATION OF "NOISE" AND SOFTWARE FILTERS OF LIGHT SCATTERING MEASUREMENTS.

Nalin J. Shah, Min-Lee Cheng and Robert J. Obremski, Beckman Instruments, Inc., 200 South Kraemer Blvd., Brea, CA 92621.

Light scattering has been used as a technique for the analysis of low level analytes in body fluids. While successful, the measurement is plagued with "noise spikes" from suspended particles, superimposed on a slowly changing signal. In this paper light scattering measurements of latex particles of known sizes and several concentrations in different matrices were collected at various angles using wavelength between 300 nm and 1400 nm. The "noise" due to the instrument and the chemistry were characterized and several filtering techniques were utilized to improve signal/background and signal/noise. The intent of this paper is to demonstrate the effectiveness of filtering techniques employed.

783 GENERAL METHOD FOR THE PRODUCTION OF BIOSPECIFIC OPTICAL FIBER SENSORS BASED ON A DYNAMICALLY ASSOCIATED SURFACE INTERACTION.

Donald R. Bobbitt, Yunlong Wang, Kim P. Titus and Faye K. Ogasawara, Department of Chemistry and Biochemistry, University of Arkansas, Fayetteville, AR 72701.

Covalent coupling of biological ligands to optical fibers to enhance the selectivity of the sensing system has proven problematic leading to nonreproducibility, loss of activity and limited usage. These limitations are compounded when the reagent is consumed as a consequence of the measurement process. This presentation will describe a new approach for the production of biospecific, optical fiber sensors which is based on a dynamic modification procedure. The optical fiber surface is first modified with a hydrophobic layer and the specified reagent is then associated with this surface through either its inherent, or designed hydrophobicity. The approach is general and can be used to fabricate optical fiber sensors for a variety of applications. Specific examples to be discussed include the use of dynamically associated 3-octylriboflavin as a probe for riboflavin binding protein in a fluorescence quenching mode, and the use of the biotin/avidin interaction as a model of an immunological sensing application.

784 OPTICAL SENSOR BASED ON POLYMER SWELLING COUPLED TO A CHANGE IN FLUORESCENCE.

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There is considerable current interest in combining immobilized indicators with fiber optics to prepare sensors that can measure chemical concentrations *in situ*. The vast majority of these sensors involve fluorescence, bio- or chemi-luminescence or absorption as a transducer for chemical reactions. Analyte induced swelling of polymers can also serve as a transduction mechanism in biosensors. The changes in polymer size may be measured either electrically or optically and related to concentration. A membrane for a fiber optic biosensor based on coupling changes in the dimensions of the polymer to a change in fluorescence has been investigated. The membrane is a hydrogel formed by immobilizing a fluorophore in a lightly crosslinked polymer. The swelling of the membrane was found to be a function of pH. The fluorescence change as a function of the swelling of the membrane was examined. Glucose oxidase was also immobilized in the fluorophore-hydrogel matrix. It has been shown in this laboratory that the conversion of glucose into gluconic acid by glucose oxidase induces a change in the hydrogel investigated. The change in fluorescence as a function of glucose was also investigated.

785 A NOVEL SUBSTRATE FOR SURFACE-ENHANCED RAMAN SCATTERING (SERS) DETERMINATION OF SULFONAMIDES.

Stefanie T. Pagano and J. D. Winefordner, Dept. of Chemistry, University of Florida, Gainesville, FL 32611.

One of the most challenging aspects of Surface-Enhanced Raman Spectroscopy (SERS) is finding a suitable substrate that will significantly enhance the signal of Raman-active compounds. If the substrate can increase the Raman signal, then lower limits of detection can be achieved. A few characteristics of a good substrate are that it be inexpensive, east to prepare, and have a uniform surface. The Anapore aluminum oxide membrane; designed by Anotec, possesses these characteristics and has been shown to be a suitable substrate for the trace-level detection of sulfonamides. The membrane is composed of a highly-ordered honeycomb structure. Its capillary pores lend to very high flow rates compared to other types of membranes with comparable pore diameters. Because of this, Syringe filtration of a Ag colloid solution can be used to deposit silver spheroids on the membrane surface. This technique is a faster and less expensive method of Ag deposition compared to other methods used, such as vapor deposition, direct silver reduction, and vacuum filtration of Ag colloids. The structure of the membrane also allows for a very even, monodispersion of Ag. The SERS activity of three sulfonamides on Ag-coated Anapore membranes has been studied using the 514.5 nm line of an argon ion laser, Spectra Physics, series 2000, and has shown promising results. The sulfa drugs are therapeutically important in controlling bacterial infections in pet and food-producing animals, and the ability to have an inexpensive, fast, and reliable method to monitor trace levels of them is clinically significant.

786 A COMPARISON BETWEEN SCANNING GRATING NIR ANALYZERS AND FIXED-FILTER PHOTOMETERS IN INDUSTRY. R. C. Moessner, E. I. Du Pont De Nemours & Co., Spruance Fibers Plant, P.O. Box 27001, Richmond, VA 23261.

This paper provides a performance comparison between NIR scanning grating spectrophotometers and NIR fixed-filter photometers. The application of each technology to measurement of the quality of an aromatic substance in an aliphatic solvent is explored. The signal-to-noise ratio for each analyzer is determined and comparisons made of relative suitability for the evaluated application. The influence of signal-to-noise on the validity of chemometric method developments (PLS & PCS) is explored and comparisons made to methods derived on a purely theoretical basis. Each analyzer is evaluated against a set of criteria developed for suitability in a production plant environment for real-time process control. Several "yardsticks" are used, including, measurement signal-to-noise, measurement stability with time, process control objective attainment, calibration requirements, support requirements, installation cost, and cost of operation. With a fuller understanding of the relative advantages and disadvantages of each technology, these analyzers can be deployed in a manner which takes full advantage of their relative strengths.

787 DIFFICULT APPLICATIONS OF NIR SPECTROSCOPY: VISCOUS FLUIDS AND MOVING FILMS, John M. Pope, Sc.D., L. T. Industries, Inc., 6110 Executive Blvd, Rockville, MD 20852.

In conjunction with the use of fiber optic technology, the development of specialized and proprietary probe technology has allowed some difficult applications of NIR spectroscopy to be pursued. Three recent successful applications dependent on specialized probe technology were measurement of hydroxyl numbers in molten polyester, measurement of moisture content in a moving film, and measurement of color level in a molten polymer. In the case of the molten polyester, a special bubble shedding design allowed a measurement of hydroxyl number in a viscous fluid at 80°C without the interference of air bubbles. Linear regression results indicated a normalized standard error (standard error/sample range) of 3.1% for the measurement. In the case of the moving film, a special probe design including fiber optics and remote pneumatic actuation for reference and sample scans allowed measurement of moisture content in a moving film in a potentially explosive environment. Linear regression results indicated a normalized standard error of 4.9%. For the measurement. In the case of the molten polymer, fiber optics combined with special probe materials and construction allowed a measurement of color level in a process stream at 250°C and 800 psi. Linear regression results indicated a normalized standard error of 2.0% for the measurement.

788 NEAR LINE PROCESS MONITORING OF TOOTHPASTE USING FTIR. James W. Rydzak, Colgate-Palmolive, 909 River Rd. Piscataway, NJ 08854-5503.

A laboratory FTIR instrument was adapted to a manufacturing floor environment to monitor the making of toothpaste. The approach to establishing an analytical process monitoring device will be discussed. Aspects of setting up the instrument and implementing the sample interface to allow production line operators to analyze batches in the manufacturing environment will be covered. The advantages of a gravimetrically prepared standard set for the PLS (partial least square software) quantitative method, will be discussed. Finally, validation results indicating that process monitoring can provide quality results, comparable to lab analysis for individual components, in a faster more cost effective manner will be presented.

789 PROCESS MONITORING OF EMULSION POLYMERIZATION OF STYRENE BY SW-NIR. Caicai Wu, J. D. S. Danielson and James B. Callis, Department of Chemistry, BG-10, University of Washington, Seattle, WA 98195.

On-line process control is regarded as the key to more rapid and reliable polymerization processes. One of the most important problems in process monitoring and control is the inadequacy of monitoring sensors. NIR spectroscopy is a non-invasive chemical measurement technique, which provides an approach to real-time monitoring of polymerization processes. In this research, SW-NIR is used to monitor the emulsion polymerization process of styrene by diffuse reflectance. A HP8452A spectrometer was modified to analyze the reflected light. An automated reaction monitoring system was built, which includes a sleeve to hold an optical fiber bundle, a propeller for stirring, a temperature sensor, and two inlets for nitrogen purging and delivery of materials. The fiber bundle introduces light from the light source and, at the same time, receives the reflected light from the sample and transfers it into the spectrometer. The monomer is delivered automatically by a computer-controlled syringe pump. A temperature controller is used to maintain the temperature of the water bath of the reactor constant. The stir rate is also controlled by a computer. The spectra, temperature, and titration of monomers are shown on a computer screen as the reaction proceeds. Multivariate statistical techniques are used to analyze SW-NIR data. Good correlation has been found between NIR data and percentage of solid polymer as measured by the ASTM method.

790 MONTE CARLO RATIONALIZATION FOR OPTIMAL SENSOR DESIGN. Zhihong Ge, Aijun Li and James B. Callis, Center for Process Analytical Chemistry, Department of Chemistry, BG-10, University of Washington, Seattle, WA 98195.

Short wave near infrared spectroscopy has previously been used to measure cell density in a fermentation process. Here the back scattered light is monitored noninvasively by means of concentric fiber optic bundle attached to the outside of the glass vessel. The logarithm of the inverse diffusely reflected intensity at 810 nm decreased exponentially as the concentration of yeast increased over the range of 0–60 g/l. The reason for this exponential decay relation are not explained by any existing theories of diffuse photon transport such as the Kubelka-Munk equation. Accordingly; we have carried out Monte Carlo simulations of photon transport in diffuse medium in order to (a) understand the current results and (b) design better sensor geometries. The Monte Carlo model was used to simulate photon transport in a fermentation medium in which the density of yeast cells was varied. The simulation results indicate that we can rationalize the experimental results over the wide range of biomass concentrations (1–60 g/l). In addition, Monte Carlo models were used to simulate the response of the different probe geometries. The results showed that the different positions of the source and receiver give different responses, and that the geometry initially chosen is actually near ideal. Clearly, by using the Monte Carlo technique, we can predict the effects of variations in irradiation and detection geometry. Thus before time consuming and expensive experiments are carried out, simulation can be performed to determine optimum conditions of probe geometry.

791 REDUCED NOISE OF QUANTITATION IN NIR THROUGH FT-SPECTROSCOPY. Marc Trygstad, Bomem/Hartmann & Braun, Quebec, Quebec, Canada.

Fourier transform (FT) technology offers distinct performance advantages in near infrared (NIR) spectroscopy compared with old technologies for quantitative analysis, i.e. those employing filters and diffraction gratings. For example, partial least squares (PLS) models for quantitative analysis developed with FT-NIR data require significantly fewer factor spectra, whether derivative spectra are used or not. This evidence minimal instrument artifacts which can increase a model's predictive error or be incorporated into the PLS factors. This also implies that the FT-NIR spectra more accurately represent sample spectra. Thus, a stable FT-spectrometer affords more sensitive quantitative analyses through reduced noise of quantitation. FT-spectroscopy provides exceptional stability in spectral band shapes and frequency through rigorous control of mirror scanning via the internal HeNe laser. Also, the statistical robustness of the interferogram provides extremely precise band heights relative to local baseline. The benefits to quantitative analysis are twofold: wider analytical range is available for single sample properties; and unambiguous determination of components in complex mixtures. In both cases PLS models can be developed using fewer factors and their predictions are more precise.

AUTHOR INDEX

Announcement and Call for Papers

Twentieth Annual Meeting of the Federation of Analytical Chemistry and Spectroscopy Societies

October 17-22, 1993

Cobo Hall, Detroit, Michigan USA

Julian Tyson
Program Chairman
413-545-0195

David Coleman and Felix Schneider
General Chairs

FACSS National Office
P.O. Box 278, Manhattan, KS 66502-0002 (301) 846-4797

Scientific Program and Submission of Papers

The FACSS meeting is one of the world's leading analytical chemistry conferences with over 2,500 delegates and an anticipated program comprising almost 1,000 presentations. This year, as well as the core topics of atomic and molecular spectrometry, chromatography, and electroanalysis, the meeting will feature a number of sessions concerned with materials characterization, including abrasives, coatings, fuels, and silicones. Contributed original research papers are solicited in all areas of analytical chemistry. Please complete the title submission form and return by February 1, 1993. Submitted papers will be given as either 20 minute talks or presented in poster sessions. Upon acceptance of your submission, final abstract materials and instructions will be sent to you prior to April, 1993. Final acceptance of your presentation is contingent upon receipt of your 250 word final camera-ready abstract by May 15, 1993.

Awards Symposia

It is anticipated that several awards symposia will be arranged including symposia for the ANACHEM Award and Society for Applied Spectroscopy (SAS) Awards such as the Lester Strock and Lippincott Awards. In addition, this conference will serve as the forum for the presentation of other SAS Awards and FACSS Student Awards.

Tomas Hirschfeld Student Awards

Nominations are requested for the Tomas Hirschfeld Student Awards which will be presented at the conference for the most outstanding papers submitted by graduate students. The student nominees will give their papers at the conference. To be considered for these awards, students must submit the titles of their papers, two letters of nomination, any reprints/preprints, and a 250 word abstract to the National Office by February 1, 1993. As many as three students will be selected as awardees and their travel expenses will be arranged and paid for by FACSS. For further information concerning these student awards, contact the FACSS National Office.

Instrument Exhibit

The instrument exhibit is one of the most useful and exciting components of the conference and is designed to complement the scientific program. The exhibition area can accommodate 125 booths and will serve as the primary gathering place for many of the social events associated with the conference.

Workshops, Short Courses, and Employment Bureau

Workshops and short courses, conducted by leading scientists, will be offered in conjunction with this conference. Typical topics include ICP-MS, GC-MS, LC-MS, Sample Preparation, Lasers in Analytical Chemistry, and Chemometrics. The Employment Bureau will offer both local and national job listings. In addition, workshops on resume preparation and career planning will assist professionals seeking employment.

1993 FACSS Meeting ◆ Title Submission Form

☞ **Please note:** *No FAX submissions will be accepted*

Title Deadline: **February 1, 1993** **Please print clearly or type**

Key Words____________________ (please select up to 3 code letters from the list below)

◆ Title:

Authors:

Corresponding Author Information:

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Company/University ____

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Preferred Format* Talk ☐ Poster ☐ Either ☐

**Actual format may be determined by space availability and format of similar talks in your topical area.*

◆ Specific references to vendor products in the title of papers will not be permitted.

Key Word Code List:

A. Atomic spectrometry
B. Applications
C. Automotive industry
D. Bioanalytical
E. Coatings
F. Chemometrics
G. Chromatography
H. Data handling/Acquisn.
I. Electroanalytical
J. Electrophoresis
K. Expert systems
L. Flow analysis/Injection
M. Fuels
N. Fundamentals/Theory
O. Imaging
P. Infrared
Q. Instrumentation
R. Lasers
S. Luminescence
T. Mass spectrometry
U. NMR
V. Process analysis
W. Raman
X. Sample preparation
Y. Sensing/Sensors
Z. Separations
AA. Medical
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Note: FACSS does not provide financial support to authors of contributed papers.

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