

# Rocky Mountain Conference on Magnetic Resonance

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Volume 24 *24th Rocky Mountain Conference*


Article 1

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8-1-1982

## 24th Rocky Mountain Conference

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## 24th Rocky Mountain Conference

### Abstract

Abstracts and meeting program from the 24th annual meeting of the Rocky Mountain Conference, co-sponsored by the Rocky Mountain Section of the Society for Applied Spectroscopy and the Rocky Mountain Chromatography Discussion Group. Held in Denver, Colorado, August 1-5, 1982.

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## ABSTRACTS & MEETING PROGRAM

Sponsored jointly by

Rocky Mountain Section  
Society for Applied  
Spectroscopy

and

Rocky Mountain Chroma-  
tography Discussion Group

**DENVER CONVENTION COMPLEX**

**Denver, Colorado**

**August 1-5, 1982**

WELCOME

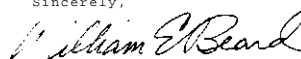
On behalf of the sponsoring organizations I am pleased to welcome you to the 24th Rocky Mountain Conference. To those of you who have travelled from other states or countries, I hope you will enjoy your stay and observe some of the area's features that make those of us living here justifiably proud of Denver and Colorado.

The Rocky Mountain Conference has grown in stature over the years and has become an outstanding summer scientific meeting in the United States. The conference has an 'international flavor' exhibited by the participation of scientists from a number of foreign countries with two of the nine symposia categorized as "International." Last year more than 800 attended the conference and about 260 papers were presented. We have 263 papers scheduled on this year's program and we hope to equal if not better the attendance of last year.

Thanks to all the exhibitors who support the conference, enabling us to have a complete scientific program. The excellent quality of the exhibits keeps us abreast of the latest developments necessary for the operation of the modern analytical laboratory.

Finally, I thank the members of *the* organizing committee and the symposia chairpersons for their efforts in keeping the annual Rocky Mountain Conference a quality program to be eagerly anticipated by a segment of the scientific community.

Sincerely,

A handwritten signature in dark ink, appearing to read 'William E. Beard', written in a cursive style.

Conference Chairman

#### REGISTRATION HOURS AND LOCATION

Sunday,	August 1,	Executive Tower Inn	4:00 p.m. - 8:00 p.m.
Monday,	August 2,	Denver Convention Complex	7:30 a.m. - 3:30 p.m.
Tuesday,	August 3,	Denver Convention Complex	7:30 a.m. - 3:30 p.m.
Wednesday,	August 4,	Denver Convention Complex	7:30 a.m. - 3:30 p.m.
Thursday,	August 5,	Denver Convention Complex	7:30 a.m. - 11:30 a.m.

#### REGISTRATION FEES

Registration at Conference	\$35.00
Registration one day only	\$20.00
Students	\$10.00
Unemployed or retired	No charge

Badges are required for admission to all technical programs and to the exhibit area, "Exhibit Area Only" badges can be obtained at the registration desk for those not wishing to attend technical meetings. No Charge.

#### VISITOR INFORMATION

Information on the Denver area may be obtained from the Denver Convention and Visitors Bureau, 225 West Colfax Avenue, Denver, CO 80202 (Phone 303/892-1112).

#### SOCIAL FUNCTIONS

##### MIXER

All conference attendees and spouses are invited to a mixer on Monday, August 2, from 5:30 p.m. to 8:00 p.m. at the Executive Tower Inn.

##### CONFERENCE BANQUET

The Conference Banquet will be held on Tuesday, August 3, at 7:00 p.m. at the Executive Tower Inn. Tickets are \$13.00 each. There will be a cash bar in the banquet area at 6:30 p.m.

This year our banquet program is presented by Dr. John Eddy, an informed and entertaining speaker from the National Center for Atmospheric Research in Boulder, who will speak on the ASTRONOMY OF THE AMERICAN INDIANS. This will be a highly illustrated talk about the Indians' knowledge of their sky and will cover such topics as medicine wheels, southwestern Indian architecture, pictographs and petroglyphs.

##### DINNER - THEATER

The conference has arranged for a limited number of tickets to the Wednesday, August 4, evening performance of "KISS ME KATE" at the Country Dinner Playhouse. This theater "in the round" is one of the better known entertainment places in the Denver area. An excellent buffet dinner is served prior to the performance. Tickets for the dinner and musical are \$13.00 each. Buses have been reserved for those requiring transportation. Cost is \$6.00 per person. Payment for the playhouse tickets and transportation (if required) must be included with your preregistration. The buffet dinner is served at 6:45 and buses will leave from the Executive Tower Inn at 6:00 p.m.

Check at the registration desk for the availability of tickets not requested with preregistration.

#### **SPOUSES' TOUR**

A 6-hour Grayline bus tour to Central City is offered to attendees' spouses and families. The trip will leave Denver and travel to Boulder, home of the University of Colorado, then up Boulder canyon to the 'peak to peak' highway where you will be treated to a view of the high Rockies. The tour continues on through Blackhawk to Central City, center of Colorado's early gold mining activity. You will be given time to shop and eat and visit historical places. The tour will return to Denver through scenic Clear Creek Canyon. Cost for this grand tour is \$11.00 per person, meals not included.

#### **FILM FESTIVAL**

EINSTEIN'S UNIVERSE, a two-hour color film produced in 1979 will be shown four times during the conference. This film presentation is open to conference attendees and families without charge. Spouses may obtain a badge for admission to the film at the registration desk.

#### **EMPLOYMENT CLEARING HOUSE**

An employment clearing house booth will be in operation during regular conference hours. This service will be available to all conferees. Location of the booth will be posted at the registration desk. Bulletin board space will be provided in the booth for employers to post job announcements. There will also be a notebook provided for conferees to post resumes. A list of Denver Metropolitan area employers will be available upon request. The conference (employment clearing house) will not assume obligation for the qualifications of job candidates, confidentiality of information exchanged, or the responsibility of employers.

#### **MESSAGE CENTER**

Mountain Bell has graciously agreed to set up a message center for Conference attendees in the registration area. The number is (303) 825-6388. The message center will be open from 8:00 a.m. to 4:30 p.m. (MDT) on Monday, Tuesday, and Wednesday and from 8:00 a.m. to 12:00 noon (MDT) on Thursday. The message center is for incoming calls only.

There are numerous pay phones in the Convention complex for outgoing calls.

#### **CONFERENCE EXHIBITION**

Exhibits of new chemical products, instruments, and services will be on display in the Denver Convention Complex. Exhibit hours will be 1:00 - 5:00 p.m. on Monday, 9:30 a.m. - 5:00 p.m. Tuesday and Wednesday, and 9:30 a.m. - 12:00 noon on Thursday. The exhibits are an important part of the Conference, so set aside time in your schedule to visit them and learn what's new in laboratory apparatus. The sponsoring societies of the Conference gratefully acknowledge the exhibitor support.

#### Future Conference Dates

August 14 -19, 1983

August 5 - 10, 1984

July 14 - 19, 1985

August 3 - 8, 1986

July 26 - 30, 1987

WORKSHOP

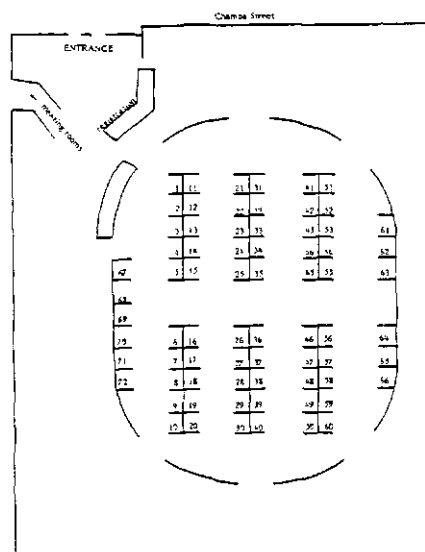
Practical Quality Control for the Chemical Laboratory  
Instructor: Dr. Dean P. Stull, Chief Chemist, Hauser Laboratories

There is increasing need for verification of results from chemical laboratories. The methods and techniques used for quality assurance of laboratory data are often overlooked or not used. This workshop reviews and examines the basic concepts of practical quality control for the chemical laboratory. Practical procedures and techniques will be covered. The basic ingredients of an in-house quality control manual will be reviewed. Participants will be given an opportunity to develop the basics for their own laboratory manual. Check sample program and round robin program will be discussed. Laboratory accreditation programs will be assessed.

CONFERENCE EXHIBITORS  
(as of June 6)

Booth No.

Analytichem	28
AXXIOM	27
Beckman Instruments	68
Brinkmann Instruments	30
Burdick & Jackson	28
Certified Balance Service	61
Cleveland Enterprises of Colorado	70
Coulometrics, Inc.	15
Digilab	69
Dionex	4-5
EG&G Ortec	65
Encyclopaedia Britannica, USA	44
Extranuclear Laboratories	60
Finnigan-MAT	56
Gow-Mac Instrument Co.	52
Hach Co.	67
H.A. Gilbert Co.	2-3
Harris Analytical	39-40
Hauser Laboratories	42
Hewlett-Packard	35
HPS Corporation	55
IBM Instruments	62-63
Instrumentation Laboratory	19-20
Instruments SA	25
JEOL USA	43
Kratos	27
Kontron	18
Lachat Instrument Division	12
Linear Instrument Corporation	7
Manville	24
MCB Manufacturing Chemists	26
Merck & Co. - Isotopes	14
Nicolet Instruments	46
Nicolet Magnetics	47
Perkin-Elmer	21-23 31-33
R.H. Allen Co.	64
Rocky Mountain Analytical Lab.	13
Sadtler Research Laboratories	41
SCT Sales	1-11
Shimadzu Corporation	17
Tracor Northern	16
Varian Instruments	36
VG Instruments	45
Western Research and Development	34
Wescan	6
Wilmad Glass Co.	51



**ORGANIZERS OF THE 24th ROCKY MOUNTAIN CONFERENCE**

Conference Chairman	W.E. Beard USDA - ARS
Conference Vice Chairman	E.A. Brovsky Rockwell International
Treasurer/Registration	J.L. Gurnsey
Exhibits/Facility	K. Brooks University of Colorado
Publicity	M. Brooks U.S. Geological Survey K.J. Grossaint Rockwell International
Printing	J.D. Grooms Rockwell International
Banquet/Mixer	B. Wiginton Marathon Oil Company B. McCarty Marathon Oil Company
Short Courses	C. Arozarena U.S. Geological Survey
Visitor Information	E. Huffman Huffman Laboratories
Audio-Visual	D. Raines Huffman Laboratories

**SYMPOSIA CHAIRPERSONS**

Atomic Spectroscopy	T. Niemczyk University of New Mexico
Chromatography	R. Barkley University of Colorado
Environmental Chemistry	J. Bonelli U.S. Geological Survey
EPR Spectroscopy	G.R. Eaton S.S. Eaton University of Denver
Ion Chromatography	M.J. Fishman U.S. Geological Survey
Mass Spectroscopy	M. Bergeron Rockwell International
NMR Spectroscopy	F. Miknis Laramie Energy Technology Center
Raman and IR Spectroscopy	M. Goldberg U.S. Geological Survey
Surface Analysis	W.H. Christie Oak Ridge National Laboratory

A W A R D

GREGORY STEPHEN CARAVAJAL

1982 Student Award Winner  
Rocky Mountain Section  
Society for Applied Spectroscopy

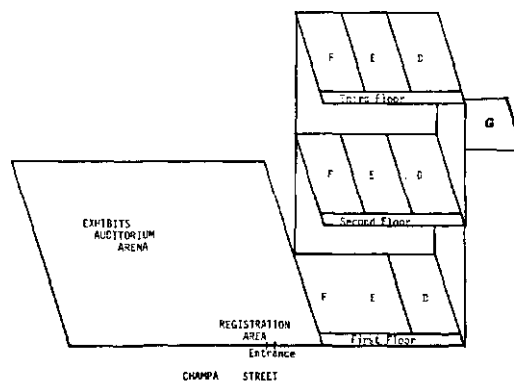
Gregory Stephen Caravajal graduated from Rocky Ford High School and came to the University of Southern Colorado on a football scholarship. Steve majored in physical education until a back injury caused him to reassess his education and career plans. He began taking mathematics and science courses, eventually concentrating on chemistry.

For the past two years Mr. Caravajal has been working on problems associated with the determination of trace metals in environmental systems. His work as an undergraduate has been outstanding as evidenced by the volume of publishable work he has produced. He is principal author for two papers and coauthor on a third paper which were presented at the 183rd National American Chemical Society Meeting at Las Vegas. In addition to these presentations, his paper, "The Determination of Uranium in Natural Waters at PPB Levels by Thin-Film X-Ray Fluorescence Spectrometry After Co-Precipitation with an Iron-Dibenzylidithio-Carbamate Carrier Complex" has been scheduled for publication in Analytica Chimica Acta. His manuscript entitled "The Analysis of River Sediments; Evaluation of Both the HNO<sub>3</sub>-HCl Extraction Procedure and the Multielement Determinations by Flame and Graphite Furnace Atomic Absorption Spectrophotometry" will be submitted to Analytica Chimica Acta.

Mr. Caravajal received his B.A. degree in chemistry from the University of Southern Colorado in May of 1982. He is continuing his work in analytical spectroscopy as a graduate student at Colorado State University.

# TECHNICAL PROGRAM

	Floor	Rm	MORNING	Floor	Rm	AFTERNOON
Monday	3rd	E	Atomic Absorption Spect.	3rd	E	Atomic Absorption Spect.
August 2	2nd	F	EPR Session I	2nd	F	EPR Session II
	2nd	E	Ion Chromatography	2nd	E	Chromatography
	3rd	F	NMR Session	3rd	F	NMR Session II
	2nd	G	Mass Spectroscopy	2nd	G	Mass Spectroscopy
	2nd	D	Chromatography	2nd	D	Chromatography
				3rd	D	Environmental Chemistry
<hr/>						
Tuesday	2nd	F	EPR Session III	2nd	F	EPR Sessions IV & V
August 3	2nd	E	Ion Chromatography	2nd	E	Ion Chromatography
	3rd	F	NMR Session III	3rd	F	NMR Session IV
	2nd	G	Mass Spectroscopy	2nd	G	Mass Spectroscopy
	3rd	D	Environmental Chemistry	3rd	D	Environmental Chemistry
	3rd	E	Surface Analysis	3rd	E	Surface Analysis
	1st	F	General Posters	1st	F	General Posters
	2nd	D	Chromatography			
<hr/>						
Wednesday	3rd	E	Atomic Emission Spect.	3rd	E	Atomic Emission Spect.
August 4	2nd	F	EPR Session VI	2nd	F	EPR Sessions VII & VIII
	2nd	E	Ion Chromatography	2nd	E	Ion Chromatography
	3rd	F	NMR Session V	3rd	F	NMR Session VI
	2nd	D	Raman & IR Spectroscopy	2nd	D	Raman & IR Spectroscopy
	3rd	D	General Session	1st	F	EPR Poster Session
<hr/>						
Thursday	2nd	F	EPR Session IX			
August 5						



INTERNATIONAL SYMPOSIUM ON ION CHROMATOGRAPHY

MONDAY MORNING, AUGUST 2 - Second Floor, Room E  
M.J. Fishman, presiding

- 8:30 INTRODUCTORY REMARKS - M.J. Fishman
- 8:35 92. Keynote Speaker - "Recent Developments in Ion Analysis," Hamish Small, The Dow Chemical Company
- 9:20 93. "Column-Eluent Selection for Single Column Ion Chromatography," J.E. Girard, J.A. Glatz, and D.Y. Badio, The American University
- 9:45 Break
- 10:15 94. "Progress in the Development of Very High Performance Ion Chromatography Columns," C. Pohl, A. Woodruff, M. Ebenhahn, and G. Hennion, Dionex Corporation
- 10:40 95. "Column/Eluent Optimization in Single-Column Ion Chromatography (SCIC)," T. Jupille and D. Togami, Wescan Instruments, Inc.
- 11:05 96. "New, High Sensitivity Universal Flame Photometric Detector For Cation Chromatography," S.W. Downey and G.M. Hieftje, Indiana University

INTERNATIONAL SYMPOSIUM ON ELECTRON PARAMAGNETIC RESONANCE

MONDAY MORNING, AUGUST 2 - Second Floor, Room F  
EPR SESSION I - Time Resolved EPR - A.D. Trifunac, presiding

- 8:30 Introductory Remarks - G.R. Eaton
- 8:35 31. Plenary Lecture - "Time Resolved EPR in Radiation Chemistry: CIDEP, Spin Exchange and Radical Recombination Rates", R.G. Lawler, Brown University
- 9:35 32. "Time Resolved EPR Applied to Study Electron Transport in Photosynthesis and Model Systems", M.C. Thurnauer, Argonne National Laboratory
- 10:35 Break
- 11:00 33. "Time Resolved EPR and ESE of Photoinduced Spin-Polarized Radicals in Photosynthetic Reaction Centers", A.J. Hoff, P. Gast, and R.A. Mushlin, Leiden

SYMPOSIUM ON NUCLEAR MAGNETIC RESONANCE

MONDAY MORNING, AUGUST 2 - Third Floor, Room F  
NMR SESSION I - Solids - F. Miknis, presiding

- 9:00 127. Robert Vaughan Plenary Lecture, "New Angles in Solid State NMR", A. Pines, University of California, Berkeley
- 10:00 128. "Carbon-13 NMR in Solids at Higher Magnetic Field's.", W.T. Dixon and J. Schaefer, Washington University and the Monsanto Company
- 10:30 Break
- 11:00 129. "Selective Carbon Excitation and Detection of Spatial Heterogeneity in Solid- State NMR," N. Zumbulyadis, Eastman Kodak Company
- 11:30 130. "A Triple-Resonance, 200 MH, Solids Spectrometer." R.A. McKay. Monsanto Company

SYMPOSIUM ON ATOMIC SPECTROSCOPY

MONDAY MORNING, AUGUST 2 - Third Floor, Room E  
ATOMIC ABSORPTION SESSION - J. Sneddon, presiding

- 8:30 1. "Automation of Trace Metal Analysis by Microcomputer Controlled-Flow Injection Flame Atomic Absorption Spectroscopy Method," R.L. Jones, T.D. Mevborn and D.P. Olander, U.S. Geological Survey
- 8:50 2. "Dealing with Matrix Interferences in Furnace Atomizer Absorption Spectroscopy," A. Rattonnetti, J. Sotera and G. Dulude, Instrumentation Laboratory Inc.
- 9:10 3. "Spatially Resolved Gas Temperatures Within the Furnace Atomizer," M.R. Riddle and J.A. Holcombe, University of Texas
- 9:30 4. "A HNO<sub>3</sub> - H<sub>2</sub>SO<sub>4</sub>/H<sub>2</sub>SO<sub>4</sub> - H<sub>2</sub>O - HNO<sub>3</sub> Solubilization Procedure for the Determination of Hg in Foods," R.W. Marts and J.J. Blaha, U.S. Food and Drug Administration
- 9:50 Break
- 10:20 5. "Quantitative Analysis of the Chemical Fill of a Metal Halide Lamp Arc Tube," R.A. Fowler, GTE Products Corporation
- 10:40 6. "Graphite Atomizer/Mass Spectrometer Measurements," G.D. Rayson and J.A. Holcombe, University of Texas
- 11:00 7. "Determination of Selenium in Siliceous Materials by a Peroxide Fusion-Hydride Evolution Technique," E.J. Cokal, Los Alamos National Laboratory
- 11:20 8. "The Determination of Refractory Elements in the Stabilized Temperature Graphite Furnace," R. Beaty, D.C. Manning and W. Slavin, Perkin-Elmer Corporation

SYMPOSIUM ON MASS SPECTROSCOPY

MONDAY MORNING, AUGUST 2 - Second Floor, Room G

- 9:00 Introductory Remarks - M.B. Bergeron
- 9:05 Plenary Lecture "Recent Advances in Mass Spectrometry," Prof. Klaus Biemann, Massachusetts Institute of Technology
- 10:00 248. "Applications of Stable Isotope Mass Spectrometry in Clinical Medicine," P.V. Fennessey, University of Colorado
- 10:30 Break
- 11:00 249. "Fast Atom Bombardment Mass Spectrometry in Biomedical Research," K.L. Clay and R.C. Murphy, University of Colorado
- 11:30 250. "Chemical Ionization Utilizing a Single High Vacuum Pump," D.E. Smith and D. Remling, Finnigan MAT Corporation

SYMPOSIUM ON CHROMATOGRAPHY

MONDAY MORNING, AUGUST 2 - Second Floor, Room D  
C.A. Burgett, presiding

- 8:40 159. "Selective Retention Using Mixed Mechanisms in High Performance Liquid Chromatography," M. Van Der Kaay and U.R. Tjaden, State University Leiden, Netherlands
- 9:00 160. "Determination of Trace Levels of Quaternary Ammonium Compounds in River Water by High Performance Liquid Chromatography/Conductimetric Detection," V.T. Wee and J.M. Kennedy, The Proctor and Gamble Co.
- 9:20 161. "HPLC Fractioned Samples of Diesel Particulate Extracts for Ames Testing," D.E. Seizinger, D.B. Eccleston, U.S. Department of Energy, and C.R. Clark and R.O. McClellan, Lovelace Inhalation Toxicology Research Institute
- 9:40 162. "Concentration and Measurement of Oxygen - Containing Organic Compounds in the Atmosphere," E.J. Williams and R.E. Sievers, University of Colorado
- 10:00 Break
- 10:30 163. "Determination of Polyolefin Additives by Normal-Phase High Performance Liquid Chromatography Following Soxhlet Extraction," J.F. Schabron, Phillips Petroleum Co.
- 10:50 164. "Analysis of Trace Levels of Explosives by High Pressure Liquid Chromatography" K.A. Carlberg and S.M. Brettbauer, Rocky Mountain Analytical Laboratory
- 11:10 165. "Analytical Evaluation of Polynaphthalenesulfonates as Oil-Well Cement Dispersants," T.G. Miller, Dowell, Inc.
- 11:30 166. "Gas Chromatographic Study of Chemically Modified Carbon Particles," J.A. Holcombe and Bunmi Ogunkeye, University of Texas

INTERNATIONAL SYMPOSIUM ON ION CHROMATOGRAPHY

MONDAY AFTERNOON, AUGUST 2 - Second Floor, Room E  
Hamish Small, presiding

- 2:00 97. "Care and Feeding of Fiber Suppressors," D. Eubanks, K. Haak, and A. Fitchett, Dionex Corporation
- 2:25 98. "Inorganic Cation and Anion Separations on Dynamically Coated Reversed Phase Columns," R.M. Cassidy and S. Elchuk, Atomic Energy of Canada Ltd. Research Company
- 2:50 99. "Automated Dialyzing Injection System for Chromatography," L.D. Hansen and F.R. Nordmeyer, Brigham Young University
- 3:15 Break
- 3:40 100. "Further Developments in the Computerized Acquisition and Reduction of Ion Chromatographic Data," C.C. Torquato, N. Latner, and D.C. Bogen, U.S. Department of Energy
- 4:05 101. "Cation Effects on Nonsuppressed Anion Chromatography at High Salt Concentrations," L.C. Stone and T.N. Andersen, Kennecott Minerals Company
- 4:30 102. "On the Ion Chromatographic Determination of S (IV)" P.K. Dasgupta, Texas Tech University

INTERNATIONAL SYMPOSIUM ON ELECTRON PARAMAGNETIC RESONANCE

MONDAY AFTERNOON, AUGUST 2 - Second Floor, Room F

EPR SESSION II - Time Resolved EPR - A.D. Trifunac, presiding

- 1:30 34. Plenary Lecture - "Transient Electron Spin Nutation - A Fast Way of Doing EPR", R. Furrer, Free University, Berlin
- 2:30 35. "Spectral and Spatial Diffusion of Triplet Spins in Organic Solids: Pulsed ODMR Studies", H.C. Brenner, New York University
- 3:30 Break
- 4:00 36. "Dynamics of the Photochemical H-Abstraction in Doped Fluorene Crystals as Studied by Time Resolved EPR, ONP, and Transient Optical Absorption", D. Stehlik, Free University, Berlin
- 4:30 37. "Time Resolved ODMR on the Yellow Phosphorescence of Benzil", R. Gilles and A.M. Ponte Goncalves, Temple University

SYMPOSIUM ON NUCLEAR MAGNETIC RESONANCE

MONDAY AFTERNOON, AUGUST 2 - Third Floor, Room F

NMR SESSION II - Solids - F. Miknis, presiding

- 1:30 131. "Optical Nuclear Polarization Enhanced Heteronuclear Cross Polarization," C.M. Oshiro and M.P. Klein, University of California, Berkeley
- 2:00 132. "Magic Angle of Spinning of Quadrupolar Nuclei," J.L. Ackerman, University of Cincinnati
- 2:30 133. "Signal Enhancement of <sup>14</sup>N Single Quantum Transitions in Solids," T.K. Pratun and M.P. Klein, University of California, Berkeley
- 3:00 Break
- 3:20 134. "NMR Studies at Surfaces." G.E. Maciel, D.W. Sindorf, M.R. Seger, I.-S. Chuang, and M.P. Shatlock, Colorado State University
- 4:00 135. "The Characterization of Silicon-Aluminum Ordering in Synthetic Zeolites by Silicon-29 NMR," M. Melchior, Exxon Research and Engineering Co.
- 4:30 136. "<sup>13</sup>C-NMR and Thermal Analysis Investigation of the State of Tetraalkyl-Ammonium and -Phosphonium Cations within the ZSM-5 AND ZSM-11 Framework," Z. Gabelica, J.B. Nagy and E.G. Derouane, Facultes Universitaires de Namur, (Belgium)

MONDAY EVENING - Tour of NSF Regional NMR Facility at Fort Collins, Colorado  
7 p.m. - 11 p.m.

SYMPOSIUM ON ATOMIC SPECTROSCOPY

MONDAY AFTERNOON, AUGUST 2 - Third Floor, Room E

T.M. Niemczyk, presiding

- 1:30 Introduction to Keynote Speaker
- 1:35 9. KEYNOTE SPEAKER  
"An Overview of Chemical Interactions Within Graphite Furnace Atomizers," J.A. Holcombe, University of Texas
- 2:15 10. "The use of Electrothermal Atomization for Simultaneous Multielement Atomic Absorption Spectrometry," J.M. Harnly, USDA
- 2:25 11. "Direct Analysis of Dust Particles in the Atmosphere by Carbon Furnace Atomic Absorption Spectrophotometry," J. Sneddon, New Mexico State University, L. Bezur and J.M. Ottaway, University of Strathelyde, Scotland
- 2:55 BREAK
- 3:20 12. "Improvement of Signal to Noise Ratios in Flame Atomic Absorption using a Zeeman Background Correction System," T.M. Vickrey, J. Liddle and J.D. Miller, Hitachi Scientific Instruments
- 3:40 13. "Applications of a Two-Channel Atomic Absorption Spectrophotometer: A Laboratory Survey," A. Rattonnetti, J. Sotera and G. Dulude, Instrumentation Laboratory Inc.
- 4:00 14. The Determination of Toxic Metals in Waters and Wastes by Automated Furnace Atomic Absorption," L.A. Covick, L.M. Voth and D.E. Shrader, Varian Instrument Group

SYMPOSIUM ON MASS SPECTROSCOPY

MONDAY AFTERNOON, AUGUST 2 - Second Floor, Room G

- 1:30 251. "Isotope Cluster Program Used to Selectively Characterize Mass Spectral Data," L. Abrams, and P.P. Dymerski, O.H. Materials Co.
- 2:00 252. "Discharge Ionization/Secondary Ion Mass Spectrometry Analysis of Biologically Important Compounds," D.E. Smith and D. Remling, Finnigan-MAT Corp.
- 2:30 253. "Characterization of Heterogeneous Metal Chelate Reactions by GC/MS," W.C. Gorman, Jr., and R.K. Skogerboe, Colorado State University
- 3:00 175. "A Retrofittable Fast Atom Bombardment Ion Source for the Hewlett-Packard 5985B GC/MS System." R.K. Latven, R.K. Goodley, and C.N. Kenyon, Hewlett-Packard Co.

SYMPOSIUM ON CHROMATOGRAPHY

MONDAY AFTERNOON, AUGUST 2 - Second Floor, Room D  
R.M. Barkley, presiding

- 1:30 167. Plenary Lecture "Micro-HPLC and Related Techniques," M. Novotny.  
Indiana University
- 2:25 168. "Applications of On-Line Direct Liquid Introduction Micro LC/MS  
to Drug Analysis," J.D. Henion, D. Skrabalak and C. Eckers,  
Cornell University
- 2:45 169. "On the Limit of Sedimentation Field Flow Fractionation for  
Characterization of Polydisperse Colloidal Samples," Feng-Shyang  
Yang. K.D. Caldwell, M.N. Meyers, and J.C. Giddings, University  
of Utah
- 3:05 Break
- 3:30 170. "Mobile Phase and Molecular Structure Effects in Normal Phase  
High Performance Liquid Chromatography Involving an Aminosilane  
Bonded Phase Column," W. Palaitis. Merck and Co., Inc.
- 3:50 171. "A Microprocessor Controlled Valve Switching Unit for Multi-  
Dimensional Liquid Chromatography and Complex HPLC Methods," J.K.  
Ung and C.J. Little, Kontron Analytical
- 4:10 172. "HPLC Tasks Using CRT Graphics on a Laboratory Microcomputer,"  
R.L. Miller and D.E. Bodwell. Perkin-Elmer Corp.
- 4:30 173. "Supercritical Chromatography on Packed Columns Using CO<sub>2</sub> and  
Polar Modifiers," R. Board. D. Gere, D. McManigill, and H.  
Weaver, Hewlett-Packard Co.

SYMPOSIUM ON ENVIRONMENTAL CHEMISTRY

MONDAY AFTERNOON, AUGUST 2 - Third Floor, Room D  
SESSION I - L. Jackson, presiding

- 1:00 Introductory Remarks
- 1:05 181. "Extraction of Humic Substances into Slightly Polar Water-  
Immiscible Organic Solvents," R.S. Allen III and P. MacCarthy,  
Colorado School of Mines
- 1:35 182. "Comparison of a Sequential Extraction Scheme to the EPA  
Extraction Procedure for Toxicants," T.E. Clevenger and W.  
Mullins, University of Missouri
- 2:05 183. "On-Site Pesticide Disposal." T.D. Spittler. J.B. Bourke, P.B.  
Baker, J.E. Dewey, F. Winkler, and T.K. DeRue, NYS Ag. Exp. Sta.,  
Cornell University
- 2:35 Break
- 3:05 184. "Analysis of Carbamate Pesticides by Capillary Gas  
Chromatography," C.P. Rzeszutko and M.K. Correa, U.S.  
Environmental Protection Agency
- 3:35 185. "Herbicide Residues Resulting from the Experimental Application  
of 2,4-D to Control Eurasian Watermilfoil in Banks Lake, WA and  
Ft. Cobb Reservoir, OK, N.E. Otto, J.C. Pringle, Jr., and D.  
Sisneros, U.S. Bureau of Reclamation
- 4:05 186. "Ruggedness Testing for Extraction and PNBDI Derivatization of  
Compound 1080 (Sodium Fluoroacetate) from Single Lethal Dose  
Baits," J. Nichols. L. Hageman, and L. Torraa, Montana Department  
of Agriculture - Laboratory Bureau

INTERNATIONAL SYMPOSIUM ON ION CHROMATOGRAPHY

TUESDAY MORNING, AUGUST 3 - Second Floor, Room E  
C.C. Torquato, presiding

- 8:30 103. "Ion Chromatographic Determination of Inorganic Anions with UV Detection - A Look at Applications," V.T. Turkelson and R.P. Himes, The Dow Chemical Company
- 8:55 104. "New Applications in MPIC," A. Fitchett, D. Eubanks, and L. Lois, Dionex Corporation
- 9:20 105. "Bromine Measurements by Ion Chromatography Using Electrochemical and Conductivity Detectors," Jann M. Frye, SOHIO Research
- 9:45 BREAK
- 10:15 106. "Ion Chromatography Exclusion Determination of Lactate in Serum," J.W. Smith and R.T. Ambrose, Eastman Kodak Company
- 10:40 107. "Ion Chromatographic Analysis of Bromate in Foods," K. Oikawa and H. Saito, Niigata College of Pharmacy, Japan
- 11:05 108. "Analysis of Metals and Metal Complexes by Ion Chromatography," J. Riviello and C. Pohl, Dionex Corporation
- 11:30 109. "Single-Column Ion Chromatographic Determination of Divalent Metal Ions and Lanthanides," G.J. Sevenich and J.S. Fritz, Department of Chemistry and Ames Laboratory, U.S.D.O.E.

INTERNATIONAL SYMPOSIUM ON ELECTRON PARAMAGNETIC RESONANCE

TUESDAY MORNING, AUGUST 3 - Second Floor, Room F  
EPR SESSION Ill-Fossil Fuels and Carbonaceous Materials-L.S. Singer, presiding.

- 8:30 38. Plenary Lecture - "ESR Study of Free radicals Produced Pyrolytically and Photolytically in Fluids Flowing at High Pressure and Temperature", R. Livingston and H. Zeldes, Oak Ridge National Laboratory
- 9:15 39. "Structure of the Electron Spin Centers in Carbonaceous Materials: 1954-1982", J.Uebersfeld, Universite Pierre et Marie Curie, France
- 9:45 40. "ESR Studies of Transient Free Radicals Produced During Coal Pyrolysis", H.L. Retcofsky and R.F. Sprecher, DOE, Pittsburgh
- 10:10 Break
- 10:40 41. "In Situ EPR Studies of Coal Hydrogenation", T.M. McKinney and I.B. Goldberg, Rockwell International
- 11:00 42. "Electron Spin Echo Studies of Natural and Solvent Refined Coal", S. Schlick, M. Narayana, and L. Kevan, University of Windsor and University of Houston
- 11:20 43. "Spin Echoes and Saturation in Coal", D.C. Doetschman, SUNY, Binghamton
- 11:40 44. "Electron Spin Resonance of Carbon/Potassium Systems", L.B. Ebert and D.R. Mills, Exxon Research and Engineering

SYMPOSIUM ON NUCLEAR MAGNETIC RESONANCE

TUESDAY MORNING, AUGUST 3 - Third Floor, Room F  
NMR SESSION III - Polymers - K. Zilm, presiding

- 8:30 137. Plenary Lecture "NMR in Solid Polymers - An Overview," D.L. VanderHart. National Bureau of Standards
- 9:30 138. "The Application of the Correlated States Model to the Analysis of NMR Relaxation Data in Polymers," P.T. Inglefield. J. Fragala, A.A. Jones, and K.L. Ngai, College of the Holy Cross, Claris. University and the Naval Research Laboratory
- 10:00 Break
- 10:30 139. "Solid State <sup>1</sup>H NMR Studies of Molecular Motion in Segmented Copolymers," L.W. Jelinski, J.J. Dumais, and A. Engel, Bell Laboratories and the DuPont Company
- 11:00 140. "NMR Studies of Ion-Containing Polymers: Solutions," A.C. Watterson, W.B. Moniz, T. Stone, T. Nagabhushanam, and J.C. Salomone, Naval Research Laboratory and University of Lowell

NMR SESSION IV - Biopolymers

- 11:30 141. "Conformational Studies of Dipeptides from Nuclear-Nuclear and Electron-Nuclear Spin Relaxation," C. Chachaty and B. Perly, C.E.N. de Saclay

SYMPOSIUM ON MASS SPECTROSCOPY

TUESDAY MORNING, AUGUST 3 - Second Floor, Room G

- 9:00 Featured Speaker. "Intermediate Range (10<sup>1</sup> - 10<sup>11</sup>) Isotope Ratio Mass Spectrometry," W.R. Shields. Los Alamos National Laboratory
- 10:00 254. "Plasma Discharge Source Mass Spectrometry," P.J. Turner. VG Isotopes Ltd.
- 10:30 Break
- 11:00 255. "Enriched Stable Isotopes as Internal Standards." S.H. Cole and P.H. Hemberger, Union Carbide (Oak Ridge)
- 11:30 256. "A Conversion and Appraisal of a Thermal Ionization Instrument to a Field Control System." V. Connolly. New Brunswick Laboratory

SYMPOSIUM ON CHROMATOGRAPHY

TUESDAY MORNING, AUGUST 3 - Second Floor, Room D  
K.C. Brooks, presiding

- 9:20 174. "Chemical Concentration Modulators for Multiplex Chromatography," J.B. Phillips. Southern Illinois University
- 9:40 176. "Combined WCOT Capillary GC/FTIR/MS Analysis of Organic Compounds," Keck. M. Schroeder, and R. Grabbe, U.S. Geological Survey
- 10:30 177. "Possibilities and Limitations of Non-Vaporizing, Cold, On-Column Injection Technique in High Resolution Gas Chromatography," G. Sisti, F. Munari, Carlo Erba Strumentazione, and B. Apon, Erba Instruments
- 10:50 178. "Studies of Complex Mixtures of Tris(*B*-Diketonato)Chromium(III) Geometrical Isomers with Fused Silica Capillary Columns," R.E. Sievers and K.C. Brooks University of Colorado

- 11:10 179. "Chromatographic Analysis of Limburger Cheese," T.H. Parliment. General Foods Corp.
- 11:30 180. "A CC-Automated Film Permeation System," J.M. Hughes. The Clorox Company

SYMPOSIUM ON ENVIRONMENTAL CHEMISTRY

TUESDAY MORNING, AUGUST 3 - Third Floor, Room D  
SESSION II - L. Jackson, presiding

- 8:30 Introductory Remarks
- 8:35 187. "The Use of Ion Exclusion Chromatography to Determine the Contribution of Weak Organic Acids to the Acidity of Precipitation in Remote Areas of the World," W.C. Keene and J.N. Galloway, University of Virginia
- 9:05 188. "Sequential Sampling of Storm Precipitation in Denver, Colorado," L.J. Schroder and A.H. Hedley, U.S. Geological Survey
- 9:35 Break
- 10:05 189. "Comparison of Storm and Weekly Composite Precipitation Samples at Raleigh, North Carolina," L.J. Schroder and R.A. Linthurst, U.S. Geological Survey and North Carolina State University
- 10:35 190. "The Impact of Lake Acidity on the Quality of Pumped Cottage Water," J.C. Meranger, T.H. Khan, C. Vairo, R. Jackson, and Wan Chi Li, Environmental Health Directorate and Barringer Magenta Ltd. (Ontario, Canada)
- 11:05 191. "The Determination of Uranium in Rocks, Soils, and Uranium Mill Tailings by a Fusion-Fluorimetric Technique." E.J. Cokal. Los Alamos National Laboratory

SYMPOSIUM ON SURFACE ANALYSIS

TUESDAY MORNING, AUGUST 3 - Third Floor, Room E  
W.H. Christie, presiding

- 9:00 Opening Remarks, W.H. Christie
- 9:05 198. Applications and Techniques of Scanning Auger Microscopy. T.J. Shaffner, Texas Instruments, Inc.
- 9:45 199. Analytical Applications of Heavy Ion Induced X-Ray Fluorescence and Auger Electrons. T.M. Rosseel, R.L. Auble, L.D. Huiett, S. Kahane, H.J. Kim, W.T. Milner, G.D. O'Kelley, S. Raman, G.G. Slaughter, C.R. Vane, and J.P. Young, Oak Ridge National Laboratory
- 10:05 200. Surface Characterization by Combined Low Energy Ion Scattering (LEIS) and Spark Source Mass Spectrometry (SSMS) Analysis. D.L. Malm, Bell Laboratories
- 10:25 Intermission
- 10:45 201. Surface Characterization of Materials for Use in Advanced Energy Conversion Systems. R.E. Witkowski, Westinghouse R&D Center
- 11:05 202. Surface Analysis of Commercially Made Mirrors. T.M. Thomas. J.R. Pitts and A.W. Czanderna, Solar Energy Research Institute
- 11:30 203. Surface Analysis of Mirrors Made From Organometallic Solutions. J.R. Pitts, T.M. Thomas and A.W. Czanderna, Solar Energy Research Institute

GENERAL SESSION - POSTERS

TUESDAY, AUGUST 3 - First Floor, Rooms E - F  
C. Arozarena, presiding

Posters displayed all day - Authors present 2:00 - 4:00

221. "The U.S. Environmental Protection Agency Analytical Reference Standards Repository for Toxic Substances," R.E. Thompson. Northrup Services, Inc.
222. "On-Site Pesticide Disposal," T.D. Spittler. J.B. Bourke, P.B. Baker, J.E. Dewey, F. Winkler, and T.K. DeRue, NYS Ag. Exp. Sta., Cornell University
223. "Calculation of the Dissociation Constants for a Humic Acid Sample Based on the Presence of Isobestic Points in the Fluorescence Spectrum." M.C. Goldberg and K.M. Cunningham, U.S. Geological Survey
224. "Chemical Ionization Utilizing a Single High Vacuum Pump." D.E. Smith. Finnigan-MAT Corporation
225. "Distribution of Uranium and Radium in Ralston Creek and Reservoir, Colorado." I.C. Yang. U.S. Geological Survey, A.M. Essed and K.W. Edwards, Colorado School of Mines
226. "Toxicity of Spent Oil Shale Leachate to a Blue-Green Alga," D. McKnight. W. Pereira, C. Rostad, and E. Stiles, U.S. Geological Survey
227. "A Computer Accessible Compendium for Selected Instrumental Methods," F.A. Settle, Jr., Virginia Military Institute, and M.A. Pleva, Washington and Lee University
228. "A Quality Assurance Plan for a Multi-Laboratory System," P.B. Peart and L.C. Friedman
229. "Chemical Characterization of Retorted Oil-Shale Leachates," S.M. Johnson, T.R. Steinheimer, U.S. Geological Survey, C.L. Grant, S.J. Endersen, University of New Hampshire, and F.J. Trujillo, University of Antioquia, Colombia
230. "Optical Nuclear Polarization Enhanced Cross Polarization," M.P. Klein. University of California, Berkeley
231. "Products of Gas Phase Alkene-Ozone Reactions," C. Rusik and L.A. Hull, Union College
232. "Characterization of Organic Compounds in Ground Water Contaminated by Coal-Tar Wastes Using Gas Chromatography-Mass Spectrometry Computer Techniques," C.E. Rostad and W.E. Pereira, U.S. Geological Survey
233. "Force Field for C4X4 Compounds," G. Diaz. Universidad Catolica, Chile
234. "Raman Spectral Studies of Rare Earth Phosphates," G.M. Begun and C.E. Bamberger, Oak Ridge National Laboratory
235. "Mass Spectrometric Study of Pyrolysis Behavior of Solid Fuels," M.N. Soltys and T.A. Milne, Solar Energy Research Institute
236. "Inductively Coupled Plasma Emission Spectroscopic Determination of Metals in Precipitation," M.M. Reddy, M. Werner and E. Zayhowski, US Geological Survey

237. "Thermal Analysis Methods at Rocky Flats," J. Palcic and P. Hyman, Rockwell International
238. "Chlorinated Hydrocarbons in Petroleum Products by Gas Chromatography/Hall Electrolytic Conductivity Detector," M.P. Phillips and O.J. Logsdon, Rocky Mountain Analytical Laboratory
239. "Determination of Total Iodine in Foods and Nutritional Products by Differential Pulse Polarography," D.D. Thompson. S. Lee, R.G. Locatelli, S. Subramanian, and R.J. Allen, Forrest C. Shaklee Research Center
240. "Determination of Selenium in Human and Quarter Horse Blood by Hydride Generated and Graphite Furnace Atomic Absorption Spectrophotometry," V.A. Fuavo, B.L. Porter, and J. Sneddon, New Mexico State University

#### INTERNATIONAL SYMPOSIUM ON ION CHROMATOGRAPHY

TUESDAY AFTERNOON, AUGUST 3 - Second Floor, Room E  
A.G. Hedley, presiding

- 2:00 110. "Determination of Acetate by Ion Exclusion Technique Using H<sub>2</sub>CO<sub>3</sub> as an Eluent." H. Itoh and Y. Shinbori, Faculty of Pharmaceutical Sciences, Josai University and I. Murata, Faculty of Science, Osaka University
- 2:25 111. "Analysis of Fermentation Broths and Raw Materials Utilizing Ion Chromatographic Techniques." T.L. Hassinger and B.A. Olsen, Eli Lilly and Company
- 2:50 112. "Ion Chromatographic Analysis of Ethanol/Ammonium Tartrate Aluminum Anodization Solutions," R.M. Merrill, Sandia National Laboratories.
- 3:15 BREAK
- 3:40 113. "Measurement of Quaternary Ammonium Ions in Zn/Br, Battery Electrolytes Using Ion Chromatography," P.G. Grimes, R.V. Kastrup, G.E. Milliman and A.R. Young, II, Exxon Research and Engineering Company
- 4:05 114. "Applications of Ion Chromatography in the Semi-Conductor Industry," K. Evans, Motorola Inc.
- 4:30 115. "Ion Chromatography Capabilities in Food Analysis." L. Angers and L. Kimball, Dionex Corporation

#### INTERNATIONAL SYMPOSIUM ON ELECTRON PARAMAGNETIC RESONANCE

TUESDAY AFTERNOON, AUGUST 3 - Second Floor, Room F  
EPR SESSION IV-Fossil Fuels and Carbonaceous Materials-L.S. Singer, presiding

- 1:30 45. "An EPR Investigation of the Bitumen, Asphaltene and Petroleum Fractions in P.R. Spring (Utah) Tar Sand", V.M. Malhotra and W.R.M. Graham, Texas Christian University
- 1:45 46. "EPR and IR Study of the Clay Fraction of a Bituminous Coal", V.M. Malhotra and W.R.M. Graham, Texas Christian University
- 2:00 47. "Effects of Catalysts and Steam Gasification on ESR of Carbon Black", K.M. Sancier. SRI International
- 2:25 Break

EPR SESSION V - G.R. Eaton, presiding

- 2:55 48. "EPR of N<sub>0</sub> in Zeolites", T.J. Schaafsma and B. Meijer, Agric. Univ. de Dreijen
- 3:25 49. "An Experimental and Theoretical Study of the Low Temperature ESR of the Cyclooctatetraene and Tetramethylcyclooctatetraene Anion Radicals in Single Crystal Environments", M.T. Jones. University of Missouri - St. Louis and E. de Boer, University of Nijmegen
- 3:45 50. "EPR and Photoluminescence Studies of Defect Centers in ZnO", W.G. McDugle and R.S. Eachus, Kodak Research Laboratories
- 4:05 51. "EPR Studies of Two Structural Phase Transitions in Doped Crystals of RbMgBr.", G.L. McPherson and K.H. Kirklin, Tulane University
- 4:25 52. "EPR Studies of the Dilute Europous Alloys Eu Tfbj<sup>^</sup>CNH<sup>^</sup>g". F.Y. Robb, T.R. White, and W.S. Glaunsinger. Arizona State University

SYMPOSIUM ON NUCLEAR MAGNETIC RESONANCE

TUESDAY AFTERNOON, AUGUST 3 - Third Floor, Room F

NMR SESSION IV (cont'd) - Biopolymers - J. Frye, presiding

- 1:30 142. "Structure, Dynamics and Interaction of 13C-Labeled Individual E. Coli Transfer RNAs," J.I. Olsen, M.P. Schweizer, I.J. Walkiw, W.D. Hamill, Jr., W.J. Horton and D.M. Grant, University of Utah
- 2:00 143. "13C NMR Study of Bovine Galactosyltransferase Specificity," E. Berman and T.L. James. University of California, San Francisco
- 2:30 144. "Multinuclide NMR Methods to Monitor Sodium Transport and other Transports Across the Renal Brush Border Membrane," A. Elgavish, G.A. Elgavish and University of Alabama, Birmingham
- 3:00 145. "Applications of Carbon-13 Labeling/NMR Detection for *in vivo* Metabolic Studies." R.E. London, T.E. Walker, C.J. Unkefer, and N.A. Matwiyoff, Los Alamos National Laboratory
- 3:30 146. "Proton Magnetic Resonance Studies on the Catalytic Center of Subtilisins and Thiolsubtilisins," F\* Jordan. Rutgers University
- 4:00 147. 15N of a Liver Alcohol Dehydrogenase - Inhibitor Complex," N.N. Becker and J.D. Roberts, California Institute of Technology
- 4:30 148. "15N NMR Studies of Amino Acids in *Neurospora Crassa* as Probes of Intracellular Environment K. Kanamori. T.L. Legerton, R.L. Weiss, and J.D. Roberts, California Institute of Technology and University of California, Los Angeles

SYMPOSIUM ON MASS SPECTROSCOPY

TUESDAY AFTERNOON, AUGUST 3 - Second Floor, Room G

- 1:30 257. "Automation of a Three Stage, Thermal Emission Isotope Ratio Instrument," L. Smith. Department of the Air Force
- 2:00 258. "Contamination, Interferences and Memory Effects in the Determination of Isotopic Ratios by Volatile Metal Chelate-Mass Spectrometry Techniques," S.R. Hill, R.K. Skogerboe, Colorado State University, and F.E. Lichte, U.S. Geological Survey
- 2:30 259. "Dynamic Mass Spectrometry: A Residual Gas Analysis Method and Some Applications," T.L. McFeeters. Rockwell International

- 3:00 260. "Application of Amberlite IRA-938 Ion Exchange Resin to Isotope Ratio Mass Spectrometry of Uranium/Plutonium Mixtures," M.B. Bergeron. Rockwell International
- 3:30 261. "The Determination of D<sub>2</sub>O by Mass Spectrometry," R.W. Looyenga, South Dakota School of Mines and Technology

#### SYMPOSIUM ON ENVIRONMENTAL CHEMISTRY

TUESDAY AFTERNOON, AUGUST 3 - Third Floor, Room D  
SESSION III - L. Jackson, presiding

- 1:00 Introductory Remarks
- 1:05 192. "The Chemistry and Health Effects of a Major Air Pollution Episode in Utah Valley," L.D. Hansen and D.J. Eatough, Brigham Young University
- 1:35 193. "Continuous Ultrasensitive Measurement of Nitric Acid and Other Oxides of Nitrogen in Air," M.J. Bollinger. R.E. Sievers, and F.C. Fehsenfeld, University of Colorado and CIRES and NOAA Aeronomy Laboratory
- 2:05 194. "Organic Air Pollutants from Shale Oil Wastewaters," S.B.Hawthorne and R.E. Sievers, University of Colorado
- 2:35 Break
- 3:05 195. "Analysis of Ambient Air Around a Hazardous Surface Impoundment," J. Broadus. G. Connolly, and M. Witt, Dept. of the Army - Rocky Mountain Arsenal
- 3:35 196. "Determination of Low Level Quantities of Chloropicrin, Chloroform, and Carbonyl Chloride in Air by Computer Assisted infrared Spectrophotometry," G.B. Mohrman. E.G. Jones, and M.E. Witt, Dept. of the Army - Rocky Mountain Arsenal
- 4:05 197. SAS STUDENT AWARD ADDRESS "The Analysis of River Sediments: Evaluation of both the Digestion Procedure and the Trace Metal Determinations by Atomic Absorption Spectroscopy," G.S. Caravajal and K.I. Mahan, University of Southern Colorado, and D.E. Leyden, University of Denver.

#### SYMPOSIUM ON SURFACE ANALYSIS

TUESDAY AFTERNOON, AUGUST 3 - Third Floor, Room E  
T.J. Shaffner, presiding

- 2:00 204. Quantitative Secondary Ion Mass Spectrometry. Peter Williams. Arizona State University
- 2:40 205. Surface Analysis of Silicon Grain Boundary Chemistry. Phillip E. Russell, L.L. Kazmerski, P.J. Ireland, Solar Energy Research Institute
- 3:20 Intermission
- 3:35 206. Combined Analysis for Semiconductor Materials Evaluation. B.F. Phillips. Perkin-Elmer Corporation
- 3:55 207. Use of the Raman Microprobe for Analysis of Optical Surfaces. F. Adar. Instruments SA, Inc.
- 4:15 208. Photoacoustic Spectroscopy Study of Metal - Support Interactions in Metal Oxide Catalysts Supported on  $\gamma$ -Alumina. L.W. Burggraf, D.E. Leyden', R.L. Chin', D.M. Hercules', 'USAF Academy, 'Colorado State University, 'University of Pittsburgh
- 4:35 209. Surface Analysis: An Overview of Techniques and Applications in an Analytical Environment. Hilary Karp, Robert Linder, Surface Science Laboratories, Inc.

# INTERNATIONAL SYMPOSIUM ON ION CHROMATOGRAPHY

WEDNESDAY MORNING, AUGUST 4 - Second Floor, Room E  
M.M. Reddy, presiding

- 8:55 116. "Airborne Formaldehyde Collection by Solid Sorbent and Analysis by Ion Chromatography," K.E. Williams. U.S. Army, Aberdeen Proving Ground.
- 9:20 117. "Automated Determination of Bromide in Water by Ion Chromatography with an Electrochemical Detector," G.S. Pyen and D.E. Erdmann, U.S. Geological Survey
- 9:45 BREAK
- 10:15 118. "A Monitoring Study of Nitrate in Drinking Water in the Federal Republic of Germany," M. Sonneborn and T. Darimont, Institute for Water, Soil and Air Hygiene, Federal Republic of Germany
- 10:40 119. "Ion Chromatographic Analysis for Chloride, Fluoride, and Sulfate in Precipitation," M.M. Reddy, Marilyn Werner, and A.G. Hedley. U.S. Geological Survey
- 11:05 120. "A Three-Minute Analysis for Acid Rain Anions by Single-Column Ion Chromatography (SCIC)," T. Jupille, D. Togami and D. Burge, Wescan Instruments, Inc.

# INTERNATIONAL SYMPOSIUM ON ELECTRON PARAMAGNETIC RESONANCE

WEDNESDAY MORNING, AUGUST 4 - Second Floor, Room F  
EPR SESSION VI - Pulsed EPR - L.B. Dalton, presiding

- 8:30 53. Plenary Lecture - "Analysis of Electron Spin Echoes by Spectral Representation," L.J. Schwartz, A.E. Stillman, and J.H. Freed. Cornell University
- 9:20 54. Plenary Lecture - "Short Pulse Saturation Recovery", A. Kusumi, J.S. Hyde and W. Froncisz, Medical College of Wisconsin
- 10:10 Break
- 10:40 55. Plenary Lecture - "Electron Spin Echo Experiments on Triplet State", D.C. Doetschman. SUNY, Binghamton
- 11:30 56. "ESE and ENDOR Studies of Pristine Polyacetylenes", H. Thomann, H. Kim, L.R. Dalton. Y. Tomkiewicz, N.S. Shiren, T.C. Clarke, B.H. Robinson, SUNY Stony Brook and University of Southern California

# SYMPOSIUM ON NUCLEAR MAGNETIC RESONANCE

WEDNESDAY MORNING, AUGUST 4 - Third Floor, Room F  
NMR SESSION V - Fossil Fuels - D. Netzel, presiding

- 9:00 149. Plenary Lecture "Magnetic Resonance in Coal Research - History, Status, Pitfalls and Needs." H.L. Retcofsky, Pittsburgh Energy Technology Center
- 10:00 150. "Application of Dynamic Nuclear Polarization in Coal Characterization by Means of Magnetic Resonance," R.A. Wind. M.J. Duijvestijn, and J. Smidt, Delft University of Technology, Netherlands
- 10:30 Break
- 11:00 151. "Characterization of Whole Coals by Carbon-13 CP/MAS Spectroscopy at High Field." R.E. Botto and R.E. Winans, Argonne National Laboratory
- 11:30 152. "Elucidation of Structural Information from Solid Fossil Fuels by Recent NMR Techniques," P.D. Murphy and B.C. Gerstein, IBM Instruments Inc. and Iowa State University

SYMPOSIUM ON ATOMIC SPECTROSCOPY

WEDNESDAY MORNING, AUGUST 4 - Third Floor, Room E

ATOMIC EMISSION SESSION - F.E. Lichte, presiding

- 8:30 15. "The Role of Three-Body Processes in the ICP Excitation Mechanism," J.W. Mills, Fort Levis College, J.W. Carr and G.M. Hieftje, Indiana University
- 8:50 16. "Determination of Halogens in Geologic Materials by Atomic Emission Spectrography of a Low-Pressure Microwave-Induced Helium Plasma," N. Rait, D.W. Golightly, and C.J. Massoni, U.S. Geological Survey
- 9:10 17. "Time Response Studies in the ICP Using RF Power Modulation," J.W. Carr, J.W. Mills and G.M. Hieftje, Indiana University
- 9:30 18. "Analysis of Wastewater with a Scanning ICP," D.D. Nygaard, D.S. Chase and D.A. Leighty, Instrumentation Laboratory
- 9:50 BREAK
- 10:20 19. "Determination of Volatile and Refractory Elements in Microliter Samples Using Electrothermal Carbon Cup Vaporization and Inductively Coupled Plasma Excitation," K.C. Ng and J.A. Caruso, University of Cincinnati
- 10:40 20. "Advantages of Synchronously-Gated Detection in Spectrochemical Alloy Analysis Using Spark Excitation," S.G. Barnhart and J.P. Walters, University of Wisconsin
- 11:10 21. "Alkali Elements in the Inductively Coupled Plasma." L.M. Faires, C.T. Apel, Los Alamos National Laboratory, T.M. Niemczyk, University of New Mexico
- 11:20 22. "Interelement Interferences and Temperature Measurements in a Microwave-Induced Nitrogen Discharge at Atmospheric Pressure (MINDAP)," R.D. Deutsch and G.M. Hieftje, Indiana University

SYMPOSIUM ON RAMAN AND INFRARED SPECTROSCOPY

WEDNESDAY MORNING, AUGUST 4 - Second Floor, Room D

FOURIER TRANSFORM INFRARED SPECTROSCOPY - M.C. Goldberg, presiding

- 8:25 Introduction - M.C. Goldberg
- 8:30 210. "An FT-IR Study of the Surface Reaction Between SO<sub>2</sub> and Soot," D.S. Robinson, M.S. Akhter, A.R. Chughtai and D.M. Smith, University of Denver
- 9:00 211. "The Infrared Spectroscopy of CO Adsorbed on Supported Molybdenum (0)," T. Puckett, H-P Lu, A.R. Chughtai and D.M. Smith, University of Denver
- 9:30 212. "The Use of FTIR to Characterize Sediment Coatings of Phosphate on the Substrates Goethite and Pyrolucite," M.C. Goldberg, E.R. Weiner and P. Boymel, U.S. Geological Survey and University of Denver
- 10:00 Break
- 10:30 213. "The Determination of Silanol in Silicones by Quantitative FTIR," G.W. Griffith, The Bendix Corporation
- 11:00 214. "Alkali Halide Pellets of Deuterated Solid Samples for Infrared Spectrometry," P. MacCarthy, Colorado School of Mines
- 11:30 215. "Filamentous Bacterial Virus, - A Realistic Model Spectrum for Alpha Helix," C. Gilon and E.J. Wachtel, Weizmann Institute of Science

GENERAL SESSION

WEDNESDAY MORNING, AUGUST 4 - Third Floor, Room D  
C.E. Andre, presiding

- 8:35           Introductory Remarks
- 8:40   241.   "Optimum Data Reduction for the Chromatographic Laboratory," D.E. Bodwell and M. Harter, Perkin-Elmer Corporation
- 9:00   242.   "A Computer Controlled Acquisition System for Atomic Absorption Data," R.E. Bostrom. Kansas Department of Health and Environment
- 9:20   243.   "The Coulometric Determination of Moisture and Combined Water in Silicate Rocks Using the Karl Fischer Titration Method," D.R. Norton, U.S. Geological Survey
- 9:40           Break
- 10:10   244.   "The Use of Bonded Phase Extraction Columns for Rapid Sample Preparation of Priority Pollutant Phenols in Water," P.A. Dimson and L.S. Yago, Analytichem International, Inc.
- 10:30   245.   "Solvolyis of 1-Butadiynylvinyl Trifluoromethanesulfonates," M. Ladika, P.J. Stang - University of Utah, M.D. Schiavelli and M. Hughey - College of William and Mary
- 10:50   246.   "Effect of Strong Complexing Agents on Response of Precipitate-Based Copper (II) Ion-Selective Electrodes," G.C. Smith and P. MacCarthy, Colorado School of Mines
- 11:10   247.   "Analytical Evaluation of Corrosion-Induced Microstructural Changes in a U.S. Core Graphite," D.A. Lee, W.P. Eatherly, and J.D. Kintigh, Oak Ridge National Laboratory

INTERNATIONAL SYMPOSIUM ON ION CHROMATOGRAPHY

WEDNESDAY AFTERNOON, AUGUST 4 - Second Floor, Room E  
M. Sonneborn, presiding

- 1:30   121.   "Applications of Ion Chromatography to Synfuels Research," R.A. Nadkarni and D.M. Pond, Exxon Research and Engineering Company
- 1:55   122.   "An Ion Chromatographic Method for the Determination of Total Sulfur in Plant Material," J.G. Zakrevsky and S.S. Sidhu, Newfoundland Forest Research Center
- 2:20   123.   "Analysis of Contaminants and Corrosion Products on Indoor Surfaces by Ion Chromatography," G.B. Munier, L.A. Psota-Kelty, and J.D. Sinclair. Bell Laboratories
- 2:45           BREAK
- 3:35   124.   "Ion Chromatographic Determination of Bromide Ion in Raw Waters Using a Concentrator Column," C.M. Morrow and R.A. Minear, University of Tennessee, and D.C.M. Hines and A.M. Yoakum, Stewart Laboratories
- 3:40   125.   "Sampling and Analyzing Mixtures of Sulfoxy Anions in Natural Waters," C.O. Moses\*, D.K. Nordstrom\*\*, and A.L. Mills\*, ^University of Virginia and \*\*U.S. Geological Survey
- 4:05   126.   "Effect of Ammonia Concentration on PPB Chloride Measurement," S. H. Peterson,. D.F. Pensensadler, and S.L. Anderson, Westinghouse Research and Development Center

INTERNATIONAL SYMPOSIUM ON ELECTRON PARAMAGNETIC RESONANCE

WEDNESDAY AFTERNOON, AUGUST 4 - Second Floor, Room F

EPR SESSION VII - G.R. Eaton, presiding

- 1:30 57. "ENDOR and TRIPLE Resonance Studies on Primary Products of Bacterial and Plant Photosynthesis", Lubitz, Free University, Berlin
- 2:00 58. "Spin-Label Technique to Detect Domain-Domain Interaction in Antibody Molecules", P. Zavodszky, F. Kilar, and T. Simon, Hungarian Academy of Sciences
- 2:20 59. "Dipolar Correlation Function in EPR (or NMR) Lineshape Analysis for a Finite Two-Dimensional Liquid", J.-P. Korb, D. Torney, and H.M. McConnell, Stanford University
- 2:40 60. "An Electron Spin Resonance Determination of Semiquinone Equilibria in Aqueous Alkali", J. Charkoudian and D. Gildea, Polaroid Research Laboratory

EPR SESSION VIII - S.S. Eaton, presiding

Poster Session - First Floor, Rooms E - F

Authors present 3:00 - 4:00 for papers labeled A,  
4:00 - 5:00 for papers labeled B.

- A 61. "Hyperfine Coupling Constants for Cobalt and Copper Bleomycin, W.E. Antholine and R.C. Sealy, Medical College of Wisconsin and D.H. Petering, University of Wisconsin - Milwaukee
- B 62. "Azethoxyl, Doxyl, Analysis: Probing Ordered Systems." M.S. Broido and E. Meirovitch, Weizmann Institute of Science
- A 63. "EPR Studies of Phenylalanine Hydroxylase - A "g=4.3" Iron Enzyme," B.J. Gaffney\*, D. Wallick\*\*, R. Lazarus\*\*, R.K. Scheule\*, and S.J. Benkovic\*\*, \*Johns Hopkins University and \*\*Pennsylvania State University
- B 64. "Saturation Transfer EPR Measurements of the Interaction of Spin Labeled Subfragment-1 and Heavy Meromyosin with F-Actin," B.A. Manuck, J.C. Seidel, and J. Gergely, Boston Biomedical Research Institute
- A 65. "Single Crystal EPR of Spin-Labeled Copper Porphyrins," D. Reddy and G.R. Eaton, University of Denver and S.S. Eaton, University of Colorado at Denver
- B 66. "Half-Field Transitions," S.S. Eaton, University of Colorado at Denver and G.R. Eaton, University of Denver
- A 67. "Metal-Nitroxyl Exchange Interaction Dependence on Pathway," J.K. More, K.M. More, G.R. Eaton, University of Denver, and S.S. Eaton, University of Colorado at Denver
- B 68. "Spin-Trapping of the Trichloromethyl Radical from a Variety of Reactions," R. Sridhar and J.L. Poyer, Oklahoma Medical Research Foundation
- A 69. "ESR Studies of Spin Probes in Sodium Dibutylphosphate Liquid Crystals," C.Chachaty, E. Stefani, S. Belaid, CEN de Saclay
- B 70. "Measurement of HFI with ID- and 2D-ESE Spectroscopy," H. Barkhuijsen, R. de Beer, K. Nederveen, and D. van Ormondt, Delft University of Technology
- A 71. "NMR-Detected Nuclear Resonance of Transient Radicals," R.H.D. Nuttall and A.D. Trifunac, Argonne National Laboratory

- B 72. "Optically Detected Time-Resolved EPR," S.M. Lefkowitz and A.D. Trifunac, Argonne National laboratory
- A 73. "ESR Studies of Lipid-Protein Interaction in Lipoprotein Recombinants," D.J. Vaughan, General Foods Research
- B 74. "EPR Studies of Surface Interactions - 0,~ on <sup>67</sup>Zn enriched ZnO," R. Clarkson, and R.G. Kooser, University of Illinois
- A 75. "Dependence of ESR and EPR Signals on Modulation Phase Angle," I. Miyagawa, F. Khalaf, B. Rakvin, and C. Alexander, Jr., University of Alabama
- B 76- "EPR Studies of Stable Free Radicals in Carbonization," I.C. Levis and L.S. Singer, Union Carbide
- A 77. "Roles of Catalyst for Coal Liquefaction Reaction by Means of High Temperature ESR and NMR," T. Yokono., T. Khono, and Y. Sanada, Coal Research Institute, Japan
- 5 78. "Oxidation of Substituted Benzo(a)pyrenes," P.D. Sullivan, L.F. Ellis, F. Bannoura, and I.J. Ocasio, Ohio University
- A 79. "EPR and Structural Studies of Intermediate pK Vanadyl (IV) a.a' - Dihydroxydicarboxylates u.b. Beeson, R.E. Tapscott, and E.N. Duesler, University of New Mexico
- B 80. "Spin-Trapping of NC2 Radicals Produced by Ultraviolet Photolysis of RDX, HMX and Nitroguanidine," M.D. Pace and W.B. Moniz, Naval Research Laboratory, Washington D.C.
- A 81. "Intra-Clathrate Trapped Radicals: Conformation and Dynamics," E. Meirovitch, Weizmann Institute of Science
- B 82. "EPR of Free Radicals Induced in L-Ascorbic Acid by Laser Radiation or X-Rays from 77K to 300K," G.C. Moulton and G. McDermon\*, Florida State University and \*Goodyear Aerospace Corp.
- A 83. "An EPR Study at 77K of Alkoxy and Hydroxyalkyl Radicals in X-Ray Irradiated Trehalose Single Crystals," P.O. Samskog, and L.D. Kispert, University of Alabama, and A. Lund, Studsvik Science Research Laboratory, Sweden
- B 84. "Resolution Enhanced EPR: Theory, Experiment, and Application," R.C. Perkins, Varian Associates
- A 85. "EPR and ST-EPR Investigations of Model Biological Systems Using <sup>15</sup>N and Deuterium Substituted Spin Labels," A.H. Beth, S.D. Venkatramu, K. Balasubramanian, A.J. Dammers, D.E. Pearson, C.R. ParV, and J.H. Park, Vanderbilt University
- E 86. "EPR Studies of Lithium Dithionite," R.L. Ake, Old Dominion University
- A 87. "Magnetization Hysteresis EPR, A New Method for Studying Slow Molecular Motion," A.I. Vistnes, University of Oslo

SYMPOSIUM ON NUCLEAR MAGNETIC RESONANCE

WEDNESDAY AFTERNOON, AUGUST 4 - Third Floor, Room F  
NMR SESSION VI - Fossil Fuels - D. Netzel, presiding

- 1:30 153. H and C Relaxation in Coals: the Effects of Paramagnetic Impurities," K.W. Zilm. University of Utah
- 2:00 154. "Geochemical Conditions and Solid State NMR Analyses: Keys to Understanding the Chemical Structure of Coal," P.G. Hatcher. I.A. Breger, N.M. Szeverenyi, and G.E. Maciel, U.S. Geological Survey and Colorado State University
- 2:30 155. "<sup>13</sup>C CP/MAS Studies of Canadian Peat Moss." D. Cory and W.M. Ritchey, Case Western Reserve University, and H. Morita, Chem. and Biol. Res. Inst., Ottawa, Ontario
- 3:00 Break
- 3:30 156. "Heteronuclear Correlated 2-D NMR of Synthetic Fuels," L.W. Dennis and R.E. Pabst, Exxon Research and Engineering Co.
- 4:00 157. "Characterization of H/D Treated Petroleum Streams," J.R. Mooney, D.R. Herrington, A.P. Schwerko, and P.A. Budinger, Standard Oil Co. (Ohio)
- 4:30 158. "A <sup>13</sup>P, <sup>13</sup>C NMR Study of Rhodium Hydroformylation Mechanisms," R.V. Kastrup, A.A. Oswald, D.E. Hendriksen, J.S. Merola, and J.C. Reisch, Exxon Research and Engineering Co.

SYMPOSIUM ON ATOMIC SPECTROSCOPY

WEDNESDAY AFTERNOON, AUGUST 4 - Third Floor, Room E  
T.M. Niemczyk, presiding

- 1:30 Introduction of Keynote Speaker
- 1:35 23. KEYNOTE SPEAKER  
"New Developments in Inductively Coupled Plasma Emission Spectrometry," G. Horlick, University of Alberta, Canada
- 2:15 24. "Pressure-limited Argon Radiation Trapping in the ICP," J.W. Mills, Fort Lewis College, and G.M. Hieftje, Indiana University
- 2:35 25. "Direct Detection of Contaminant in Liquids via Laser-Induced Break-Down Spectroscopy (LIBS)," D.A. Cremers, L.J. Radziemski and R.J. Martinez, University of California - Los Alamos National Laboratory
- 2:55 BREAK
- 3:20 26. "Near-Infrared Nonmetal Atomic Emission from Organic Samples in a Microwave-Induced Plasma," J.E. Freeman and G.M. Hieftje, Indiana University
- 3:40 27. "Inductively Coupled Plasma Emission Spectrometric Detection for High Pressure Liquid Chromatography of Metal Complexes," W. Nisamanepong, and J.A. Caruso, University of Cincinnati

- 4:00 28. "Establishment of Correct Analytical Parameters for a Multielement Rapid Scanning Sequential ICP," A<sup>^</sup> Rattonetti, Instrumentation Laboratory
- 4:20 29. "Design and Performance Characteristics of a New Paschen-Runge Sequential Monochromator for ICP Applications," L.P. Morgenthaler, D.J. Comaford and K. Kondo, Bausch and Lomb
- 4:40 30. "Automated Oil Analysis: AIDS for the ICP," S<sup>±</sup> Evans, R.J. Klueppel, J.-C. Schmitt, and P. Gilles, Baird Corporation Corporation

#### SYMPOSIUM ON RAMAN AND INFRARED SPECTROSCOPY

WEDNESDAY AFTERNOON, AUGUST 4 - Second Floor, Room D  
RAMAN AND INFRARED SPECTROSCOPY - P.J. Trotter, presiding

- 1:30 216. "Software Methodology for Path Length Indeterminate Quantitative Analysis," R.J. Obremski, J. Bernard and L. Sims, Beckman Instruments, Inc.
- 2:00 217. "Resonance Raman Selectivity in Metal-Metal Bonds, Metal-Indicator Dyes, and One-Dimensional Organic Conductors." P.J. Trotter, Eastman Kodak Company
- 2:30 216. "Enhanced Raman Scattering from Metal Electrode Surfaces," M.V. Johnston, A.B. Apkarian, B.E. Miller, and R.P. Van Duyne, Northwestern University
- 3:00 Break
- 3:30 219. "A Raman Spectroscopic Analysis of Volcanic Ash from Mt. St. Helens and Mt. Sakurajima (JAPAN)," Hiroyuki Ishizaki and A.T. Tu, Colorado State University
- 4:00 220. "Raman Microprobe Analysis of Polymers, Ceramics, and Corrosion," Fran Adar, Instruments SA, Inc.

#### INTERNATIONAL SYMPOSIUM ON ELECTRON PARAMAGNETIC RESONANCE

THURSDAY MORNING, AUGUST 5 - Second Floor, Room F  
EPR SESSION IX - Pulsed EPR - L.R. Dalton, presiding

- 8:30 88. Plenary Lecture - "Effects of Motion on ESE and ESEEM Signals," B.H. Robinson, University of Washington
- 9:20 89. "Electron Spin Echo Studies of Doped Poly(p-Phenylene Sulfide) and p-Terphenyl", L.P. Kispert, M.K. Bowman, and J.R. Norris, University of Alabama and Argonne National Laboratory
- 9:45 Break
- 10:15 90. Plenary Lecture - "Techniques for Fourier Transform EPR Spectroscopy", M.K. Bowman and J.R. Norris, Argonne National Laboratory
- 11:05 91. Plenary Lecture - "Pulsed Electron Magnetic Resonance of Transient (10 - nsec) Radical Pairs," J.R. Norris, Argonne National Laboratory

i n

- 1 AUTOMATION OF TRACE METAL ANALYSIS BY MICROCOMPUTER CONTROLLED-FLOW INJECTION FLAME ATOMIC ABSORPTION SPECTROSCOPY METHOD. R. L. Jones, T. D. Mewborn, and D. P. Olander. U.S. Geological Survey, National Water Quality Laboratory, 6481-H Peachtree Industrial Boulevard, Doraville, Georgia 30340

A multielement microcomputer-controlled, flow injection, atomic absorption spectrometer system has been extended to incorporate automatic data handling and real-time quality control. This permits high sample throughput for routine analysis, while maintaining precision and accuracy. The system permits the rapid entry of sample identifiers and method determination codes into a preestablished autosampler tray pattern which includes blank, standard, and reference samples. After entry, the system generates a hard-copy listing of tray assignments. In order to eliminate variability introduced by different analysts, the microcomputer automatically establishes certain critical instrument settings. During analysis, the sample and reference identifiers are matched with the analytical data, permitting real-time quality control by randomly selected standard references, which are systematically spaced within a sample tray. Precision and accuracy are monitored throughout the analytical run by checking instrument generated data, for the standards, against stored values of acceptable concentration ranges. The analyst is warned by an audio signal, and by a description of the error on a video display, whenever a quality control problem occurs and is given the option of stopping or continuing the analysis. An editing program automatically corrects for dilutions, checks for upper and lower detection limits, and permits the deletion of improper samples. Subsequently, individual data files are merged prior to electronic transmission to a central data base.

- 2 DEALING WITH MATRIX INTERFERENCES IN FURNACE ATOMIZER ATOMIC ABSORPTION SPECTROSCOPY. Anthony Rattonnetti, John Sotera, and Gerald Dulude. Instrumentation Laboratory Inc., Analytical Instrument Division, Jonspin Road, Wilmington, MA 01887.

A new sample has been developed where the sample is deposited as an aerosol mist onto a microboat placed in the furnace cuvette. The presence of the microboat removes many of the matrix interferences associated with complex samples. This reduction in interferences is attributed to the fact that the temperature of the microboat lags behind that of the graphite tube wall because of the relatively poor thermal contact with the cuvette wall. This temperature lag delays atomization until the gases in the furnace are at a higher and a more nearly constant temperature. Atomizing into a hotter environment reduces vapor-phase interferences and matrix effects caused by the presence of other salt-like materials. Furthermore, the microboat may be chemically pre-treated to prevent chemical attack by strong oxidizing acids. The technique has been applied to the determination of lead, bismuth, tellurium, and thallium in nickel alloys which have been dissolved in a 5% solution of HF and HNO<sub>3</sub>. These acids tend to oxidize the pyrolytic graphite surface of the microboat when it is untreated. However, application of a boric acid solution tends to neutralize the HF and extend the life of the graphite. A study of interferences and results for the nickel alloys will be presented.

- 3 SPATIALLY RESOLVED GAS TEMPERATURES WITHIN THE GRAPHITE FURNACE ATOMIZER Mary R. Riddle and James A. Holcombe, Department of Chemistry, University of Texas at Austin, Austin, Texas 78712

The two-line absorbance method (e.g., ref. 1) is used to determine the gas phase temperature at selected spatial zones within a graphite furnace atomizer. Initial work using Ga as the photometric species produced anomalous results and the cause of these errors will be discussed. A simple alteration in the graphite furnace was made to make reliable temperature measurements from which basic physical constants were derived. The use of these constants in calculating spatially resolved, vapor phase temperatures in a furnace with and without a platform will be presented.

<sup>1</sup>R. Browner and J. D. Winefordner, Anal. Chem., 44, 247 (1972).

4 A  $\text{HNO}_3$  -  $\text{H}_2\text{SO}_4$  /  $\text{H}_2\text{SO}_4$  -  $\text{H}_2\text{O}$  -  $\text{NO}_2$  SOLUBILIZATION PROCEDURE FOR THE DETERMINATION OF MERCURY IN FOODS. R.W. Marts and J.J. Blaha, U.S. Food and Drug Administration, 1009 Cherry Street, Kansas City, Missouri, 64106.

Abstract: A method for the determination of mercury in foods has been developed. Depending on the sample matrix, two solubilization procedures can be used to allow the analysis of essentially all foods. For foods that are low in lipid, cellulose, and sugar, a direct  $\text{HNO}_3$ - $\text{H}_2\text{SO}_4$  digestion is used. Foods that have high concentration of lipid, cellulose, and sugar, a two phase digestion using  $\text{H}_2\text{SO}_4$  -  $\text{H}_2\text{O}_2$  -  $\text{HNO}_3$  works best. Both digestion schemes utilize one digestion vessel, and a heated block digester programmed to a final temperature of 200 C and are completed in about three hours. The  $\text{HNO}_3$  -  $\text{H}_2\text{SO}_4$  digestion is accomplished directly in the heated block digester. The  $\text{H}_2\text{SO}_4$  -  $\text{H}_2\text{O}_2$  -  $\text{HNO}_3$  digestion requires the sequential addition of the reagents with water condensers in place for refluxing to avoid elemental losses. Samples are then transferred to the block digester for the final phase of digestion.

The determinative step for both digestions is AA using the cold vapor technique. Data will be presented showing the mercury determination and recovery studies for selected food items and NBS Standard Reference Materials.

5 QUANTITATIVE ANALYSIS OF THE CHEMICAL FILL OF A METAL HALIDE LAMP ARC TUBE  
R. A. Fowler, GTE Products Corporation, Sylvania Lighting Center, Danvers, MA 01923

Metal Halide lamps are an important light source for nonresidential lighting applications with about 1.5 million units sold annually. The light source is primarily emissive radiation from the excited metal atoms of the chemical fill. Since the characteristics of the source are governed by the composition of the chemical fill, detection and quantization of the fill additives is vital for lamp engineering and production. Arc Tube fill is both qualitatively and quantitatively monitored by several analytical techniques. A broad qualitative examination of an acid extract of the arc tube contents is done by SSMS. Both qualitative and quantitative analysis are done by examination of the optical spectra of the light source. The primary topic of this paper will be the quantitative analysis of the arc tube contents utilizing A.A.S. and I.C.P.E.S. techniques for metals analysis and ion chromatography for halide content. Sodium, scandium, cadmium and mercury are determined by atomic spectroscopy utilizing Perkin Models 503 and 5500 Spectrophotometers. Iodide is determined by ion chromatography using a Dionex Model 16 Chromatograph and a bicarbonate-carbonate-uric acid eluent. Chloride and bromide are determined using a carbonate-bicarbonate eluent. Thorium present in water soluble form is determined by the Thoron spectrophotometric method. Determination of thorium by I.C.P.E.S. will be discussed.

6 GRAPHITE ATOMIZER/MASS SPECTROMETER MEASUREMENTS Gary D. Rayson and James A. Holcombe  
The University of Texas at Austin, Austin, Texas 78712

A mass spectrometer is used to monitor the gas phase products and reactants evolved from a heated graphite atomizer. The system was designed to provide an experimental approach to determine what species are being vaporized from the surface as a function of time and temperature. The sample is deposited on the graphite as a solution and can be dried and ashed at any given temperature under any desired sheath gas composition. The atomizer is then transferred to an analyzing chamber through a gate valve where it undergoes atomization. The mass spectrometer is capable of monitoring and storing time variations of seven different masses as well as the atomizer temperature and the atomic absorbance signal. Data will be presented for a variety of sample matrices to illustrate the information available from this diagnostic approach for GFAA.

7 DETERMINATION OF SELENIUM IN SILICEOUS MATERIALS BY A PEROXIDE FUSION - HYDRIDE EVOLUTION TECHNIQUE. E. J. Cokal, Los Alamos National Laboratory, P.O. Box 1663, Los Alamos, New Mexico 87545.

The determination of selenium in materials of geochemical and environmental interest is complicated by the complex oxidation-reduction properties of the element and by the volatility of many of its compounds. Several techniques for determination of Se and several methods for sample preparation exist, but the combination of an efficient and reliable routine dissolution method with an appropriate and dependable determination technique has been somewhat elusive. This paper describes the sodium peroxide fusion of siliceous rocks and wastes and the conditions under which the necessary reduction of Se(VI) to Se(IV) is accomplished without loss of selenium. The determination of the resultant Se(IV) is accomplished by means of the hydride evolution AA technique, using borohydride pellet reduction. The method is suitable for routine use and requires only apparatus and materials already common in laboratories that perform selenium determinations by the hydride technique. Results are presented for the selenium content of several reference materials.

- 8 THE DETERMINATION OF REFRACTORY ELEMENTS IN THE STABILIZED TEMPERATURE GRAPHITE FURNACE. R. Beaty, O. C. Manning and W. Slavin, The Perkin-Elmer Corporation, Main Avenue, Norwalk, CT 06855.

Most of the work to date with graphite furnaces that provide a stable thermal environment during atomization has involved elements that are highly or moderately volatile. There have been relatively few reports of success in determining elements that form refractory compounds. Previous workers have shown that if the furnace tube has a coating of pyrolytic graphite, the analytical sensitivity for these refractory elements is significantly increased. Even with the pyrolytic coating, however, the refractory elements exhibit a memory effect which is not seen with more volatile elements.

Several of the elements provide adequate sensitivity for many applications. Conditions must be optimized to achieve this sensitivity. Optimization includes a study of charring and atomization conditions, as well as the possible addition of a matrix modifier. We have also studied the effect of rapid heating, purge gas flow and furnace tube design and coating on the absorption signal shape and memory.

- 9 AN OVERVIEW OF CHEMICAL INTERACTIONS WITHIN GRAPHITE FURNACE ATOMIZERS James A. Holcombe, Department of Chemistry, University of Texas at Austin, Austin, Texas 78712

Furnace AA is often plagued by "matrix effects" which are presently minimized by employing a variety of approaches which would include separation techniques, matrix modification, standard additions, or a combination of these schemes. It would appear ideal to avoid these analyte specific operational modes by designing the "perfect atomizer" or developing the "universal" matrix modifier. To intelligently approach the accomplishment of either goal, one must understand what chemical and physical processes are occurring within the graphite furnace prior to, during and after atomization. Atomic absorbance peak height and area changes due to concomitants in the sample do not provide sufficient information to make any conclusive statement regarding these interactions.

Discussion will concentrate on: (1) what occurs within the graphite furnace, (2) means of monitoring these reactions, and (3) implications toward the improved operational criteria of the "perfect atomizer".

- 10 THE USE OF ELECTROTHERMAL ATOMIZATION FOR SIMULTANEOUS MULTIELEMENT ATOMIC ABSORPTION SPECTROMETRY. J. M. Harnly, USDA, Nutrient Composition Laboratory, Building 161, BARC-East, S MD 20705.

A simultaneous multielement atomic absorption spectrometer has been developed based on a continuum source, an echelle polychromator modified for wavelength modulation, and a dedicated minicomputer. This instrument has two unique features, the multielement aspect and the ability to extend the calibration range to cover 5 to 6 orders of magnitude of concentration. While the application of the extended range technique to flame atomization is relatively straight forward, the nature of electrothermal atomization requires special considerations. Optimum compromise conditions must consider the atomization mode (off the wall vs. off a platform), the atomization rate (stepped vs. ramped heating), and the nature of the data (peak height vs. peak area). Each of these variables will influence the shape of the calibration curves, the detection limits, contamination carry-over between atomizations and analytical accuracy. Of these effects, carry-over contamination has presented the most serious problem.

- 11 DIRECT ANALYSIS OF DUST PARTICLES IN THE ATMOSPHERE BY CARBON FURNACE ATOMIC ABSORPTION SPECTROPHOTOMETRY, N. Liddle Department of Chemistry, New Mexico State University, Las Cruces, New Mexico 88003 and L. Bezur and J.M. Ottaway, Department of Pure and Applied Chemistry, University of Strathclyde, Glasgow GL 1XL, Scotland, U.K.

The development and construction of a prototype particulate matter-in-air monitor based on commercially available carbon furnace atomic absorption instrumentation will be described. Results on the performance of the monitor for the measurement of potentially hazardous metals in the atmosphere, e.g., lead, cadmium and beryllium will be presented. Three methods for the collection of dust particles were investigated and the results will be reviewed. The methods were:

- (1) Electrostatic precipitation on a tungsten rod followed by the introduction of the rod into the carbon furnace.
- (2) Electrostatic precipitation and impaction into the carbon furnace.
- (3) Direct impaction into the carbon furnace.

Collection efficiency of particles generated by a carbon rod atomizer will be shown to be greatest for the direct impaction system.

Incorporation of this method of dust collection, the design of a monitor controller and standardization procedure using aerosol generated by the nebuliser as the standard, and the other for sampling dust. The two cycles are interchanged at a frequency given by the preset cycle counter, e.g., if the cycle counter is set at 5, a standardization is carried out after every 4 samples. A maximum flow rate of  $10 \text{ l min}^{-1}$  with a programmable sampling time of 12 seconds to 99 minutes is possible. An interconnection between a computer and the monitor controller allows a one point calibration system based on the previous standard measurement.

- 12 IMPROVEMENT OF SIGNAL TO NOISE RATIOS IN FLAME ATOMIC ABSORPTION USING A ZEEMAN BACKGROUND CORRECTION SYSTEM - T.M. Vickrey, J. Liddle, J.D. Miller  
Hitachi Scientific Instruments, 460 E. Middlefield Road, Mountain View, CA 94043

For many elemental analyses by flame atomic absorption, the background absorption of the flame is small (less than 2.0 AU vs Air) and constant (in the steady state sampling method). Therefore, the rationale for application of analyte shifted Zeeman background correction techniques may seem unnecessary. However, because of the reduction in drift, long term and short term noise inherent in the double beam method, an improvement in signal to noise ratio is seen over the single beam method. The noise reduction will be discussed for several elements in different matrices and flame conditions. The origin of the reduction in the noise will also be discussed.

- 13 APPLICATIONS OF A TWO-CHANNEL ATOMIC ABSORPTION SPECTROPHOTOMETER: A LABORATORY SURVEY. Anthony Rattonnetti, John Sotera, and Gerald Dulude. Instrumentation Laboratory Inc., Jonspin Road, Wilmington, MA 01887.

Laboratories with large numbers of samples to be analyzed are often-times faced with conflicting requirements. On the one hand they want to analyze as many samples as possible, but on the other hand they must maintain a high degree of accuracy. The incorporation of micro-computer technology into atomic absorption spectrophotometers has enabled automatic computation of curve fitting equations and direct readout of sample concentrations. These advancements have simplified laboratory workloads by reducing analysis times. The availability of two channel atomic absorption spectrophotometers has made the simultaneous determination of two elements possible, which has the potential of increasing the efficiency of analysis twofold. In addition, two channel spectrophotometers can be used to compute ratios, to perform internal standardization, and to perform simultaneous background correction using the non-absorbing line technique. All of the capabilities expand the analytical power of the analyst. The applications will be taken from an analytical survey of 10-25 participating laboratories. Examples will range from routine simultaneous determinations of trace elements to specialized applications of the internal standard technique.

- 14 THE DETERMINATION OF TOXIC METALS IN WATERS AND WASTES BY AUTOMATED FURNACE ATOMIC ABSORPTION, L.A. Covick, L.M. Voth, D.E. Shrader. Varian Instrument Group, AA Resource Center, 205 W. Touhy Avenue, Park Ridge, IL 6006B (312) 825-7772 x231.

With the increasing awareness of the significance of many trace metals at ultratrace as well as toxicological levels, there is a continuing need for improvement of existing methods for determining those elements. Analysts must monitor elements such as As, Se, Pb, and Cd in a rapidly increasing number of samples. The maximum allowable concentration levels of these toxic metals in waters and wastes is regulated by the U.S. EPA and individual states. Because of extremely low concentrations encountered in many samples, furnace AA methods are EPA approved. The furnace AA analytical methods and required sample preparation procedures for waters and wastes are given in two EPA publications, "Methods for Chemical Analysis of Waters and Wastes" and "Test Methods for Evaluating Solid Wastes". Seven metals (As, Ba, Cd, Cr, Pb, Se, and Ag) regulated in drinking water and categorized as hazardous wastes to be checked for characteristic of EP Toxicity may be determined by furnace AA. A study was undertaken to ascertain optimum parameters, necessary matrix modifiers, and performance characteristics for the seven elements. The applicability of an automated furnace atomic absorption system was investigated. Equipment utilized in the study was the new Varian AA-975, GTA-95 Graphite Tube Atomizer with programmable sample dispenser, and HP-85 Computer for AA. Optimum parameters, necessary matrix modifiers, and performance for the seven elements will be presented. Results for numerous samples (drinking water, extracts, effluents, and reference standards) will be shown along with interference and accuracy data.

- 15 THE ROLE OF THREE-BODY PROCESSES IN THE ICP EXCITATION MECHANISM. J. W. Mills, J. W. Carr\* and G. M. Hieftje\*. Department of Chemistry, Fort Lewis College, Durango, Colorado 81301. \*Department of Chemistry, Indiana University, Bloomington, Indiana 47405.

The mechanism for analyte excitation and ionization in the argon inductively coupled plasma (ICP) remains unclear. Plasma temperatures and electron densities are thought to play key roles in determining how plasma energy is transferred to the analyte. These crucial plasma properties have not, however, been satisfactorily reconciled with argon plasma models in which energy transfer occurs primarily by electron-impact and radiative processes. Such models are derived for low-pressure plasmas dominated by two-body collisions. Furthermore, at low pressures, atomic metastable states can be important agents for storing plasma energy and for transferring that energy to analytes, a situation unlikely to exist at atmospheric pressure.

Kinetic and spectral data for "physical" argon plasmas indicate that three-body reactions might contribute significantly to processes occurring in the ICP. Calculations show that electron-ion recombination occurs at high pressure mainly by dissociative rather than radiative means. In particular, the principal electron interceptor at elevated pressure appears to be  $\text{Ar}^+_2$ ; after electron capture, the product dimer immediately dissociates to form atomic 4p excited states. Consequently,  $\text{Ar}^+_2$  should be the predominant ionic species in the upper region of the ICP. Moreover,  $\text{Ar}^*_2$  excimer formation by three-body collisions provides radiative and non-radiative relaxation pathways among atomic excited states, in competition with the atomic radiative decay responsible for the ICP's argon line spectrum.

- 16 DETERMINATION OF HALOGENS IN GEOLOGIC MATERIALS BY ATOMIC-EMISSION SPECTROGRAPHY OF A LOW-PRESSURE MICROWAVE-INDUCED HELIUM PLASMA. N. Rait, D. W. Golightly, and C. J. Massoni, U.S. Geological Survey, 957 National Center, Reston, Virginia 22092.

Excitation of the common halogens and other nonmetals to produce bright atomic spectra has been effected in rare-gas plasmas induced by a 2.45 GHz field. Direct electrothermal vaporization of samples of whole coal or of solution residues into a 100-120-watt low-pressure helium plasma maintained in a TM010 cavity (1, 2) has enabled the convenient spectrographic determination of nanogram-to-microgram quantities of the naturally occurring halogens. Topics discussed include basic experimental configuration, conditions for operation of a stable plasma, vaporization and transport of samples into the microwave-induced plasma, and the measurement capabilities of the system for the multiple-element determination of halogens in geologic materials.

- 1) C.I.M. Beenakker, et al., Philips Tech. Rev. 1980, 39, 65-77.  
2) C.I.M. Beenakker, Spectrochim. Acta 1976, 31B, 483-486.

17 TIME RESPONSE STUDIES IN THE ICP USING RF POWER MODULATION. J. W. Carr, J. W. Mills and G. M. Hieftje. Department of Chemistry, Indiana University, Bloomington, Indiana 47405.

Fundamental investigations into excitation mechanisms in the inductively coupled argon plasma (ICP) might lead to improved performance in analytical applications. For example, the spatial distribution and absolute intensity of analyte emission are determined at least in part by the mechanism of energy transfer from the argon plasma. Knowledge of this mechanism should aid in controlling plasma conditions so maximum analyte emission can be generated in low-background plasma zones.

To better understand energy flow and distribution in the ICP, the rate of plasma relaxation was measured by monitoring plasma emission and electron density fluctuations as the RF power was modulated. The amplitude spectrum of the modulated signal then yields plasma relaxation times ranging from 0.3 msec in the plasma skin region near the load coils to 1.1 msec in the analytical zone. These relaxation times are characteristic of the plasma region being observed, but independent of the property under observation, e.g. continuum emission, emission from argon 4s or 4p levels, or electron density.

Such relaxation times can be interpreted in terms of the rates of ion-electron recombination, argon-ion production, ambipolar diffusion and relaxation of excited states.

18 ANALYSIS OF WASTEWATER WITH A SCANNING ICP J. V. Nygaard, D.S. Chase, and D.A. Leighty. Instrumentation Laboratory, Analytical Instrument Division, Jonspin Rd., Wilmington, MA 01887.

Wastewaters present a challenging analytical problem. Priority pollutants (Ag, As, Be, Cd, Cr, Cu, Hg, Ni, Pb, Sb, Se, Tl, and Zn) and other metals (Ba, Co, Mn, and V) must be determined at trace levels near their detection limits. At the same time, metals such as Al, Ca, Fe, Mg, and Na may be present at high concentrations, thereby causing continuum emission, spectral line overlap, and other spectral interference problems. The challenges associated with analyses near the detection limit will be discussed, and suggestions will be made for priority pollutant emission lines which are both useful at trace levels and relatively free from serious spectral interferences. In cases where such ideal emission lines do not exist, methods of compensation for remaining spectral problems will be discussed. In addition, analytical emission lines will be suggested for Al, Ca, Fe, Mg, and Na. For these elements, the suggested lines meet the criteria of being free from spectral interference, and having sufficiently wide dynamic range to be useful at high concentration.

19 DETERMINATION OF VOLATILE AND REFRACTORY ELEMENTS IN MICROLITER SAMPLES USING ELECTROTHERMAL CARBON CUP VAPORIZATION AND INDUCTIVELY COUPLED PLASMA EXCITATION. K. C. Ng and J. A. Caruso. Department of Chemistry, University of Cincinnati, Cincinnati, Ohio 45221.

An atomic spectrometric system is described for trace element analysis of micro-volume samples. The system involves vaporizing the sample by electrothermal carbon cup vaporization followed by the atomization and excitation of the vapor cloud in an inductively coupled plasma (ICP). The detection limits for 20 elements in 10 microliter samples are at the ng/ml and sub-ng/ml levels with linear dynamic ranges of over four orders of magnitude. Pyrolytic graphite coated carbon cups are overcoated with tantalum carbide. These Ta-carbidized cups have resulted in improved detection levels for Al, As, Bi, Co, Cu and Sn relative to those not containing Ta. However, the non-carbidized pyrocoated cups were superior for Cd, Ge, Hg, K, Li, Mg, Mn, Rb and Zn. Comparisons using the two types of carbon cups are presented and discussed. Results also are compared with literature values available for other electrothermal vaporization systems.

The determination of refractory elements such as Zr, V, U, O, and Cr was attempted. Some of these elements were not detectable without chemical volatilization. Addition of  $\text{NH}_4\text{Cl}$  (71 w/v) into solution of these elements has allowed their determinations to proceed with low detection levels and good precision.

20 ADVANTAGES OF SYNCHRONOUSLY-GATED DETECTION IN SPECTROCHEMICAL ALLOY ANALYSIS USING SPOT EXCITATION. Steven G. Barnhart and John P. Walters, Department of Chemistry, University of Wisconsin-Madison, Madison, WI 53706.

The use of synchronously-gated detection with spark excitation introduces a new form of signal averaging in a spectrochemical experiment. This technique reduces the contribution of spectral background to analytical lines leading to a higher signal-to-background ratio and increased sensitivity. Spectral simplification can be realized when interfering lines exhibit temporal behavior different from that of analytical lines of interest. The utility of this technique in alloy analysis will be illustrated and the gains in sensitivity and spectral simplification discussed.

21 ALKALI ELEMENTS IN THE INDUCTIVELY COUPLED PLASMA. Lynda M. Faires, C. T. Apel, Los Alamos National Laboratory, Group CMB-1, Los Alamos, NM 87545, and T. M. Niemczyk, Department of Chemistry, University of New Mexico, Albuquerque, NM 87131.

The alkali elements constitute a unique analyte subset in atomic spectroscopy. This study examines their behavior in the inductively coupled plasma. Using an all-mirror optical design and a Los Alamos-built, high-resolution, dual-grating, direct-reading spectrometer, emission from the alkalis in the plasma source is viewed in both the conventional side-on optical configuration and in the new top-down configuration. Top-down viewing allows the use of either a standard short torch or an extended long torch assembly. Differences in analytical performance of the two torch assemblies will be discussed. Emission profiles of intensity versus observation position in the plasma will be presented, and analytical results for the alkali elements observed side-on and top-down will be discussed in terms of sensitivity, linearity, detection limits, self-reversal effects, and viewing position in the plasma.

22 INTERELEMENT INTERFERENCES AND TEMPERATURE MEASUREMENTS IN A MICROWAVE-INDUCED NITROGEN DISCHARGE AT ATMOSPHERIC PRESSURE (MINDAP). R. D. Deutsch and G. M. Hieftje. Department of Chemistry, Indiana University, Bloomington, Indiana 47405.

The microwave-induced nitrogen discharge at atmospheric pressure (MINDAP) is a recently developed atomic emission source. In earlier work, the MINDAP was shown to yield low detection limits (ng/mL for most elements), long linear dynamic range ( $10^5$ ) and adequate precision (1 - 5%). In the present study, the magnitude of several kinds of interferences is investigated, particular situations involve matrix interferences ( $\text{PO}_4^{3-}$  on Ca), cation interferences (Al on Ca), and ionization interferences (Na on Ca). It will be discussed how each interferent affects the neutral atom and ion line emission of the analyte and how "releasing agents" influence the degree of interference. Particular releasing agents studied for the matrix interference were identical to those commonly employed in flame spectrometry (e.g. EDTA). The results of these studies will be compared with other plasma and flame techniques. Interestingly, in the  $\text{N}_2$ -MIP system, as in some other MIP discharges emission from neutral atom lines is more intense than from ion lines, and interference effects can be eliminated by using a known suppressant reagent. These results are typical of flame-based systems rather than of high-frequency plasma systems such as the ICP. Because the flame is considered to be in thermodynamic equilibrium (LTE), temperature measurements were performed to determine the extent to which MINDAP approaches LTE. Excitation, rotation and ionization temperatures were determined as a function of applied power and gas flow rate. The methods for these determinations and their results will be discussed in detail.

- 23 NEW DEVELOPMENTS IN INDUCTIVELY COUPLED PLASMA EMISSION SPECTROMETRY. G. Horlick,  
Department of Chemistry, University of Alberta, Edmonton, Alberta, Canada, T6G 2G2.

While the inductively coupled argon plasma is currently the most widely used system for the simultaneous multi-element analysis of solution samples several aspects of the ICP require further development and understanding. In this presentation four main areas will be addressed. To date only a limited number of investigators have varied the plasma gas composition. Plasma gas composition is an important and useful experimental variable and the analytical and spectral characteristics of  $N_2/Ar$ ,  $He/Ar$ ,  $O_2/Ar$  and  $AIR/Ar$  mixed gas ICP's will be presented. Advances in ICP sample introduction systems for the direct analysis of solid samples and the direct nebulization of solution samples (ie no spray chamber) will be outlined. The spatial emission structure of the ICP will be outlined with reference to understanding the ICP emission characteristics and interference effects at a fundamental level and a new direct reading spectrometer will also be described in which the conventional PMT channels have been removed and several short segment (128 element) photodiode arrays have been mounted in their place. Its measurement capabilities will be compared to spectrometers of more conventional design.

- 24 PRESSURE-LIMITED ARGON RADIATION TRAPPING IN THE ICP. J. W. Mills and G. M. Hieftje\*. Department of Chemistry, Fort Lewis College, Durango, Colorado 81301.  
\*Department of Chemistry, Indiana University, Bloomington, Indiana 47405.

Argon resonance radiation at 106.7 nm and 104.8 nm is trapped in the inductively coupled plasma (ICP). This radiation trapping serves to lengthen the apparent lifetime (T) of the energetic  $^3P$  and  $^1P_1$  argon 4s states, and consequently must be considered in analyte excitation mechanisms.

Radiation trapping arises from the repetitive absorption and re-emission of resonant photons in an optically dense medium; this process has been theoretically considered in detail. During radiation trapping,  $\tau$  increases with pressure at low pressure, but becomes independent of pressure when pressure broadening dominates spectral line profiles. In this high-pressure limit, expected in the ICP,  $\tau$  is calculated to be 13 and 3  $\mu s$  for the  $^3P_1$  and  $^1P_1$  states, respectively. These values agree with experimental emission decay rates for argon plasmas having argon atom densities comparable to those found in the ICP, but are considerably shorter than values from earlier estimates for the ICP.

Argon plasma temperatures and geometry do not appreciably alter the pressure-limited  $\tau$ . On the other hand,  $\tau$  will be shortened further through excimer formation and emission. Excited Ar 4s atoms combine efficiently with ground-state Ar to form  $Ar^*$  excimer states, which subsequently emit at 126 nm to generate unbound argon ground state atoms. The presence of this 126 nm band in the ICP emission spectrum suggests that the  $\tau$  values calculated above are indeed upper limits, and urge that alternative vehicles be considered for analyte excitation.

- 25 DIRECT DETECTION OF CONTAMINANT IN LIQUIDS VIA LASER-INDUCED BREAK-DOWN SPECTROSCOPY (LIBS). D. A. Cremers, L. J. Radziemski, and R. d. Martinez, University of California, Los Alamos National Laboratory, P.O. Box 1663, Los Alamos, NM 87545.

We have used laser-induced break-down spectroscopy (LIBS) to monitor trace levels of species directly in liquids. When a Q-switched laser pulse is tightly focused in a liquid, a small intense spark is formed. By temporally and spectrally resolving the spark radiation, emitting species can be identified. Preliminary work indicates that a low concentration of some materials can be readily measured. A detection limit of 17 ppb (w/w) of Na/H<sub>2</sub>O has been established. We will present information of the characteristics of the spark in a liquid medium and current detection limits for some elements.

- 26 EAR-INFRARED NONMETAL ATOMIC EMISSION FROM ORGANIC SAMPLES IN A MICROWAVE-INDUCED PLASMA. J. E. Freeman and G. M. Hieftje. Department of Chemistry, Indiana University, Bloomington, Indiana 47405.

Microwave-induced plasmas in helium have been shown to be capable of electronically exciting even atomic species with relatively high ionization potentials. Among such species are the nonmetals and metalloids, most of whose more intense emission lines are in the experimentally inconvenient vacuum ultraviolet spectral region. In the present paper, these same species (C, N, O and Cl) are examined, but the emission lines employed lie in the near-infrared spectral region (between 8,000 and 20,000 Å). In this technique, simple organic compounds are introduced into an atmospheric-pressure helium microwave-induced plasma. The high thermal conductivity and excitation energy of the plasma enable it to fragment sample molecules and electronically excite their constituent atoms.

Several previously unobserved emission lines from atoms in the helium plasma will be reported. Emission intensities as a function of various plasma parameters such as power, helium flow rate, and plasma length will also be discussed. The suitability of this new technique for the quantitative detection of atoms in various molecular forms will be considered by examining emission from molecules of varying complexity and by comparing line intensity ratios for atoms of different elements.

- 27 INDUCTIVELY COUPLED PLASMA EMISSION SPECTROMETRIC DETECTION FOR HIGH PRESSURE LIQUID CHROMATOGRAPHY OF METAL COMPLEXES. Wipawan Nisananepong and Joseph A. Caruso, Department of Chemistry, University of Cincinnati, Cincinnati, OH 45221.

Speciation at trace levels of organometallic compounds is an important area of study in analytical chemistry. High pressure liquid chromatography (HPLC) coupled with inductively coupled plasma emission spectroscopy (ICP) is capable of sensitive, element specific detection of wide range of molecular substances containing a metal on other elements providing line emission. In addition to being specific for a given element, the method is free of some of the constraints associated with conventional uv absorption and refractive index detectors commonly used with HPLC. The (ethylenedinitrile)tetraacetic (EDTA) and diethyldithiocarbamate (DDTC) chelates of nickel(II) are separated by HPLC on 10 µm ODS spherisorb using uv detector at 254 nm. The ICP system is used to confirm the metal content of eluted peaks and permit specific element detection. Column effluent from the HPLC is fed directly to the ICP nebulizer. Relative sensitivities of the HPLC-ICP system for the various compounds are reported as a function of operational parameters. Variation of retention time and resolution with respect to changes in ligand structure and metal chelates will be investigated by varying the mobile phase. This necessitates discussion of the differing plasma characteristic as the solvent varies from 100% water.

- 28 ESTABLISHMENT OF CORRECT ANALYTICAL PARAMETERS FOR A MULTIELEMENT RAPID SCANNING SEQUENTIAL ICP. Anthony Rattonetti, Instrumentation Laboratory Inc., 115 Constitution Drive, Menlo Park, CA 94025.

Scanning ICP spectrophotometers have the ability to analyze a variety of elements in differing matrices because the programing is flexible. Observation height; nebulization rate, and pressure; power; need, and kind of background correction; and wavelength can be changed for each analytical task. The parameters that yield the best elemental sensitivity may result in increased interferences; however, when correctly selected interferences are nominal. Considerations in the selection of these parameters will be discussed.

- 29 DESIGN AND PERFORMANCE CHARACTERISTICS OF A NEW PASCHEN-RUNGE SEQUENTIAL MONO-CHROMATOR FOR ICP APPLICATIONS. L. P. Morganthaler, D. J. Comaford, K. Kondo, Bausc & Lomb, Spectroscopy Systems Division, 9545 Wentworth, Sunland, CA 91040.

A novel optical design of a fast sequential scanning 1.0 meter monochromator is described. Because only one optical element, (a concave grating) is employed, efficiency in the vacuum ultra violet, and spectral selectivity are optimal. Drive mechanisms are located at the focal plane so that critical grating deflection maneuvers and peak-peak routines are rendered unnecessary. 250 spectral windows on 2mm centers are located at the focal plane by an etched slit array. A stepper motor driven carriage places one of two optimized PMT detectors within the spectral window of interest. The primary slit is stepper motor driven  $\pm 1$  mm along the focal curve to place any spectrum line within the secondary slit in the range 165-790 nm. The primary slit drive reproducibility is 1.0 micrometer. Maximum access time to any line peak is 1.5 seconds. With the 1080 g/mm grating used in spectral orders up to the 4th, FWHM bandpass of 0.007 nm may be achieved with a step resolution of 0.0003 nm.

- 30 AUTOMATED OIL ANALYSIS: AIDS FOR THE ICP. S. J. Evans, R. J. Klueppel, J.-C. Schmitt, and P. Gilles, Baird Corporation, 124 Middlesex Turnpike, Bedford, MA 01730.

Inductively coupled plasma emission spectrometry has been shown to be an effective technique for the simultaneous measurement of trace metals in crudes and lubricating fluids. Determinations on a prepared sample may be made at the rate of approximately one sample per minute. Prior to the actual analysis, an aliquot of sample is drawn up, weighed, and diluted to a known volume or weight with an organic solvent. It is this prior step that poses the main time limitation. Sample preparation not only reduces real throughput to somewhere near 15 samples per hour (allowing three minutes for preparation), but also requires a specially trained technician to work with highly volatile and flammable solvents which may pose a health hazard. Our efforts have been directed at removing this preparation step so as to attain total system automation once the raw sample has arrived at the laboratory. To this end, we are introducing the AIDS accessory as a means of delivering a diluted, thoroughly mixed, and highly reproducible sample flow to the nebulizer assembly without any pretreatment step. With this Automatic Injection and Dilution System, solvent is pumped to the sample simultaneously with sample uptake to the ICP. Dilution is operator controllable, and the original sample remains undisturbed. Throughput rates of 80 samples per hour have been experimentally achieved. In this report, we will detail the construction of the device, and discuss its performance on used lubricating oils. While this presentation relates to oil based systems, potential applications on a variety of sample types will be outlined.

- 31 TIME-RESOLVED EPR IN RADIATION CHEMISTRY: CIDEP, SPIN EXCHANGE AND RADICAL RECOMBINATION RATES.\* Ronald G. Lawler, Department of Chemistry, Brown University, Providence, R.I. 02912.

The interaction between pairs of free radicals in solution is manifested in the EPR spectra of these species via the phenomena of second-order chemical decay, spin-exchange, and Chemically Induced Dynamic Electron Polarization (CIDEP). Each of these processes, however, is sensitive to a different aspect of radical pair chemistry; e.g. decay occurs, by definition, only via reactive encounters, whereas spin-exchange and CIDEP are by-products of chemically ineffective collisions with differing magnitudes of the exchange interaction. By combining submicrosecond intense pulsed electron radiolysis with pulsed EPR it is possible to measure simultaneously all three of these effects for simple radicals in solution. Experimental methods and a theoretical model used to extract this information from time-resolved spectra will be discussed using the acetate radical anion,  $\cdot\text{CH}_2\text{CO}_2^-$ , as an example.

\*Work performed in part at Argonne National Laboratory under the auspices of the Office of Basic Energy Sciences, Division of Chemical Sciences, U.S. Department of Energy.

- 32 TIME RESOLVED EPR APPLIED TO STUDY ELECTRON TRANSPORT IN PHOTOSYNTHESIS AND MODEL SYSTEMS. M. C. Thurnauer, Chemistry Division, Argonne National Laboratory, 9700 S. Cass Ave., Argonne, Illinois 60439

The first microsecond time resolved EPR spectrometer was described in 1968. Although the techniques still remain somewhat specialized, several laboratories have been involved with not only applications of the method, but also with spectrometer development in order to achieve shorter time resolution. Applications have been to the study of transient intermediates in liquid solution with emphasis on understanding the observed electron spin polarization and to the study of photoexcited states in molecular crystals. In the last few years several groups have applied the methods to less well defined biological systems, in particular photosynthetic systems. These studies provide examples of several different technical approaches to the same problem. These will be discussed in relation to our application of time resolved pulsed epr methods to study green plant photosynthetic systems. In this work we have found a new way to study short-lived radical pair interactions. Our recent application of this method to study photoreactions taking place in micelles will be discussed.

- 33 TIME-RESOLVED EPR AND ESE OF PHOTOINDUCED SPIN-POLARIZED RADICALS IN PHOTOSYNTHETIC REACTION CENTERS, A. J. Hoff, P. Cast and R.A. Mushlin, Biophysics Department, Huygens Laboratory of the State University, Leiden, The Netherlands

The primary act of photosynthesis is the conversion of a light quantum into two geminate radicals. Through the radical-pair mechanism, the EPR signals of the donor radical and of secondary acceptor radicals may become spin-polarized. If the secondary acceptor is chemically pre-reduced, the geminate radicals recombine to the triplet or singlet-ground or-excited state of the donor molecule. In this case, during the lifetime of the geminate pair polarization may be transferred to the prerduced acceptor, which becomes emissively spin-polarized.

We have further studied this process of transfer of spin-polarization in reaction centers of photosynthetic bacteria. It has been established that the transfer is non-uniform over the dark EPR lineshape of the prerduced acceptor (a semiquinone). Possible mechanisms that may produce this non-uniformity have been investigated by measurements of polarization,  $T_1$  and  $T_2$  as a function of magnetic field within the resonance line. It was found that neither  $T_1$  or  $T_2$  is responsible for the observed non-uniformity, which may be caused by anisotropic exchange or dipolar magnetic interactions between the anion of the gemmate pair and the semiquinone.

- 34 TRANSIENT ELECTRON SPIN NUTATION - A FAST WAY OF DOING EPR, Reinhard Furrer, Department of Physics, Free University Berlin, W. Germany

Time resolved EPR spectroscopy has received attention because it allows the direct study of the dynamics of spin systems. But even static quantities such as the fine- or hyperfine splitting in molecular crystals can frequently be measured with much higher sensitivities in a time resolved experiment than with conventional EPR. This is because of the high spin polarization in triplet states immediately after an exciting laser pulse.

Very often transient microwave experiments include the generation and the detection of electron spin echos (ESE). This method is well developed because it is an established standard procedure in the field of NMR. Today we have reached a high level of theoretical understanding as well as highly developed experimental capabilities. Other transient methods, such as electron spin nutation (ESN), on the contrary are often believed not to be suitable for high time resolution experiments.

In this talk it will be shown that the rise of the transverse magnetization after a populating laser pulse is determined not only by the microwave field strength,  $B_1$ , but also by the off-resonance contribution within an inhomogeneous EPR line, and can easily be dominated by the latter. Signals appear as fast as 15 ns in conventional molecular crystals after the excitation event, even at low microwave power levels. The time dependence of the nutation signal can be analyzed and gives information about the shape of an inhomogeneously broadened EPR-line; it allows the determination of unresolved hyperfine splittings and it carries information about  $T_2$ -times. A modification of the method where the electron spin nutation is started some time after the exciting light pulse (delayed transient nutation), allows the measurement of spin-lattice relaxation data even in cases where ESE-experiments fail because of too short  $T_2$ -times.

There are also other methods that have sometimes advantage over electron spin echo experiments because they avoid the problems that usually arise from high microwave powers. Their principles will be outlined and examples of experimental results from liquid solutions as well as from the solid state will be presented.

- 35 SPECTRAL AND SPATIAL DIFFUSION OF TRIPLET SPINS IN ORGANIC SOLIDS: PULSED ODMR STUDIES. Henry C. Brenner. Department of Chemistry, New York University, New York, NY 10003.

The decay of two-pulse *Hahn* and three-pulse stimulated echoes has been measured in several mixed organic crystals in zero external magnetic field, using phosphorescence detection and a probe pulse technique. In deep trap systems, where energy exchange between triplet traps is negligible at pumped helium temperatures, echo lifetimes are found to be sensitive to host deuteration, indicating that host nuclear spin flips contribute substantially to trap spin coherence decay. Effects of nearby host protons are probed with impurity-induced traps, in which the dopant induces a triplet trap on an adjacent host molecule. Effects of impurity deuteration on echo decay profiles are determined. Preliminary stimulated echo results are also presented for isotopic mixed crystals under conditions where trap to trap energy migration rates are appreciable. Variation of the first timing time in the stimulated echo pulse sequence allows one to determine the effective rate constants for jumps in local field of various magnitudes, and to map out the spectral diffusion function.

This work was supported by NSF Grant DMR-8024275.

- 36 DYNAMICS OF THE PHOTOCHEMICAL H-ABSTRACTION IN DOPED FLUORENE CRYSTALS AS STUDIED BY TIME RESOLVED EPR, ONP AND TRANSIENT OPTICAL ABSORPTION. D. Stehlik, Free University of Berlin, Inst. fur Atom Und Festborphys., Konigin-Luise-Str 34a, D-1000, Berlin 33, West Germany

Solid state photochemical reactions are particularly interesting when the molecular structure of the reactants and the product are known in detail [1] as for the H-abstraction in doped fluorene single crystals. Kinetic data for both, the triplet state sublevels of the unreacted acceptor and the radical pair product provide the most conclusive results for the determination of the reaction pathway. Time resolved EPR-data using the electron spin echo as well as transient nutation technique are supplemented by new ONP-detected time resolved EPR results and data from fast transient optical absorption experiments. Conclusions will be presented concerning the reaction mechanism and the potential of the methods to study high temperature nonradiative decay channels of molecular triplet states.

[1] D. Stehlik, R. Furrer, V. Macho, J. Phys. Chem. 83, 3440 (1979).

- 37 TIME-RESOLVED ODMR ON THE YELLOW PHOSPHORESCENCE OF BENZIL. R. Gilles and A. M. Ponte Goncalves, Department of Chemistry, Temple University, Philadelphia, PA 19122.

A great deal of evidence in the literature indicates that when benzil in its ground state adopts a trans-planar configuration for the two carbonyls, the phosphorescence (green in neat crystals) changes to yellow. While optically-detected magnetic resonance (ODMR) studies of the green phosphorescence of benzil have been in the literature for some time, no studies of the triplet state responsible for the yellow phosphorescence have been reported. We have used time-resolved ODMR to investigate this triplet state in polycrystalline toluene. At least two major triplet species are observed, depending on the detection wavelength. Double resonance techniques were used to establish the interdependence of the observed magnetic resonance transitions. Spin-lattice and spin-spin relaxation processes were examined from 77 K up to the melting point of toluene (178 K).

This research was supported by the National Science Foundation under Grant CHE-8009219.

38 ESR STUDY OF FREE RADICALS PRODUCED PYROLYTICALLY AND PHOTOLYTICALLY IN FLUIDS FLOWING AT HIGH PRESSURE AND TEMPERATURE. Ralph Livingston and Henry Zeldes, Chemistry Division, Oak Ridge National Laboratory, Oak Ridge, Tennessee 37830.

Short lived chemical free radicals with well resolved hyperfine structure have been observed in fluids that slowly flow under pressure through the microwave cavity of an ESR spectrometer and are heated as they pass through the cavity. Pressures to 21 MPa (3000 psi) and temperatures to 700°C may be used. These conditions are adequate to produce free radicals pyrolytically from many hydrocarbons, and a number of examples involving aromatic hydrocarbons will be described. Included will be a discussion of the evaluation of two important equilibrium constants for the bibenzyl system:  $C_6H_5CH_2CH_2C_6H_5 \rightleftharpoons 2C_6H_5CH_2$  and  $C_6H_5CH_2CH_2C_6H_5 + C_6H_5CH_2 \rightleftharpoons C_6H_5CHCH_2C_6H_5 + C_6H_5CH_3$ . Photolyses, usually with initiators, may also be carried out over the above temperature and pressure ranges. Experiments on benzyl ether will be described where the benzyl radical is observed in a chain reaction that occurs during the pyrolytic decomposition of the ether. Photolytic experiments with an initiator and at somewhat lower temperature allow one of the important reactions of the chain process to be singled out:  $C_6H_5CHOCH_2C_6H_5 \rightarrow C_6H_5CHO + C_6H_5CH_2$ . The activation energy for this reaction has been measured. This research was sponsored by the Division of Chemical Sciences, Office of Basic Energy Sciences, U. S. Department of Energy, under Contract W-7405-eng-26 with Union Carbide Corporation.

39 STRUCTURE OF THE ELECTRON SPIN CENTERS IN CARBONACEOUS MATERIALS: 1954-1982

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It has now been 28 years since the discovery of electron spin resonance (ESR) in coals and charcoals. The structure of the paramagnetic centers responsible for the ESR is well understood, at least for the products of pyrolysis below 600°C. These centers are odd-alternate neutral free radicals such as the perinaphthyl free radical. Such a conclusion was reached by observing ESR hyperfine structure during carbonization in thermally inert solvents. ESR spectroscopy is now a powerful tool for studying the structure of coals and carbonaceous materials, the process of hydrogenation and liquefaction of coals, and more generally the process of carbonization. The very important role of odd-alternate neutral free radicals in the carbonization process should be more precisely determined as should the process which transforms the free radicals to free electrons in high temperature carbons and graphites. The relation between free radical content and the graphitization process should be carefully investigated.

40 ESR STUDIES OF TRANSIENT FREE RADICALS PRODUCED DURING COAL PYROLYSIS. H. L. Retcofsky and R. F. Sprecher. Pittsburgh Energy Technology Center, P. O. Box 10940, Pittsburgh, PA 15236.

Transient free radicals have been observed via electron spin resonance (ESR) during rapid pyrolysis of coals directly within the microwave cavity of the instrument. The presence of such radicals was inferred from maxima in both the free spin concentration and in the ESR linewidth. The times of occurrence of the maxima coincided and were dependent on the temperature at which the pyrolysis was carried out. When the pyrolysis was performed in the presence of a good hydrogen donor, no maxima were observed and the concentration of free radicals was reduced to half its initial value in the first thirty seconds of pyrolysis. In contrast to the results for the whole coal, vitrains from a series of coals (subA, hvAb, and 1vb) showed no maxima in free spin concentrations upon pyrolysis. The results demonstrated that free radicals are important intermediates in coal pyrolysis and are consistent with currently proposed reaction mechanisms for the conversion of coals to liquid products. Preliminary experiments involving extracted coals and coals impregnated with metal salts, as well as initial attempts to trap small radicals generated pyrolytically, will also be described.

- 41 IN SITU EPR STUDIES OF COAL HYDROGENATION. Ted M. McKinney and Ira B. Goldberg, Rockwell International Science Center, Thousand Oaks, California 91360.

Bituminous, subbituminous or lignite coals were heated with  $N_2$  or  $H_2$  at pressures to 10.3 MPa and temperatures between 400° and 500° C in a unique high-pressure high temperature microwave cavity. These coals exhibit a rapid increase in radical concentration over a 100 to 300 s interval followed by a constant or slowly decreasing radical content. The maximum radical concentration in the coal depended slightly on the  $H_2$  pressure and on the temperature. The Illinois No. 6 bituminous coal was also heated to 800° C. Under high temperature conditions, the radical concentration was much greater than at low temperatures, but the rise time to that value was relatively slower than at 500° C.

The same coals were also reacted in an equal weight mixture with 9,10-dihydroanthracene at similar temperatures and pressures. In this case, the radical concentration first decreased on heating, then gradually increased, not approaching the initial value within 5000 s. The initial radical decay rate increased with increasing temperature. Hyperfine structure was observed only in samples of bituminous coal heated by itself or in a 50% mixture with p-quaterphenyl. These experimental results and an overview of cavity performance will be discussed.

- 42 ELECTRON SPIN ECHO STUDIES OF NATURAL AND SOLVENT REFINED COAL. Shulamith Schlick, Department of Chemistry, University of Windsor, Windsor, Ontario N9B 3P4 and M. Arayana and Larry Kevan, Department of Chemistry, University of Houston, Houston, Texas 77004.

Spin echo spectrometry is uniquely suited for study of radicals in polycrystalline and disordered systems. By analyzing the 2- or 3-pulse echo decay envelope, it is possible to identify the number and positions of nuclei interacting with the radical. This technique has been applied in this study to obtain structural information on the environment of the unpaired spin in natural Pittsburgh #8 coal and in the corresponding solvent-refined coal (SRC). Two-pulse spin echoes from SRC have been detected in a wide temperature range, from room temperature down to 4K. Clear proton modulation has been observed and the experimental results were simulated assuming an environment consisting of 16 protons at a distance of 0.5nm. Spin echoes have also been observed from the natural coal with a proton modulation pattern too shallow for a quantitative analysis. We deduce that there are less protons in the vicinity of the unpaired spin in natural coal. These results, as well as previous ENDOR and CW ESR studies on coal, will be discussed.

- 43 SPIN ECHOES AND SATURATION IN COAL. D. C. Doetschman. Department of Chemistry, SUSY Binghamton, Binghamton, NY 13901.

Coal free radical spectra are comprised of unresolved hyperfine multiplets with widths of 770 kHz, at 90-110K according to the spin echo decay times. Unresolved hyperfine interaction are indicated by the spin echo decay modulation and are consistent with perinaphthyl type centers in the vitrainite component. The fusain and vitrain EPR components are separable from one another by judicious choices of temperature, pulse interval and echo repetition rate. The  $T_1$  and  $T_2$  relaxation times are measured with spin echoes at several temperatures.

- 44 ELECTRON SPIN RESONANCE OF CARBON/POTASSIUM SYSTEMS. L. B. Ebert and D. R. Mills, Exxon Corporate Research--Science Laboratories, P. O. Box 45, Linden, NJ 07036

Potassium can reduce benzenoid systems ranging from graphite to bituminous coals (ACS Symposium Series #169, 73 (1981)). In the case of the coals, reduction by potassium naphthalene (Fuel, 53, 172 (1974)) or by potassium metal (Fuel, 61, 58 (1982)) followed by alkylation can enhance product solubility in common organic solvents. To determine the mechanism of this enhancement, we have studied the reduction by potassium of various "carbon" systems (graphite, spherocarb, tetrahydropyrene, naphthalene, Illinois #6 coal) by electron spin resonance. For graphite and spherocarb, at a loading of 1 K/8 C, we find considerable atomic character of added potassium, as evinced by spin orbit effects in linewidth and g value. This inference is confirmed by the observation of  $H_2$  on contacting these systems with  $H_2O$ . Naphthalene and tetrahydropyrene form radical ions (but not dianions) with potassium in THF, and yield no  $H_2$  on  $H_2O$  quench. The reaction of Illinois #6 coal with K/naphthalene/THF does not yield a significant increase in radical density, thereby suggesting this reduction to be distinct from the other reactions. This divergence arises from substituents on the coal (as-R, -OH, -OR) which not only destabilize anions but also react with the potassium naphthalene directly. Thus, the reductive chemistry of coals is not analogous to that of simple aromatic hydrocarbons (ACS Advances in Chemistry #192, 225 (1981)).

- 45 AN EPR INVESTIGATION OF THE BITUMEN, ASPHALTENE, AND PETROLENE FRACTIONS IN P.R. SPRING (UTAH) TAR SAND<sup>\*</sup> V.M. Malhotra and W.R.M. Graham. Department of Physics, Texas Christian University, Fort Worth, Texas 76129.

Bitumen and its asphaltene and petroleene fractions which were extracted from a sample of P.R. Spring (Utah) tar sand have been investigated by EPR at 9.2 GHz over the temperature range 10-340 K. The temperature dependence of the relative intensity of the organic free radical signal indicates the presence of both monoradicals and exchange coupled spins in all three fractions. Asphaltene contains the highest percentage of monoradicals followed by bitumen and petroleene. It is argued that the principal mechanism resulting in singlet, ground and triplet, excited states is exchange coupling among stacked aromatic sheets containing similar heteroatoms in alternate sheets. Calculation of the singlet-triplet energy separation indicates that for all three organic components the core sheet structure is the same. The observation of temperature dependent g-values arising from magnetic interactions suggests that only g-values measured at low (~10 K) temperatures should be used in attempting to make correlations with structural parameters. The effects on asphaltene of oxygen exposure and heat treatment are also discussed.

Supported in part by The Robert A. Welch Foundation.

- 46 PR AND IR STUDY OF THE CLAY FRACTION OF A BITUMINOUS COAL V.M. Malhotra and W.R.M. Graham. Department of Physics, Texas Christian University, Fort Worth, Texas 76129.

The 9.2 GHz EPR spectrum of a high-volatile bituminous (Pittsburgh No. 8 seam) coal's clay fraction has been measured and analyzed at 90-600 K. The clay fraction, which is believed to play a catalytic role in hydroliquefaction, was hand picked from 3/8 x 28 mesh, ground coal. The prominent features of the spectra are: (1) a well resolved Mn<sup>2+</sup> spectrum showing doubling of each of the hyperfine lines of the fine structure 1/2 ↔ -1/2, which is attributed to perturbation effects, (2) a spectrum of V<sup>4+</sup> showing typical hyperfine structure and (3) transitions due to Fe<sup>3+</sup> at g~14.64, 11.13, 5.96, 4.24, 4.23 and 2.94. The origin of the Fe<sup>3+</sup> spectra can be associated with the presence of kaolinite and muscovite clays. From the temperature dependence of the EPR spectra it is argued that these clays have different degrees of crystallinity. The results of acid treatment are presented. The IR spectra of the clays were recorded in the 200-4000 cm<sup>-1</sup> range.

Supported in part by The Robert A. Welch Foundation.

- 47 EFFECTS OF CATALYSTS AND STEAM GASIFICATION ON S.R. OF CARBON BLACK. Kenneth M. Sancier, SRI International, Menlo Park, California 94025

The effects of temperature and steam concentration on Spheron 6 carbon black with and without impregnated K<sub>2</sub>CO<sub>3</sub> and diluted with alumina were measured by in situ electron spin resonance (e.s.r.). For samples in flowing helium, heating from 290 to 1070 K resulted in a small increase in the line width of the resonance of carbon but a large and largely irreversible increase of that of carbon with K<sub>2</sub>CO<sub>3</sub> starting above 650 K.

We studied the effect of steam concentration on the e.s.r. of carbon with K<sub>2</sub>CO<sub>3</sub> at 75 K. Increasing the steam concentration from 0 to 6.5 vol% resulted in reversible narrowing of the line width while hardly changing the free radical concentration.

The e.s.r. line of the carbon black is attributed to localized spin centers. The mechanism of the line broadening of the resonance resulting from heating the carbon with K<sub>2</sub>CO<sub>3</sub> may be due to two processes: an unresolved nuclear hyperfine interaction between the unpaired electron of the carbon free radical and potassium or to an increased mobility of charge carriers produced by potassium. The reversible effects of steam are attributed to a modification of these processes and may be related to catalyzed gasification of coal products.

- 48 EPR OF  $\text{NO}_2$  IN ZEOLITES. T.J.Schaafsma and B.Meijer, Dept. of Mol. Physics, Agric. Univ., De Dreijen 11, 6703 BC Wageningen (Neth.).

The ESR spectrum of  $\text{NO}_2$  absorbed in 13X-type molecular sieve has been studied, changing the concentration of adsorbed  $\text{NO}_2$ , and varying the temperature between 100 and 300 K.  $\text{NO}$  is strongly bound to the zeolite surface such that dimerization to  $\text{N}_2\text{O}_4$  has become endothermic, in contrast to the  $\text{NO}_2 \rightleftharpoons \text{N}_2\text{O}_4$  equilibrium mixture having no interaction with the zeolite surface.

At low concentration, increased mobility of the  $\text{NO}_2$  molecule results in nearly isotropic ESR spectra, which are also observed at room temperature. This increased mobility affects the  $\text{NO}_2$  librational motion, which is the main mechanism causing the ESR spectra to lose their anisotropy at low concentration. Half-field transitions with large temperature-dependent shifts are tentatively attributed to spin-spin interaction between several  $\text{NO}_2$  molecules in the same zeolite-cavity.

- 49 AN EXPERIMENTAL AND THEORETICAL STUDY OF THE LOW TEMPERATURE ESR OF THE CYCLOOCTATETRAENE AND TETRAMETHYLCYCLOOCTATETRAENE ANION RADICALS IN SINGLE CRYSTAL ENVIRONMENTS. M.T.Jones, Department of Chemistry, University of Mo.-St. Louis, St. Louis, Missouri 63121 and E. de Boer, Research Institute for Materials, University of Nijmegen, Toernooiveld, Nijmegen, The Netherlands.

Experimental and theoretical investigations are reported of the ESR spectroscopy of cyclooctatetraene (COT) and 1, 3, 5, 7 -tetramethylcyclooctatetraene (TMCOT) monoanion radicals oriented in single crystals of dialkali metal cyclooctatetraene diglyme ( $\text{M}_2\text{COT dg}$ ), where  $\text{M}=\text{K}$ ,  $\text{Rb}$  or  $\text{Cs}$ , and dipotassium 1, 3, 5, 7 -tetramethylcyclooctatetraene bis (diglyme) ( $\text{K}_2\text{TMCOT 2 dg}$ ), respectively. Calculations are presented of the ion pair association energies (due to the electrostatic interactions of the nearest neighbor alkali metal ions and COT monoanion) which show that a) the orbital degeneracy of the free, unperturbed COT monoanion is removed and b) the lowest energy state of the COT monoanion (in agreement with experiment) is antisymmetric with respect to reflection through a mirror plane perpendicular to the COT plane. Measurements of the principal components of the g-tensor of the oriented COT monoanion are also reported. They show that two of the components are independent and one ( $g_{zz}$ ) is dependent upon temperature. For the TMCOT monoanion all three principal components of the g-tensor are independent of temperature. Calculations of the values of the principal components of the g-tensor for the COT and TMCOT monoanions are presented. It is shown that the sign of the change in  $g_{zz}$  with temperature, as well as the change itself, for the COT monoanion can be accounted for, if interactions between the COT monoanion and the nearest neighbor alkali metal ions are taken into account.

- 50 EPR AND PHOTOLUMINESCENCE STUDIES OF DEFECT CENTERS IN  $\text{ZnO}$ . W. G. McDugle and R. S. Eachus. Research Laboratories, Eastman Kodak Company, Rochester, N. Y. 14650

Various intrinsic and extrinsic defects in  $\text{ZnO}$  have been studied with electron paramagnetic resonance (EPR) and photoluminescence (PL). The extrinsic acceptor centers due to lithium or sodium impurities have been well characterized, but little is known about the extrinsic donor centers. Most of our present efforts are directed toward understanding the shallow indium donor centers in  $\text{ZnO}$ . For low indium concentrations, well-defined donor states are observed. This is evidenced in the EPR by the formation of paramagnetic  $\text{In}^{2+}$  centers at temperatures below 80°K, as conduction-band electrons are trapped at the shallow  $\text{In}^{3+}$  centers. As the indium concentration increases, indium impurity bands evolve and coalesce with the conduction band. The previously observed EPR signals are now no longer resolved. Indium incorporation can be greatly enhanced if the  $\text{ZnO}$  materials are co-doped with compensating lithium. This has resulted in the use of lower annealing temperatures and shorter annealing times to incorporate a given concentration of substitutional indium centers. The above results also apply to the incorporation of thallium donor centers. Lithium co-doping, in fact, may provide a simple method to readily incorporate other  $\text{n}^+$  ions, where n is larger than two, into  $\text{ZnO}$ .

- 51 EPR STUDIES OF TWO STRUCTURAL PHASE TRANSITIONS IN DOPED CRYSTALS OF  $\text{RbMgBr}_3$ . Gary L. McPherson and Kelley H. Kirklin. Department of Chemistry, Tulane University, New Orleans, LA 70118.

The EPR spectra of doped crystals of  $\text{RbMgBr}_3$  indicate that the host material undergoes two structural phase changes between the melting point (748K) and liquid nitrogen temperature. Above 449K  $\text{RbMgBr}_3$  adopts a hexagonal lattice which is isostructural with  $\text{CsNiCl}_3$ . The  $\text{MgBr}_6^{2-}$  octahedra share opposite faces to form infinite linear  $[\text{MgBr}_3]_n$  chains which are identical and have axial symmetry. At 449K the lattice transforms to a more complex hexagonal structure in which the  $[\text{MgBr}_3]_n$  chains are no longer all equivalent. A second transformation occurs at 223K where the axial symmetry of  $[\text{MgBr}_3]$  chains is lost. These structural changes were investigated by monitoring the spectra of a variety of paramagnetic ions including some magnetically coupled pairs. The nature of these two phase changes and the impact that the structural modification has on the magnetic properties of the various paramagnetic centers will be discussed in detail.

- 52 EPR STUDIES OF THE DILUTE EUROPEAN ALLOYS  $\text{Eu Yb}_{1-x}(\text{NH}_3)_6$ , F.Y. Robb, T.R. White, W.S. Glaunsinger. Department of Chemistry, Arizona State University, Tempe, Arizona 85287

Electron paramagnetic resonance has been as a function of composition and temperature in  $\text{Eu Yb}_{1-x}(\text{NH}_3)_6$  alloys. The only detectable paramagnetic center in these alloys is  $\text{Eu}^{2+}$ . The observation of exchange-narrowed linewidths as well as the onset of critical broadening below 10 K in  $\text{Eu}(\text{NH}_3)_6$  provides qualitative evidence of magnetic exchange interactions between the  $\text{Eu}^{2+}$  moments. However, the experimental exchange field is very small and in reasonable agreement with that using the RKKY theory of magnetic interactions, with an estimated ordering temperature of about 0.2 K. A line-shape transition occurs near 160 K in  $\text{Eu}(\text{NH}_3)_6$ , and this transition diminishes with decreasing  $x$  and disappears for  $x \leq 0.1$ . It is proposed that this transition diminishes from a crystallographic distortion at the Eu site and that its disappearance is associated with rapid  $\text{NH}_3$  diffusion above about 100 K in these alloys. Characteristic  $\text{Eu}^{2+}$  hyperfine structure is observed for  $x < 0.01$ , which further supports the view that magnetic exchange interactions are very weak. The origin of the weak exchange interactions in  $\text{Eu}(\text{NH}_3)_6$  is discussed in the light of recent theoretical calculations on the electronic structure of electron and metal-NH complexes.

- 53 ANALYSIS OF ELECTRON SPIN ECHOES BY SPECTRAL REPRESENTATION. Leslie J. Schwartz, Arthur E. Stillman, and Jack H. Freed. Baker Laboratory of Chemistry, Cornell University, Ithaca, New York 14853.

Motional effects can easily be incorporated into calculated spin echo decay envelopes by idealizing the effects of the pulses and by using the Stochastic Liouville Equation (SLE) to govern the time dependence of the density matrix between pulses. The spectral representation of the  $90^\circ$ - $\tau$ - $180^\circ$ - $\tau$  envelope is  $\sum_i a_i \exp[-(\lambda_i + i\omega_i)\tau]$ , where  $\lambda_i$  is the  $i$ th eigenvalue of the SLE matrix, and  $a_i$  are products of relevant components of eigenvectors. The long time (large  $\tau$ ) phase memory times  $T_2$  are equal to  $\text{Re}(\lambda_1)^{-1}$  where  $\lambda_1$  is the smallest eigenvalue. For an axially symmetric  $g$ -tensor case in the slow motional region  $T_2 = 3(\tau/F)^{1/2}$ ,  $2(\tau^2/F)$  and  $\tau$  for Brownian, free and jump models, resp., with  $F = \frac{2}{3}|g_w - g_z|^2 B_0^2/\hbar$ ,  $\tau_F$  = motional correlation time. Analogous results hold for nitroxides with  $A$ -tensor. The overall shape of an echo envelope in the low motional region is  $\exp(-bF^2\tau^3/\tau_F)$  for very short times and  $\exp(-\tau/T_2)$  for the longer times.  $\text{rr-Purcell}$  (CP) sequences suppress the initial exponential in  $\tau^3$  and increase  $T_2$  as a function of decreasing  $\tau$ . Detailed analysis of CP sequences can provide information on motional model. The analysis of motional averaging of nuclear modulation effects by our methods will also be discussed. Despite the simplicity of our methods, we are able to fit experimental data from the tempone/glycerol-water system in both the fast and slow motional regions. Experimental techniques and other relevant experiments will be discussed.

- 54 SHORT PULSE SATURATION RECOVERY. Akihiro Kusumi, James S. Hyde and Wojciech Froncisz  
National Biomedical ESR Center, The Medical College of Wisconsin, 8701 Watertown  
Plank Road, Milwaukee, Wisconsin, 53226.

The short pulse saturation recovery (SPSR) technique has been used to measure directly relaxation processes that give rise to spectral diffusion of saturation, with particular emphasis on application to nitroxide radical spin labels. These spectral diffusion mechanisms include nitrogen nuclear relaxation, Heisenberg exchange, chemical exchange, physical exchange, and, in the case of very slowly tumbling spin labels, rotational diffusion. Following a very short saturating pulse, preferably  $180^\circ$ , recovery is monitored using a weak observing microwave power. This approach is particularly applicable when the spectral diffusion rate is much greater than the electron spin-lattice relaxation rate. Initial fast recovery is then followed by slower recovery because of electron spin-lattice relaxation. The ability to measure very fast spectral diffusion processes is limited in principle to about 20 ns, when using the recently developed "loop-gap" resonator (1), where the limitation is determined by a combination of the following: the Q of the structure, the rf magnetic field intensity obtainable with the available power, pin-diode switching time, and the speed of A-D converters. SPSR has been applied to very slowly diffusing spin labels, to nitrogen nuclear relaxation in the slow tumbling domain, to Heisenberg exchange in the fast tumbling domain, and to physical exchange of bulk and boundary layer lipids in membranes.

- (1) W. Froncisz and J.S. Hyde (1982) J. Mag. Reson., May issue.

- 55 ELECTRON SPIN ECHO EXPERIMENTS ON TRIPLET STATE. David C. Doetschman. Department of Chemistry, SUNT Binghamton, Binghamton, NY 13901.

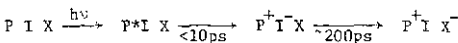
A number of kinds of electron spin echo experiments on the triplet states of organic molecules have been possible in magnetic fields at low temperature with conventional  $10^2$ – $10^3$  mW sources and ordinary cavities. A brief theoretical introduction will emphasize some of the differences between the spin echoes of triplets and doublets. Characteristic triplets spin echo studies will be presented followed by a number of applications to the structure and dynamics of the triplet molecules.

- 56 ESE AND ENDO STUDIES OF PRISTINE POLYACETYLENES. H. Thomann, H. Kim, L. R. Dalton, Y. Tomkiewicz, N. S. Shiren, T. C. Clarke, and B. H. Robinson. Department of Chemistry, University of Southern California, University Park, Los Angeles, California 90007.

Pristine samples of various polyacetylenes have been investigated by electron spin echo (ESE) and ENDOR methods in order to define the paramagnetic electron wavefunction and dynamics for these materials. At 136°K, the following  $^{13}\text{C}$  and hyperfine tensors are measured for cis-rich polyacetylene: (site 1),  $A_{xx}(^1\text{H}) \approx -0.5$  MHz,  $A_{yy}(^1\text{H}) \approx -2.1$  MHz,  $A_{zz}(^1\text{H}) \approx -1.1$  MHz,  $A_{xx}(^{13}\text{C}) \approx A_{yy}(^{13}\text{C}) \approx -1.3$  MHz,  $A_{zz}(^{13}\text{C}) = 2.1$  MHz; (site 2),  $A_{xx}(^1\text{H})$  (not resolved),  $A_{yy}(^1\text{H}) \approx -7.0$  MHz,  $A_{zz}(^1\text{H}) \approx -3.9$  MHz,  $A_{xx}(^{13}\text{C}) = A_{yy}(^{13}\text{C}) \approx -3.1$  MHz, and  $A_{zz}(^{13}\text{C}) \approx 7.0$  MHz. The relative magnitudes of the  $^1\text{H}$  and  $^{13}\text{C}$  tensors and the ratios of the tensor elements establish that the paramagnetic electron resides in a delocalized orbital. The extent of delocalization is observed to increase with increasing trans isomer content. ESEEM is observed for all polyacetylene samples studied (although only at temperatures below 150°K for trans-rich polyacetylene) consistent with electron motional correlation times characteristic of slow diffusion (motional frequencies less than the frequencies of the magnetic interaction modulated). In this region, motional correlation times are obtained directly from ESE decays and hyperfine interactions modulated by the electron diffusion are obtained from the ESEEM. Measurements on pure polyacetylene samples are compared with those for polyacetylene prepared in matrices of various high structural strength polymers.

57 ENDOR AND TRIPLE RESONANCE STUDIES ON PRIMARY PRODUCTS OF BACTERIAL AND PLANT PHOTOSYNTHESIS, Wolfgang Lubitz, Tnstitut fur Organische Chemie, Freie Universitat Berlin, West Germany

The primary process of light-induced charge separation in photosynthesis can generally be written as



where P is the primary electron donor, I the first, and X the second acceptor. In bacterial photosynthesis only one photosystem (PS) is involved; the primary donor is believed to be a bacteriochlorophyll (Bchl) dimer and I is a bacterio-pheophytin (BPh). Plant photosynthesis functions via two PS's; in PS 1 both P and I are believed to be a monomeric chlorophyll (Chl) species; in PS 2, P is again a Chl species and I is a pheophytin (Ph). Since paramagnetic intermediates are formed in the charge separation process, ESR and, in particular ENDOR, with its much higher resolution, are suitable techniques for the structural characterization of these species. However, ESR and low-temperature ENDOR spectra obtained so far, suffer from a lack of spectral resolution. We have therefore employed high-power/high-resolution ENDOR and TRIPLE resonance spectroscopy in liquid solution. By these techniques the set of hyperfine couplings (hfc's) - including signs - can be greatly extended. This is demonstrated for the various pigment -radicals (Bchl<sup>+</sup>a<sup>-</sup>, Chl<sup>+</sup>a<sup>-</sup>, Bchl<sup>+</sup>a<sup>-</sup>, Chl<sup>+</sup>a<sup>-</sup>, and Ph<sup>+</sup>a<sup>-</sup>) in vitro, which are involved in primary photosynthesis. Different experimental approaches for the assignment of hfc's to specific molecular positions are discussed. The hfc's are compared with these which have been calculated using advanced MO methods. The feasibility of ENDOR to detect different nuclei (H, D, N, etc.) in such radicals is discussed. In bacterial reaction centers (RC's) from R.rubrum G-9 and Rp.spaeiroids R-26 the in situ light-induced radical cation of the primary donor, P<sub>870</sub><sup>+</sup>, in aqueous solution, as observed by ENDOR/TRIPLE at room temperature for the first time. Seven H-hfc's including signs were measured. The observed differences for the two bacteria might be explained by the different protein environment. Specifically deuterated RC's were prepared by biosynthetic labeling techniques in order to elucidate proton assignments. The comparison with the in vitro Bchl<sup>+</sup>a<sup>-</sup> show that the overall reduction factor of the hfc's is very close to 2, supporting the "dimer model". The different shifts of the individual hfc's, however, reflect local geometrical changes within this dimer.

58 SPIN-LABEL TECHNIQUE TO DETECT DOMAIN-DOMAIN INTERACTION IN ANTIBODY MOLECULES, Peter Zavodszky, Ferenc Kilar and Istvan Simon, Institute of Enzymology, Biological Research Centre, Hungarian Academy of Sciences, Budapest, H-1502 P.O.B.7. Hungary

At molecular level the immune response is mediated through antibodies. The multiple functions of antigen recognition and the secondary effector processes are associated with discrete domains within the antibody molecule. The mechanism by which the initial antigen recognition on the Fab part of the molecule is communicated to the distant /7 nm/ secondary binding sites on the Fc part, is still a matter of controversy. We used spin-label probes to detect interactions and information transfer between the Fab and Fc parts of rabbit IgG antibody molecule. 3-/2-iodoacetamido/-2,2,5,5-tetramethylpiperidino-1-oxyl label was used. Under properly selected conditions this spin-label covalently binds to some hyperreactive lysine residues of the Fab part of the molecule, while no bound label is observed on the Fc part. The selective labelling on the Fab was controlled by ESR measurements on the Fab and Fc fragments obtained by limited proteolysis of the spin-labelled IgG. No paramagnetic signal was observed with the Fc fragment, while the intensity of the spectra obtained with Fab fragment corresponded to the full intensity of the labelled intact IgG molecule. Staphylococcus protein A is a bacterial cell wall protein, which specifically binds to the Fc part of the IgG molecule. Monovalent fragment of SpA were prepared and bound to the spin-labelled IgG. A slight, but reproducible and significant change was observed in the ESR spectra upon binding of SpA. The rotational correlation times were calculated and ~ = 2.26 nsec and t = 1.44 nsec values were obtained for the IgG and IgG complexed with monovalent SpA molecule, respectively. The observed decrease in the t value suggests that information is transferred from the Fc part to the Fab through the bing region and, the conformational motility around the spin-labelled site is increased in the Fab, upon binding of SpA to an other domain located in the Fc part of the .

- 59 DIPOLAR CORRELATION FUNCTION IN EPR (OR NMR) LINESHAPE ANALYSIS FOR A FINITE TWO-DIMENSIONAL LIQUID, J.-P. Korb\*, D. Torney and H.M. McConnell, Stauffer Laboratory for Physical Chemistry, Stanford University, Stanford, California 94305

We have shown that for a finite two-dimensional (2D) liquid sample the dipolar correlation function  $G(\tau)$  decays faster at long-time than that of an infinite 2D system. This facilitates an understanding of the paradoxical divergence of the zero-frequency spectral density found in previous 2D theories (1,2). We have obtained an exponential decay for  $G(\tau)$  in the case of spins,  $S=\frac{1}{2}$ , diffusing laterally at the surface of a plane and a sphere, of the same area, in a high constant magnetic field. The translational correlation times derived can be useful in the measurement of the constant of diffusion  $D$  of spin labels embedded in a plane or a spherical biological membrane (4).

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\*On leave from C.M.O.A. du C.N.R.S., Paris, France, with a NATO Fellowship. This work has been supported by NSF Grant PCM 8021993 (HMMcC).

- 60 AN ELECTRON SPIN RESONANCE DETERMINATION OF SEMIQUINONE EQUILIBRIA IN AQUEOUS ALKALI. John Charkoudian and David Gildea. Polaroid Corporation, 750 Main Street, Cambridge, MA. 02139.

p-Benzosemiquinone radical anion (SQ) and its derivatives exist in equilibrium with corresponding dianions (D) and quinones (Q) in aqueous alkaline solvents. The concentration of various SQ's was studied as a function of hydroxide concentration, ionic strength, and temperature. The equilibrium concentration of SQ was determined by double integration of the SQ ESR spectrum. These evaluations required an analysis of potassium nitrosyldisulfonate as a primary standard and an error analysis of the overall methodology. Plots of relationship  $1/\epsilon K_e = 1/K_s + K_c/K$  ( $OH^-$ ) were used to determine SQ formation constants,  $K_s$ , for p-benzosemiquinone and its 2-methyl, 2-methylphenyl, and 2,5 dimethyl derivatives. In general both  $K_s$  and  $K_c$  decrease when the ionic strength is increased from 0.375 to 1.75. The temperature dependence for SQ formation was found to be endothermic with  $\Delta H$  values in the range of 4.9 kcal/mole. Given  $K_s$  values of about 5 at 25°C, these endothermic enthalpies indicate significant entropy effects favoring semiquinone formation.

- 61 HYPERFINE COUPLING CONSTANTS FOR COBALT AND COPPER BLEOMYCIN. W. E. Antholine and R. C. Sealy, Department of Radiology, Medical College of Wisconsin, 8701 Watertown Plank Road; . H. Petering, Department of Chemistry, University of Wisconsin-Milwaukee, Milwaukee, Wisconsin.

The glycopeptide bleomycin, Blm, is a clinically useful antitumor agent. Although attention has been focused on the iron complex due to its DNA strand-scission activity, CuBlm and CoBlm are of interest since the former is inactive in the strand-scission reaction but is active as an antitumor agent, while the latter is inactive. Resolution of the  $M = -3/2$  X-band epr line in the  $g$  region into an apparent 1,2,3,2,1-like pattern indicates that Co(II)Blm can be six coordinate with two axial nitrogen donor atoms. For CuBlm, single-crystal-type ENDOR spectra were selected by saturating the  $M = -3/2$  line in the  $g_{||}$  region of the epr spectrum of  $^{63}CuBlm$  frozen in 80% ethylene glycol or  $D_2O$ . Five of the six lines attributable to protons give ENDOR transitions at frequencies  $\nu_1 = \nu_{free-proton} \pm \frac{1}{2}A_1$ . In the absence of comparative studies with altered structures or deuterated analogs only tentative assignment of the proton resonances are made. Lines centered at 15 MHz and 20 MHz ( $A_N/2$  and  $A_N'/2$ ) arise from nitrogen nuclei because the positions of these lines do not change as the magnetic field is shifted. The matrix ENDOR signal diminishes in the presence of  $D_2O$ , showing that solvent water molecules are within about 6 Å of the cupric ion and are accessible to the metal site.

Supported by NIH grants CA-22184 and RR-01008 and funds from the University of Wisconsin-Milwaukee.

62 AZETHOXYL, DOXYL, ANALYSIS: PROBING ORDERED SYSTEMS. M. S. Broido and E. Meirovitch. Isotope Department, The Weizmann Institute of Science, 76 100 Rehovot, Israel.

Doxyl-nitroxide labeled fatty acids are commonly used to probe dynamics of, and conformations in, ordered media. We have performed temperature dependent studies of both doxyl-labeled and azethoxyl (minimum steric perturbation)-labeled fatty acids dissolved in several liquid crystalline mesophases, and our results indicate that many of the ambiguities in interpretation inherent in using doxyl probes and motional narrowing theory spectral analysis are relieved by using azethoxyl probes, or slow-motional lineshape analysis, or both. Deviations of doxyl-labeled chains from all-trans conformations cannot be deduced from single-label experiments, whereas the azethoxyl probes can, and do, show deviations from all-trans chains, with great sensitivity to their specific environment. For azethoxyl probes, the relative magnitudes of the hyperfine splittings,  $a$ , are  $a_s$  (isotropic)  $>$   $a_{all-trans}$ ; hence,  $a_{(experimental)} > a_{(isotropic)}$  immediately yields conformational information. In anisotropic media, slow-motional effects are apparent in relatively high temperature spectra; motional narrowing analyses provide little dynamical information and can lead to large errors in deduced order parameters. We find that full lineshape analysis provides many details of ordering and dynamic behavior of probes in such systems, including anisotropies and magnitudes of rotational diffusion rates and order parameters.

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EPR STUDIES OF PHENYLALANINE HYDROXYLASE - A " $g = 4.3$ " IRON ENZYME. B.J. Caffney,\* D. Wallick,\*\* R. Lazarus,\*\* R.K. Scheule,\* and S.J. Benkovic\*\*, Department of Chemistry, \*The Johns Hopkins University, Baltimore, MD 21218 and \*\*Pennsylvania State University, University Park, PA 16802

The role of iron in the catalytic action of phenylalanine hydroxylase has been investigated. This enzyme contains four iron atoms per tetramer. The EPR signal of the resting enzyme, or the enzyme which has been activated by incubation at room temperature with the substrate, phenylalanine, gives an EPR signal at approximately  $g_{eff} = 4.3$  with a peak-to-peak width of  $\sim 45$  gauss. Conversion of phenylalanine to tyrosine requires addition of a cofactor, 6-methyltetrahydropterin, to the activated enzyme. Upon addition of a saturating amount of the pterin, the EPR signal at  $g_{eff} = 4.3$  sharpens to a width of 25 gauss. Titration of the activated enzyme with pterin in the presence and absence of oxygen suggests iron involvement in the catalysis.

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SATURATION TRANSFER EPR MEASUREMENTS OF THE INTERACTION OF SPIN LABELED SUBFRAGMENT-1 AND HEAVY MEROMYOSIN WITH F-ACTIN. B.A. Manuck, J.C. Seidel, and J. Gergely, Boston Biomedical Research Institute, Boston, MA 02114

Heavy meromyosin (HMM) and subfragment-1 (S-1) rigidly spin labeled with a maleimide spin probe were used to study rotation of myosin heads by saturation transfer EPR (ST-EPR). Binding to F-actin increases the correlation time ( $\tau_c$ ) for rotation of labeled S-1 or HMM, from 200 ns to 400  $\mu$ s, the value found for a spin label bound to F-actin (Thomas et al. 1975). When bound heads are dissociated by AMPPNP, a non-hydrolyzable analog of ATP, the dependence on AMPPNP concentration, of the motional parameter,  $L^2/L$ , and that of the fraction of HMM bound determined by centrifugation, follow the same simple binding isotherm. This suggests either that both heads of HMM always participate in the binding or that only one head participates but it immobilizes the free head. The shape of the binding isotherm indicates that a single molecule of AMPPNP dissociates both heads. MSL-S-1 crosslinked to F-actin with a water soluble carbodiimide is immobilized,  $\tau_c \approx 400$   $\mu$ s, but ATP reduces  $\tau_c$  to about 10  $\mu$ s, a value longer than that found with uncrosslinked acto-S-1, but shorter than that for MSL-S-1 covalently bound to immobile supports. This lower value of  $\tau_c$ , which persists until ATP has been hydrolyzed and then returns to the original value, may reflect increased motion of part of the myosin head while it is attached to actin.

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SINGLE CRYSTAL EPR OF SPIN-LABELED COPPER PORPHYRINS. D. Reddy and G.R. Eaton, Department of Chemistry, University of Denver, Denver, CO 80208 and S. S. Eaton, Department of Chemistry, University of Colorado at Denver, Denver, CO 80202

Nitroxyl spin labeled copper porphyrins have been doped into single crystals of diamagnetic hosts. X-band EPR spectra were obtained as a function of rotation angle about three orthogonal axes. The spectra are interpreted in terms of an isotropic exchange and anisotropic dipole interaction between the copper and nitroxyl unpaired electrons.

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HALF-FIELD TRANSITIONS S.S. Eaton, Department of Chemistry, University of Colorado at Denver, Denver, CO 80202, and G.R. Eaton, Department of Chemistry, University of Denver, Denver, CO 80203

Interaction of two spins yield EPR transitions near those of the non-interacting spins and also at  $1/2$  this magnetic field. These "half-field" transitions are characteristic of interacting spin systems. Calculations indicate that the intensity of the half-field transition depends on the spin-spin distance  $r$  as  $r^{-6}$ . The shape of the half-field transition depends on the relative orientations of the spin coordinate systems. Calibrations using small molecules will be presented.

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METAL-NITROXYL EXCHANGE INTERACTION DEPENDENCE ON PATHWAY. J.K. More, K.N. More, and G.R. Eaton, Department of Chemistry, University of Denver, Denver, CO 80208, and S.S. Eaton, Department of Chemistry, University of Colorado at Denver, Denver, CO 80202.

The exchange interaction between a paramagnetic metal (Cu(II) or VO(IV)) and a nitroxyl spin label in the same molecule depends on the bond pathway between the metal and the nitroxyl. By comparison of cis, trans isomers, saturated versus unsaturated pathways, isoelectronic substitutions, ring positional isomers, and the effect of an additional atom (e.g. urea versus amide linkage) on the metal nitroxyl exchange, relative  $\sigma$  and  $\pi$  delocalization pathways can be identified in several classes of compounds.

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SPIN-TRAPPING OF THE TRICHLOROMETHYL RADICAL FROM A VARIETY OF REACTIONS. Rajagopalan Sridhar and J. Lee Poyer, Oklahoma Medical Research Foundation, Oklahoma City, Oklahoma 73104.

Carbon tetrachloride is an hepatotoxic halocarbon which is used as a fumigant for grain. This chemical is also employed as a versatile solvent in research laboratories and in industry. Metabolic degradation of carbon tetrachloride by liver enzymes both in vivo and in vitro produces the trichloromethyl free radical as demonstrated by spin-trapping with  $\alpha$ -phenyl- $t$ -butylnitrone (PBN). The ability of various antioxidants and free radical scavengers to intercept this radical can be tested by using PBN in competition kinetic studies. Therefore we have studied the spin-trapping of trichloromethyl and other radicals that are formed during the interaction of carbon tetrachloride with (i) metal ions, (ii) free metals, (iii) electron-donating organic compounds, (iv) ultraviolet light and (v) enzymes.

- 69 ESR STUDIES OF SPIN PROBES IN SODIUM DIBUTYLPHOSPHATE LIQUID CRYSTALS  
C. CHACHATY, E. STEFANI, S. BELAID, Département de Physico-Chimie, CEN de SACLAY  
91191 - GIF-SUR-YVETTE CEDEX, FRANCE.

Concentrated aqueous solutions of sodium dibutylphosphate ( $3M < (DBP^-) < 4M$ ) give a lamellar phase between 285 K and 330 K. The dynamical behavior of spin probes such as  $VO_2^{2+}$ , tempamine and tempohexanamide dissolved in this phase has been investigated by ESR. The  $VO_2^{2+}$  ion, bound to the phosphate group undergoes a quasi isotropic motion, the correlation time of which is given by an empirical relation of the form  $\tau_R = a(1 - \frac{A_2}{A_7})^b$ . The constants  $a = 2.9 \times 10^{-11}s$  and  $b = -1.42$  have been obtained from the ESR spectra of vanadyl acetylacetonate / dibutylphosphoric acid solutions in the fast and slow motion ranges. The motions of nitroxide probes have been investigated by computer simulations as a function of order parameters and diffusion constants about a molecular axis. The tempamine, located in the polar layers undergoes an anisotropic motion about the N - O bond, the average orientation of which is perpendicular to  $H_0$ . A similar motion is observed for tempohexanamide in a range of  $20^\circ$  below the melting point (330 K). At lower temperatures the motion of this probe appears to be quasi isotropic suggesting that the nitroxide group reorients about an effective direction nearly parallel to the axis of the unpaired spin  $2p_z$  orbital. Correlations are established between the ESR of spin probes and NMR experiments on guest molecules.

- 70 MEASUREMENT OF HFI WITH 1D- AND 2D-ESE SPECTROSCOPY, H. Barkhuijsen, R. de Beer, K. Nederveen and D. van Ormondt, Applied Physics Laboratory, Delft University of Technology, P.O. Box 5046, Delft The Netherlands.

Recently it has been shown that Fourier transformation of the electron spin echo (ESE) envelope modulation signal yields a spectrum that compares favourably with that obtainable with regular electron nuclear double resonance (ENDOR) (R.P.J. Merks and R. de Beer, J.Magn.Reson. 37, 305(1980)). The results are especially promising at the low frequency end of the spectrum. By applying so-called maximum entropy spectral analysis (MEM) the resolution of the method can be enhanced significantly in those cases where the signal record is short (D. van Ormondt and K. Nederveen, Chem.Phys.Lett. 82, 443 (1981)). Moreover, when the technique is used in two dimensions, relations between peaks are revealed that facilitate the interpretation of the spectrum (R.P.J. Merks and R. de Beer, J.Phys.Chem. 83, 3319(1979)). In order to further investigate the merits of the technique a case study is being carried out for F-centres in KCl, in which signals from nuclei as far away as the ninth shell can be observed (with ENDOR (B.G. Grachev and M.F. Deigen, Sov.Phys.Usp. 21, 674(1978)), as well as ESE). Results of studies of the resolving power, peak intensities and properties of the 2D-spectrum, among other things, will be presented. An important future application of the technique will be the measurement of HFI in short-lived systems, where continuous wave ENDOR fails.

- 71 NMR-DETECTED NUCLEAR RESONANCE OF TRANSIENT RADICALS. R. H. D. Nuttall, A. D. Trifunac, Argonne National Laboratory, Chemistry Division, 9700 S. Cass Ave., Argonne, Illinois 60439

Nuclear resonances in transient radicals produced by pulse radiolysis can be detected via NMR of their reaction products. The product NMR intensities are perturbed by application of rf corresponding to nuclear resonances of the precursor radical intermediates. Computer controlled NMR-detected Nuclear Resonance Experiments will be described. Results of studies of NMR-detected nuclear resonance spectra for several chemical systems will be illustrated. From these studies detailed population pictures of the radical magnetic energy levels are obtained, and are explained using the radical pair theory of Chemically Induced Magnetic Polarization. A study of time dependence of transient radicals will also be illustrated.

72 OPTICALLY DETECTED TIME-RESOLVED EPR. S. M. Lefkowitz, and A. D. Trifunac, Argonne National Laboratory, Chemistry Division, 9700 S. Cass Ave., Argonne, Illinois 60439

The EPR spectra of radical ions which recombine to yield an excited singlet state is detected by the decrease in fluorescence intensity occurring after the application of a single microwave pulse at the magnetic field of resonance. Since recombination of geminate radical ions is often a very important pathway for excited state production, this ODMR technique can be used to study a variety of radical ion species in radiation and photochemistry. Both radical ion kinetics and EPR spectra have been studied illustrating several features of this time resolved EPR technique.

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ESR STUDIES OF LIPID-PROTEIN INTERACTIONS IN LIPOPROTEIN RECOMBINANTS. D.J. Vaughan, General Foods Research Department, Cobourg, Ontario, K9A 4L4

Isomeric 5'-, 12'- and 16'-(N-oxyl-4'',4''-dimethyloxazolidine) stearoyl spin-labeled phosphatidylcholines have been used to monitor lipid-protein interactions in sonicated vesicles of sn-3-dimyristoyl phosphatidylcholine and sn-3-dimyristoyl phosphatidylcholine:cholesterol (10:1, mol:mol) reconstituted with apolipoproteins A-I, A-II, C-I and C-III<sub>2</sub> isolated from human plasma. The gel to liquid crystalline phospholipid phase transition was observed to broaden for reconstituted vesicles containing apolipoprotein A-I or A-II when probed by 5'- and 12'-(N-oxyl-4'',4''-dimethyloxazolidine) stearoyl phosphatidylcholines relative to the phase transition reported by 6'-(N-oxyl-4'',4''-dimethyloxazolidine)stearoyl phosphatidylcholine. Conversely, phase transitions in reconstituted vesicles containing apolipoproteins C-I or C-III<sub>2</sub> reported by 5'-(N-oxyl-4'',4''-dimethyloxazolidine)stearoyl phosphatidylcholine were broader than these reported by 12' and 16'-(N-oxyl-4'',4''-dimethyloxazolidine)stearoyl phosphatidylcholines.

In summary, the results indicate that apolipoproteins A-I and A-II in these model lipoprotein recombinants are partially embedded within the hydrocarbon region of the lipid bilayer but do not span the complete bilayer. Apolipoproteins C-I and C-III<sub>2</sub> appear to be localized closer to the surface of the bilayer at the lipid-water interface.

74 EPR STUDIES OF SURFACE INTERACTIONS- $O_2^-$  on  $^{67}Zn$  Enriched ZnO. R. B. Clarkson and R. G. Kooser, Laboratory for Molecular Spectroscopy, University of Illinois, Urbana, IL 61801, Department of Chemistry, Knox College, Galesburg, IL 61401

In the EPR spectrum of a surface radical, the interaction of adsorbed paramagnetic species with  $I \neq 0$  nuclei in the solid substrate may be reflected by hyperfine structure. Although in most cases unresolved, the hfs can modify EPR lineshapes, giving important information concerning the strength of chemisorption and the mobility of the adsorbed radical.

In this work, we have investigated the conditions, both chemical and instrumental, affecting hyperfine structure in the EPR spectrum of  $O_2^-$  adsorbed on the surface of  $^{67}Zn$ -enriched ZnO. The  $O_2^-$ - $^{67}Zn$  hyperfine interaction also was compared with the  $O_2^-$ -Ag interaction seen when oxygen adsorbs on metallic silver.

- 75 DEPENDENCE OF ESR AND ENDOR SIGNALS ON MODULATION PHASE-ANGLE. I. Miyagawa, F. Khalaf, B. Rakvin, and C. Alexander, Jr., Department of Physics and Astronomy, The University of Alabama, University, Alabama 35486

In previous investigation, ESR and ENDOR signals from coal samples were found to depend on phase-angle of magnetic field modulation. The present work was conducted with the aim to clarify the nature of the phase dependence, studying succinic acid crystals irradiated by x-rays for varying periods of time ranging from 10 sec to 10 h. Analysis of the result indicated that the radicals which appeared isolated for ESR experiments actually occurred in at least three different types of clusters, the ENDOR mechanism being entirely different from one type to another. It was shown that ENDOR signal from cluster I in which radicals are relatively isolated was negative rather than positive, probably contrary to the common view. In contrast, ENDOR signal from cluster II with a fairly high radical density was positive; each signal line was much sharper than the corresponding one from cluster I under a given radiofrequency field, indicating that a substantial exchange interaction occurred between radicals. ENDOR signal from cluster III with a higher radical density was broad and negative, indicating a relatively strong exchange interaction. These results suggested a similar cluster formation of radicals in coal which resulted in the phase dependence of the signals. In conclusion, ENDOR techniques appeared to be useful for study of radical distributions rather than radical structures in the case of coal samples. The work was supported by a grant from the School of Mines and Energy Development, The University of Alabama.

- 76 EPR STUDIES OF STABLE FREE RADICALS IN CARBONIZATION. I. C. Lewis and L. S. Singer. Union Carbide Corporation, Carbon Products Division, Parma Technical Center, P. O. Box 6116, Cleveland, Ohio 44101.

Large concentrations of stable free radicals are formed during carbonization of all organic materials. There is now substantial evidence that for at least the early reaction stages, the unpaired electrons are stabilized in odd-alternate aromatic ring systems. EPR studies have been used to demonstrate the extreme thermal stability of odd-alternate radicals such as phenalenyl and its larger aromatic analogs naphthanthryl and benzanthryl. EPR investigations of the pyrolysis of model aromatic hydrocarbons have provided further evidence concerning the nature of odd-alternate radical structures in carbonaceous materials and their role in the overall polymerization-condensation scheme of carbonization.

- 77 ROLES OF CATALYST FOR COAL LIQUEFACTION REACTION BY MEANS OF HIGH TEMPERATURE ESR AND NMR. Tetsuro Yokono, Taro Khono and Yuzo Sanada. Coal Research Institute, Faculty of Engineering, Hokkaido University, North 13, West 8, Sapporo, Japan

The high temperature ESR and NMR were used in order to obtain in-situ information on the behavior of catalysts during coal pyrolysis. The free radical population in coal was observed in the presence of catalyst at the pyrolysis temperature. The spin concentration increased drastically for the coal/ZnCl<sub>2</sub> system while that of coal alone showed a small increase at 420°C. This increase in the spin concentration may result from the formation of complexes between zinc chloride and polyaromatic compounds and/or the cleavage of some heterolinkage. Marked broadening of the line width of <sup>1</sup>H NMR spectrum occurred correspondingly above 430°C in the presence of zinc chloride. Activity of MOO<sub>3</sub> over the various metal oxides was discussed relating to the concentration of Mo<sup>5+</sup>.

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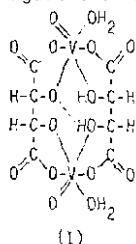
OXIDATION OF SUBSTITUTED BENZO(A)PYRENES. Paul D. Sullivan, Larry E. Ellis, F. Bannoura and I. J. Ocasio, Department of Chemistry, Ohio University, Athens, Ohio 45701.

Multiple pathways may exist for the activation of polycyclic aromatic hydrocarbons to ultimate carcinogenic forms. Substitution particularly at positions 7,8,9 or 10 of the benzo(a)pyrene molecule may block the well established diol-epoxide pathway and other alternate pathways may be particularly important for such derivatives. In view of this it seemed worthwhile to investigate the oxidative behavior of BP derivatives to further understand possible activation pathways. This paper reports our investigations into the chemical oxidations of several mono- and dimethyl substituted BP's and several mono-fluoro BP's. EPR spectroscopy was used to detect radical intermediates and HPLC was employed to separate reaction products. Radical cations were generally observed on oxidation with sulfuric acid or with thallium trisulfate, although in the latter case the radicals were often due to substituted derivatives. Fenton's reagent or trifluoroacetic acid/hydrogen peroxide generally produced 6-oxy radicals unless the 6-position was blocked by substitution.

79 EPR AND STRUCTURAL STUDIES OF INTERMEDIATE pH VANADYL(IV)  $\alpha,\alpha'$ -DIHYDROXYDICARBOXYLATES. Harold D. Beeson, Robert E. Tapscott, and Eileen N. Duesler, Department of Chemistry, The University of New Mexico, Albuquerque, NM 87131.

EPR studies have shown a large increase in internuclear distance in binuclear vanadyl(IV) tartrates as the solution pH is decreased. These studies also show that the stereoselectivity observed at high pH, where there is a preferential formation of complexes with two bridging ligands of opposite enantiomeric form (dl complexes), apparently disappears as the pH is lowered. Thus, at intermediate and low pH, there is little difference discernable between EPR spectra of active and racemic systems. Our past EPR investigations on the high pH system have shown V-V distances in excellent agreement with

those determined by x-ray diffraction studies. We have now determined x-ray structures of a binuclear vanadyl(IV) tartrate(3-) complex isolated from both active and racemic systems which show larger internuclear distances, again in excellent agreement with those found in EPR studies. The dinegative complex (1) in (dl)-K [(VO) $_2$ (C<sub>4</sub>H<sub>3</sub>O<sub>6</sub>)<sub>2</sub>(H<sub>2</sub>O)<sub>2</sub>] $\cdot$ 2H<sub>2</sub>O (P2<sub>1</sub>/c) and K<sub>2</sub>[(VO) $_2$ ((d)-C<sub>4</sub>H<sub>3</sub>O<sub>6</sub>)<sub>2</sub>(H<sub>2</sub>O)<sub>2</sub>] $\cdot$ H<sub>2</sub>O (P2<sub>1</sub>2<sub>1</sub>2<sub>1</sub>) show internuclear distances of 5.382(2) and 5.386(2). The increase in internuclear distance from about 4.0 Å at high pH is due to a change in coordination geometry from quadrilateral pyramidal or trigonal bipyramidal to octahedral with water coordination. A reversal in isomer stability from d>dd=c at high pH to dd>dd=c at intermediate pH gives rise to the "apparent" lack of stereoselectivity. In fact the stereoselectivity is high with preferential formation of active isomer in both active and racemic systems.



80 SPIN-TRAPPING OF NO RADICALS PRODUCED BY ULTRAVIOLET PHOTOLYSIS OF RDX, HMX AND NITROGUANIDINE. M. B. PAGE and J. B. Moniz, Chemistry Division, Naval Research Laboratory, Washington, DC 20375

Electron spin resonance studies of nitroxide radicals formed by the reaction between nitrogen dioxide and dimethyl sulfide (DMSO) have been reported. (1) Lagercrantz carried out the reaction by bubbling NO<sub>2</sub> gas through DMSO solutions and irradiating with ultraviolet light. We have applied this spin trapping capacity of DMSO in the study of several energetic materials. The compounds cyclotrimethylene-trinitramine (RDX), cyclotetramethylene-tetranitramine, or nitroguanidine (NQ) were dissolved in DMSO or deuterium substituted. Irradiation of these solutions with ultraviolet light was carried out in the EPR cavity at 298 K. EPR spectra were recorded which indicate that nitroxide radicals are formed from NO<sub>2</sub> and the solvent molecules. This provides evidence that NO<sub>2</sub> radicals are formed from RDX, HMX, and NQ by uv radiation at room temperature but rapidly decay in the absence of a spin trapping agent. The EPR spectra and implications of this finding will be presented.

(1) C. Lagercrantz, Acta Chem. Scand. 23, 3259 (1969).

81 INTRA-CLATHRATE TRAPPED RADICALS: CONFORMATION AND DYNAMICS. E. Meirovitch. Isotope Dept., The Weizmann Institute of Science, 76 100 Rehovot, Israel.

Thiourea clathrates are built of a channel-type framework wherein the guest molecules reside. The dynamic behavior and the conformation of intrachannelly located molecules is investigated using ESR by spin-probe doping the guest. Elongated radicals were found to be highly ordered orientationally and to exhibit various degrees of mobility. Complete lineshape analysis of slow motional orientation and temperature dependent cholestane spectra provided accurate order parameters, motional rates and related activation energies. At approximately -40°C an unusual conformer, associated tentatively with oxazolidine ring pucker, was detected. Small and nearly spherically shaped radicals reorient isotropically within the channels. The unusually high hyperfine constants and extremely narrow lines suggest conformational changes imposed by the restrictive environment. Intrachannel clustering was detected at lower temperatures.

82 EPR OF FREE RADICALS INDUCED IN L-ASCORBIC ACID BY LASER RADIATION OR X-RAYS FROM 77K TO 300K, Grace C. Moulton and Graham McDermott\*, Florida State University, Tallahassee, Florida, 32306; \*Goodyear Aerospace Corp., Akron, Ohio, 44315

Single crystals of 1-ascorbic acid and partially deuterated 1-ascorbic acid have been irradiated with either x-rays or 337.1 nm laser radiation at 77K or 300K. The same types of radicals are produced by either type of radiation, but their EPR spectra differ in relative intensity. Four different radicals have been characterized and models have been suggested for each of them. At 77K two oxidation products are produced, radical I, monodehydroascorbic acid, and IV, produced by the loss of the H attached to C<sub>4</sub> of the ring, and one reduction product, III. At 140K radical I decays with the loss of the second hydroxyl-H to form dehydroascorbic acid, and the adduct radical II is produced in the process. Further warming to 300K produces no other changes in the radicals. The unpaired electron in each of the radical species observed is in a \* molecular orbital on the furan ring, as evidenced by the eigenvector of the minimum g eigenvalue. The hyperfine tensors and g-tensors determined from EPR data will be reported.

83 AN EPR STUDY AT 77 K OF ALKOXY AND HYDROXYALKYL RADICALS IN X-RAY IRRADIATED TREHALOSE SINGLE CRYSTALS. P. O. Samskog and L. D. Kispert, Chemistry Department, The University of Alabama, Tuscaloosa, AL 35486 and A. Lund, The Studsvik Science Research Laboratory, S-611 82Nyköping, Sweden.

Recent EPR and ENDOR studies of irradiated single crystals of polyhydroxy compounds at low temperatures (77 K and 4.2 K) have shown that the primary reduced species, the electron, is trapped at intermolecular sites. One of the primary oxidation products formed is the oxygen-centered alkoxy radical RO. In the present work we report the radicals trapped in single crystals of trehalose dihydrate at 77 K. Four different alkoxy radicals were identified, three being of the type >CHO while the fourth is tentatively identified as the radical cation formed on the ring oxygen O5. The radical sites are O<sub>2</sub>'(I), O<sub>2</sub>(II), O<sub>3</sub>'(III) and the ring oxygen O<sub>5</sub>(IV). Proton hyperfine tensors and g values were recorded for each species. The principal direction of each tensor was used to assign the radical site of each species in terms of the known crystal structure. The magnitude of the g tensors were found to be sensitive to the type of hydrogen bond (OH or H<sub>2</sub>O protons) formed with the alkoxy radicals. In addition two hydroxy alkyl radicals were produced at 77 K. A decay mechanism for one of the alkoxy radicals was deduced. The interesting new observation is that a variety of oxidation products are possible in X-ray irradiated trehalose, while it is more usual to observe a very specific product formation in solids.

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## Resolution Enhanced - EPR: Theory, Experiment and Applications

Ray c. Perkins, Jr., Varian Associates

Recent experimental reports cite substantial enhancement in resolution through detection 90° out-of-phase with the incident field modulation (1. R.B. Clarkson and D.S. Leniart, Magnetic Resonance in Chemistry, Biology and Physics, Argonne National Laboratory, June, 1979. 2. E. Perez-Reyes and R.P. Mason, Molecular Pharmacology, 18, 594-597). Theoretical simulations which include the details of phase sensitive detection confirm earlier experimental results and demonstrate the general utility of RE-EPR. Simulations of both first and second harmonic, out-of-phase absorption lines exhibit narrower line widths than their in-phase counterparts for a wide range of modulation frequencies (35Hz - 2MHz). Experimental spectra of widely dissimilar samples such as strong pitch, immobilized spin label and perylene radical anion demonstrate the general utility of RE-EPR.

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EPR AND ST-EPR INVESTIGATIONS OF MODEL BIOLOGICAL SYSTEMS USING  $^{15}\text{N}$  AND DEUTERIUM SUBSTITUTED SPIN LABELS. A.H. Beth, S.D. Venkatramu, K. Balasubramanian, A.J. Dammers, D.E. Pearson, C.R. Park and J.H. Park, Vanderbilt University, Nashville, TN 37232

The sensitivity and resolution of EPR and ST-EPR spectra are greatly enhanced when  $^{15}\text{N}$  and deuterium substituted maleimide spin probes are used for spin labeling of proteins (PNAS 73, 957 and 4955, 1976). EPS studies on the binding of coenzymes, NAD and NADH, to enzymes are likewise facilitated by deuteration of spin labeled analogs (BBR 701, 224, 1982). For investigations of biological membranes and model lipid bilayers, we have now synthesized  $^{15}\text{N}$ -5-stearate ( $^{15}\text{N}$ -5-NS) and  $^{15}\text{N}$ -cholesterol ( $^{15}\text{N}$ -CSL). These compounds were synthesized by converting  $^{15}\text{N}$ -glycine to  $^{15}\text{N}$ -2-amino-2-methyl-1-propanol and subsequent condensation with  $\alpha$ -keto stearate or cholesterol. The signal heights of freely tumbling  $^{15}\text{N}$ -5-NS were increased 1.7 fold. Spectral simplifications afforded by the  $^{15}\text{N}$  substitution enabled more detailed and quantitative analysis of the structural characteristics of bound to bovine serum albumin or inserted into the plasma membrane of intact red blood cells. Model membranes have been prepared with  $^{15}\text{N}$ -CSL incorporated into dispersed and highly ordered DPPC-cholesterol bilayers. EPR and ST-EPR spectra were recorded with  $\text{H}_0 \parallel$  and  $\text{H}_0 \perp$  to the membrane normal axis for the ordered system over a temperature range of -18° to 40° C. Modeling of this system has enabled a more rigorous definition of the diffusional model for  $^{15}\text{N}$ -CSL in these model membrane systems.

## 86 EPR STUDIES OF LITHIUM DITHIONITE. R. L. Ake, Old Dominion University, Department of Chemical Sciences, Norfolk, VA 23508.

Lithium dithionite has been recently synthesized and studied by ESR spectroscopy. The characteristic  $\text{SO}_2^{\cdot -}$  spectra is present, but the spectrum, except for very low temperatures appears to be a composite of two resonances from two species. The shape and the linewidth of the signal changes dramatically from -172°C to 300°C. At low temperatures a single very broad resonance is seen. At room temperature the spectrum narrows and splits into two similar overlapping spectra. As the temperature approaches 200°C the intensity of the signal increases dramatically although it decays away rather quickly as a function of time at a constant temperature. The maximum intensity, is achieved at 220°C, approximately the temperature of the exothermic decomposition of  $\text{Li}_2\text{S}_2\text{O}_4$ . Above 250°C the signal decreases in intensity and the shape changes as well. The changes described are irreversible because the room temperature spectrum is not recovered by lowering the temperature. Crystalline  $\text{Li}_2\text{S}_2\text{O}_4$  also displays a half-field signal at low temperature similar to that seen for  $\text{Na}_2\text{S}_2\text{O}_4$ . However, the spectrum of the lithium salt shows two sets of absorptions.

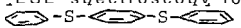
88 EFFECTS OF MOTION ON ESE AND ESEEM SIGNALS, Bruce H. Robinson, Department of Chemistry, University of Washington, Seattle, WA 98195

The effects of motion upon Electron Spin Echo (ESE) relaxation curves are examined. The density matrix for the spin response incorporates the stochastic motional operator following the work of Freed and Stillman and Schwartz (in Time Domain EPR). We assume that a single unpaired electron is coupled to many nuclei via scalar coupling. The first dynamic model to be considered is the two jump model, characterized by a single hopping rate ( $k$ ) from one site to another. Numerical calculations were carried out to simulate the ESE following two pulse (90-180) and three pulse (180-90-180) sequences. The appropriate Hamiltonian for a single electron coupled to a single proton is:

$$H_0 S_z + a S_z I_z + a_2 (S_+ I_- + S_- I_+).$$

Analytic results show that the ESE is composed of three exponential relaxation terms after a 90-180 pulse sequence when the jump rate is greater than the splitting. The phase memory time ( $T_M$ ), for the long time relaxation is related to the jump rate, by the expression:  $T_M = k - (k - (a/2))$ . When the rate is less than  $(a/2)$  envelope modulation (EM) of the ESE is seen on a single exponential relaxation. The effects of multiple exponential relaxation when  $k > a/2$  as well as the ESEEM when  $k < a/2$  will be discussed. The phase memory time will be a minimum when  $k = a/2$ . This model may be generalized to study the multiple site systems where only two resonance lines are seen. This model is applied to the ESE of pristine samples of cis and trans (CH) and (CD). The rate constant is assumed to arise from diffusion across a barrier. ESE results do not distinguish between a one dimensional diffusion model and concerted motion of the electron (as a soliton) through the lattice. Since the phase memory times for (CH) differ from those of (CD) the motional processes must be connected to the lattice.<sup>x</sup> The above techniques are used to consider the effects of the continuum motional process of Brownian rotational reorientation on the ESE relaxation curves. The sensitivity of the ESE signals to the motional process in the slow motional regime, the effects of presaturating spectral lines, and the effects of finite pulse power will be discussed.

89 ELECTRON SPIN ECHO STUDIES OF DOPED POLY(p-PHENYLENE SULFIDE) AND p-TERPHENYL. L. D. Kispert, Chemistry Department, The University of Alabama, Tuscaloosa, AL 35486 and M. K. Bowman and J. R. Norris, Chemistry Division, Argonne National Laboratory, Argonne, Illinois 60439.

Highly conducting polymers can be prepared by doping poly(p-phenylene), [PPP], poly(p-phenylene sulfide), [PPS], or various crystalline oligomers with either strong electron acceptors (ASF<sub>5</sub>, SO<sub>3</sub>) or donors (Na, K, Li). EPR studies over a wide range of dopant concentration reveals a line narrowing with dopant concentration. It has been shown by Dalton et.al. that it is very difficult to extract motional information for a system giving rise to a narrow EPR line. To get around this problem electron spin echo (ESE) measurements are carried out. We have measured  $T_2$  as a function of temperature by ESE spectroscopy for several doped systems. For instance  $T_2$  for SO<sub>3</sub> doped  (Trimer) between -150°C to 25°C is essentially temperature independent and equal to 200 ns. On the other hand  $T_2$  for SO<sub>3</sub> doped PPS varies from 600 ns at -150°C to 400 ns at -60°C. In contrast SO<sub>3</sub> doped p-terphenyl varies from 500 ns at 36°C to 3.5 us at -150°C. The conductivity for these samples varies from SO<sub>3</sub> doped trimer (an insulator) to highly conductive p-terphenyl. The temperature independent  $T_2$  behavior of SO<sub>3</sub> doped trimer suggests the presence of a localized radical. This is in contrast to the temperature dependence of the weakly conducting doped PPS or the highly conducting p-terphenyl. These  $T_2$  measurements will be compared to those found for Li, K and Na doped PPP and deuterated PPP.

96 NEW, HIGH SENSITIVITY UNIVERSAL FLAME PHOTOMETRIC DETECTOR FOR CATION CHROMATOGRAPHY. S. W. Downey and G. M. Hieftje. Department of Chemistry, Indiana University, Bloomington, Indiana 47405.

A novel detection scheme for ion chromatography has been devised in which cations separated in an ion chromatograph are stoichiometrically replaced by a sensitive, photometrically active species. Following cation replacement, the eluent is nebulized into a flame where emission from the photometric species is measured by a filter photometer.

In this new technique, cations are separated as usual on a strongly acidic ion-exchange resin. Following separation, the eluent is neutralized with a basic suppressor column, and passes through a "replacement" column. The replacement column contains a strongly acidic ion-exchange resin in the  $A^+$  form where  $A^+$  is an alkali metal. Sample cations have stronger affinities for the resin and are therefore replaced by  $A^+$  in the eluent. Chromatograms are produced by monitoring the alkali metal concentration with a simple, inexpensive flame photometer consisting of a photomultiplier tube, the appropriate wavelength filter for the replacement ion used, and necessary electronics.

The conditions necessary for useful operation and performance of the system are presented and evaluated. Emphasis will be placed upon predictable replacement efficiency, single-channel operation and the sensitivity afforded by flame-photometric detection of the replacement alkali cations.

97 CARE AND FEEDING OF FIBER SUPPRESSORS. D. Eubanks, K. Haak, A. Fitchett. Dionex Corporation, 1228 Titan Way, Sunnyvale, CA 94086.

The use of Ion Chromatography has in the past been sometimes complicated by the need to periodically regenerate the suppressor column. The introduction of the Fiber Suppressor had eliminated this problem since it is constantly regenerated while in use. When using the Fiber Suppressor, the eluent flow is directed through the interior of a semi permeable ion exchange fiber while the exterior of the fiber is constantly in contact with flowing regenerant solution. With the Fiber Suppressor, baseline conditions (stability, magnitude) will be dependent on eluent composition, eluent flowrate, regenerant composition and regenerant flowrate. This paper will address the optimization of these parameters for baseline stability and low background conductivity. The practice aspects of using fiber suppressors will be emphasized as well as tips on their handling.

98 INORGANIC CATION AND ANION SEPARATIONS ON DYNAMICALLY COATED REVERSED PHASE COLUMNS. Richard M. Cassidy, Steven Elchuk; Atomic Energy of Canada Ltd., Research Company, Chalk River Nuclear Laboratories, Chalk River, Ontario, Canada, K0J 1J0.

A number of hydrophobic molecules containing ionic functional groups were dynamically coated onto 5 and 10  $\mu\text{m}$  reversed phases, and these phases were evaluated for the separation of cations and anions. Quaternary ammonium salt ( $C_8$ ,  $C_{16}$ ,  $C_{25}$ ,  $C_{32}$ ,  $C_{37}$ ) anion systems, and sulfate ( $C_{12}$ ,  $C_{20}$ ) and sulfonate ( $C_6$ ,  $C_8$ ) cation systems were examined, and column efficiencies were compared. Both  $C_{18}$  bonded phases and a styrenedivinylbenzene phase were used either under dynamic equilibrium conditions, or with eluents that would not elute the dynamically coated modifier. This approach permitted the rapid and reproducible preparation of ion exchangers having variable capacity and excellent efficiency; column efficiencies of 0.03 to 0.1 mm at 1  $\text{mL}\cdot\text{min}^{-1}$  were commonly observed. Both variable wavelength UV-visible and conductivity detectors have been used for test ions such as  $F^-$ ,  $Cl^-$ ,  $I^-$ ,  $Br^-$ ,  $NO_3^-$ ,  $NO_2^-$ ,  $SO_4^{2-}$ ,  $S_2O_3^{2-}$ ,  $IO_4^-$ ,  $IO_3^-$ ,  $Cu^{2+}$ ,  $Pb^{2+}$ ,  $Ni^{2+}$ ,  $Co^{2+}$ ,  $Zn^{2+}$ , and  $Mn^{2+}$ . A variety of eluent options were examined for conductivity detection and the results obtained are illustrated and compared. Examples are given which illustrate the flexibility and potential of this approach for the determination of ions in the picogram and nanogram range.

- 99     AUTOMATED DIALYZING INJECTION SYSTEM FOR CHROMATOGRAPHY. L.D. Hansen and F.R. Nordmeyer, Department of Chemistry and Thermochemical Institute, Brigham Young University, Provo, Utah 84602 .

The presence of soluble polymeric materials in a sample often makes it difficult to **analyze** a **sample** by liquid chromatography **because** the polymeric material must first be removed or it will foul the chromatographic column. Also it is often of interest to know the equilibrium or free **concentration** of the species being determined as opposed to the total **concentration**. Both of these problems can be solved **by** dialysis of the sample and injection of the dialysate into the **chromatograph**. However, normal dialysis procedures are slow, require relatively large **samples**, and usually result in severe dilution of the **sample**. We have developed a dialyzing injection system which uses as little as 40  $\mu$ L of **sample** and delivers a precisely **measured, ultrafiltered** dialysate to the eluent stream. The **system** described provides an attractive way to handle any chromatographic samples containing **undesired ultrafilterable** material. This injection system should be useful for the analysis of ions and drugs in **blood**, small molecules and ions in soil extracts, ions and small molecules in polymer containing **pharmaceuticals**, and the equilibrium concentrations of unbound ions and small molecules in complex **fluids**.

- 100 FURTHER DEVELOPMENTS IN THE COMPUTERIZED ACQUISITION AND REDUCTION OF ION CHROMATOGRAPHIC DATA. C. C. Torquato, N. Latner and D. C. Bogen. Environmental Measurements Laboratory, U. S. Department of Energy, 376 Hudson St., New York, NY 10014.

At the 23rd *Rocky Mountain Conference*, we reported the interfacing of a Hewlett-Packard-85 microcomputer to a Dionex Model 10 Ion Chromatograph. The development of a BASIC program to acquire and reduce ion chromatographic data was also reported. As a first step toward automation, a  $4\frac{1}{2}$  digit, 30,000-part resolution, auto-ranging digital voltmeter replaced the digital voltmeter formerly in use. The new voltmeter's resolution and auto-ranging capabilities permit calibration from  $\mu$ g/L to mg/L concentrations. A single sensitivity scale setting can now be used when the instrument is calibrated. Conductivity detector response was monitored using both peak height and peak area measurements. Detector response was found to be linear for the concentration ranges studied. In addition, the microcomputer program has been modified to expand its data reduction capability.

- 101 CATION EFFECTS ON NONSUPPRESSED ANION CHROMATOGRAPHY AT HIGH SALT CONCENTRATIONS. L. C. Stone and T. N. Andersen. Kennecott Minerals Company, Process Technology, 1515 Mineral Square, Salt Lake City, Utah 84147

Nonsuppressed anion chromatography was applied to aqueous solutions containing up to 2,000 ppm salts to determine high-level ( $\sim$ 1,000 ppm) and low level ( $\sim$ 10 ppm) anions simultaneously. Anion response at a given level was found to depend on the cation present. Double peaks and other anomalies also occurred which varied with the cation, column condition, and pH. Reasons for and ways to overcome the problem are discussed.

- 102 ON THE ION CHROMATOGRAPHIC DETERMINATION OF S(IV). Purnendu K. Dasgupta. Department of Chemistry, Texas Tech University, Lubbock, Texas 79401.

Ion chromatographic determination of S(IV) is described with special reference to the determination of  $\text{SO}_2(\text{g})$  and/or aerosol S(IV) along with chloride, nitrate and sulfate in particulate matter. A method is presented for the baseline separation of the above species. The chromatographic behavior of hydroxymethanesulfonate under various eluent conditions is discussed. Novel developments in ion chromatographic suppression and detection methods are presented.

- 103 ION CHROMATOGRAPHIC DETERMINATION OF INORGANIC ANIONS WITH UV DETECTION - A LOOK AT APPLICATIONS. V. T. Turkelson and R. P. Himes. The Dow Chemical Company, Midland, Michigan 48640.

During the past two years, ion chromatography (IC) coupled with UV detection has been successfully applied to the separation and determination of iodate ( $\text{IO}_3^-$ ), bromate ( $\text{BrO}_3^-$ ), nitrite ( $\text{NO}_2^-$ ), bromide ( $\text{Br}^-$ ), nitrate ( $\text{NO}_3^-$ ), chromate ( $\text{CrO}_4^-$ ), thiosulfate ( $\text{S}_2\text{O}_3^{2-}$ ), iodide ( $\text{I}^-$ ), and thiocyanate ( $\text{SCN}^-$ ) in a variety of sample matrices. As compared to the determination of these anions via IC with conductivity detection, the IC/UV technology has provided notable improvements in specificity and sensitivity (e.g., as much as 50-100 times). Parts per billion (ppb) concentrations of these anions have been routinely determined without the use of concentrator columns and common conductimetric interferences, encountered in many inorganic materials and process streams (e.g., high chloride and sulfate concentrations), have effectively been eliminated. In addition, use of UV detection has introduced single column simplicity to the IC system since the second column normally required for eluent conductivity suppression is not needed.

This paper describes the eluents, and those UV detectors and appropriate wavelengths chosen for the noted anions and presents applications of the IC/UV methodology as an indication of its scope and impact.

- 104 NEW APPLICATIONS IN MPIC. A. Fitchett, D. Eubanks, L. Lois, Dionex Corporation, 1228 Titan Way, Sunnyvale, CA 94086.

Since the introduction of Mobile Phase Ion Chromatography, MPIC, a new series of applications have been developed which utilize this unique separation mode. The MPIC separation mode is characterized by the use of neutral macroporous resins and specialty Ion Sep reagents. Some of these new applications include the separation of ferri- and ferro- cyanide complexes, the separation of nitrate and chlorate, and the ability to analyze a wide variety of ionic organic compounds. This paper will discuss these new applications and will show comparisons between MPIC and other separation modes (HPIC and HPLC). The ability to use MPIC for difficult sample types will be demonstrated, as well as the use of different detection modes.

- 105 BROMINE MEASUREMENTS BY ION CHROMATOGRAPHY USING ELECTROCHEMICAL AND CONDUCTIVITY DETECTORS. Jann M. Frye. SOHIO Research, 4440 Warrensville Center Road, Warrensville Ohio, 44128.

A comparison was made of bromide measurements by Ion Chromatography using two different detectors; the conductivity detector and the electrochemical detector. Selectivity, sensitivity, and linearity of the two detectors was investigated. Application of both detectors to the measurement of bromide in polymers following Schoeniger combustion is also discussed.

- 106 ION CHROMATOGRAPHY EXCLUSION DETERMINATION OF LACTATE IN SERUM. John W. Smith and Robert T. Ambrose. Research Laboratories, Eastman Kodak Company, Rochester, New York 14650.

This method was developed in our laboratory as a potential reference method. Lactate ion and other anionic species were removed from the bulk of the serum matrix on an anion exchange resin. The lactate was eluted quantitatively from the resin with 0.01 M  $\text{H}_2\text{SO}_4$ . We then separated the lactate from other organic acids present on a Bio-Rad HPX-87H organic analysis column, using 0.005 M  $\text{H}_2\text{SO}_4$  as eluent and monitoring the absorbance of the lactate at 214 nm. With 0.5 ml serum samples, a level of 0.1 mM was easily measured, and the calibration obtained was linear to at least 15 mM. Recoveries of lithium lactate standards put through this procedure ranged from 98.7 to 100%. Recoveries of known amounts of lactate added to serum pools ranged from 98.9 to 102.6% at levels from 1.0 to 10.0 mM lactate. The precision of the method was measured at three levels on 16 days over a 52-day period. The CV's obtained were 3.5% at 1.62 mM, 2.2% at 2.87 mM, and 2.1% at 8.44 mM. No interferences have been found. The anion column pretreatment excludes neutral and cationic species, and the measurement of the retention of a number of organic acids showed no interfering species. Comparison with a method in use in many hospitals will show the superiority of the chromatographic procedure, particularly for samples which are icteric, hemolytic, or lipemic.

107 ION CHROMATOGRAPHIC ANALYSIS OF BROMATE IN FOODS. K. Oikawa and H. Saito. Niigata College of Pharmacy, 5329, Kamichinei-cho, Iigata, Japan, 950-21.

Potassium bromate( $\text{KBrO}_3$ ) is used in bread-making as an oxidizing agent. Recently, it has been positive in its carcinogenic tests, and its safety when as a food additive is being doubted. Therefore, it is important for securing the safety of food to check residue  $\text{KBrO}_3$  in food. We found that bromate ion can be determined easily and rapidly by the use of Ion Chromatography(IC) which is recently much diffused as a means for determining ions. For the analysis of bromate ion,  $0.0035\text{ M Na}_2\text{B}_4\text{O}_7$  was used as the eluent, and the large interference of chloride ion with the ion chromatographic analysis was eliminated easily by the silver coated resin treatments. The determination limit of bromate ion was  $0.1\mu\text{g/g}$ . By this method, the presence of residual bromate in bread was clarified. It was confirmed that this method was also effective for the bromate ion determination of fish paste and other food.

\* This work was supported by the Japanese Ministry of Health and Welfare.

108 ANALYSIS OF METALS AND METAL COMPLEXES BY ION CHROMATOGRAPHY. J. Riviello and C. Pohl. Dionex Corporation, 1228 Titan Way, Sunnyvale, CA 94086

Ion Chromatography has been widely accepted as an analytical tool for solving anion analysis problems in all types of matrices. The ability to analyze such common anionic species as fluoride, chloride and sulfate at  $\text{g/L}$  levels in water, wastewater and water soluble samples is well documented. The ability to analyze metals by Ion Chromatography has not enjoyed the same popularity. One reason for this had been the ability to analyze only group Ia and IIa metals. This limitation was the result of the detection system employed. Many of the metal species of interest underwent undesirable reactions in the suppressor column when using an IonChrom/Cond conductivity detection mode. In most cases, the transition metals would form insoluble hydroxides or oxides during the chemical suppression reaction. Now by using specially prepared resins and a new detection system, transition metal capability is a reality. The detection system employed uses a post column reaction followed by an Opti-Ion/UV-VIS detector. This system now permits metal profiles to be done quickly and with speciation  $\text{Fe}^{2+}$  and  $\text{Fe}^{3+}$  on very small samples. Metal-ion complexes such as  $\text{Fe}(\text{CN})$  and  $\text{Fe}(\text{CN})$  have been successfully separated and detected using Mobile Phase Ion Chromatography (MPIC) with IonSep reagents and onChrom/Cond conductivity detection. This paper will discuss the separation of transition metals by Ion Chromatography along with the mechanisms and principles of post column reactor detection.

109 SINGLE-COLUMN ION CHROMATOGRAPHIC DETERMINATION OF DIVALENT METAL IONS AND LANTHANIDES. Gregory J. Sevenich and James S. Fritz. Department of Chemistry and Ames Laboratory, U.S.D.O.E. Iowa State University, Ames, Iowa 50011.

The scope of ion chromatography has been extended to include the separations of transition metal ions and lanthanides as well as the alkaline earths. The system uses a separating column filled with a cation-exchange resin of low capacity, connected directly to a conductivity detector. Separations are achieved using an ethylenediammonium cation as the eluting agent with a complexing anion incorporated in this eluent. The separations are thus obtained through a combination of mass-action and complexation effects. Exceptional resolution of iron(II), cobalt(II), manganese(II), cadmium(II), calcium(II), lead(II), and strontium(II) was obtained in 12 minutes using an eluent containing ethylenediammonium tartarate. Several of the lanthanide cations were well resolved using an eluent containing ethylenediammonium tartarate or  $\alpha$ -hydroxyisobutyrate. Calibration curves based on peak height are linear and good quantitative results were obtained.

110 DETERMINATION OF ACETATE BY ION EXCLUSION TECHNIQUE USING  $H_2CO_3$  AS AN ELUENT.

H. Itoh and Y. Shinbori, Faculty of Pharmaceutical Sciences, Josai University, Sakado, Saitama, Japan ; and I. Murata, Faculty of Science, Osaka University, Osaka, Japan.

Using a Dionex Model 10 Ion Chromatograph equipped with conductivity detector and ICE separator, and a carbonic acid eluent, the analyses of weak acids can be performed without using the Ag column as a halide suppressor. In our system, an anion suppressor is introduced between the pump and the injection valve in order to convert sodium bicarbonate/ sodium carbonate solution into carbonic acid solution. This weakly acidic solution can be used as an eluent in ion exclusion technique.

The elution profile of weak acids ( formate, acetate, propionate, butyrate and lactate ) was examined as a function of the concentration of eluent and flow rate. The technique was applied to the analysis of acetate in serum and in some pharmaceutical samples.

111 ANALYSIS OF FERMENTATION BROTHS AND RAW MATERIALS UTILIZING ION CHROMATOGRAPHIC TECHNIQUES. T. L. Hassinger and B. A. Olsen, Eli Lilly and Company, P.O. Box 685, Lafayette, Indiana 47902.

Knowledge of the concentrations of inorganic ions and organic acids in fermentation broths is useful in optimizing broth conditions to produce a maximum yield of the desired product. Common methods for the determination of these species can be cumbersome, time-consuming and sensitive to interferences. For these reasons, many ionic species in broths are not determined on a routine basis.

Ion chromatography and ion chromatography exclusion have, proven extremely useful for the determination of inorganic ions and organic acids, respectively, in fermentation broths. Minimal sample preparation and short analysis time make it possible to profile the concentrations of ionic species during the course of a fermentation. Accurate and sensitive analyses are obtained despite the complex sample matrix. Examples and evaluation data for assays of three types of broth will be presented.

Various fermentation raw materials were analyzed utilizing ion chromatography to determine the major sources of certain ionic components in the broth make-up. Results will be presented for the analysis of corn starch, corn meal, and corn steep liquor.

112 ION CHROMATOGRAPHIC ANALYSIS OF ETHANOL/AMMONIUM TARTRATE ALUMINUM ANODIZATION SOLUTIONS. R. M. Merrill. Sandia National Laboratories, Organization 5821, P.O. Box 5800, Albuquerque, New Mexico 87185.

A solution which is 98% ethyl alcohol saturated with ammonium tartrate (0.12 gm/L) is used as an electrolyte in the formation of anodic aluminum oxide barrier film capacitor dielectrics. Bath composition affects the dielectric strength and thickness of these films. Anions in the electrolyte may cause poor barrier coatings by migrating to the aluminum anode and forming porous films or providing pathways for electrical breakdown. Ion chromatography has been found to be an ideal tool for both qualitative and quantitative analysis for anions in the anodization baths. A method for replacing the ethanol solvent with standard anion eluent prior to analysis was developed and used to analyze for chloride in the range of 0.1 to 0.7  $\mu\text{g/mL}$ .

The formation of formate and acetate ions in the electrolyte solution as a function of anodization was discovered during the course of these studies. Ion chromatography exclusion can simultaneously determine these two ions as well as the tartrate ion without prior removal of ethanol, and was used to monitor changes in bath composition. Acetate and formate levels ranged from undetectable in a fresh 114 Liter bath to 15  $\mu\text{g/mL}$  after the anodization of 96,000 cm of aluminum. Tartrate levels in the same bath ranged from 97  $\mu\text{g/mL}$  to 56  $\mu\text{g/mL}$ .

\*This work was performed at Sandia National Laboratories supported by the U.S. Department of Energy under contract number DE-AC04-76DP00789.

113 MEASUREMENT OF QUATERNARY AMMONIUM IONS IN Zn/Br<sub>2</sub> BATTERY ELECTROLYTES USING ION CHROMATOGRAPHY. P. G. Grimes, R. V. Kastrup, G. E. Milliman, and A. R. Young, II. Exxon Res. and Eng. Co., Linden, NJ, 07036.

Advanced battery systems which are based on the Zn/Br<sub>2</sub> couple employ circulating electrolytes containing a bromine complexing agent(s). A system under investigation in our laboratories uses N-ethyl-N-methylpyrrolidinium bromide and N-ethyl-N-methylmorpholinium bromide for bromine complexation. The concentrations of these quaternary ammonium ions vary in the anode and cathode compartments of the battery as a function of the state-of-charge of the battery, and it is necessary to know these concentrations in order to gain insight into battery performance. A method has been developed to measure these quaternaries in electrolytes. It involves complexation of Zn(II) with chloride ion, removal of the ZnCl<sub>4</sub><sup>2-</sup> complex by passage through an anion exchange resin, and the determination of the quaternaries in the zinc-free effluent by ion chromatography. The individual quaternaries can be measured to at least 0.05M in the presence of 1M ZnBr<sub>2</sub>. The results of the determinations of the quaternaries by ion chromatography compare favorably with those obtained by <sup>13</sup>C and N NMR measurements.

114 APPLICATIONS OF ION CHROMATOGRAPHY IN THE SEMICONDUCTOR INDUSTRY. Keenan Evans. Motorola Inc., 5005 E. McDowell Rd., Phoenix, AZ 85008.

In the electronics materials analytical laboratory at Motorola ion chromatography has been applied to the analysis of a wide spectrum of materials.

The analyses performed can be categorized according to the source of the problem or sample; e.g., 1) A-quality assurance of incoming raw materials, 2) QC-quality control of finished products and process controls, 3) acute problem solving, and 4) chronic problem solving.

Typical QA functions include determination of ionic species in aqueous extracts of incoming die attach and encapsulation grade molding compounds, monitoring etch mixtures for proper acid ratios, and determination of impurities in a variety of chemicals.

QC analyses may include determination of contaminants or carry-over species in process rinse waters and testing aqueous extracts of devices at various stages of production.

An example of IC use in acute problem solving is the determination of possible contamination sources by analyzing polymeric packing materials for heteroatom content.

In a chronic problem solving situation ion chromatography is used to monitor levels of various plating bath species as part of an overall effort to correlate bath and deposit chemistry with device performance.

115 ION CHROMATOGRAPHY capabilities in food analysis. L. Angers and L. Kimball. Dionex Corporation, 1228 Titan Way, Sunnyvale, CA 94086.

This paper discusses the application of old and new technologies of Ion Chromatography to the analysis of ionic species in the complex matrices of food. Anion High Performance Ion Chromatography (HPIC-AS1-4/Cond) can be used for the analysis of strong anion species such as fluoride in milk, nitrite and nitrate in meat and oxalate in whiskeys. High Performance Ion Chromatography Exclusion (HPICE-AS1/Cond) can be used for the analysis of weaker anionic species such as organic acids in dairy products, vinegars and soy sauce. The determination of specific amino acids present in various food matrices is accomplished by the use of another HPICE Separator (HPICE-AA), a Post Column Reactor (PCR) with Fluoropa reagent and an Opti-Ion Fluorescence Detector. The HPIC-CS2 Separator with an electrical conductivity detector (HPIC-CS2/Cond) can be used for the analysis of physiologically significant monovalent cations such as sodium and potassium. Using the same type of separator, but a different eluent, the analysis for trace nutrients such as magnesium and calcium can be accomplished. The analysis of trace metals such as iron and zinc can be performed through the use of an HPIC-CS2 Separator, a PCR utilizing PAR reagent and an Opti-Ion UV/VIS Detector (HPIC-CS2/Opti-Ion UV/VIS). The analysis of more hydrophobic anions and cations such as sulfonic acid detergents and quaternary ammonium disinfectants or more neutral species such as vitamins can be analyzed by the use of Mobile Phase Ion Chromatography with an electrical conductivity detector (MPIC-NS1/Cond) or an Opti-Ion UV/VIS Detector (MPIC-NS1/Opti-Ion UV/VIS).

- 116 AIRBORNE FORMALDEHYDE COLLECTION BY SOLID SORBENT AND ANALYSIS BY ION CHROMATOGRAPHY.  
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A rapid and accurate method for the ion chromatographic analysis of formaldehyde in air is presented. Atmospheric concentrations of formaldehyde are collected on sampling tubes containing activated 13X molecular sieve. The formaldehyde is desorbed with an aqueous solution of sodium bisulfite that forms an ionic addition product. The excess bisulfite which coelutes with the addition product is selectively oxidized allowing for the quantitation of the formaldehyde bisulfite. The elution time for this addition product is approximately 14 minutes when using the standard anion system. Analysis time of less than 1 hour is achieved. Concentrations generated from a dynamic standards generator ranging from 1.3 mg/m<sup>3</sup> to 6.6 mg/m<sup>3</sup> (1.1 to 5.4 ppm) in air were collected and a mean recovery of 102% was obtained. Sensitivity of 1 ng formaldehyde per mL of desorbant (25 mL) is obtained when using a 500 uL sample loop.

- 117 AUTOMATED DETERMINATION OF BROMIDE IN WATER BY ION CHROMATOGRAPHY WITH AN ELECTROCHEMICAL DETECTOR. G. S. Pyen and D. E. Erdmann. U.S. Geological Survey, National Water Quality Laboratory, 6481-H Peachtree Industrial Boulevard, Doraville, Georgia 30340

An automated ion chromatograph with an electrochemical detector was used to develop a rapid, sensitive, and accurate procedure for the determination of bromide in rain water and most ice and ground waters. By using a program controller, an automatic sampler, and an integrator, approximately 10 minutes is required to complete a chromatogram. The detection limit for bromide is 0.01 milligram per liter. Relative standard deviations of less than five percent were obtained for six U.S. Geological Survey Standard Reference Water Samples. Erratic results are obtained if the chloride to bromide ratio is greater than 1,000:1 and 5,000:1 for working calibration ranges of 0.01-0.1 and 0.1-1.0 milligram per liter of bromide, respectively, with maximum limit of 2,000 milligram per liter of chloride. To determine accuracy of results, several samples were spiked with known concentrations of bromide. Recoveries ranged from 97 to 110 percent. Bromide in several samples also was determined independently by a catalytic oxidation colorimetric procedure. Recovery data obtained proved to be less accurate than the automated ion chromatographic method.

- 118 A MONITORING STUDY OF NITRATE IN DRINKING WATER IN THE FEDERAL

REPUBLIC OF GERMANY. M. Sonneborn and T. Darimont. Institute for Water, Soil and Air Hygiene, Federal Health Office, D-1000 Berlin 33, Fed. Rep. of Germany

Nitrate is considered as a substance whose presence in drinking water is not considered as desirable. If reduced to nitrite it may cause methemoglobinemia in infants. Onward reaction of nitrite with organic amines will result in the formation of nitrosamines. More than 1000 samples of drinking water were examined for their content of nitrate and other anions by means of ion chromatography (IC). Clearly elevated nitrate contents in drinking water were revealed by the results of measurements in wine-growing areas, caused by the extensive use of fertilizers. Also high nitrate levels in drinking water are attributed to the use of nitrogen fertilizers for other special agricultural crops. The type and amount of nitrate pollution are discussed and the analytical conditions of the IC are described in detail.

119 ION CHROMATOGRAPHIC ANALYSIS FOR CHLORIDE, FLUORIDE, AND SULFATE IN PRECIPITATION. M. M. Reddy, Marilyn Werner, and A. G. Hedley, United States Geological Survey, 5293 Ward Road, Arvada, Colorado 80002.

Characterization of precipitation water quality by ion chromatography is an important new area of research. This technique offers the potential of automated, highly accurate, and reproducible analyses. The purpose of this paper is to assess the precision, accuracy, and limitations of ion chromatography for the determination of fluoride, chloride, and sulfate in precipitation samples collected in remote areas of Colorado. The samples analyzed included precipitation from several remote sites in central and southwestern Colorado, and a spring water. Two SRWS (standard reference water samples) prepared by the U. S. Geological Survey, Water Resources Division were also analyzed. One, a dilute surface-water SRWS, and the other, a precipitation SRWS, have proven to be valuable in this program. Optimum precision, expressed as the percent RSD (relative standard deviation), for analyses of the precipitation SRWS was 15 percent for fluoride, and 2 to 3 percent for chloride and sulfate. Comparison of sample analyses employing two different ion chromatography systems and three analysts showed good agreement for mean concentrations; there were significant differences in precision. Analyses of the diluted surface-water SRWS were within the acceptable range. A paired comparison of 19 spring-water analyses exhibited no significant difference between ion chromatography and the reference procedure for fluoride and sulfate. Chloride determinations, on the other hand, showed a significant difference between the ion chromatography and the reference procedure at greater than the 99 percent confidence level. Results from this study emphasize the need for incorporation of appropriate reference materials in a quality-assurance program involving ion chromatographic analyses of low-level environmental samples.

120 A THREE-MINUTE ANALYSIS FOR ACID RAIN ANIONS BY SINGLE-COLUMN ION CHROMATOGRAPHY (SCIC). Thomas Jupille, David Togami, and David Burge. Wescan Instruments, Inc. 3018 Scott Blvd., Santa Clara, CA 95050

Single-Column Ion Chromatography (SCIC) can be defined as the analysis of dissolved ions by liquid chromatographic separation coupled directly to an appropriate detector. In practice, the most commonly used combination is ion exchange separation coupled with electrical conductivity detection.

Because SCIC allows direct coupling of the detector to the column, extremely efficient HPLC columns can be used. Extra-column dead volume can be minimized to allow high-speed/high-resolution analysis. In the present instance, a new, high-speed anion exchange column 100 mm long by 4.6 mm id has been developed which allows the resolution of chloride, nitrate, bicarbonate, and sulfate in less than three minutes. Detection sensitivity down to the 100 ug/L (ppb) level can readily be obtained.

A complete discussion of buffer and system optimization parameters is presented.

121 APPLICATIONS OF ION CHROMATOGRAPHY IN SYNFUELS RESEARCH • R A Nadkarni and D. M. Pond, Analytical Research Laboratory, Exxon Research and Engineering Company, P. O Box 4255, Baytown, Texas 77520

Ion Chromatography (IC) is proving to be a valuable tool in the developing synthetic fuels industry for monitoring various environmentally important anions. Some examples of this will be presented: (1) Halogens including F, Cl, and Br can be determined in coal or oil shale feedstock by combustion in a Parr oxygen bomb followed by IC. (2) The above method also determines nitrogen and sulfur in these fuels. (3) Sulfur forms such as sulfate and pyrite in coal can be rapidly determined by acid digestion followed by IC, instead of the much longer ASTM procedure. (4) Hexavalent and trivalent chromium in effluent waters can be determined by IC. (5) Halides, sulfate, thiosulfate, and sulfite are routinely monitored using IC in the coal gasification, and coal and shale liquefaction product effluent streams. (6) These methods are also used for the determination of halogens, nitrogen, and sulfur in polymer samples. Validity of the IC results has been compared with other instrumental methods for anions such as XRF and measurements using ion selective electrodes. Stability of calibration over a one year period for IC is compared and found to be substantially constant. The new fast run anion columns have proved to have higher sensitivity for some anions, with shorter retention times.

- 122 AN ION CHROMATOGRAPHIC METHOD FOR THE DETERMINATION OF TOTAL SULFUR IN PLANT MATERIAL. J.G. Zakrevsky and S.S. Sidhu, Newfoundland Forest Research Centre, Canadian Forestry Service, P.O. Box 602S, Pleasantville, St. John's, Nfld. A1C 5X3,

A new method for the determination of total sulfur in plant material is presented. The sample is first combusted in an oxygen flask and the sulfate content of the absorbing solution is subsequently determined by ion chromatography. The combustion procedure is rapid, simple and efficient. Because of the excellent sensitivity and precision of the ion chromatographic analysis and its relative freedom from interferences, results are reproducible and accurate. The method was used to determine total sulfur in tree foliage and lichens. Results are compared with those obtained by the turbidimetric determination of sulfate following a magnesium nitrate ashing procedure.

- 123 ANALYSIS OF CONTAMINANTS AND CORROSION PRODUCTS ON INDOOR SURFACES BY ION CHROMATOGRAPHY BY G. B. Murder, L. A. Psota-Kelty and J. D. Sinclair. Bell Laboratories, Crawford's Corner Road, Holmdel, New Jersey 07733.

Water soluble contaminants and corrosion products that accumulate on zinc and aluminum electronic equipment surfaces have been analyzed by ion chromatography. Samples are extracted from field surfaces with filter papers ~~intened~~ with distilled water. The dried papers are re-extracted in the laboratory and the sample solutions are then split and appropriately prepared for automated analysis. Chloride, sulfate, nitrate, bromide, sodium ammonium, potassium, calcium, and magnesium concentrations have been measured. At the cities observed to date, the ranges of accumulation rates for chloride and sulfate are approximately 0.05-0.7 ug chloride/cm<sup>2</sup>/yr on zinc, 0.02-0.4 ug chloride/cm<sup>2</sup>/yr on aluminum, 0.1-1.3 ug sulfate/cm<sup>2</sup>/yr on zinc, and 0.1-0.9 ug sulfate/cm<sup>2</sup>/yr on aluminum. Cities studied include New York, Cleveland, Houston, Council Bluffs (Iowa), Boulder, Colorado Springs, Denver, Orlando, Minneapolis, Seattle, Indianapolis, Chicago, Philadelphia and Newark. The data generally indicate that in addition to some tropospheric influences, the amounts of water soluble ionic contaminants and corrosion products on indoor surfaces depend in a very complex manner on engineering, design, housekeeping, and human factors as well as on temperature and humidity patterns. It is also found that some surfaces seem to emit significant amounts of ionic contaminants, particularly chloride from aluminum surfaces.

- 124 ION CHROMATOGRAPHIC DETERMINATION OF BROMIDE ION IN RAW WATERS USING A CONCENTRATOR COLUMN. C.M. Morrow and R.A. Minear. The University of Tennessee Department of Civil Engineering, Knoxville, TN 37996. D.C.M. Hines and A.M. Yoakum. Stewart Laboratories, Inc., 5815 Middlebrook Pike, Knoxville, TN 37921.

The presence of trace level bromide (<0.5 mg/l) in raw waters produces significant effects on both the total formation potential and the percent distribution of the four trihalomethanes (THMs): CHCl<sub>3</sub>, CHCl<sub>2</sub>Br, CHClBr<sub>2</sub>, CHBr<sub>3</sub> produced when chlorine is used for disinfection. Quantification of bromide allows development of reaction kinetic models regarding rate of THM formation. Such models could provide a vehicle for manipulation of water quality and concentrations of THMs delivered to the consumer. Few data regarding bromide levels are currently available since most conventional colorimetric applications lack desired sensitivity, as does direct ion chromatography (IC). Although Fishman's kinetic permanganate method is adequate in the 1-100 ug/l range, it is time consuming. An IC method employing a sample preconcentration column has been evaluated. The method produced a 1 ug/l limit of detection using DI-based standards, with a 3% relative precision at 20 ug/l. Concentrator capacity varied and the highest-capacity column was selected, followed by examination of raw waters sampled regarding ranges and types of other ions present, such that the maximum concentration volume selected resulted in 100% retention of bromide.

125 Sampling and Analyzing Mixtures of Sulfoxy Anions in Natural Waters  
C.O. Moses\*, D.K. Nordstrom\*\*, and A.L. Mills\* \*Dept. of Environmental Sciences, Univ. of Virginia, Charlottesville, VA 22903 \*\*U.S. Geological Survey, Menlo Park, CA 94025

A chief obstacle to elucidating the redox chemistry of sulfur in natural waters is the difficulty encountered in analyzing mixtures of sulfoxy anions. Previous methods have been too involved to permit high sample throughput while maintaining good quality control. Methods based on Ion Chromatography (IC) were developed for the direct analysis of  $\text{SO}_3^{2-}$ ,  $\text{S}_2\text{O}_3^{2-}$ , and  $\text{SO}^{\cdot -}$ , as well as  $\text{SCN}^-$ . The latter permits the indirect analysis of sulfane disulfonates (polythionates,  $\text{SxO}_2^{6-}$ ,  $3 < x < 6$ ) after cyanolysis, which yields  $\text{SCN}^-$  equal to original  $\text{SxO}_2^{6-}$ . The average value of x is determined by the  $\text{S}_2\text{O}_3^{2-}/\text{SCN}^-$  ratio. Formate, acetate,  $\text{F}^-$ ,  $\text{Cl}^-$ ,  $\text{CO}_3^{2-}$ , and  $\text{PO}_4^{3-}$  do not interfere;  $\text{NO}_2^-$  and  $\text{NO}_3^-$  interfere with  $\text{SO}_3^{2-}$  determination. Sulfite oxidation is initially inhibited by  $\text{SO}_3^{2-}/\text{S}_2\text{O}_3^{2-}$  of 37% formalin. The rearrangement of  $\text{SO}_3^{2-}/\text{S}_2\text{O}_3^{2-}$  mixtures by nucleophilic displacement ( $\text{S}_x^{2-}$ ) reactions is also retarded.

shows that analytical quality assurance is best served by analysis as soon as possible after sample collection. The methods reported here have been applied to field and lab studies of sulfide mineral oxidation and acid mine drainage, as well as to field studies of thermal waters.

126 EFFECT OF AMMONIA CONCENTRATION ON PPB CHLORIDE MEASUREMENT. ~~Steven H. Peterson~~, D. F. Pensensstadler, and S. L. Anderson. estinghouse Research & Development Center, 1310 Beulah Road, Pittsburgh, Pennsylvania 15235.

Ion chromatography with the use of concentrator columns has made possible the analysis of chloride ion at the part Per billion concentration range in high purity water samples. Such analyses are particularly important in the power generation industry, since low levels of chloride in power plant steam have been implicated in the formation of corrosive deposits on turbine blades. However, in some power plants ammonia is added to feedwater for pH control, and the high ammonia concentration (part per million) has appeared to cause low analytical values for chloride. Results will be presented to illustrate the mechanism by which ammonia interferes with chloride determination and possible corrective procedures will be discussed.

127 NEW ANGLES IN SOLID STATE NMR. A. Pines. Department of Chemistry, University of California, Berkeley, CA 94720.

I shall discuss some recent developments in solid state NMR, both from my own group and from related work of other groups. These include spin diffusion, magic angle spinning, multiple quantum spectroscopy, decoupling and correlated motions.

128 CARBON-13 NMR IN SOLIDS AT HIGHER MAGNETIC FIELDS, W. T. Dixon and J. Schaefer, Washington University Chemistry Department, St. Louis, Missouri 63130 and Monsanto Company, Physical Science Center, St. Louis, Missouri 63166

The sensitivity of C-13 spectra can be increased by cross polarization from protons. Magic-angle spinning and high power proton decoupling greatly improve resolution and therefore increase sensitivity as well. For years the best solid C-13 spectra have been obtained by combining these three techniques. To improve results further we are now using the high field of a superconducting magnet. Higher fields have been very effective for liquids but cause new problems in solids not seen in the liquids; spinning sidebands are the best known but not the only example. Solutions to these new problems will be discussed.

- 129 SELECTIVE CARBON EXCITATION AND DETECTION OF SPATIAL HETEROGENEITY IN SOLID-STATE NMR. N. Zumbulyadis. Research Laboratories, Eastman Kodak Company, Rochester, New York 14650.

A new class of cross-polarization experiments will be described that can be used to selectively excite carbons in different domains of an inhomogeneous solid, provided the domains differ in their proton relaxation properties. The techniques rely on bringing the rare spins into thermal contact with a nonequilibrium proton magnetization. Examples of applications include selective observation of spectra from crystalline and amorphous domains of poly(ethylene terephthalate) and the suppression of the spinner signals.

- 130 A Triple - Resonance, 200 MHz Solids Spectrometer: Robert A. McKay, Monsanto Co., 800 N. Lindbergh Blvd., St. Louis, MO

A 200 MHz, triple-resonance H,  $^{13}\text{C}$ ,  $^{15}\text{N}$ ), high resolution solids spectrometer will be described. Some of the features required to do triple-resonance will be outlined. High rf power is required to generate adequate H levels in a 12 mm diameter (700 l) sample coil and a typical kilowatt level amplifier will be described. Some of the newer solids experiments require rf pulses synchronized with rotor period and the design of a control unit to regulate rotor speed will be given.

- 131 OPTICAL NUCLEAR POLARIZATION ENHANCED HETERONUCLEAR CROSS POLARIZATION. C. M. Oshiro and M. P. Klein. Laboratory of Chemical Biodynamics, Lawrence Berkeley Laboratory, University of California, Berkeley, CA 94720.

Optical Nuclear Polarization (ONP) of protons has been combined successfully with the cross-polarization double resonance experiment to produce large Carbon-13 signals at natural abundance in acridine-doped fluorene single crystals. The C-13 signals were enhanced by a factor of approximately 200 over that expected for a Boltzman population distribution at room temperature in a 14 KGauss Zeeman field. The seven incongruent C-13 chemical shielding tensors of fluorene have been determined.

Supported by the U. S. Department of Energy under Contract DE-AC03-76SF00098.

- 132 MAGIC ANGLE OF SPINNING OF QUADRUPOLEAR NUCLEI, Jerome L. Ackerman, Department of Chemistry, #172, University of Cincinnati, Cincinnati, OH 45221

The possibility of obtaining isotropic chemical shifts from solid phase quadrupolar nuclei with magic angle spinning (MAS) was recognized long ago by Andrew. Much more recently, Maricq and Waugh proposed the application of synchronous sampling of rotational echoes for quadrupolar nuclei such as deuterium.

Deuterium MAS has been explored in detail by Pines, et. al., who have demonstrated the practicality of obtaining useful information from such experiments. Finally, within the last year or so, Oldfield, et. al., and other groups have extended the domain of nuclei susceptible to the magic bullet of MAS to include the half-integral spin quadrupolar nuclei.

The talk will contain a synopsis of instrumental requirements and our recent results on deuterium labeled hydrocarbons, as well as a brief review of half-integral spin work conducted while the author was a guest of the University of Illinois NMR group.

133 SIGNAL ENHANCEMENT OF  $^{14}\text{N}$  SINGLE QUANTUM TRANSITIONS IN SOLIDS. T. K. PRATUM and M. P. Klein. Laboratory of Chemical Biodynamics, Lawrence Berkeley Laboratory, University of California, Berkeley, CA 94720

Nitrogen-14 is a rather unfavorable nucleus with respect to its' observation due to a large quadrupole moment and a low gyromagnetic ratio.  $^{14}\text{N}$  double quantum transitions have been enhanced and indirectly detected by Ernst et al. using spin lock (J. Chem. Phys. 73,3,1086) and ADRF (J. Chem. Phys. 74,1,184) techniques, but there are many instances where one would not like to lose the information provided by the first order quadrupole. We have been studying nitrogen nuclei in relatively high symmetry environments via their quadrupolar powder patterns, and have found that conventional direct detection spin lock cross polarization experiments will provide signal enhancements over a large range of quadrupolar frequencies. The effective fields and mixing coefficients are easily derived using the formalism of Vega and Pines (J. Chem. Phys. 66,12,5624), and agreement with experiment is observed. For large quadrupoles, it will be easier to cross polarize the double quantum coherence and transfer its' polarization to single quantum coherence using known techniques. Additionally, conventional nuclear overhauser enhancement experiments have been attempted; and they can, in some cases, provide a degree of signal enhancement which is independent of quadrupolar frequency.

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134 NMR STUDIES AT SURFACES. Gary E. Maciel, Dean W. Sindorf, Mark R. Seger, I.-S. Chuang and Michael P. Shatlock, Department of Chemistry, Colorado State University, Fort Collins, Colorado 80523

Magic-angle spinning (MAS) NMR studies have been carried out on the surface structures and reactivities of various oxides. The nuclides involved include  $^{29}\text{Si}$ ,  $^{27}\text{Al}$ ,  $^{13}\text{C}$ ,  $^{15}\text{N}$ ,  $^{113}\text{Cd}$  and  $^{119}\text{Sn}$ . Magnetic fields of 1.4 T, 3.5 T, and 4.7 T and 8.5 T and MAS speeds ranging from 2 to 7 KHz have been employed. Detailed studies on silica systems include the examination of dehydration/rehydration processes and reactivity with silylation agents.  $^{27}\text{Al}$  studies of alumina are complemented by  $^{15}\text{N}$  and  $^{13}\text{C}$  studies of pyridine adsorption.  $^{113}\text{Cd}$  and  $^{119}\text{Sn}$  studies of the surfaces of  $\text{CdO}$  and  $\text{SnO}_2$  show considerable promise. Prospects for NMR studies of surface phenomena are discussed.

135 THE CHARACTERIZATION OF SILICON-ALUMINUM ORDERING IN SYNTHETIC ZEOLITES BY SILICON-29 NMR. M. T. Melchior. Exxon Research and Engineering Co., Linden, NJ 07036.

This paper describes the application of solid state high-resolution  $^{29}\text{Si}$  NMR to the study of framework metals distribution in synthetic zeolites. Within a given crystal framework the  $^{29}\text{Si}$  chemical shifts for tetracoordinate silicon can be correlated with the number of nearest neighbor Al atoms, an observation first noted by Lippmaa, et al. (1). To the extent that a given  $^{29}\text{Si}$  NMR absorption can be identified with a particular Si environment  $[\text{Si}(n\text{Al})]$ ,  $n \approx 0, 1, 2, 3, 4$  the NMR data provide a direct measurement of the average distribution of Al nearest neighbors. It will be shown that these distributions are consistent with strict adherence to Loewenstein's rule (2) which excludes Al-O-Al linkages. The NMR data provide evidence of a high degree of local ordering of Si and Al, beyond the constraint of Loewenstein's rule. For a given Si/Al ratio the distribution  $[\text{Si}(n\text{Al})]$ ,  $n = 0, 1, 2, 3, 4$  can be calculated by considering a narrow distribution of secondary building units which minimize Al-O-Si-O-Al linkages. It will be shown that the details of the calculated Al neighbor distribution depend on the choice of secondary building unit. Thus  $^{29}\text{Si}$  NMR not only provides previously unavailable information concerning framework metals ordering in solid zeolites but may provide important information on the mechanism of formation.

(1) E. Lippmaa, M. Mazi, A. Samason, G. Engelhardt, and A. R. Grimmer, 3. Am. Chem. Soc. 102, 4889 (1980).  
(2) W. Loewenstein, Am. Mineral 39, 92 (1954).

- 136 A <sup>13</sup>C-NMR AND THERMAL ANALYSIS INVESTIGATION OF THE STATE OF TETRAALKYL-AMMONIUM AND -PHOSPHONIUM CATIONS WITHIN THE ZSM-5 AND ZSM-11 FRAMEWORK. Z. Gabelica, J. B. Nagy and E. G. Derouane, Facultes Universitaires de Namur, Departement de Chimie, Laboratoire de Catalyse, 61, rue de Bruxelles, B-5000 - Namur (Belgium).

Thermogravimetry (TG) and high resolution NMR spectroscopy (HRNMR), using cross-polarization (CP) and magic angle spinning (MAS), enable the characterization of the configuration (conformation ?) of tetrapropylammonium (TPA) and tetrabutylammonium (TBA) or tetrabutylphosphonium (TBP) cations within ZSM-5 and ZSM-11 frameworks respectively.

It is observed by thermal analysis that 3.6 to 3.9 TPA cations are present per unit cell of the ZSM-5 precursor while for ZSM-11 the corresponding values are 2.6-2.9 for TBA and 2.5-2.6 for TBP.

HRNMR shows for all species two types of terminal methyl groups. Differences in chemical shift values can be interpreted by a consideration of their environment, locating these cations at the channel intersections can be evidenced : they account for the variations which occur in the NMR parameters (shifts, linewidths and relative intensities).

While each channel intersection in zeolite ZSM-5 tends to be occupied by a TPA cation at the synthesis stage, the largest intersections (that is two per unit cell) are preferentially occupied by the bigger TBA and TBP cations in the ZSM-11 framework.

- 137 NMR IN SOLID POLYMERS - AN OVERVIEW, David L. VanderHart, Polymers Division, National Bureau of Standards, Washington, D.C. 20234

In the early days of solid-state NMR experiments usually had to be performed on sensitive and abundant nuclei in systems i.e. H or F. The many-body nature of the dipolar interaction gave rise to broad, often featureless resonances in polymers. Analysis of these resonance lines was often limited to moment methods. Molecular motion evidenced itself by a change in the linewidth and second moment, indicating correlation times for molecular motion in the range of 10<sup>-8</sup> - 10<sup>-6</sup>s. The past 10-15 years has been a time when a large range of new NMR techniques has been applied to polymer systems. Some of these techniques have been based on new ideas and others on combinations of previously established principles. Also the introduction of mini-computers and the rapid expansion of their capabilities contributed heavily to the growth and implementation of NMR techniques during this period. Among the techniques to be discussed are cross-polarization, magic angle sample spinning, multiple pulse methods (including techniques for suppressing spin diffusion), and 2-Dimensional NMR. The range of nuclei that can now be observed is also greatly expanded. As a result one typically can use NMR to study structure (internuclear distances up to 0.4nm), domain structure (1.0 to 30 nm) in polymers with heterogeneous morphologies, molecular motion at different sites in a monomeric unit, and orientation of polymer chains. Techniques and applications to polymers will be discussed as time permits.

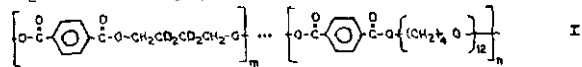
- 138 THE APPLICATION OF THE CORRELATED STATES MODEL TO THE ANALYSIS OF NMR RELAXATION DATA IN POLYMERS. P. T. Inglefield and J. S. Fragala, Chemistry Department, College of the Holy Cross, Worcester, MA 01610; A. A. Jones, Chemistry Department, Clark University, Main Street, Worcester, MA 01610; and K. L. Ngai, Naval Research Laboratory, Washington, D. C. 20375.

The quantitative treatment of NMR relaxation data using a correlation function-spectral density approach is considered. In particular, correlation functions having fractional exponential form are used:  $\phi(t) \propto \exp[-(t/\tau)^n]$ , 0 < n < 1. This correlation function has been developed on the basis of correlated state excitations in condensed matter (K. L. Ngai, Comments Solid State Phys. 9 127 (1979)) and has been proposed previously on empirical grounds. n determines the shape of the frequency dispersion of the spectral density and  $\tau$ , the position of the dispersion on the time axis. The model predicts an asymmetric dependence of T<sub>1</sub> on temperature on either side of the T minimum. The details of the analysis of experimental relaxation data over a wide range of frequency and temperature for solid bisphenol polymer systems illustrates that the model successfully characterizes the molecular dynamics in terms of a thermal activation for  $\tau$ . Both the derived activation parameters and n for a given polymer are shown to characterize the microscopic details of the motion.

139 SOLID STATE <sup>1</sup>H NMR STUDIES OF MOLECULAR MOTION IN SEGMENTED COPOLYMERS.

Lynn W. Jelinski, J. J. Dumais, and A. Engel,\* Bell Laboratories, Murray Hill, NJ 07974 \*duPont company, Wilmington, DE 19898.

We report here solid state <sup>1</sup>H NMR experiments on the specifically deuterated copolymer, I. These studies are designed 1) to assess the heterogeneity or homogeneity of the polybutylene terephthalate hard segment environments and 2) to deduce models for the motions of the CD<sub>2</sub> carbons in copolymer I.



At 20°C, copolymer I exhibits a nearly  $\eta \approx 1$  quadrupolar pattern with a 120 kHz width, upon which is superimposed a small but nearly isotropic signal. As the temperature is raised to 40°C the isotropic signal sharpens, but the  $\eta \approx 1$  pattern remains intact. At low temperatures (-70°) a classical quadrupolar pattern is observed with  $\Delta\nu \approx 120$  kHz. The T<sub>1</sub> values for these deuterons at 20°C are very short (<1s) and thus do not allow discrimination of the two types of signals based on T<sub>1</sub> differences. The inhomogeneous T<sub>2</sub> is also very short at 20°C and much signal intensity is lost from the spectrum at long (>50 ps) quadrupolar echo delay times. These data suggest 1) that a small fraction (<5%) of the hard segments reside in nonlamellar regions, in which nearly isotropic reorientation may occur, and 2) that the motions of the rest of the deuterons must involve conformational transitions which are in the fast exchange limit at 20°C.

140 NMR STUDIES OF ION-CONTAINING POLYMERS: SOLUTIONS

A. C. Watterson and W. B. Moniz, Code 6120, Naval Research Laboratory, Washington, D.C. 20375, and T. Stone, I. Nagabhushanam and J. C. Salamone, Polymer Science Program, Department of Chemistry, University of Lowell, Lowell, MA 01854

Recently, terpolymers have been prepared containing small, variable amounts of cationic and anionic sites incorporated into the polymer chain. These ionomers exhibit interesting solution properties in comparison with the uncharged and fully charged materials. Solution carbon-13 T<sub>1</sub> studies over a wide range of concentrations were possible utilizing synthetic techniques to enrich the ionic site with carbon-13. Terpolymers of polyacrylamide and poly(3-methacrylamidopropyltrimethyl-ammonium-2-methylpropanesulfonate) containing 2-15% of the ionic groups were used in these studies. The relaxation studies in dilute solution as well as in the presence of added salts,

complemented by a temperature dependent 14N-13C coupling indicated a greater degree of motional freedom for the ionic sites of the terpolymers.

141 CONFORMATIONAL STUDIES OF DIPEPTIDES FROM NUCLEAR-NUCLEAR AND ELECTRON-NUCLEAR SPIN RELAXATION.

C. CHACHATY, B. PEPLY, Département de Physico-Chimie, CEN de SACLAY, 91191 Gif-sur-Yvette Cedex, France.

The conformations and dynamical behavior of alanyl-tryptophan (AW) and glycyl-histidine (GH) in aqueous solutions have been investigated by 1H and <sup>13</sup>C NMR and relaxation, some experiments being performed in the presence of Gd<sup>3+</sup> ions. The <sup>13</sup>C relaxation in diamagnetic solutions shows that the rates of internal motions are slow compared to the overall motion of these molecules. The main conformers of these dipeptides have been determined by means of the <sup>13</sup>C and <sup>1</sup>H longitudinal relaxations enhanced by Gd<sup>3+</sup> selectively bound to the carboxylate residue. It is shown that the G' rotamer about the tryptophane or histidine C<sub>α</sub> - C<sub>β</sub> bond (X<sub>1</sub> = 80°) is the most populated with P<sub>G'</sub> ≈ 0.7 and that the orientations of the indole or imidazole residues about C<sub>β</sub> - C<sub>γ</sub> are independent of X<sub>1</sub>. <sup>13</sup>C and proton-proton relaxation measurements on free AW and GH molecule indicate that the binding of Gd<sup>3+</sup> does not change appreciably the conformations of dipeptides and allows an unambiguous determination of the torsional angles X<sub>2</sub> and φ, the latter defining the relative orientations of the two amino acid residues.

142 STRUCTURE, DYNAMICS AND INTERACTION OF  $^{13}\text{C}$ -LABELED INDIVIDUAL E. COLI TRANSFER RNAS  
J.I. Olsen, M.P. Schweizer, I.J. Walkiw, W.D. Hamill, Jr., W.J. Horton and D.M. Grant  
Departments of Medicinal Chemistry and Chemistry, University of Utah, Salt Lake City, Utah 84112

In this paper we report 67.8 MHz carbon-13 spin-lattice relaxation studies on [4- $^{13}\text{C}$ -uracil] labeled transfer RNAs purified from E. coli 50-187. We have monitored  $^{13}\text{C}$ -enriched  $\text{C}_4$  carbonyl resonances from modified and unsubstituted uridines scattered throughout the polymer backbone which enables us to determine dynamical features in both loop and helical stem regions. The experimental results have been analyzed in terms of a model of isotropic overall molecular reorientation. In the case of  $\text{tRNA}^{\text{Val}}$ , we have estimated contributions to the measured T1 values from chemical shift anisotropy (CSA; 60-75%); proton dipolar (20-30%) and nitrogen dipolar (6-8%) relaxation mechanisms. There are "anomalous" residues for which the experimental data cannot be accounted for in terms of the model; they provide an assessment of local and regional properties. Thus, "native"  $\text{tRNA}^{\text{Val}}$  under physiological conditions of magnesium (10 mM) and temperature (20°-40°C), exhibits the following characteristics: 1) uridines held rigidly in helical stems and tertiary interactions display correlation times for rotational reorientation of 15-20 nsecs, typical for overall tRNA motion; 2) uridines in loops such as the wobble residue uridine-5-oxyacetic acid ( $\text{U}_{54}$ ) are quite accessible to solvent; moreover  $\text{U}_{54}$  and another loop residue,  $\text{U}_{17}$ , exhibit local mobility; 3) the tertiary interactions involving 4-thio uridine ( $\text{S}^4\text{U}_8$ ) and A and ribothymidine ( $\text{rT}_{54}$ ) and  $\text{A}_5$  are weakened as temperature increases. We are studying other tRNAs and their complexes. This work is supported by USPHS grants GM-25512 (MPS) and GM-08521 (DMG).

143  $^{13}\text{C}$  NMR STUDY OF BOVINE GALACTOSYLTRANSFERASE SPECIFICITY. E. Berman and T.L. James,  
Department of Pharmaceutical Chemistry, School of Pharmacy, University of California, San Francisco, California 94143.

Galactose, uniformly enriched in  $^{13}\text{C}$ , was attached to terminal N-acetylglucosamines (GlcNAc) of the carbohydrate side chain of hen ovalbumin using bovine galactosyltransferase. Previous reports indicate that there are 9 different carbohydrate side chains in ovalbumin which satisfy the initial requirement of having at least one nonreducing GlcNAc residue. However, it was also established that there are three different types of glycosidic linkages of those GlcNAc residues to the contiguous mannose residues, i.e.  $\beta 1,4$ ,  $\beta 1,2$  and a small amount of  $\beta 1,6$  linkages. Thus, it is possible that the enzymatic attachment of a galactose residue to a carbohydrate side chain may be influenced by the enzymatic specificity toward the various types of GlcNAc linkages present in the structure. In order to investigate this point, we have isolated the corresponding crude glycopeptide fractions of galactose-labeled ovalbumin and studied their  $^{13}\text{C}$  NMR spectra. In the  $^{13}\text{C}$  NMR spectra, we observed two types of galactose residues corresponding to attachment to GlcNAc residues linked via  $\beta 1,4$  and via  $\beta 1,2$  to mannose residues. Quantitative analysis showed that the enzyme-catalyzed reaction is not specific for the type of anomeric linkages of GlcNAc to mannose residues. This has implications for the use of the enzyme in labeling cell surface glycoproteins with isotopically enriched galactose. We have also compared the motions of galactose residues in the glycopeptides (M.W. ~1500) with that found in the intact glycoprotein (M.W. ~45000).

144 MULTINUCLEIDE NMR METHODS TO MONITOR SODIUM TRANSPORT AND OTHER RELATED TRANSPORTS ACROSS THE RENAL BRUSH BORDER MEMBRANE. Ada Elgavish,\* and Gabriel A. Elgavish,†  
\*Department of Pharmacology, †Department of Biochemistry and the Comprehensive Cancer Center, University of Alabama in Birmingham, Birmingham, AL 35294.

The transporting properties of the brush border membrane are crucial for the proper functioning of the kidney. It has been widely accepted that the transport of most solutes across this membrane is sodium dependent. Sodium transport at low concentrations has been followed by radioactive techniques.  $^{23}\text{Na}$  NMR can monitor sodium transport at the higher, physiological concentrations of this cation. Concurrently, NMR of other nuclides can be used to follow the transport of other species. To achieve these the magnetic degeneracy of the intravesicular and extravesicular space in the sample has to be lifted. Methods to do this, especially for cationic species, using aqueous lanthanide relaxation and shift reagents will be demonstrated along with results relevant to the brush border membrane system.

- 145 APPLICATIONS OF CARBON-13 LABELING/NMR DETECTION FOR IN VIVO METABOLIC STUDIES. Robert E. London, Thomas E. Walker, Clifford J. Unkefer, and N.A. Matwiyoff. Los Alamos National Laboratory, P.O. Box 1663, Los Alamos, NM 87545.

Since the initial application of isotopic labeling in combination with NMR detection to study glucose metabolism by yeast cells Eakin, et al., FEBS Lett. 28, 259 (1973)], applications of magnetic resonance for in vivo metabolic studies have been extended to a wide variety of *microorganisms* and cells, perfused organs, and intact animals. We have recently used this approach in studies of *microorganisms* which excrete large quantities of amino acids into the medium and, therefore, provide a basis for the bio-synthetic production of selectively enriched amino acids. Studies on the production of carbon-13 labeled glutamate and proline from carbon-13 labeled glucose and acetate precursors by *M. ammoniaphilum* and *B. flavum* will be described. In these systems, blockage of the Krebs cycle at ketoglutarate dehydrogenase provides the basis for the accumulation of glutamate or proline, which is derived directly from the glutamate. The labeling patterns and multiplet intensities in the products can be used to interpret the flux through several competing pathways, and this data can, in turn, be used to develop more optimal labeling strategies. We have recently developed a second strategy for studying metabolic regulation involving enrichment of the pyridine nucleotide pool by the addition of carbon-13 labeled nicotinic acid. The approach allows simultaneous monitoring of both the metabolic flux and the pyridine nucleotide reduction charge, which is involved in metabolic regulation. Studies using a nicotinic acid requiring mutant of *E. coli* will be discussed.

\* This work performed under the auspices of the U.S. Dept. of Energy.

- 146 PROTON MAGNETIC RESONANCE STUDIES ON THE CATALYTIC CENTER OF SUBTILISINS AND THIOL-SUBTILISINS. F. Jordan, Department of Chemistry, Rutgers, the State University of New Jersey, Newark, N.J. 07102.

The imidazole of His at the catalytic center of the serine protease, subtilisin has been examined by two proton approaches. In aqueous solutions of serine proteases and their zymogens at ca. 17-1 ppm downfield from DSS there is found a resonance pertaining to the AspCOO<sup>-</sup>...H-N<sup>δ</sup>His hydrogen bonded proton of the catalytic Asp...His...Ser triad (Robillard and Shulman (1912) J. Biol. Chem. 71, 507-511). While this resonance was absent from the spectra of native subtilisins at pH 6.0, -2°C, it was present in thiolsubtilisins and in the phenylboronic acid derivatives of the serine enzymes (Jordan and Polgar 1981) Biochemistry, 20, 6366-6370) as well as in the presence of saturating concentration of -acetyl-L-tryptophan (but absent in the presence of -acetyl-D-tryptophan or L-tryptophanamide). The resonance was also visible in carboxymethylthiolsubtilisin but not in carboxamidothiolsubtilisin. Therefore, the hydrogen bond between Asp and His is particularly stable if a - + - charge distribution is present at the catalytic center, as for example in the tetrahedral transition state. Resolution and assignment of the His C2-H resonances in D<sub>2</sub>O for two sources of the native enzyme allowed us to conclude that the tertiary structures of the enzymes from Carlsberg and 3PN strains are remarkably conserved, notwithstanding differences in their primary sequences.

- 147 <sup>15</sup>N NMR OF A LIVER ALCOHOL DEHYDROGENASE-INHIBITOR COMPLEX  
Nancy N. Becker and John D. Roberts, Department of Chemistry, California Institute of Technology, Pasadena, CA 91125

Alcohol dehydrogenase from horse liver is a dimeric, zinc-containing enzyme of MW 80,000 which forms a tight ternary complex with NAD<sup>+</sup> and pyrazole. The results of a <sup>15</sup>N NMR investigation of the structure of the ternary complex containing <sup>15</sup>N-labeled inhibitor and coenzyme will be presented. The role of the metal ion in inhibitor binding will be discussed.

148 <sup>15</sup>N NMR STUDIES OF AMINO ACIDS IN NEUROSPORA CRASSA AS PROBES OF INTRACELLULAR ENVIRONMENT. K. Kanamori\*, T. L. Legerton†, R. L. Weiss† and J. D. Roberts\*. \*California Institute of Technology, Pasadena, CA 91125. †University of California, Los Angeles, CA 90024.

<sup>15</sup>N NMR spectra of suspensions of intact *N. crassa* mycelia showed well-resolved resonances for intracellular glutamine, arginine, alanine and histidine. The <sup>15</sup>N spin-lattice relaxation time, T<sub>1</sub>, has been measured for intracellular glutamine and arginine to probe their various intracellular environments. For <sup>15</sup>N of glutamine in the cytoplasm, the intracellular T<sub>1</sub> (4.1 s) was only slightly shorter than that in the culture medium (4.9 s). By contrast, for <sup>15</sup>N of arginine, which is sequestered in vacuoles, the intracellular T<sub>1</sub> (1.1 s) was one-fourth of that in the medium (4.3 s). These results indicate either that the vacuolar viscosity is substantially higher than that in the cytoplasm or that the guanidino nitrogens of arginine are highly associated with a polyanion in the vacuole.

The intracellular pH values in the vacuole and cytoplasm of *N. crassa* were estimated from the <sup>15</sup>N chemical shift of the imidazole nitrogen of vacuolar histidine and the line shape of proton-coupled <sup>15</sup>N resonance of cytoplasmic alanine which are functions of pH. The pH in the vacuole (6.0) was found to be substantially lower than that in the cytoplasm (~7.0). The potential utility of <sup>15</sup>N NMR as in vivo probes of intracellular environments will be discussed.

149 MAGNETIC RESONANCE IN COAL RESEARCH -- HISTORY, STATUS, PITFALLS, AND NEEDS. H. L. Retcofsky. Pittsburgh Energy Technology Center, P. O. Box 10940, Pittsburgh, PA 15236.

Magnetic resonance spectrometries, both nuclear magnetic resonance (NMR) and electron spin resonance (ESR), were first applied to the study of coal structure just nine years after detection of the respective resonances in bulk matter. Since that time, these techniques have proven to be among the most powerful means for elucidating the chemical structure of coal and for following the changes that occur in chemical structure during coal conversion processes. The history of NMR in coal research will be traced from early applications of broadband proton NMR to applications of the much more sophisticated techniques that are currently available. Of particular interest are those techniques that allow high resolution spectra of solid coals, a feat thought impossible only a few years ago. Applications of ESR spectrometry in coal research have advanced from the early work of the 1960's in which resonances were often detected under non-quantitative conditions to more recent studies using double resonance techniques and high pressure, high temperature cavities. Examples of pitfalls that may confront the unwary magnetic resonance investigator and methods for avoiding them will be discussed. The current status of magnetic resonance techniques in coal research as well as the need for additional research in certain areas will also be addressed.

150 APPLICATION OF DYNAMIC NUCLEAR POLARIZATION IN COAL CHARACTERIZATION BY MEANS OF MAGNETIC RESONANCE. R. A. Wind, M. J. Duijvestijn and J. Smidt. Department of Applied Physics, Delft University of Technology, P.O. Box 5046, 2600 GA Delft, the Netherlands.

Coal contains a lot of free electrons, typically of the order of 10<sup>17</sup>-5. 10<sup>18</sup> g depending on the coal rank. Irradiation near the electron frequency enhances the NMR signals of other spin species present in the coal such as protons or <sup>13</sup>C, due to the Dynamic Nuclear Polarization (DNP) effect. This facilitates the determination of various parameters that can be determined by NMR, such as the proton and <sup>13</sup>C relaxation times, the DNP enhancement factors, the aromaticity etc. All parameters depend on the coal rank, and can be used as a fast means (in the order of minutes) of coal characterization. Moreover, DNP opens the possibility of a more detailed study of the coal structure than could be performed before.

151 CHARACTERIZATION OF WHOLE COALS BY CARBON-13 CP/MASS SPECTROSCOPY AT HIGH FIELD\*  
Robert E. Botto and Randall E. Winans, Chemistry Division, Argonne National  
Laboratory, Argonne, IL 60439

A number of whole coals have been characterized by  $^{13}\text{C}$  CP/MASS spectroscopy at a high field employing pulse methods to suppress spinning sidebands. Solid-state 50-MHz  $^{13}\text{C}$  spectra essentially free of spinning sidebands can be constructed by the addition of echo spectra having phase-altered spinning sidebands (PASS). The echo spectra are produced by a modified version of the Dixon pulse sequence which shows promise for use in PASS experiments performed at higher magnetic field strengths where one is likely to be operating near maximum proton decoupling amplitudes. Quantitative analysis of the aromatic carbon content from PASS data for the coals compares favorably with results obtained by other methods. Removal of the unwanted spinning bands enables one to distinguish and assign absorptions for specific structural units present in the coals. Reasonably versatile pulse programming capabilities and very stable sample spinning ( $\pm 2\text{Hz}$ ) are necessary to perform experiments of this type.

\*Work performed under the auspices of the Office of Basic Energy Sciences, Division of Chemical Sciences, U.S. Department of Energy under contract W-31-109-ENG-38.

152 Elucidation of Structural Information from Solid Fossil Fuels  
by Recent NMR Techniques  
Paul D. Murphy, IBM Instruments, Inc., Orchard Park, Danbury, CT 06810 and  
Bernard C. Gerstein, 229 Spedding Hall, Ames Lab, Iowa State Univ., Ames,  
Iowa 50011

The recently exploited technique of  $^1\text{C}$  heteronuclear dipolar dephasing is used to simplify the complicated carbon NMR spectra of solid fuels. As a result, considerably more structural information is obtained than what would be obtained from a simple cross-polarization experiment on the same material.

When used as an analytical tool, the dephasing technique provides estimates of the relative concentrations of the various carbon types such as primary, secondary, tertiary and quaternary carbons. When the dephasing results are used to supplement those of x-ray, IR and others, estimates of structure such as polynuclear ring size, degree of ring substitution and degree of side-chain branching are possible. The present results will deal with the recent applications of the dephasing technique to estimation of: 1) the average polynuclear ring size in an anthracite coal and, 2) the average molecular structure in two asphaltene.

153  $^1\text{H}$  AND  $^{13}\text{C}$  RELAXATION IN COALS: THE EFFECTS OF PARAMAGNETIC IMPURITIES. K. VI Zilm  
\*Department of Chemistry, University of Utah, Salt Lake City, UT 84112.

Proton  $T_1$  and  $T_{1\rho}$  along with  $^{13}\text{C}$   $T_{1\rho}$  data on a set of coals ranging in rank from lignite through anthracite will be discussed. The effects of absorbed  $\text{O}_2$  on  $\text{H}_2\text{O}$  and coal proton relaxation will be demonstrated. In coals, the protons usually exhibit a single  $T_1$  but always seem to have double or multiple exponential behavior. This can be explained by a spin-diffusion limited relaxation pathway. The theory predicts that the field dependence of  $T_{1\rho}$  is a function of the number of paramagnetic impurities and the electron  $T_1$ . This is confirmed for the entire set of coals.

\* Permanent Address: Yale University, New Haven, CT

154 Abstract not available

155 <sup>13</sup>C CPMAS STUDIES OF CANADIAN PEAT MOSS. D. Cory, and W. H. Ritchey. Dept. of Chemistry, Case Western Reserve U., Cleveland, Ohio 44106. and H. Morita. Chem. & Biol. Res. Inst., Central Experimental Farm, Ottawa, Ontario K1A0C6.

Peat Mosses offer an abundant energy and raw chemicals *source* in Canada and in the northern United States, they also demonstrate chemical features of more intractable coal samples while allowing considerably easier chemical analysis. We have investigated peat moss samples from a variety of Canadian bogs by C13 CPMAS NMR and are able to qualitatively account for differences observed by more conventional chemical analysis, particularly variation in the hydrogen content. In addition depth profiles have been studied in an attempt to relate changes in spectroscopic observations with aging of the samples. Contamination of the surface samples by iron rich ground water also enabled us to investigate the degradation of the spectra by iron impurities.

156 HETERONUCLEAR CORRELATED 2-D NMR OF SYNTHETIC FUELS. L. W. Dennis and R. E. Pabst. Exxon Research and Engineering Company, Baytown Research and Development Division, P. O. Box 4255, Baytown, Texas 77520

C-13 and H-1 NMR spectroscopy has been used extensively in the study of the complex mixtures that occur in synfuel liquids such as coal liquids or shale oils. Proton NMR has been a valuable tool for a considerable time, whereas Carbon NMR characterization of such liquids is a relatively new and ongoing development. The greatest understanding is, of course, obtainable when the two are used in conjunction. In these complex mixtures, however, the chemical shifts of various carbons or protons overlap and as a result unequivocal assignments of spectral regions and peaks are not always possible.

This problem has been partially solved by the development of Heteronuclear Correlated NMR Spectroscopy (2-D NMR). This technique yields a two dimensional plot which correlates a particular carbon chemical shift with the chemical shift of associated protons. In addition, the resultant plot often spreads a congested area in the one dimensional spectrum into the second dimension, making possible a detailed analysis of the region.

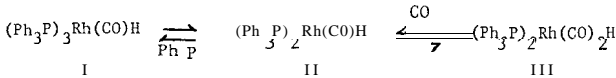
Heteronuclear Correlated 2-D NMR Spectroscopy has been applied to the analysis of several synthetic fuel liquids. Both whole liquids and fractions have been examined. The results obtained range from confirmation of previously used correlations and assignments to identification of specific compounds and compound types that had not been previously observed. This talk will present a survey of some recent results.

157 CHARACTERIZATION OF H<sub>2</sub>/D<sub>2</sub> TREATED PETROLEUM STREAMS. J.R. Mooney, D.R. Herrington, A.P. Schwerko and P.A. Budinger. The Standard Oil Company (Ohio), 4440 Warrensville Center Road, Cleveland, Ohio .

A highly aromatic decanted oil extract was hydrogenated at temperatures of 343-399°C, liquid hourly space velocities of 1.0-4.0(v/v/hr), and 500 psig over a sulfided NiO/MoO<sub>3</sub>/Al<sub>2</sub>O<sub>3</sub> catalyst. In a parallel series of experiments, deuterium was substituted for hydrogen in order to achieve a clearer understanding of the mechanisms of aromatics hydrogenation, desulfurization, and denitrogenation. Detailed spectroscopic characterization of the gaseous overheads and liquid products was accomplished using infrared, mass spectroscopy, Fourier transform infrared, and proton, <sup>13</sup>C, and deuterium NMR measurements.

158 A 31P, 13C NMR STUDY OF RHODIUM HYDROFORMYLATION MECHANISMS. R. V. Kastrup, A. A. Oswald, D. E. Hendriksen, J. S. Merola and J. C. Reisch. Exxon Research and Engineering Co., P.O. Box 121, Linden, New Jersey 07036.

Low pressure rhodium hydroformylation catalyzed by tris(triphenylphosphine) rhodium carbonyl hydride complex based catalyst [Ph<sub>3</sub>P-Rh] systems is a recently commercialized, rapidly developing area of catalytic synthesis gas chemistry. The early mechanisms of rhodium hydroformylation were developed by its discoverer, Prof. Wilkinson, and his co-workers largely on the basis of IR studies of isolated potential intermediates. To better describe the highly selective Ph<sub>3</sub>P-Rh systems recently commercialized by Union Carbide, the present work on selective hydroformylation mechanisms emphasized P and NMR studies of dissolved catalyst species under a variety of simulated reaction conditions. The NMR studies of ligand exchange and equilibria among various complexes were correlated with catalysis studies of the effect of broad ranges of Ph<sub>3</sub>P concentrations, CO and H<sub>2</sub> partial pressures and temperatures. It was concluded that rhodium hydroformylation of terminal olefins can proceed via multiple mechanisms to yield n- and/or i-aldehydes, mainly dependent on the following equilibria:



The new findings emphasize the importance of complex I as a stable, reversible reservoir for the generation of highly reactive catalytic intermediate, II, in selective hydroformylation and provide a consistent explanation of known catalysis results.

159 Title: Selective Retention Using Mixed Mechanisms in High Performance Liquid Chromatography Authors: Marianne Van Der Kaay and Ubbo R. Tjaden, State University, Leiden, Netherlands

Since the early seventies, detergent-based high performance liquid chromatography has been of great importance to the determination of ionogenic compounds in biological matrices. In principle gradient systems can be applied. However, we prefer isocratic systems for trace analysis, especially if electrochemical detection is used. In bio-medical analysis often separation problems are met concerning compounds varying strongly in polarity e.g., pharmaceuticals and their metabolites c.q. degradation products.

The investigated solutes include cations, anions, zwitterions and neutral components. Therefore we investigated the possibility to apply selective retention to the more polar e.g. ionogenic compounds.

The opinions given in literature about the postulated mechanism(s) in detergent-based high performance liquid chromatography are various. In literature many procedures are described, concerning the "loading" and "working" concentration of ionogenic detergents in the eluent, but they do not discuss the influence of added counter ions (usually sodium or chloride c.q. phosphate) in detail.

However it appeared that the sodium concentration is of great influence on the relative retention. Therefore the associating ion concentration was varied with and without keeping the sodium ion concentration constant by adding sodium chloride to a mixture of phosphatebuffer and methanol. A number of alkylsulfonates and -sulphates (sodium salts) were used as an associating ion in the eluent. Loading of the column material results in a considerable increase of the life-time of the column, especially when the support material was loaded with dodecylsulphate.

Preliminary experiments were done in order to relate the chromatographic behavior to some physico-chemical parameters of the eluent.

The selected phase systems were applied to the determination of the compounds of interest in biological matrices by means of detergent-based high performance liquid chromatography.

- 160 DETERMINATION OF TRACE LEVELS OF QUATERNARY AMMONIUM COMPOUNDS IN RIVER WATER BY HIGH PERFORMANCE LIQUID CHROMATOGRAPHY/CONDUCTIMETRIC DETECTION. V. T. Wee and J. M. Kennedy, The Procter & Gamble Company, Environmental Safety Department, Ivorydale Technical Center, Cincinnati, Ohio 45217.

An analytical method has been developed to determine trace levels of UV and non-UV absorbing long alkyl chain quaternary ammonium compounds. It consists of a simple solvent extraction scheme followed by separation and quantitation using high performance liquid chromatography coupled with a conductivity detector. The unique feature of this method is the chromatographic system. For the first time, non-UV absorbing long alkyl chain quaternaries are determined at submicrogram quantity without any form of derivatization. Furthermore, ion chromatography is performed in a non-aqueous media, without ion-pairing, and in the absence of a suppressor column.

An application of the method is demonstrated in river water samples where concentrations of four different quaternaries: ditallow dimethyl ammonium chloride, dodecyl trimethyl ammonium chloride, stearyl dimethyl benzyl ammonium chloride and 1-hexadecylpyridinium chloride were measured.

- 161 HPLC FRACTIONATED SAMPLES OF DIESEL PARTICULATE EXTRACTS FOR AMES TESTING. D. E. Seizinger and D. B. Eccleston., U.S. Dept. of Energy, Bartlesville Energy Technology Center, P.O. Box 1398, Bartlesville, OK 74005; C. R. Clark and R. O. McClellan, Lovelace Inhalation Toxicology Research Institute, P.O. Box 5890, Albuquerque, NM 85117.

Diesel vehicles in the automotive fleet are increasing annually, and the particulate emissions from these vehicles have raised some questions concerning human health based on Ames test results of the particulate extracts. Therefore, we have been involved in a characterization study of the particulate extract. Our study has involved collecting exhaust particulates on large filters which are solvent extracted. The extract is separated into three fractions using liquid-solid chromatographic (LSC) techniques. The first LSC fraction is separated into six different HPLC fractions using an automated semipreparative gradient HPLC system equipped with a silica column. The resulting chromatograms are very reproducible for a gradient silica column separation. The fractions from both LSC and HPLC separations are forwarded to Lovelace Inhalation Toxicology Research Institute for Ames testing. These Ames test results are used to limit an identification study of biologically active species to only those fractions which contain direct-acting mutagenic components. Three HPLC fractions containing nitro PAH's, dinitro PAH's, and oxygenated hydrocarbons (phenols and carboxylic acids) represent 90+ percent of the original samples mutagenicity (without S-9 activation). Routine chemical methods are being developed to measure the levels of the identified mutagenically active species such as nitropyrene in the original exhaust.

- 162 CONCENTRATION AND MEASUREMENT OF OXYGEN-CONTAINING COMPOUNDS IN THE ATMOSPHERE. E.J. Williams and R.E. Sievers, Chemistry Dept. and CIRES, University of Colorado, Campus Box 449, Boulder, CO 80309.

Oxygenated organic compounds, especially aldehydes and ketones, are important species in the photochemistry of the troposphere. Unfortunately, these species are present at low concentrations and, with respect to gas chromatographic analysis, are usually masked by the more abundant hydrocarbons. The use of a lanthanide metal-containing polymer which selectively retains oxygen-containing nucleophilic compounds is described. The polymer is employed in either of two ways. First, it can be used in a pre-column which separates samples of atmospheric organic compounds into retained or non-retained fractions followed by gas chromatographic analysis using a fused silica capillary column. Second, the polymer can be employed as a trapping medium which selectively concentrates nucleophilic species present in ambient air followed by gas chromatographic analysis. Synthetic mixtures of different classes of compounds were used to show that reproducible and nearly complete recovery of sorbed compounds is possible, which allows one to use the sorbent for quantitative analysis. The selectivity of the polymer has been shown to be temperature dependent. In addition, the polymer may be coated with liquid phases to enhance selectivity. A description of the preparation and characterization of the polymer will be presented, and the use of the polymer for ambient air analysis will be demonstrated.

- 163 DETERMINATION OF POLYOLEFIN ADDITIVES BY NORMAL-PHASE HIGH PERFORMANCE LIQUID CHROMATOGRAPHY FOLLOWING SOXHLET EXTRACTION, J. F. Schabron, Phillips Research Center, Phillips Petroleum Company, Bartlesville, Oklahoma 74004

Methods were developed for the determination of three classes of polyolefin additives. These classes are: mono and diglycerides, tertiary C<sub>12</sub>-C<sub>16</sub> alkyldiethanolamines, and alkyldithiopropionates. Soxhlet extractions were performed on 50 g ground samples with chloroform for 2 hours. The extracts were concentrated and the additives were determined by high-performance liquid chromatography on a u-Porasil stationary phase. The methods were studied with both polyethylene and polypropylene.

- 164 ANALYSIS OF TRACE LEVELS OF EXPLOSIVES BY HIGH PRESSURE LIQUID CHROMATOGRAPHY Kathy A. Carlberg and Susan M. Bretthauer, Rocky Mountain Analytical Laboratory, 5530 Marshall Street, Suite D, Arvada, Colorado 80002

The contamination of groundwater by organic chemicals has become a national concern in the last decade. Among the classes of compounds of concern are nitrogen containing explosives such as HMX, RDX and PETN.

Routine analysis of nonogram levels of these nitramines and nitrate esters has always proven difficult. Gas chromatographic techniques are impractical due to the thermal instability and nonvolatility of these compounds.

This paper describes the use of reverse-phase high pressure liquid chromatography to determine the part per billion levels of explosives in groundwater. The technique involves the use of a C<sub>18</sub> Sep-Pak™ Cartridge for extraction of the explosives from the samplematrix and concentration prior to analysis.

- 165 ANALYTICAL EVALUATION OF POLYNAPHTHALENESULFONATES AS OIL-WELL CEMENT DISPERSANTS. T. G. Miller, Dowell Inc., p. O. Box 21, Tulsa, Okla 74102.

An analytical method has been developed to evaluate the performance of polynaphthalenesulfonates as cement dispersants based upon their relative molecular weight distributions. Since the performance of the dispersants may vary widely among different sources, or even different samples from the same source, a simple, rapid analytical method to compare their performances would be of great value. A series of these dispersants was prepared and studied to follow the events occurring during their production, in order to understand in detail what chemical compositions produce a quality dispersant. The liquid chromatographic method used to produce the analytical information combines the techniques of solvent programming and ion-pairing. The liquid chromatographic method with other analytical techniques shows the "low" and "high" molecular weight components to be "linear" and "branched" molecules, respectively. Chromatograms show that the linear molecular components are formed initially. As the reaction proceeds, the higher molecular weight, branched molecules are formed. A plot of the ratio of the high-to-low molecular weight fraction against the experimental performance data of the dispersants reveals a very surprising correlation. The plot showed a linear relationship between the ratios of high-to-low molecular weight components and their performances. The liquid chromatograms can easily be used to monitor the production of this dispersant and to analytically predict the relative performances of dispersants from different sources.

- 166 AS CHROMATOGRAPHIC STUDY OF CHEMICALLY MODIFIED CARBON PARTICLES. J. A. Holcombe and Burmi Ogunkeye, University of Texas, Department of Chemistry, Austin, Texas 78712 .

Studies were directed towards the improvement of the chemical properties of carbon as an adsorbent in gas chromatography. Alterations in the chemical nature of the particle surface were used to change the adsorption characteristics of this substrate. The chemical modification involved an initial solution oxidation of the surface followed by a series of other reactions ultimately leading to chemical binding of the desired functional group on the carbon surface.

The effect of benzene pyrolysis on the heated particles prior to chemical modification will be considered. Characterization based on column efficiency, specificity, and stability of columns packed with these particles will be discussed as well as the effect of binding different functional groups on the particles. The feasibility of synthesizing such specific carbon adsorbents for specific tasks will also be presented.

- 167 MICRO-HPLC AND RELATED TECHNIQUES. M. Gvotny, Department of Chemistry, Indiana University, Bloomington, Indiana 47405.

The rationale behind developing the microcolumns for liquid chromatography includes: (a) the potential for high resolution of complex mixtures; (b) drastically decreased consumption of mobile phases; and, (c) improved detection possibilities due to extremely low flow-rates. High column efficiencies have already been demonstrated with microbore columns and packed capillaries, but the realization of HPLC in open tubular columns will first require the development of extremely small sampling and detection units (of the order of nanoliters). However, significant improvements in small-volume technology have lately been made. The detection aspects of micro-HPLC are rapidly gaining importance, as evidenced by new laser spectroscopic devices, flame-based (flame-photometric and thermionic) detectors, and the liquid chromatography/mass spectrometry coupling. Conventional spectroscopic and electrochemical detectors have also been miniaturized for micro-HPLC. Recently, capillary supercritical fluid chromatography has become another attractive method for efficient separations of non-volatile mixtures; this is primarily due to greater solute diffusivities and low viscosities in the supercritical fluids as compared to "true liquids." Finally, high-voltage capillary electrophoresis developed recently by Jorgenson and co-workers is yet another promising technique that resembles micro-HPLC in certain instrumental aspects.

- 168 APPLICATIONS OF ON-LINE DIRECT LIQUID INTRODUCTION MICRO LC/MS TO DRUG ANALYSIS. J. D. Henion, D. Skrabalak and C. Eckers.

Many liquid chromatography/mass spectrometry (LC/MS) systems utilize conventional high performance liquid chromatography (HPLC) operating at eluant flow rates of 0.5-2.0 mL per minute. Conventional mass spectrometer (MS) pumping systems require that such HPLC effluent volumes be split prior to introduction into the MS. This diverts substantial portions of the EC solute away from the MS ion source and causes reduced LC/MS sensitivity. Trace level environmental analyses and drug metabolism studies require low part per billion (ppb) detection limits which currently are difficult to achieve in many conventional LC/MS systems. It is possible to interface homemade or commercially available micro LC columns to the mass spectrometer placing little or no restriction on the type of micro column using this system. This interface serves the increasing interest in micro LC resulting from the need for increased LC/MS sensitivity. A variety of drugs and their metabolites have been examined using the system to explore the utility of the technique. Construction details will be shown as well as examples of micro LC separations and micro LC/MS analyses. The advantages and limitations of the system and earlier DLI LC/MS probe designs.

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ON THE LIMIT OF SEDIMENTATION FIELD FLOW FRACTIONATION FOR CHARACTERIZATION OF POLYDISPERSE COLLOIDAL SAMPLES, [Feng-Shyang Yang\\*](#) [Karin D. Caldwell](#), [Marcus N. Myers](#), and [J. Calvin Giddings](#). Department of Chemistry, University of Utah, Salt Lake City 84112. (\*now with Chemistry Division, Research and Development, China Steel Co. Kaohsiung, Taiwan, R.O.C.)

The particle size distribution is an important characteristic of colloidal samples, as such information is often used to follow the stability of a given product as well as to explain its physicochemical behavior. Sedimentation Field-Flow Fractionation (Sed FFF) is a high resolution technique for yielding size spectra for colloidal samples in the 0.1 to 1.0  $\mu$ m range. Its performance will be illustrated by characterizations of intravenous fat emulsions, homogenized milk and blood substitutes. However, the steric effect which will influence both the retention and resolution appears as a limiting factor to the separation of highly polydisperse sample by Sed FFF. A thorough study of the magnitude of the steric effects under various conditions has been carried out. These include a retention change by varying the centrifugal field, flow rate and carrier fluid in the transition region between Sed FFF and Steric FFF. The understanding of steric effects will help us to choose proper experimental conditions in the sizing of polydisperse sample by Sed FFF.

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MOBILE PHASE AND MOLECULAR STRUCTURE EFFECTS IN NORMAL PHASE HIGH PERFORMANCE LIQUID CHROMATOGRAPHY INVOLVING AN AMINOSILANE BONDED PHASE COLUMN. [W. Palaitis](#), Merck & Co., Inc., Rahway, New Jersey, 07065.

A Waters  $\mu$ -Bondapak-NH<sub>2</sub> HPLC column proved to be highly effective in separating the antihypertensive, Methyldopa (L-2-amino-2-methyl-3-(3,4-dihydroxyphenyl) propionic acid), from a variety of analogous compounds. The mobile phase used was 80/20:CH<sub>3</sub>CN/H<sub>2</sub>O(buffered with triethylammonium phosphate or diethylammonium phosphate). Related experiments showed a normal phase dependence of capacity factors on the concentration of water in the mobile phase. The pH dependence of these factors over the range 2.5 to 7.0 (for buffer, prior to mixing with CH<sub>3</sub>CN), however, indicated at least two kinds of interactions of the compounds with the column. One of these, observed only for Methyldopa, resulted in increased retention with increasing pH. This interaction undoubtedly has an ionic component, as severe tailing was observed at the higher, but not at the lower, pH levels. The other, observed for 3-O-methylmethyldopa (L-2-amino-2-methyl-3-(3-methoxy-4-hydroxyphenyl) propionic acid) and some of the other compounds, resulted in complete preservation of peak symmetry, over the pH range studied, but decreased retention with increasing pH. A mechanistic model that covers both of these interactions will be presented, as will details of an assay procedure for Methyldopa.

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A MICROPROCESSOR CONTROLLED VALVE SWITCHING UNIT FOR MULTI-DIMENSIONAL LIQUID CHROMATOGRAPHY AND COMPLEX HPLC METHODS. [J. K. Ung](#), Kontron Analytical, 630 Price Avenue, Redwood City, California 94063, and [C. J. Little](#), Kontron Electrolab Ltd., Ashford, Middlesex, United Kingdom.

Chromatographic techniques such as automatic sample clean-up, automatic trace enrichment, and automatic method development would be more attractive if the procedure could be accurately controlled and automated. In this paper, we utilized the combined technology of a microprocessor controlled valve switching unit and an automatic sampler to achieve all the methods described. The most useful of these methods is automatic sample clean-up, which includes a wide range of multi-dimensional chromatographic techniques such as front, heart and end cutting. Typically, a preliminary separation is made on a pre-column or a suitable analytical column. Part of that solution is then transferred to another column where the analytical separation takes place. The method is particularly useful for cleaning up samples of biological origin, foodstuffs, drinks, etc. Automatic solvent selection is achieved by sequential switching of two 6-port valves. These are particularly useful for automating trace enrichment methods where large volumes of sample are pumped through a pre-column in order to concentrate the solutes. Subsequently, these solutes are eluted from the pre-column onto an analytical column for separation or even through a further sample clean-up sequence. An alternative use for these selector valves allows the generation of step gradients, formation of ternary and multi-solvent systems and automating pH changes in ion-pair and ion-exchange chromatography. Automatic method development enables us to carry out a series of separations on one column, then switch to a different column, and carry out the same separations. The unit allows for the switching of up to four different columns.

- 172 HPLC TASKS USING CRT GRAPHICS ON A LABORATORY MICROCOMPUTER. R. L. Miller and D. E. Odwell. Chromatography Division, The Perkin-Elmer Corporation, Main Avenue, Norwalk, CT 06856.

The small computer is becoming increasingly popular in the analytical laboratory. This popularity has been enhanced by the availability of turnkey software packages to perform specific tasks. The presence of a **microcomputer** in the laboratory also allows the more sophisticated **chemist** to develop special purpose programs to perform tasks specific to his or her needs. This paper describes three tasks which utilize the CRT graphics capability of a laboratory microcomputer to enhance and assist calculations in three areas of liquid **chromatography**. One such application is in gel permeation chromatography. The **microcomputer** is used to display calibration curves and normalized molecular weight distributions calculated by the software. **Chromatograms** and molecular weight distributions may be **replotted**, overlaid, and even subtracted to facilitate comparison of similar materials. A graphic display is used to define baseline and the summation limits to be used in the **calculations**. A second application deals with the ability to reconstruct baseline and reintegrate after a chromatographic run. This capability is **present** ed in the context of the hydrocarbon group-type separation by **LC**. The third application is the analysis of chromatographic data for systematic trends. In this case, data from repetitive measurements is plotted on the microcomputer CRT against time, and regression curves and prediction intervals plotted to visualize the statistical calculations.

- 173 SUPERCRITICAL CHROMATOGRAPHY ON PACKED COLUMNS USING CO<sub>2</sub> AND POLAR MODIFIERS. R. Board D. Gere, D. McManigill, H. Weaver. Hewlett-Packard Company, Applied Physics Laboratory, 165] Page Mill Road, 28C, Palo Alto, California 94304.

A liquid **chromatograph** has been modified to enable operation as a supercritical **fluid chromatograph** using CO<sub>2</sub> as the mobile phase. The system has been used to study the chromatographic characteristics of 10, 5 and 3 μ particle diameter reversed phase packed **columns**. Reduced plate heights between 2.0 and 3.0 are achieved in the region of the van Deemter minimum. Provision is made for the addition of polar **modifiers** to the mobile phase. The theoretical and practical chromatographic implications of modifiers **will** be reported.

- 174 CHEMICAL CONCENTRATION MODULATORS FOR MULTIPLEX CHROMATOGRAPHY. John B. Phillips, Department of Chemistry & Biochemistry, Southern Illinois University, Carbondale, IL 62901

Multiplex chromatographic methods require that the sample stream be modulated in concentration at the head of the column. Each modulated substance travels through the column at its own migration rate carrying the modulation signal with it. The **chromatogram** of the sample stream mixture may be recovered by cross correlating the detector output signal with the modulation signal. For good results the modulation must be linear, reproducible, of sufficient amplitude to be measured by the detector, and of small enough amplitude to avoid driving the column into non-linear behavior. Various mechanical stream switching valves have not been very successful in either multiplex GC or HPLC. Fluidic, or Coanda effect, valves may be useful in GC, but they still require a reference gas stream and dilute the sample stream. Concentration modulators based on a variety of chemical effects including thermal, photochemical, and electrochemical processes are mechanically simple and rugged devices. Their operating characteristics can usually be tailored to match the modulation requirements of a multiplex chromatographic technique. They can be chemically tailored to modulate only specific substances in the sample stream adding selectivity to the chromatographic determination. And, they do not dilute the sample stream. Several of these chemical concentration modulators and their application to multiplex chromatography will be described.

- 175 A RETROFITTABLE FAST ATOM BOMBARDMENT ION SOURCE FOR THE HEWLETT-PACKARD 5985B GC/MS SYSTEM. R.K. Latven, P.C. Goodley and C.N. Kenyon. Hewlett-Packard Company, 3003 Scott Blvd., Santa Clara, CA 95050.

Sample ionization induced by momentum transfer from a fast atom beam can provide abundant molecular ion for polar, thermally labile or involatile compounds. Since fast atom bombardment (FAB) ionization is a surface sputtering phenomenon, it is useful for many cases in which substances decompose prior to reaching the vapor state, so precluding the use of electron impact (EI) or chemical ionization (CI). The FAB source conversion assembly consists of a Fast Atom Capillaritron Source (Phasor Scientific) which is mounted on a flange external to the ion source. Only minor changes are required in the existing source, which remains unaffected for normal CI/EI operation. A conventional 1/2 inch direct insertion probe is used with a modified tip, on which is placed the sample in a nonvolatile matrix, e.g., glycerol. Ionization occurs within the ion source region from the particle beam which enters through an orifice from above. The technique is demonstrated for a variety of compounds including peptides, carbohydrates, sugars, and bile acids. The spectra obtained provide abundant molecular ion, have excellent signal to noise, and show high mass sensitivity comparable to that found on magnetic instruments.

- 176 Abstract not available

- 177 POSSIBILITIES AND LIMITATIONS OF NON-VAPORIZING, COLD, ON-COLUMN INJECTION TECHNIQUE IN HIGH RESOLUTION GAS CHROMATOGRAPHY, G. SISTI, F. MUNARI, Carlo Erba Strumentazione P.O. Box 10364, I-20100 Milan, Italy, S. TRESTIANU, Vel, Parkstraat 169, Leuven, Belgium and B. APON, Erba Instruments Inc, 12015 Slauson Ave. Ste. F, Santa Fe Springs, Ca. 90605

The non-vaporizing septumless, cold, on-column injection technique requires samples highly diluted in adequate solvents. These are generally volatile and therefore impose a relatively low oven temperature (around the b.p. of the solvent) during the injection. For many samples containing heavy components this is not convenient, since the elution of the sample components requires much higher oven temperature. The possibilities and limitations of sample injection at oven temperatures higher than the boiling point of the solvent, using the special cooling system developed by us, are discussed.

The benefits of the carrier gas supply in a constant flow mode when the non-vaporizing on-column system is used is also discussed in the paper. The column flow rate variation during the temperature programming is eliminated and the column operation better optimized. Some examples are also presented.

A limitation of the non-vaporizing, on-column injection arises from the fact that the syringe injection technique is not reliable below 0.2 - 0.3 µl. Therefore for undilutable liquid samples this technique is hardly applicable. The above mentioned limitation can be overcome if small sample amounts can be reproducibly injected into the capillary.

The decomposition of high molecular weight by-products inside the capillary during the on-column injection and their subsequent pyrolysis and decomposition during the temperature programming can also cause problems by creating adsorption sites inside the capillary column. The possibilities to avoid these undesired processes are also mentioned.

- 178 STUDIES OF COMPLEX MIXTURES OF TRIS(β-DIKETONATO)CHROMIUM(III) GEOMETRICAL ISOMERS WITH FUSED SILICA CAPILLARY COLUMNS. R.E. Sievers and K.C. Brooks, Department of Chemistry and Cooperative Institute for Research in Environmental Sciences, University of Colorado, Campus Box 449, Boulder, CO 80309.

Combined gas chromatography/mass spectrometry (GC/MS) using a fused silica capillary chromatographic column has been employed in a study of the geometrical isomers of tris(β-diketonato)Cr(III) complexes. One sample of mixed ligand chelates of Cr(III) prepared from a reaction of Cr(III) and equimolar amounts of the symmetrical bidentate ligand 1,1,1,5,5,5-hexafluoro-2,4-pentanedione, Hfa, and two unsymmetrical bidentate ligands 1,1,1-trifluoro-2,4-pentanedione, Htfa, and 6,6,7,7,8,8,8-heptafluoro-2,2-dimethyl-3,5-octanedione, Hfod, contains 25 distinct chemical species (counting geometrical isomers but excluding enantiomers). Twenty four of these species were separated and tentatively identified from analysis of GC/MS data. The electron impact mass spectra of the geometrical isomers are very similar but, with one exception, they have distinctive chromatographic retention times and the coupling of the techniques provides much more information than either technique alone. Another mixture studied included Cr(III) chelates prepared from equimolar amounts of Hfod (1,1,1,5,5,6,6,6-octafluoro-2,4-hexanedione), Htfa and Hfod (three unsymmetrical bidentate ligands). Some 28 of a possible 38 species were separated in this experiment.

- 179 CHROMATOGRAPHIC ANALYSIS OF LIMBURGER CHEESE. THOMAS H. PARLIMENT  
GENERAL FOODS TECHNICAL CENTER, WHIT PLAINS, NEW YORK

THE VOLATILE CONSTITUENTS OF LIMBURGER CHEESE WERE OBTAINED BY DISTILLATION-EXTRACTION, SEPARATED BY CAPILLARY GAS CHROMATOGRAPHY AND SUBJECTED TO MASS SPECTRAL ANALYSIS. MORE THAN TWENTY NEUTRAL AND ACIDIC COMPOUNDS WERE IDENTIFIED. THE MAJOR COMPONENT PRESENT IS PHENOL, WHICH CAN ARISE FROM THE MICROBIAL DECOMPOSITION OF TYROSINE. ALSO AT RELATIVELY HIGH LEVELS ARE THE ODOROUS COMPOUNDS DIMETHYL DISULFIDE AND INDOLE. OTHER COMPOUNDS IDENTIFIED INCLUDE A HOMOLOGOUS SERIES OF METHYL KETONES, ACETOPHENONE AND HIGHER DIMETHYL POLYSULFIDES.

IN THE ACIDIC FRACTION, BUTYRIC, ISOBUTYRIC, HEXANOIC, OCTANOIC AND DECANOIC ACIDS WERE IDENTIFIED. THESE CONTRIBUTE TO THE STRONG CHARACTERISTIC AROMA OF LIMBURGER.

- 180 A GC-AUTOMATED FILM PERMEATION SYSTEM. J. M. Hughes. The Clorox Company, Clorox Technical Center, P. O. Box 493, 7200 Johnson Drive, Pleasanton, CA 94566.

An automated system for carrying out permeation measurements on packaging materials was developed using commercially-available instrumentation and components. The system is flexible and modular, avoids tying up analysts with tedious manual sampling, and is also designed to provide for automated method development and parameter optimization.

The automated permeation system consists of a heated permeation cell (Harvey Instrument Co.) configured for both gases and liquids, interfaced through miniature solenoid valves to a Hewlett-Packard 5880A Gas Chromatograph. The chromatograph is equipped with a 10-port gas sample valve, valve driver board, and BASIC programming capability. The Harvey cell provides rapid sample changeover, above-ambient temperature control, and exposes a representative sample of the material to be tested (an 80mm circle) to the permeating medium. The microprocessor GC controls sampling of the cell using the solenoid valves to fill the gas sample loops via an inert gas purge. The GC's internal clock and BASIC programming provide for automated sampling and data handling over short or long intervals, and expedite methods development by allowing automated optimization of sampling parameters. The system has been utilized to investigate permeation of packaging films by permanent gases and organic solvents with optimal use of personnel.

- 181 EXTRACTION OF HUMIC SUBSTANCES INTO SLIGHTLY POLAR WATER-IMMISCIBLE ORGANIC SOLVENTS. Ralph S. Allen III and Patrick MacCarthy, Dept. of Chemistry and Geochemistry, Colorado School of Mines, Golden, Colorado 80401.

Many extracted humic acids, and particularly those from commercial sources, possess a high ash content. This ash content frequently complicates experimental work with these substances and interferes with the study of the organic matter per se. There are a variety of published procedures for diminishing this ash content, but these are usually rather tedious and time-consuming. The problem is compounded by the fact that the humic substances are not generally extractable into water immiscible non-aqueous solvents, which would tend to leave the mineral matter in the aqueous phase. This paper describes a simple procedure for pretreating the humic substances in a manner which renders them extractable into a variety of slightly polar water-immiscible organic solvents (either in solution or in suspension). This leads to a convenient and rapid method for significantly diminishing the ash content of humic substances, and also opens the possibility for carrying out other experiments with humic materials which require a two-phase liquid system.

182 COMPARISON OF A SEQUENTIAL EXTRACTION SCHEME TO THE EPA EXTRACTION PROCEDURE FOR TOXICANTS. Tom E. Clevenger and William Mullins, Environmental Trace Substances Research Center, University of Missouri, Route 3, Columbia, Missouri 65201.

Most leaching tests, including the Extraction Procedure for Toxicants required by EPA for determination of hazardous waste status, predict the amount of possible contamination that could occur from wastes under set conditions. No attempt is made to evaluate the forms of metals and their availability under differing conditions. The chemical form of the metals may be critical as to an acceptable disposal method. The use of sequential extractions rather than single extractants is of greater value in determining metal distribution. In this study 12 municipal wastewater treatment sludges were characterized using sequential extraction. The separation scheme selected for this study consisted of five sequential extraction steps. The fractions produced correspond to the following general species (1) Exchangeable, (2) Bound to carbonates, (3) Bound to iron and manganese oxides, (4) Bound to organic matter, and (5) Residual. The following metals were tested by ICP: Cd, Zn, B, Ni, Mn, Cu, Cr, Fe and Ca. Several different speciation patterns were noted. Variations were even noted for the same metal between samples. Comparison is made between the results of the EPA method and those of the sequential extraction. The sequential extraction scheme provides much more information as to the leachability of a waste under different conditions.

183 ON-SITE PESTICIDE DISPOSAL. T.D. Spittler, J. B. Bourke, P. B. Baker, J. E. Dewey, F. Winkler and T. K. Rue. NYS Agricultural Experiment Station, Cornell University, Geneva, NY 14456.

In cooperation with the USDA-Soil Conservation Service, Chemical Control Centers have been installed on many small fruit farms in the 20-300 acre range. These facilities, consisting of a water source, catch basin, leach lines, and pesticide storage, help minimize danger to the worker and damage to the environment in the mixing and filling stages of pesticide spraying operations. In this study a series of surface water and deep soil samples were analyzed to detect any migration or runoff of waste pesticides from typical Chemical Control Centers. Entomological evaluation of soil biota and monitoring of dermal exposure to pesticides of mixer-applicators took place throughout the 1980 season. No adverse effects as a result of the Chemical Control Centers were detected.

184 ANALYSIS OF CARBAMATE PESTICIDES BY CAPILLARY GAS CHROMATOGRAPHY. C. P. Rzeszutko and M. K. Correa. U.S. Environmental Protection Agency-National Enforcement Investigations Center, Bldg. 3 Box 25227 Denver Federal Center, Denver, CO 80225

The gas chromatographic behavior of 21 carbamate pesticides were investigated using a nitrogen-specific detector (NPD). Relative retention indices were successfully determined for 19 carbamates while achieving resolution for 16 of the carbamates using a 15 meter, thick film chemically bonded fused silica capillary column. Levels of detection obtained via the capillary-NPD gas chromatographic system will be compared with those obtained from conventional packed column gas chromatography and reverse phase high performance liquid chromatography. Analytical procedures developed for the analysis of carbamate pesticides at residue levels in water and soil using capillary column gas chromatography will also be discussed.

185 HERBICIDE RESIDUES RESULTING FROM THE EXPERIMENTAL APPLICATION OF 2,4-D TO CONTROL EURASIAN WATERMILFOIL IN BARKS LAKE, WA AND FORT COBB RESERVOIR, OR. N. E. Otto, J. C. Pringle, Jr., and D. Sinneros. U.S. Bureau of Reclamation, PO Box 25007, Denver Federal Center, Code D-1522, Denver CO 80225.

An interagency effort between the Bureau of Reclamation and the Army Corps of Engineers was initiated to amend established 2,4-D tolerances and registrations. Such an amendment would permit nationwide use of this herbicide in conjunction with water level management and other measures in integrated programs for the control of eurasian watermilfoil in multiple-use reservoirs managed by Federal, state, and local government agencies and by certified applicators under contract to these agencies. To accomplish this goal, a study was initiated to obtain necessary residue data under authority of Experimental Use Permits granted by the Environmental Protection Agency. Experimental small-plot applications of the liquid amine formulation and granular butoxyethanol ester formulation were done at rates of 22.5 and 45 kg ae/ha and samples of water, hydrosol, and fish were collected for chemical analysis 1-day pretreatment, and 1, 4, 7, 14, 28, and 56 days posttreatment.

186 RUGGEDNESS TESTING FOR EXTRACTION AND PNBDI DERIVATIZATION OF COMPOUND 1080 (SODIUM FLUOROACETATE) FROM SINGLE LETHAL DOSE BAITS. John A. Nichols, Lynn Hageman, and Laszlo Torto, Montana Department of Agriculture, Laboratory Bureau, McCall Hall, Bozeman, Montana 59717.

A simple extraction with hot water was developed for sodium fluoroacetate, which is being considered for use as a predator control agent in the form of single lethal dose bait (SLDB). The SLDB consists of about 3 mg sodium fluoroacetate, 28 g tallow, 3 g beeswax, and is coated with fishmeal. Part of the aqueous extract is partitioned into ethyl acetate, and the para-nitrobenzyl ester of fluoroacetic acid is formed. This derivative may be quantified using either high pressure liquid chromatography or gas chromatography with mass spectrometric or thermionic detection.

A ruggedness test, following the approach of Youden (1), was performed to assess the susceptibility of the analytical procedure to variations in technique which might commonly be encountered. After incorporating a few procedural specifications suggested by the results of the ruggedness test, the procedure was quite rugged. Careful statistical analysis of the ruggedness test led to some interesting insights about statistical evaluations.

(1) Youden, W.J., and Steiner, E.H., Statistical Manual of the AOAC, Association of Official Analytical Chemists, 1975.

187 THE USE OF ION EXCLUSION CHROMATOGRAPHY TO DETERMINE THE CONTRIBUTION OF WEAK ORGANIC ACIDS TO THE ACIDITY OF PRECIPITATION IN REMOTE AREAS OF THE WORLD. W. C. Keene and J. N. Galloway. Department of Environmental Sciences, Clark Hall, University of Virginia, Charlottesville, Virginia 22903.

The Global Precipitation Chemistry Project collects precipitation by event to determine the composition of precipitation and the processes controlling it in five remote regions. After analysis for major inorganic species, ion balances revealed that samples from certain sites, were consistently deficient in anions. This and other evidence suggested that weak organic acids were contributing to free acidity. Therefore, a technique incorporating Ion Exclusion Chromatography was developed to measure weak organic acid anions. Eluent strength was optimized to decrease analytical time while maintaining peak integrity. A 500  $\mu$ l injection increased resolution when samples were spiked with concentrated eluent to prevent interference. Samples were treated with a biocide immediately after collection to prevent microbial activity. Using the technique, formate, acetate and citrate were found in samples. These anions are now routinely measured to a precision of  $\pm 10\%$  at sub ppm levels. Verification includes standard additions, ion balances and total acidity balances using Gran's titrations optimized for the range 1 to 25  $\mu$ eq/l. Results indicate that at three sites in or near the southern hemisphere, organic acids contributed between 13% and 66% of the free acidity in precipitation.

188 SEQUENTIAL SAMPLING OF STORM PRECIPITATION IN DENVER, COLORADO. LeRoy J. Schroder and A.H. Hedley, U. S. Geological Survey, 5293 Ward Road, Arvada, Colorado 80002

Six manually operated precipitation collectors have been installed in the northwest Denver, Colorado metropolitan area. Five collectors form a pentagon with the sixth collector at the center. The sides of the pentagon are 3 meters long and each collector is equidistant from the center collector. Each collector opening is 1 meter above land surface. The five collectors forming the pentagon are opened and closed sequentially during a storm; the center collector is open during the entire storm. All samples are filtered and split into two subsamples as soon as possible after the end of the storm. Subsamples analyzed by inductively-coupled plasma-emission techniques are acidified with 0.1 milliliter nitric acid. Samples analyzed by ion-exchange, chromatography techniques are chilled to 4 Celsius. Snow-sample analyses indicate that inorganic contaminants tend to decrease during a storm, but may be effected by local point sources. Soil-derived particles scavenged by precipitation may be the primary source of inorganic contaminants during the initial stage of the storms

189        COMPARISON OF STORM AND WEEKLY COMPOSITE PRECIPITATION SAMPLES  
AT RALEIGH, NORTH CAROLINA. L. J. Schroder, U. S. Geological Survey, 5293  
Ward Road, Arvada, Colorado 8002 and R. A. Linthurst, North Carolina State  
University, Raleigh, North Carolina.

Ten precipitation collectors are operated at Finley Farm, North Carolina State  
University, in Raleigh, North Carolina. Four collectors sample only storm precipitation,  
and six collectors sample weekly composite precipitation. Each precipitation sample is  
analyzed for Ca, Mg, Na, K, Cl, F, NO<sub>3</sub>, PO<sub>4</sub>, SO<sub>4</sub>, pH, and specific conductance, if at  
least 90 milliliters of precipitation is obtained. If less than 90 milliliters of precipitation  
is collected, only selected chemical constituents are analyzed. These collectors have  
been operated for more than 20 weeks; storm precipitation samples are compared with  
weekly composite samples for contaminant concentration and volume collected.  
Distribution of chemical constituents in precipitation is not uniform throughout areas as  
small as 10,000 square meters. Sulfate and Cl concentrations in storm samples vary  
considerably, compared to cation concentrations.

190 THE IMPACT OF LAKE ACIDITY ON THE QUALITY OF PUMPED COTTAGE WATER  
J.C. Mearns<sup>1</sup> and M. Khan and C. Vairo<sup>2</sup>, R. Jackson<sup>2</sup> and Wan Chi Li<sup>2</sup>, National Health  
and Welfare, Ottawa, Ontario, K1A 0L2, <sup>1</sup>Barringer Magenta Ltd., Rexdale, Ontario, M9W 5G2<sup>2</sup>,  
Canada.

Studies of the effects of standing time on the leaching of metals from the plumbing  
systems of cottages on three acid-rain sensitive lakes have been carried out. A survey  
of 14 cottages on Lake of Bays was also carried out to collect samples of first drawn  
water after over-night stagnation in the plumbing system, and flushed water samples.  
Passage of the lake waters through the plumbing system results in increases in pH, al-  
kalinity and the concentrations of the metals measured: Cd, Cu, Pb and Zn. The maximum  
rate of leaching of metals occurs in the first 2 hours of contact time, although levels  
continue to rise up to 10 days. The concentrations of Pb and Cu were closely related to  
the contact time and rise to or exceed the maximum acceptable concentration in the first  
litre of water drawn from the tap after 2 to 12 hours contact time. These levels de-  
creased by up to 95% in the third litre of water sampled. Concentrations of all metals  
in water taken after flushing of the system were all well below the maximum recommended  
limit, although still higher than those found in the corresponding lake water.

191 THE DETERMINATION OF URANIUM IN ROCKS, SOILS, AND URANIUM MILL TAILINGS  
BY A FUSION - FLUORIMETRIC TECHNIQUE. E. J. Cokal, Los Alamos National Laboratory,  
P.O. Box 1663, Los Alamos, New Mexico 87545.

This paper describes the determination of uranium in the sub-ppm to several hundred ppm  
range by means of a sodium hydroxide fusion - phosphoric acid dissolution combined with an  
appropriate time-gated fluorimetric measurement technique. A Scintrex UA-3 fluorimeter used in  
a standard addition mode provides a high degree of specificity and sensitivity. Sample preparation  
is simple and requires only zirconium crucibles and standard membrane filtration apparatus.  
The UA-3 fluorimeter is rugged and reliable, and is suitable for field laboratory applications. Results  
are presented for the uranium content of several reference materials. The suitability of the  
technique for determination of uranium in acid mill tailings leachates will be discussed. The  
efficacy of ICP spectrometry in uranium determinations will also be described.

192 THE CHEMISTRY AND HEALTH EFFECTS OF A MAJOR AIR POLLUTION EPISODE IN UTAH  
VALLEY. L.E. Ansen and D.J. Eatough. Department of Chemistry and  
Thermochemical Institute, 267 FB, Brigham Young University, Provo, Utah 84602.

During a two week period in December, 1980, Utah Valley in north-central Utah  
was covered by a strong, continuous temperature inversion. Total suspended  
particulate concentrations reached 700 µg/m<sup>3</sup> in parts of the valley. Airborne  
particles collected during the month of December, 1980 have been analyzed for water  
soluble anions and cations by ion chromatography. Hospital records in the  
respiratory care center at Utah Valley Hospital have been examined for correlation  
between airborne particle concentration, other meteorological parameters and hospital  
admissions. The results of these studies will be presented.

193 CONTINUOUS ULTRASENSITIVE MEASUREMENT OF NITRIC ACID AND OTHER OXIDES OF NITROGEN IN AIR. M. J. Bollinger,\* R. E. Sievers, Dept. of Chemistry and CIRES, Univ. of Colorado, Boulder, CO, 80309, and F. C. Fehsenfeld, CIRES and NOAA Aeronomy Laboratory, Boulder, CO, 80303 (\*Work done at NOAA Aeronomy Lab).

Because of the importance of  $\text{HNO}_3$  in the atmosphere, efforts are being made to devise a simple method for continuous analysis by chemiluminescence. A novel method has been developed for the conversion of oxides of nitrogen to  $\text{NO}$ , which is then determined by the sensitive and selective chemiluminescent technique. The conversion process involves heterogeneous catalysis of the reduction of the oxides of nitrogen on a gold surface in the presence of  $\text{CO}$ . The relatively low conversion temperatures required are believed to result from the exothermicity of the oxidation of  $\text{CO}$  to  $\text{CO}_2$ . At  $300^\circ\text{C}$ , conversion of  $\text{NO}_2$ ,  $\text{HNO}_3$ , and n-propyl nitrate is quantitative when 1 ppth of  $\text{CO}$  is added to the air sample flowing through a fused silica tube coated with gold. The limit of detection of  $\text{NO}_2$  and  $\text{HNO}_3$  with the chemiluminescent detector is ca. 0.02 part per billion for a ten second averaging time using photon counting techniques. The response time of the instrument is sufficiently short to allow essentially real-time analysis of the oxides of nitrogen. Simultaneous measurements of the "total" odd nitrogen oxides,  $\text{NO}_y$  ( $\text{NO}$ ,  $\text{NO}_2$ ,  $\text{HNO}_3$ , organic nitro-compounds,  $\text{NO}_3$ ,  $\text{N}_2\text{O}_5$ ,  $\text{HNO}_2$ ,  $\text{HO}_2\text{NO}_2$ , excluding  $\text{N}_2\text{O}$ ), and  $\text{NO}_x$  ( $\text{NO} + \text{NO}_2$ ) may yield valuable information about these environmentally important species as to the conversion processes of  $\text{NO}_x$  and  $\text{HNO}_3$  and organic nitrates.

194 ORGANIC AIR POLLUTANTS FROM SHALE OIL WASTEWATERS. S. B. Hawthorne and R. E. Sievers, Dept. of Chemistry and Cooperative Inst. for Research in Environmental Sciences (CIRES), Univ. of Colorado, Boulder, CO 80309.

The production of shale oil in western Colorado will generate several different waste materials that will require control and disposal in an environmentally safe manner. Although many aspects of this problem have been studied, little work has been done on the nature of organic compounds that are likely to be volatilized from shale oil wastewaters during storage, handling, and disposal. These emissions may constitute a significant and difficult to control source of air pollutants. The identities and relative concentrations of volatilized organic compounds vary greatly with the type of shale-oil wastewater. Gas chromatographic/mass spectral analysis of static headspace samples of several different wastewaters has revealed the presence of alkanes, alkenes, alkyl biophenes, alkyl benzenes, and alkylated nitrogen-containing heterocycles that can be expected to volatilize from holding ponds and from shale piles wetted with retort water. The use of fused-silica capillary columns coated with a cross-linked silicone polymer has allowed large volumes of water-saturated air to be injected into the column for cryogenic trapping and subsequent analysis of the vapor-phase organic compounds. Sample preparation and gas chromatographic injection devices have been developed in order to avoid the cross-contamination experienced with standard injection techniques. The analytical methodology employed and the results of these analyses will be discussed.

195 ANALYSIS OF AMBIENT AIR AROUND A HAZARDOUS SURFACE IMPOUNDMENT. J. Broadus, G. Connolly and Dr. M. Witt, Department of the Army, Rocky Mountain Arsenal, Commerce City, Colorado 80022

Efforts are continuing to close a hazardous surface impoundment at the Rocky Mountain Arsenal under the RCRA legislation. The safety of the workers in and around this site is of prime concern. In order to evaluate the hazard, a program for monitoring selected organic contaminants in the air was developed along with the chromatography technique needed to quantify selected compounds. The presentation will include a sampling procedure and its validation a discussion of GC/MS utilized to determine the major pollutants in the ambient air as well as the surface liquid, determination of desorption efficiencies, and the selection of analytical equipment, parameters and procedures developed for a routine gas chromatographic method.

196 DETERMINATION OF LOW LEVEL QUANTITIES OF CHLOROPICRIN, CHLOROFORM AND CARBONYL CHLORIDE IN AIR BY COMPUTER ASSISTED INFRARED SPECTROPHOTOMETRY. Gregory B. Mohrman, Elijah G. Jones and Michael E. Witt, Department of the Army, Rocky Mountain Arsenal, Commerce City, Colorado 80022

The operation of an industrial disposal facility requires the monitoring of the plant working environment to ensure worker safety. In order to support the Army disposal of chemical waste, analytical instrumentation and methodology had to be developed which provided sensitive, accurate and rapid testing of chloropicrin, chloroform, and carbonyl chloride. A programmable, single beam infrared spectrophotometer was selected to fulfill these requirements. The instrument utilizes an infrared analyzer fitted with a twenty meter gas cell to enhance sensitivity. This instrument provides near real time monitoring capabilities in the parts-per-billion range. Selected wavelengths for individual compounds in the 2.5 to 14.5 microns ( $4000-650\text{ cm}^{-1}$ ) range are used for quantitative determination. The integral micro-processor permits rapid analysts and reporting of compound concentrations with correction for interferences due to overlapping infrared absorbances. Calibration is performed using a permeation standards generator simulating actual environmental monitoring sampling techniques. Calibration gas containing a known concentration of an individual contaminant is passed through the cell at a constant flow rate with continuous analysis of all pre-selected wavelengths. A concentration versus absorption matrix, which includes interference absorbances, is developed using data from all the analytical wavelengths.

197 THE ANALYSIS OF RIVER SEDIMENTS: EVALUATION OF BOTH THE DIGESTION PROCEDURE AND THE TRACE METAL DETERMINATIONS BY ATOMIC ABSORPTION SPECTROPHOTOMETRY. G. S. Caravajal and K. I. Mahan, University of Southern Colorado, Pueblo, Co. 81001 and D. E. Leyden, University of Denver, Denver, Co. 80208.

A procedure for the digestion of river sediments with concentrated  $\text{HNO}_3$  and  $\text{HCl}$  followed by flame and flameless atomic absorption spectrophotometry is investigated and evaluated with the use of NBS/SRM-1545 river sediment. Twenty ml. of concentrated are added to previously dried .5 g samples and subsequently evaporated to dryness. This procedure is done twice followed by the addition of 20 ml. of hot concentrated  $\text{HCl}$  and gentle boiling for 15 minutes. River sediments, including NBS/SRM-1645, were analyzed for Na, K, Ca, Mg, Fe, Mn, Cu, Cd, V, Co, Cr, Ni, As, Sb, Tl, Pb, Zn and Hg. The method of standard additions was used to evaluate the accuracy of the determinations made on the river sediments. Very good accuracy was obtained for all NBS/SRM-1645 certified metals determined except for Fe.

198 APPLICATIONS AND TECHNIQUES OF SCANNING AUGER MICROSCOPY. T. J. Shaffner, Texas Instruments Inc., P.O. Box 225936, M/S 118, Dallas, Texas 75265.

Technologies in electron optics, detector design, vacuum science and sputter etching have been combined in the scanning Auger microprobe to open a new realm for surface measurement and understanding at the submicron level. Ultimate spatial resolution is determined by the diameter of the probing electron beam (near 500Å) and vacuums of  $10^{-10}$  torr are now routinely achieved with modern pumping stations which insure that contamination rates are held below one monolayer per hour. Scanning Auger is capable of detecting groups of atoms as small as 100,000 within 10Å of the surface, but on the atomic percent scale this amounts to only 1 to 5%. Poor detectability and spectrum distortion from charge buildup on insulating specimens are some limitations of the instrument. Experience has defined reasons why scanning Auger can solve failure analysis questions other techniques leave unanswered. Submicron spot surface analysis capability, freedom from nearby surface and sub-surface signals and sensitivity to the cleanup related elements C, O and N are three. Production applications will be given which stress the synergism of these advantages. Atomically clean standards and an understanding of the role of backscattered electrons in Auger production are topics of current interest relating to quantitative procedures. Developments in vacuum performance and automation can be expected to continue to serve the evolution of Auger microscopy.

199 ANALYTICAL APPLICATIONS OF HEAVY ION INDUCED X-RAY FLUORESCENCE AND AUGER ELECTRONS. T. M. Rosseel, R. L. Auble, L. D. Hulett, S. Kahane, H. J. Kim, W. T. Milner, G. D. O'Kelley, S. Raman, G. G. Slaughter, C. R. Vane, and J. P. Young. Oak Ridge National Laboratory,\* Oak Ridge, Tennessee 37830

Heavy ion bombardment at intermediate velocities (1 MeV/amu) produces a higher degree of multiple ionization than electron bombardment or photoionization of target atoms. The resultant x-ray fluorescence and Auger electrons excited by heavy ions exhibit prominent satellite lines corresponding to various states of multiple ionization. Recent experiments have shown that the intensity distribution of x-ray satellite lines display variations which depend on the chemical state or environment of the emitting target atom. These variations are being systematically explored in order to evaluate heavy ion induced x-ray fluorescence as a new analytical method for characterizing chemical speciation of materials. Correlation of the intensity distribution with parameters describing the chemical environment of a series of sulfur, molybdenum and selenium compounds will be presented. Possible chemical information from heavy ion induced Auger electrons will also be discussed.

\*Research sponsored by the Office of Energy Research sponsored by the U. S. Department of Energy, under Contract W-7405-eng-26 with the Union Carbide Corporation.

200 SURFACE CHARACTERIZATION BY COMBINED LOW ENERGY ION SCATTERING (LEISS) AND SPARK SOURCE MASS SPECTROMETRY (SSMS) ANALYSIS. D. L. Malm. Bell Laboratories, 600 Mountain Avenue, Murray Hill, NJ 07974.

The combined use of low energy ion scattering (LEISS) and spark source mass spectrometry (SSMS) for the analysis of hard gold electroplate surface provides a much more comprehensive surface characterization than when either technique is used alone. For example, SSMS can supply an unambiguous, semi-quantitative survey analysis for most of the impurities that may be present on a surface. This information is significantly enhanced by LEISS profiles which show the relative distribution of these impurities as a function of depth below the surface. The unique features and limitations of each method will be presented, and the value in the use of combined techniques discussed.

201 SURFACE CHARACTERIZATION OF MATERIALS FOR USE IN ADVANCED ENERGY CONVERSION SYSTEMS. R. E. Witkowski. Westinghouse R&D Center, 1310 Beulah Road, Pittsburgh, Pennsylvania 15235.

This paper surveys the surface microcharacterization studies carried out on selected materials that have been recommended and subsequently evaluated for use in advanced energy conversion systems. The presentation will include results obtained primarily by scanning electron microscopy studies of (1) high alloy steels exposed to high temperature liquid sodium and lithium for breeder and fusion reactor applications, (2) structural metallic and organic materials exposed to eutectic Al-K for advanced electrical current collection schemes for motors and generators, and (3) thin film polycrystalline silicon produced by fused-salt electrodeposition for photovoltaic solar energy conversion. In all the work presented, the importance of the use of SEM coupled with energy dispersive analysis by x-rays for rapid specimen screening through monitoring changes in surface morphology and elemental composition will be emphasized; supporting techniques such as SIMS, electron microprobe and optical microscopy will also be discussed where applicable. Also, the highly specialized environmental test systems, that are required to properly expose specimens to the various liquid metals (Na, Li, NaK73) under prototypic conditions and the electrodeposition fused-salt bath, will be briefly described.

232 SURFACE ANALYSIS OF COMMERCIALY MADE MIRRORS\*. T. M. Thomas, J. R. Pitts, and A. W. Czanderna. Solar Energy Research Institute 1617 Cole Boulevard, Golden, Colorado 80401.

Most commercially made mirrors, consisting of a multilayer stack of glass/Ag/Cu/paint, are made using a wet electroless process. Two of the failure modes of atmospherically weathered mirrors are delamination at the Ag/glass interface and electrochemical corrosion of the copper and silver. AES, XPS, SIMS, and ISS have been used for surface analysis during profiles to reach the glass/Ag, Ag/Cu, and Cu/paint interfaces as well as to analyze for impurities present in each layer of the mirror. Surface analysis results will be presented from studies of complete mirror stacks and of partially made mirrors prepared in our laboratory. Emphasis in the discussion will be to elucidate the chemistry of the Ag/glass interface and the corrosion induced by impurities trapped in the mirror during fabrication. A model for the mechanism of bonding silver to glass during mirror preparation will be discussed.

\*Work performed under U.S. E Contract No. EG-77-C-01-4042.  
A U.S. DOE facility.

233 SURFACE ANALYSIS OF SILVER MIRRORS MADE FROM ORGANOMETALLIC SOLUTIONS\*. J. R. Pitts, T. M. Thomas, and A. W. Czanderna. Solar Energy Research Institute 617 Cole Boulevard, Golden, Colorado 80401.

Silver mirrors, made by decomposing organometallic solutions, have been studied using surface analysis techniques to secure information about the silver/glass interface. Depth profiles using XPS, AES, ISS, and SIMS for analysis have been taken on the mirrors. From these studies, it appears that direct silver to silicon bonds are formed between the silver film and the glass substrate. A mechanism is proposed for forming these bonds during the preparation of the mirror. In the process, it is thought that the silver-containing Lewis base decomposes when in contact with glass at elevated temperatures ( $T > 500^{\circ}\text{C}$ ). The initial decomposition process depletes the glass of surface oxygen, leaving a reactive surface which can form silver to silicon covalent bonds. A second decomposition process plates silver onto the covalently bonded silver layer. Physical characteristics of the silver films prepared using the organometallic process will be presented. The mirrors exhibit excellent adhesion at the Ag/glass interface and good corrosion resistance.

\*Work performed under U.S. DOE Contract No. EG-77-C-01-4042.  
†A U.S. DOE facility.

204 Q SECONDARY ION MASS , Peter Williams. Arizona state University, Tempe, Arizona 85287

Ion microanalysers can be considered three-dimensional chemical microscopes without gross astigmatism. Thus, x-y resolution is measured in microns, whereas in-depth (z) resolution can be some tens of Angstroms. This talk will concentrate on z-analyses, or depth profiles. In this mode an ion microanalyser is a one-dimensional chemical microscope of unusual sensitivity, detection limits below the ppm level being achieved for many elements in depth profiles with 100 Angstrom resolution. Major problems with the technique are those of quantifying the analyses. Ion yields are exceptionally sensitive to the nature of the sputtered matrix, which imposes severe constraints on the use of external standards. Only in analyses of dilute impurities and dopants can linearity of working curves safely be assumed. In this regime, ion-implanted standards have proved invaluable. Our research in recent years has been aimed at developing the understanding of the physics of the sputtering and ion emission processes necessary to extend quantitative ion microanalysis beyond dilute samples. The talk will discuss the extension of quantitative ion microanalysis using ion-implanted standards to two important new areas: analysis of interfacial impurity layers, and analysis of major elements levels, in particular of H, C, N, O, and S.

205 SURFACE ANALYSIS OF SILICON GRAIN BOUNDARY CHEMISTRY. Phillip E. Russell, L.L. Kazmerski and P.J. Ireland, Solar Energy Research Institute, 1617 Cole Blvd., Golden, Colorado 80401.

The electrical properties of polycrystalline silicon are known to be influenced by grain boundary properties. Grain boundaries can serve as potential barriers to majority carrier **transport**, **recombination** sites for minority carriers, segregation sites and paths for rapid diffusion. We have used in-situ ultra high vacuum fracturing techniques combined with Auger Electron Spectroscopy (AES) and Secondary Ion Mass Spectroscopy (SIMS), to investigate grain boundary chemistry. These data have been combined with electron microscopy and electrical measurements to correlate grain boundary chemistry with electrical properties. Heat treatment to temperatures appropriate for device processing, have been shown to increase the impurity content of grain boundaries, and concurrently increase the recombination rate of grain boundaries.

206 COMBINED ANALYSES FOR SEMICONDUCTOR MATERIALS EVALUATION. B. F. Phillips. Physical Electronics Division Laboratories, Perkin-Elmer Corporation, 6509 Flying Cloud Drive, Eden Prairie, Minnesota 55344.

The use of multiple analysis techniques for the characterization of semiconductor materials has become more popular as the interactions of the various surface analytical techniques are being discovered. In particular the complementary nature of Auger Electron Spectrometry (AES) and Secondary Ion Mass Spectrometry (SIMS) has become better appreciated as smaller surface dimensions and thinner layer growths or depositions have been achieved. In particular the development of materials for Very Large Scale Integration (VLSI) has pushed the limits of sensitivity of the AES technique until it is being best applied to **quantitate** the major and minor elements present while SIMS is used to point out the differences in trace impurities. This **complementary** nature will be demonstrated by the presentation of results obtained upon analyzing Si oxide and Si nitride layers, thin metal films and semiconductor dopants.

207 USE OF THE RAMAN MICROPROBE FOR ANALYSIS OF OPTICAL SURFACES, Fran Adar, Instruments SA, Inc., 173 Essex Avenue, Metuchen, N.J. 08840

The independent development of the Raman **microprobe** at the National Bureau of **standards** in Washington, and at the University of Lille in France, has provided the capability to determine molecular composition and crystalline phases of material on surfaces. The spatial resolution of the technique is determined by optical **considerations**. In transparent heterogeneous samples, the lateral and axial resolution are determined by the wavelength of the light, the **n.a.** of the optics, and field limiting apertures. Multiphase ceramic materials from D. Clarke at Rockwell International are being examined to verify the theoretical estimates of resolution (1um lateral resolution and 5um depth **resolution**). In opaque materials only the upper layer, where the radiation can penetrate, can be probed. This layer can be as thin as several **100A's** in carbon and in transition metal oxide samples. We have been successful characterizing several types of corroded **metal** surfaces - such as ferrous metals corroded in a high temperature **brine**, stainless steel corroded in a high **tempera-**ture coal gasifier (in collaboration with J. Hamilton, Sandia) and lead oxides on lead and platinum electrodes (in collaboration with Bill **Adams**, Canada Government **Lab**).

208 PHOTOACOUSTIC SPECTROSCOPY STUDY OF METAL-SUPPORT INTERACTIONS IN METAL OXIDE CATALYSTS SUPPORTED ON  $\gamma$ -ALUMINA. L. W. Burggraf, Department of Chemistry, USAF Academy, Colorado 80840; D. E. Leyden, Department of Chemistry, Colorado State University, Fort Collins, Colorado 80523; R. . Chin and D. M. Hercules, Department of Chemistry, University of Pittsburgh, Pittsburgh, Pennsylvania 15260.

Photoacoustic spectroscopy (PAS) was used to study metal-support interactions in  $\text{Ni}/\gamma\text{-Al}_2\text{O}_3$ ,  $\text{Co}/\gamma\text{-Al}_2\text{O}_3$  and  $\text{Co-Mo}/\gamma\text{-Al}_2\text{O}_3$  catalysts which had been previously characterized by various surface spectroscopy techniques. The objective was to better understand the influence of preparation parameters on the nature of these catalyst surfaces. Qualitative and quantitative PAS results were in agreement with ESCA, ISS and SIMS studies. Metal-support interactions were found to increase with increasing calcination temperature and with decreasing metal loading. Features in the visible PAS spectra were identified with tetrahedrally and octahedrally coordinated metal ions. The distribution of metal ions in tetrahedral and octahedral interstices of the  $\gamma$ -alumina lattice was estimated. The dependence of the tetrahedral metal ion fraction and the octahedral metal ion fraction on metal loading and calcination temperature is explained by a simple model which describes competition between tetrahedral metal ion formation and inversion of the spinel at the surface of the support.

209 SURFACE ANALYSIS: AN OVERVIEW OF TECHNIQUES AND APPLICATIONS IN AN ANALYTICAL ENVIRONMENT H. A. Karp and R. Linder, Surface Science Laboratories, Inc., 1206 Charleston Road, Mt. View, California 94043.

Characterization of the surface and near surface properties of materials in terms of chemical composition, lateral homogeneity and depth variations is of fundamental importance in a wide variety of applications. ESCA (Electron Spectroscopy for Chemical Analysis) and AES (Auger Electron Spectroscopy) are two very powerful analytical techniques which can provide detailed information on such surface properties. A discussion of these techniques both in the context of fundamental principles and in the nature of the chemical information attainable is presented. ESCA can provide information on the elemental composition and chemical bonding present in the surface region for both organic and inorganic constituents. Such information is often not attainable by other analytical techniques. AES is particularly well suited to the elemental characterization of surfaces on the microscopic scale and to the determination of lateral homogeneity. In conjunction with inert gas ion bombardment both techniques can be utilized to provide chemical information as a function of depth. Specific applications of these techniques will be discussed relating to the analysis of organic materials, thin film composition and thickness, and the microelectronics industry.

210 AN FT-IR STUDY OF THE SURFACE REACTION BETWEEN  $\text{SO}$  AND  $\text{SOOT}$ . D. S. Robinson, M. S. Akhter, A. R. Chughtai, and D. M. Smith. Department of Chemistry, University of Denver, Denver, Colorado 80208.

The interaction of sulfur dioxide with the surface of soot produced by the combination of n-hexane, selected as a petroleum fuel model, has been examined by Fourier transform infrared spectroscopy (FT-IR). The reactions between  $\text{SO}_2$  and oxygen-containing functionalities on the soot surface have been examined as a function of temperature and  $\text{SO}_2$  pressure. The species on the carbon surface, as previously characterized in these laboratories, include acid anhydride, alkyl and aryl carbonyl groups, carbon-hydrogen bonds, and aryl ether linkages. Surface species produced through reaction with  $\text{SO}_2$  include sulfate, apparently formed at the expense of carbonyl and carbon-hydrogen groups. The results of isotopic substitution and rate studies are reported.

211 THE INFRARED SPECTROSCOPY OF CO ADSORBED ON SUPPORTED MOLYBDENUM (0). T. Puckett, H-P Lu, A. R. Chughtai, and D. M. Smith. Department of Chemistry, University of Denver, Denver, Colorado 80208.

Infrared studies of CO adsorbed on  $\text{SiO}_2$ - and  $\text{Al}_2\text{O}_3$ - supported molybdenum (0) are reported. While previous studies of CO on Mo film have indicated dissociative chemisorption, molecular chemisorption on the supported metal is revealed from these experiments. A significant influence of the support material is evident. The effect on the adsorption of temperature and CO pressure are discussed.

212 THE USE OF **FTIR** TO CHARACTERIZE SEDIMENT COATINGS OF PHOSPHATE ON THE SUBSTRATES GOETHITE AND PYROLUCITE. Marvin **C. Goldberg**, U.S. Geological Survey, P.O. Box **25046**, MS , Denver Federal Center, **Lakewood, CO 80225**, and Eugene R. Weiner and Paul **Boymel**, University of Denver, Department of Chemistry, Denver, CO 80210.

**FTIR** is a particularly powerful tool for examining surface coatings over substrates and can indicate bonding **configurations** as well as molecular species. **FTIR** studies were made from prepared KBr pellets that **contained solid** substrates between 2 and 20 microns in size to examine the extent of surface coating as **well** as the bonding **configuration** for selected systems. It was established that sorption of phosphate to goethite results in the formation of binuclear complexes rather than bidentate or **monodentate** complexes. Similar studies using the same technique for phosphate sorption onto pyrolucite revealed that the sorption **configuration** is **bidentate**. In the presence of mixtures of the sub-**strates** the phosphate bonding retains the bonding geometry **characteristic** of each substrate, nevertheless, as the coating becomes thicker than a monolayer this information is not sufficient to **allow** one to **quantitatively** distinguish the equilibrium distribution of phosphate between the two substrates. In some related work with quartz there were indications that the spectral **resolution** depended upon particle size. The **FTIR** spectra of quartz were better resolved as the quartz **size** was reduced from 20 to 2 microns.

213 THE DETERMINATION OF **SILANOL** IN SILICONES BY QUANTITATIVE FTIR. G. W. Griffith. The Bendix Corporation, P.O. Box 1159, Kansas City, Missouri 64141.

A great many two component silicone resins depend upon the reaction of a **silane-hydrogen** containing (SiH) material with a silanol containing (SiOH) material". There are many methods that work quite well for the quantitation of SiH. There are probably even more methods available for SiOH **determination**. Unfortunately, most of them suffer from large **disadvantages**. The disadvantages range from **interferences** (i.e., water) to poor quantitation (i.e., condensation **reactions**) to dangerous (**i.e.**, hydride reactions). This laboratory has tried nearly every available method for silanol analysis in an effort to find a reliable one. As a result, we have developed an infrared method that is **not** only fast and reliable but has very few **interferences**. The method involves measuring the absorbance of the non-bonded SiOH band (3685 **cm<sup>-1</sup>**) of very dilute solutions of the silanol in carbon **tetrachloride**. The analysis is performed on an FTIR **spectrophotometer**, and the effects of moisture and other interfering species are digitally subtracted. The choice of a suitable standard silanol proved to be one of the most difficult **problems** to overcome, since the absorptivity coefficient is somewhat structure dependent. The method is now being used on a routine basis.

214 ALKALI HALIDE PELLETS OF DEUTERATED SOLID SAMPLES FOR INFRARED SPECTROMETRY.

Patrick MacCarthy, Dept. of Chemistry and Geochemistry, Colorado School of Mines, Golden, Colorado 80401.

It is generally difficult to prepare samples, deuterated at active proton sites, for infrared spectrometry. The deuteration per se is rather trivial, but in preparing the samples in a form suitable for infrared **spectrometry**, the samples frequently revert to hydrogen (H) form. This problem can be avoided or minimized by resorting to dry-box techniques, but even then it is not uncommon to find that the final samples prepared for infrared measurements are only partially deuterated. The objective of this work was to develop a rapid and convenient method, which would avoid the tedium and expense of a dry-box, for preparing KBr pellets of compounds deuterated at active proton sites. It was intended that the method be inexpensive and be generally suitable for routine bench-top use. A comparable procedure involving the use of mulls was recently reported for this purpose, and the present paper describes an alternative method involving the KBr pellet technique. Basically, the procedure involves the application of the KBr-sample mixture to the die. Prior to pressing the pellet, the mixture is slightly dampened with a small amount of deuterating solvent or solvents. The mixture is then evaporated to dryness in a desiccator. This **dampening-drying** process may be repeated a number of times prior to actually pressing the pellet. Precautions, pitfalls and idiosyncrasies of the method will be discussed.

215 FILAMENTOUS BACTERIAL VIRUS - A REALISTIC MODEL SPECTRUM FOR ALPHA HELIX. C. Gilon and E. J. Wachtel, Department of Chemical Physics, Weizmann Institute of Science, Rehovot, Israel.

The coat protein of the filamentous bacterial virus Pfl has a molecular weight of approximately 5000 daltons and is one of the most helical proteins found in nature. Using Fourier transform spectroscopic techniques, we have studied the infrared active Amide bands of thin films of the virus, and the kinetics of the changes induced in these bands by the exchange of deuterium for hydrogen. We derive spectral parameters which are more appropriate for the characterization of helical regions of globular proteins than the commonly used parameters obtained from the spectra of synthetic polypeptides.

216 SOFTWARE METHODOLOGY FOR PATH LENGTH INDETERMINATE QUANTITATIVE ANALYSIS. R. J. Obrebski, J. Bernard and L. Sims. Beckman Instruments, Inc., Scientific Instruments Division, Irvine, CA 92713.

Materials which are conveniently dissolved in a solvent of suitable viscosity, can be sampled and subsequently removed from fixed path liquid cells. Since the path length of this type of cell is either known or easily determined, routine quantitative analysis methods using Beer's Law can be employed. However, in cases where the materials under study cannot be dissolved or the viscosity of the resultant solution is too high for convenient liquid transfer, the use of fixed path liquid cells becomes a problem. This is particularly true in infrared methodology where cell paths are relatively small. In such cases, demountable cells, ATR methods, cast films or other indeterminate path length sampling methodology is usually employed.

In order to alleviate the problem of a known path length in administering Beer's Law, several methods have been developed. In this paper, we will review those methods and discuss their implementation in current software. Since the methods are truly different, each method is well suited to a particular set of sampling conditions. The sample requirements, uses and performances of each method, as implemented in software, will be discussed and applied to various sampling conditions. Recommendations will be made for the optimum utilization of each software method relative to the sampling conditions available.

217 RESONANCE RAMAN SELECTIVITY IN METAL-METAL BONDS, METAL-INDICATOR DYES, AND ONE-DIMENSIONAL ORGANIC CONDUCTORS. P. J. Trotter. Eastman Kodak Research Laboratories, Rochester, NY 14650.

A series of tellurium compounds of the general formula  $ArTeMPh_3$  ( $Ar$  = phenyl, p-tolyl, p-anisyl, p-bromophenyl;  $M$  = Ge, Sn, Pb) were examined by Raman spectroscopy for characterization of metal-metal bond vibrations. Further information on Raman spectra of M-Te bands was obtained using the known symmetric model compounds:  $Ph_3MTeMPh_3$  ( $M$  = Ge, Pb, Sn). The very intense symmetrical M-Te-M( $\nu_s$ ) bond vibrations appear at  $113\text{ cm}^{-1}$  (Pb-Te-Pb),  $153\text{ cm}^{-1}$  (Sn-Te-Sn) and  $167\text{ cm}^{-1}$  (Ge-Te-Ge). Some of these compounds, along with  $Os_3(CO)_{12}$  and  $Ir_4(CO)_{12}$ , yielded M-M' overtones when excited in UV-Laser resonance. Micro-Raman studies of metal compound films were also carried out.

Some pyridyl azonaphthol dyes showed a well-resolved vibronic manifold in adsorption spectra. The vibrations and groups causing this vibronic activity were investigated by resonance Raman, absorption spectroscopy, and molecular orbital calculations. Resonance Raman intensity enhancements of up to  $5 \times 10^4$  were observed, and all of the major group vibrations were strongly enhanced. The resolvable vibronic manifold has its origin in several group vibrations.

The organic conductor bis-tetrathiotetracene triiodide,  $(TTT)_2I_3$ , was also examined by resonance Raman spectroscopy. Resonance Raman spectra yielded overtone patterns beginning at  $\approx 108\text{ cm}^{-1}$  and up to seven overtones could be measured. These were assigned to a linear-symmetric  $I_3^0$  species.

- 218 ENHANCED RAMAN SCATTERING FROM METAL ELECTRODE SURFACES. M. V. Johnston, A. B. Apkarian, B. E. Miller, and R. P. Van Duyne, Department of Chemistry, Northwestern University, Evanston, IL. 60201

Normal Raman spectroscopy usually does not provide enough intensity to study reactions or adsorption dynamics of molecules at electrode surfaces. However, the discovery of the surface enhanced Raman (SER) effect, whereby the Raman scattering efficiency of a molecule near a metal substrate can be amplified by up to six orders of magnitude, has stimulated many new and exciting applications. SER scattering has been definitively reported and confirmed on silver, copper, and gold surfaces. The nature of the metal substrate is found to dramatically affect the observed Raman signals. Comparisons of smooth versus rough surfaces will be made to help clarify the role of surface roughness in obtaining strong signals. Methods to achieve optimal intensities on a given substrate in electrochemical media will also be considered.

- 219 A RAMAN SPECTROSCOPIC ANALYSIS OF VOLCANIC ASH FROM MT. ST. HELENS AND MT. SAKURAJIMA (JAPAN). Hiroyuki Ishizaki and Anthony T. Tu. Department of Biochemistry, Colorado State University, Fort Collins, Colorado 80523.

A Raman spectroscopic investigation of the volcanic ash from Mt. St. Helens (May 18, 1980 eruption) and Mt. Sakurajima in Japan (September 16 and October 2, 1981 eruptions) was made. The Raman spectrum of Mt. St. Helens volcanic ash showed the peaks at 403, 481, 508, 564, 794, 963, and 1602  $\text{cm}^{-1}$ . The bands observed at 508, 794, 963, and 1602  $\text{cm}^{-1}$  were identified as due to the vibrational mode of silica (not free silica), which is the most abundant element in the ash. The Raman bands observed at 564  $\text{cm}^{-1}$  for  $\text{Al}_2\text{O}_3$ , and 403 and 481  $\text{cm}^{-1}$  for  $\text{Fe}_2\text{O}_3$  were also identified. The Raman spectra of volcanic ash from Mt. Sakurajima showed the peaks at 474, 506, 1006, and 1595  $\text{cm}^{-1}$  for the September 16 eruption, and 507, 1007, and 1609  $\text{cm}^{-1}$  for the October 2 eruption, which were identified as due to the vibrational mode of silica. The Raman bands at 563  $\text{cm}^{-1}$  (September 16 eruption) and 560  $\text{cm}^{-1}$  (October 2 eruption) due to  $\text{Al}_2\text{O}_3$ , and 480  $\text{cm}^{-1}$  (October 2 eruption) due to  $\text{Fe}_2\text{O}_3$  were also observed. The Raman bands observed at 627, 662, and 749  $\text{cm}^{-1}$  (September 16 eruption), and 629, 662, and 782  $\text{cm}^{-1}$  (October 2 eruption) may be due to the vibrational mode of both  $\text{Al}_2\text{O}_3$  and silica. Thus, the Mt. Sakurajima volcanic ash from the eruptions of the two separate dates essentially gives identical spectra. When the Raman spectra of volcanic ash from Mt. Sakurajima are compared to that of Mt. St. Helens, there are considerable similarities in the spectra. However, no bands at 452-454, 629, 662, and 1007  $\text{cm}^{-1}$  are observed for Mt. St. Helens volcanic ash, which are probably masked by the high intensity background. By examining many more Raman spectra of other volcanic ash, Raman spectroscopy can be a simple and rapid analytical method which provides an overall fingerprint pattern of the volcanic ash.

- 220 Raman MICROPROBE ANALYSIS OF POLYMERS, CERAMICS, AND CORROSION, Fran Adar, Instruments SA, Inc., 173 Essex Avenue, Metuchen, N.J. 08840

Recent successful applications of Raman microanalysis allowing identification of chemical composition and crystalline phase of polymers, ceramics and corroded metal surfaces will be presented. In all cases the examples are chosen to demonstrate the capabilities of microRaman spectroscopy to provide information not available by other techniques. Differences in crystalline phase of microregions of polymers that reflect differences in thermal history will be documented. Variations in metal-oxygen stoichiometry and crystalline polymorphs have been clearly defined on corroded metallic surfaces. Changes in crystalline phase and chemical composition of ceramics during processing will be documented. There is particular importance in being able to characterize materials composed of light elements, such as BN, where EPMA has not been successful.

221 THE U.S. ENVIRONMENTAL PROTECTION AGENCY ANALYTICAL REFERENCE STANDARDS REPOSITORY FOR TOXIC SUBSTANCES. Robert E. Thompson. Health Effects Research Program, Northrop Services, Inc., P.O. Box 12313, Research Triangle Park, North Carolina 27709.

The Reference Standards Repository of the Health Effects Research Laboratory, was established in 1965 at Perrine, FL as a central source of high-purity pesticide reference standards for the U.S. Public Health Service. Now at Research Triangle Park, NC, under EPA's Environmental Toxicology Division, its services have been extended to all **non-profit** research and monitoring laboratories worldwide. Inventory has continually increased, first including only pesticidal compounds, later those industrial chemicals EPA identifies as "priority **pollutants**", and most recently incorporating the former Beltsville, MD Food and Drug Administration standards repository. Because demand has grown for standardized **materials**, now over 1000 pesticidal compounds and **150 industrial** chemicals are continuously available to over 2600 facilities in 81 countries. Larger quantities of selected **technical-grade** materials for inhalation research, feeding studies, etc., can also be supplied. Emergency service is always provided for pesticide fires, hazardous materials spills and human poisonings. Related services include provision of analytical methodology and quality control manuals. Any relevant technical information is available upon request. All services are totally **free-of-charge**. The modern **laboratory/office** facility encompasses some 5000 square feet and includes all appropriate storage and processing equipment, operated under the strictest of safety protocols. The staff takes pride in routinely shipping materials within 12 hours of receiving requests, and in 1981, responded to 3500 requests, **distributing** over 30,000 standards.

222 **ON-SITE** PESTICIDE DISPOSAL. T. D. Spittler, J.B. Bourke, P. B. Baker, J. E. Dewey, F. Winkler and T. **K. DeRue**. NYS Agricultural Experiment Station, Cornell University, Geneva, NY 14456.

In cooperation with the USDA-Soil Conservation Service, Chemical Control Centers have been installed on many small fruit farms in the **20-300** acre range. These facilities, consisting of a water source, catch basin, leach lines, and pesticide storage, help minimize danger to the worker and damage to the environment in the mixing and filling stages of pesticide spraying operations. In this study a series of surface water and deep soil samples were analyzed to detect any migration or **runoff** of waste pesticides from typical Chemical Control **Centers**. Entomological evaluation of soil biota and monitoring of dermal exposure to pesticides of mixer-applicators took place throughout the 1980 season. No adverse effects as a result of the Chemical Control Centers were **detected**.

223 CALCULATION OF THE DISSOCIATION CONSTANTS FOR A HUMIC ACID SAMPLE BASED ON THE PRESENCE OF ISOBESTIC POINTS IN THE FLUORESCENCE SPECTRUM. M. C. Goldberg and **K. M. Cunningham**. U.S. Geological Survey, P.O. Box 25046, MS **424**, Denver Federal Center, Lakewood, CO 80225.

The fluorescence spectra of humic acid at various pH values are readily available. Some of these spectra, especially those measured on solutions of constant ionic strength, display isobestic points which are an indication that two fluorescence species (presumably an ionized and **un-ionized** form) are in equilibrium. By using this model of the equilibrium and the fluorescent properties of the two species it is possible to calculate an ionization constant for the ionizable moiety of the humic acid. The calculation is an iterative solution of an nth dimensional power function where n is determined by a set of values taken from the fluorescence spectrum at three different pH values. In the case under discussion the ionization content **K<sub>a</sub>** was **3.13 x 10<sup>-9</sup>**. This value agrees with similar constants obtained from the Manning model and related studies.

- 224 CHEMICAL IONIZATION UTILIZING A SINGLE HIGH VACUUM UMP. David E. Smith, Finnigan MAT Corporation, 355 River Oaks Parkway, San Jose, California 95134.

Mass spectrometers usually rely on costly, differential high vacuum pumping when performing chemical ionization (CI). This is necessary because flow rates and ion source pressures required for CI are high relative to the analyzer pressure. A new CI ion source is available that allows for high ion source pressure (~ 1 torr) and low analyzer pressure ( $10^{-4}$  torr) while utilizing a single high vacuum pump. By reducing gas flow rates to the ion source, high sensitivity and good spectral quality chemical ionization can be performed without differential high vacuum pumping. The novel CI ion source design permits analysis by gas chromatography mass spectrometry (GC/MS) using packed or capillary columns, solids probe, direct exposure probe, and batch inlet for gas analysis. There is no limit on the choice of CI reagent gas or combinations of reagent gas for the GC columns or CI ion source other than they be non-oxidizing. Data will be presented on the design of the ion source as well as applications of the different modes of operation utilizing the Finnigan MAT 1020 GC/MS system. Specific analyses include: erythromycin, glucose, adenosine and routine monitoring of biological fluids for drugs and metabolites.

- 225 DISTRIBUTION OF URANIUM AND RADIUM IN RALSTON CREEK AND RESERVOIR, COLORADO. I. C. Yang. U.S. Geological Survey, Water Resources Division, P.O. Box 25046, Mail Stop 407, Denver Federal Center, Lakewood, Colorado 80225; A. M. Essed and K. W. Edwards. Colorado School of Mines, Golden, Colorado 80401.

Contaminated water from uranium mining operations is discharged into Ralston Creek and Reservoir near Golden, Colorado. Samples of water and sediment were collected from this creek and reservoir for uranium and radium-226 analyses. Dissolved uranium concentrations in water were approximately 1,000 micrograms per liter in the creek water and 240 micrograms per liter in the reservoir. Radium-226 concentrations were less than 1 picocurie per liter in both the creek and reservoir waters. For sediment samples, uranium concentrations ranged from 100 to 500 micrograms per gram in dry sediment with greater concentrations in the finer particle-size fractions. Much greater radium-226 concentrations (400-600 picocuries per gram) were found in the suspended materials than in the bottom sediment (40-60 picocuries per gram).

- 226 TOXICITY OF SPENT OIL SHALE LEACHATE TO A BLUE-GREEN ALGA, Diane McKnight, Wilfred Pereira, Colleen Rostad, and Eric Stiles. U.S. Geological Survey, Water Resources Div., 5293 Ward Rd., Arvada, CO 80002.

In the event of the development of the oil shale reserves of northwestern Colorado, large volumes of spent shale will be produced. Leaching of spent shale piles may then effect the water quality of streams in the area. We studied the effect of spent shale leachate on a common blue-green alga, Anabaena flos-aquae. When leachate from spent shale retorted by the Paraho process was mixed with culture medium at a concentration of 4.0 % by volume,  $\text{CaCO}_3$  precipitated and prevented the growth of A. flos-aquae. The same high concentration (40%) of leachate from spent shale retorted by the TOSCO II process, caused a 3-fold decrease in the cellular content of C-phyococyanin; an important pigment in the photosynthetic lamellae system. Further experiments showed that the reduced C-phyococyanin content was not caused by major cations, heavy metals (Mo), or the organic acid (benzoic acid, and 3,5-dimethylbenzoic acid) present in the TOSCO II leachate. At lower concentrations (8% and 0.4%), both leachates had only minor effects on the growth in Anabaena flos-aquae.

227 A COMPUTER ACCESSIBLE COMPENDIUM FOR SELECTED INSTRUMENTAL METHODS. Frank A. Settle, Jr., Dept. of Chemistry, Virginia Military Institute, Lexington, VA 2445G, Michael A. Pleva, Dept. of Chemistry, Washington & Lee University, Lexington, VA 24450.

A series of instructional/information modules containing materials for persons using chemical instrumentation has been developed by the Scientific Instrumentation Information Network and Curricula (SIINC) Project.<sup>1</sup> At the present time modules covering three areas of analytical instrumentation are available on a Burroughs 6800 computer system at VMI and may be accessed through telecommunications terminals. The system provides the user with a basic understanding of the selected instrumental method and references him to more detailed information. Materials can be kept current and the use of individual sections (files) of each instrument module is monitored. Each of the existing modules has been developed by a task force headed by a recognized expert in the instrumental method:

Gas chromatography - Dr. Harold McNair, VPI&SU, Blacksburg.  
Gas chromatography/mass spectrometry - Dr. Frank Karasek, Waterloo University.  
Atomic Absorption Spectroscopy - Mr. Theodore Rains, The National Bureau of Standards.

The modules are composed of files that fall into one of the following general types:  
) How it works, (2) What it does, (3) Nuts and Bolts, (4) Illustrative application, (5) Latest developments. The system will be demonstrated using a video terminal.

<sup>1</sup>Project funded by National Science Foundation Grant # SED-79-19780.

THE U.S. GEOLOGICAL SURVEY QUALITY-ASSURANCE PROGRAM FOR A MULTI-  
228 LABORATORY SYSTEM. D. B. Peart and L. C. Friedman. U.S. Geological Survey, P.O. Box 25046, Mail Stop 407, Denver Federal Center, Denver, Colorado 80225.

Within the multi-laboratory system of the U.S. Geological Survey, the levels of quality assurance for major constituents, trace elements, and some organic constituents involve the analyst, the laboratory manager, and a quality-assurance specialist for the system. On the first level, the analyst is responsible for performing routine quality-control procedures. Secondly, the laboratory manager and his staff use computerized data processing to review each analytical report and to maintain an "in-house" program using Standard Reference Water Samples. At the third level, the quality-assurance specialist for the system, working independently of any individual laboratory, uses reference materials to document the quality of data produced by the laboratories.

CHEMICAL CHARACTERIZATION OF RETORTED OIL-SHALE LEACHATES.  
229 S. M. Johnson and T. R. Steinheimer, U. S. Geological Survey, Box 25046, MS 407, Denver Federal Center, Lakewood, Colorado 80225, C. L. Grant and S. J. Endersen, Dept. of Chemistry, University of New Hampshire, Durham, New Hampshire 03824-3598, and F. J. Trujillo, Chemistry Dept., University of Antioquia, Medellin, Columbia, S. A.

Retorted oil-shale (ROS) is an unusual solid waste from a geochemical viewpoint, and, therefore, prediction of potential water-pollution impacts requires much new information. ROS contains (a) several classes of organic compounds, (b) high concentrations of alkali and alkaline-earth metals, and (c) several trace metals which may serve as catalysts for various organic reactions. When water infiltrates ROS, dissolved-solids concentrations in the resulting leachate increase rapidly to excessively high values and the pH can be as great as 12. This study provides extensive analytical data on the composition of aqueous leachates obtained with ROS samples from a 50-year-old retorted shale pile generated by the U. S. Bureau of Mines-Ruisson Project. Batch extractions were performed in polyethylene bottles with a reciprocating shaker operated at 90 cycles/min times ranging from 0.5 to 72 hrs. Distilled water was the extractant and 1-10 solid-to-liquid ratio generally was used. Leachate was separated from solids by vacuum filtration on 0.45-um membrane filters. Metal analyses were performed by ICP and AAS and anion analyses by ion chromatography and titrimetric methods. Organic extracts and prepared in glass and analyses made by HPLC, GC-FTIR, and GC-MS. The data are discussed from the perspective of weathering processes and rates and potential water-pollution impacts.

230 Abstract not available

- 231 PRODUCTS OF GAS PHASE ALKENE-OZONE REACTIONS.  
C. Rusik, L.A. Hull. Union College, Department of Chemistry, Schenectady, NY 12308

The reactions of several alkenes with ozone in the gas phase have been studied. The products of reaction of tetramethylethylene (TME) and ozone were studied in the concentration range 10-800 ppm for both alkene and ozone under conditions of both excess alkene and excess ozone. With either component in excess the  $[TME\ consumed]/[ozone]$  was about 0.8-0.9. The  $[acetone\ produced]/[TME\ consumed]$  varied from 0.1-0.35 in excess ozone to 0.9-1.6 in excess alkene. Products of the gas phase reactions of alpha-pinene and beta-pinene and ozone were also studied in a flow system. A combination of GC/MS, NMR and chemical synthesis were used to identify some of the products.

- 232 CHARACTERIZATION OF ORGANIC COMPOUNDS IN GROUND WATER CONTAMINATED BY COAL-TAR WASTES USING GAS CHROMATOGRAPHY-MASS SPECTROMETRY-COMPUTER TECHNIQUES. C. E. Rostad and W. E. Pereira. U.S. Geological Survey, P.O. Box 25046, Mail Stop 407, Denver Federal Center, Denver, Colorado 80225.

In order to have a detailed understanding of the origin, transport, and fate of organic contaminants in ground-water systems, first it is essential to have a thorough knowledge of the chemistry of the organic compounds involved as well as the geochemistry of the subsurface environment. In 1978, the U.S. Geological Survey began a series of studies to obtain a comprehensive understanding of the movement and fate of coal-tar derived organic compounds through ground water in St. Louis Park, Minnesota. Operation of a coal-tar-distillation and wood-preserving facility between 1918-72 resulted in extensive ground-water contamination in the area. A ground-water sample from the site consisted of two phases, a lower oily-tar phase and an upper aqueous-fluid phase. The aqueous phase was separated from the oil phase by filtration, and fractionated into acid-neutral and base fractions by pH adjustment followed by solvent extraction. The acid-neutral fraction was fractionated further by adsorption chromatography using a silica-gel microcolumn. Separation and definitive chemical characterization of the organic compounds were accomplished using fused-silica capillary gas chromatography-mass spectrometry-computer techniques. Classes of compounds identified included alkanes, aromatic and polycyclic aromatic hydrocarbons, phenols and alkylated phenols, aromatic amines, and azaarenes. Twelve aromatic amines and azaarenes were quantitatively determined. The persistence, toxicity, and environmental impact of some of these compounds will also be discussed.

- 233 HARMONIC FORCE FIELD AND MEAN AMPLITUDES  $C_4Cl_4$  AND  $C_4F_4$  COMPOUNDS.  
Guillermo Diaz, Academia Superior de Ciencias Pedagógicas de Valparaíso.  
Sección Química. Casilla 34-V Valparaíso, Chile.-

Normal coordinate analysis of  $C_4Cl_4$  and  $C_4F_4$  has been carried out on the basis of general valence force field, using Wilson's FG matrix method. Approximate vibrational frequencies are calculated from very simple force field and used as an aid in tentative assignments of observed frequencies from literature. Next the force fields are refined by adjustments to the experimental bands assigned as fundamentals. The final force fields have been used to calculate the mean amplitudes of vibration for both molecules, according to well-established methods. The force constants obtained give an accurate description of the normal modes of vibration in terms of the potential energy distribution matrix (PED), and the calculated mean amplitudes of vibration seem to have reasonable values which are considered characteristics in a large number of polyatomic molecules.

- 234 RAMAN SPECTRAL STUDIES OF RARE EARTH PHOSPHATES, G. M. Begun and C. E. Bamberger.  
Chemistry Division, Oak Ridge National Laboratory, P.O. Box X, Oak Ridge, TN 37830.

Raman spectra of rare earth phosphates have proven to be very useful in studying the purity and reactions of these compounds. Characteristic Raman spectra of all the lanthanide ortho- and trimeta-phosphates have been observed. The frequencies of the phosphate stretching vibrations of the orthophosphates were found to increase systematically with atomic number of the lanthanide while the increases observed with the trimeta-phosphate salts were quite small. The presence of small amounts of oxide could be detected by observation of their strong Raman bands at levels considerably below those detectable by X-ray diffraction measurements. Various methods of preparation were found to lead to different proportions of ortho to trimetaphosphate as shown by the Raman spectra of the samples. The ignition at 1200°C of samples formed by the precipitation of Ce(IV) from nitric acid solutions with phosphate ion showed that precipitates with  $\text{PO}_4/\text{Ce} > 1$  yielded products consisting of  $\text{CePO}_4$  and  $\text{Ce}(\text{PO}_3)_3$ . The ratio of these two compounds depended on the ratio of  $\text{PO}_4/\text{Ce}$  and also on the temperature and duration of heating since  $\text{P}_2\text{O}_5$  is volatilized during extended heating above 1100°C. Reversibility of the reaction  $\text{CePO}_4(\text{c}) + \frac{1}{2}\text{P}_4\text{O}_{10}(\text{g}) \rightleftharpoons \text{Ce}(\text{PO}_3)_3(\text{c})$  was also confirmed by Raman spectral observations.

\*Research sponsored by the Division of Material Sciences of the Office of Basic Energy Sciences, U.S. Dept. of Energy under contract W-7405-eng-26 with Union Carbide Corporation.

- 235 MASS SPECTROMETRIC STUDY OF PYROLYSIS BEHAVIOR OF SOLID FUELS. M.N. Soltys and T.A. Milne, Solar Energy Research Institute, 1617 Cole Boulevard, Golden, Colorado 80401.

A new pyrolysis/analytical system will be described which permits the primary and secondary molecular processes of pyrolysis of solid fuels (eg. wood) to be observed in real time, under conditions that simulate those in practical systems. This is achieved by using a burner system that produces hot steam/argon to heat solid samples suspended in the flame gases. A direct, free-jet, molecular beam mass Spectrometric sampling system is used to rapidly quench and obtain mass spectra of both condensible and non-condensable gases. Typical data will be shown for the primary pyrolysis products of cellulose, lignin, wood, coal and oil shale and for the secondary cracking of tars and oils from cellulose. Identification of many of the primary pyrolysis products will be shown.

- 236 INDUCTIVELY COUPLED PLASMA EMISSION SPECTROSCOPIC DETERMINATION OF METALS IN PRECIPITATION. M. M. Reddy, Marilyn Werner, and E. J. Zayhowski, U. S. Geological Survey, 2593 Ward Road, Arvada, Colorado 80002.

Determination of metal concentrations in atmospheric precipitation plays an important role in assessing the impact of acid inputs to terrestrial ecosystems. Inductively coupled plasma emission spectroscopy offers the potential of automated, accurate, and reproducible determinations for the constituents of interest at concentration levels encountered in precipitation from remote areas. In the work reported here precision, accuracy and limits of quantitation (Anal. Chem. 52, 2242-2249, (1980)) for simultaneous determination of 17 metals in precipitation will be discussed. Standard reference water samples (SRWS) prepared by the United States Geological Survey, Water Resources Division, have been particularly useful in the program. Samples analyzed included a dilute surface-water reference sample, a precipitation reference sample, and precipitation from several remote sites in central and southwestern Colorado. Optimum precision, expressed as relative standard deviation (in percent), for major metals was 5 percent or less. Trace metals typically exhibited relative standard deviations of greater than 10 percent. Analysis of a low ionic-strength standard reference sample yielded concentration values well within one standard deviation of the mean value. Results of this investigation support incorporation of appropriate reference materials in a quality-assurance program for determination of metals in precipitation.

- 237 Title: Thermal Analysis Methods at Rocky Flats Authors: Pat Hyman and Judy Palcic  
Rockwell International, P. O. Box 464, Golden, CO 80401

A pictorial and graphic representation of the thermal analysis techniques used at Rocky Flats Analytical Laboratories will be presented. Photos and text will illustrate and describe the thermal instrumentation available in the labs. Typical data output will be illustrated for thermo gravimetric analysis (TGA), differential thermal analysis (DTA), differential scanning calorimetry (DSC), and thermal mechanical analysis (TMA).

- 238 CHLORINATED HYDROCARBONS IN PETROLEUM PRODUCTS BY GAS CHROMATOGRAPHY/  
HALL ELECTROLYTIC CONDUCTIVITY DETECTOR. M. P. Phillips and O. J. Logsdon. Rocky  
Mountain Analytical Laboratory, 5530 Marshall Street, Arvada, Colorado 80002.

The Hall Electrolytic Conductivity Detector (HECD) can be used as a specific detector in gas chromatography (GC) for trace quantities of halogen, sulfur, nitrogen or ester-containing compounds. Typical applications of the HECD have been in the areas of pesticide, herbicide and nitrosamine analysis. Chief advantages of this detector are its high degree of selectivity and wide linear dynamic range. These characteristics allow analysis of complex sample matrices with a minimum of sample preparation and interferences. An example is the use of the HECD in the halogen-specific mode to detect the presence of chlorinated solvents in petroleum products. The HECD is particularly suited to this analysis because of its extreme selectivity for halogenated species over hydrocarbons and sulfur-containing components. This analysis is important in the refining industry because the presence of chlorinated compounds can lead to problems such as poisoned catalysts used in refining processes and increased corrosion of cooling towers. A description of this type of analysis applied to crude oils and reclaimed oils will be presented. Sample preparation is extremely simple, consisting of a single 1 to 10 dilution in dodecane to decrease the viscosity of the sample before injection into the GC/HECD.

- 239 DETERMINATION OF TOTAL IODINE IN FOODS AND NUTRITIONAL PRODUCTS BY DIFFERENTIAL  
PULSE POLAROGRAPHY. D. Thompson, S. Lee, R. Locatelli, S. Subramanian and  
R. Allen, Forrest C. Shackle Research Center, 1992 Alpine Way, Hayward, CA 94545

Total iodine was determined in several foods and nutritional products by a differential pulse polarographic procedure. Recoveries of 97% and a precision of 4.7% were found in the analysis of vitamin-mineral nutritional supplements. Samples analyzed by this technique include: Sea Kelp, non-fat dry milk, whole milk, whey protein concentrate, soy protein isolate, fortified nutritional supplements, high protein fortified food bars, meal replacement products, and whole grain cereals. The procedure appears well suited for routine analysis of a wide variety of nutritionally significant samples.

- 240 DETERMINATION OF SELENIUM IN HUMAN AND QUARTER HORSE BLOOD BY HYDRIDE GENERATED AND  
GRAPHITE FURNACE ATOMIC ABSORPTION SPECTROPHOTOMETRY, Vili A. Fuavao, Britt L. Porter  
and Joseph Sneddon, Department of Chemistry, New Mexico State University, Las Cruces,  
New Mexico 88003.

The development of a hydride generated atomic absorption method for the determination of selenium in human and quarter horse blood will be described. Blood samples are digested in a mixture of nitric and perchloric acids and selenium is generated by a solution of sodium borohydride. The selenium is then analyzed in an air-acetylene flame. Calibration is achieved by aqueous standards. The method was compared to a graphite furnace atomic absorption method which involved the addition of nickel to allow an ashing stage of 1000 C to be used. Good correlation between the methods was obtained. Results of both methods will be presented.

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OPTIMUM DATA REDUCTION FOR THE CHROMATOGRAPHIC LABORATORY

DAVID E. BODWELL and MICHAEL HARTER, The Perkin-Elmer Corporation,  
Main Avenue, Norwalk, Connecticut 06856

When choosing the proper instrumentation for chromatographic data reduction, one must account for the factors involved and its ultimate use. Chromatographic factors include the number of instruments for which data reduction is required, the type of calculations required, and the complexity of the data to be analyzed. Chromatography data handling systems rely on the real-time integration, and some of them allow a limited form of recalculation of the stored data. The new system described in this paper has been designed with full flexibility in mind and allows the user to interact with the system to a level never achieved in previous instrumentation.

The use of an intelligent terminal with built-in storage capability, floppy disk, and user programmability allows even complex chromatograms to be stored in memory and on microfloppy disk, displayed as chromatograms on the screen, and reintegrated. This system is ideally suited for those laboratories that require the most advanced integration capabilities and run analyses of a different nature that are now very difficult because of an inability to preoptimize parameters before injection of the sample. This system also has the ability to archive and retrieve chromatograms from a micro-floppy disk system which is incorporated into the terminal giving an even greater flexibility than has been available in previous chromatography systems. The architecture and the use of this new system will be described in this paper.

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A COMPUTER CONTROLLED ACQUISITION SYSTEM FOR ATOMIC ABSORPTION DATA,  
Robert L. Bostrom, Kansas Department of Health and Environment, Office  
of Laboratories and Research, 74 Forbes Field, Topeka, Kansas 66620.

Since the introduction of the microprocessor a few years ago, there has been great interest in the development of automated, microprocessor controlled, data acquisition devices. These devices should, theoretically, free the analyst for more worthwhile pursuits and manipulate the great volume of data produced by laboratory instrumentation. This paper discusses the data acquisition system and software developed by the Kansas Department of Health and Environment for acquiring data in the Air Quality Laboratory from a PerkinElmer 61 5000 flame atomic absorption spectrophotometer using a DEC miniVAX microcomputer. The Air Quality Laboratory is responsible for the analysis of filters obtained from high volume air samplers located across the state and reports the results to the Kansas Bureau of Air Quality. The laboratory performs eighteen analyses, twelve of which are performed on the flame atomic absorption spectrophotometer. In addition, the paper describes plans for the interfacing of a Perkin Elmer Model 306 spectrophotometer fitted with an EA 500 graphite furnace and a Dionex System 12 ion chromatograph to the same computer.

243 THE COULOMETRIC DETERMINATION OF MOISTURE AND COMBINED WATER IN SILICATE ROCKS USING THE KARL FISCHER TITRATION METHOD. Daniel R. Norton. U.S. Geological Survey, Box 25046, MS 923, Denver Federal Center, Denver, Colorado 30225.

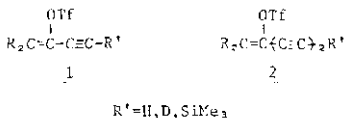
A study is presented of the coulometric determination of moisture and combined water in silicate rocks using the Karl Fischer titration method. Moisture is released from the samples at 105°C, and the combined water is released with the aid of a flux at 900°C. Dry nitrogen is used as a carrier gas to drive the water into the Karl Fischer reagent contained in the titration cell. In the presence of the reagent, water reacts quantitatively with coulometrically generated iodine. The instrument selected for this study allows for the rapid and accurate determination of moisture and combined water through an automated titration system using controlled electrolysis current and blank compensation. The accuracy and precision of this method are comparable to those of the Penfield method used in classical rock analysis. The advantages of this method are the substantially reduced analysis time and sample size. Data are presented on U.S. Geological Survey and National Bureau of Standards reference materials, and on various types of rocks that were previously analyzed by the Penfield method.

244 THE USE OF BONDED PHASE EXTENDED COLUMNS FOR RAPID SAMPLE PREPARATION OF PRIORITY POLLUTANT PHENOLS IN WATER. Philip A. Mason and Lane S. Yago. Analytichem International, Inc., 24201 Frampton Ave., Harbor City, California 90710

Representatives from various classes of phenols were evaluated as to their retention and elution behavior onto and off of several bonded phases such as octadecyl, octyl, phenyl, cyanopropyl, cyclohexyl among others. Typical examples of compounds screened were phenol, 2-4 dinitrophenol, 2-4 dichlorophenol, and pentachlorophenol. Retention and recovery data are discussed. Analysis was by High Performance Liquid Chromatography with Electrochemical Detection using a glassy carbon electrode.

245 SOLVOLYSIS OF 1-BUTADIENYL VINYL TRIFLUOROMETHANESULFONATES. Mladen Ladika and Peter J. Stang, Department of Chemistry, University of Utah, Salt Lake City, Utah 84112, and Melvyn D. Schiavelli and Michael Hughey, Chemistry Department, College of William and Mary, Williamsburg, Virginia 23185.

The solvolytic reactivity of various 1-butadienyl vinyl triflates **2** was investigated in aqueous ethanol and 2,2,2-trifluoroethanol (TFE). Activation parameters, solvent  $\rho$  values and deuterium isotope effects were determined for compounds **2** and compared with corresponding parameters for 1-ethynyl vinyl triflates **1**.



For  $\text{R}=\text{CH}_3$  and  $\text{R}'=\text{H}$ , ester **2** solvolyzes in 60% EtOH 2.1 times faster than **1**, and both compounds show almost the same isotope effects of 1.05 and 0.94 in 60% EtOH and 97% TFE respectively.

- 246 EFFECT OF STRONG COMPLEXING AGENTS ON RESPONSE OF PRECIPITATE-BASED COPPER (II) ION-SELECTIVE ELECTRODES. Garon C. Smith and Patrick MacCarthy, Dept. of Chemistry and Geochemistry, Colorado School of Mines, Golden, Colorado 80401.

Copper (II) ion-selective electrodes possessing a precipitate-based membrane exhibit confounding behavior in the presence of strong complexing agents. Potentiometric titration studies have been conducted to characterize the copper (II) electrode response to three polyamine chelating reagents (en, trien and tetren) and four polyamino-polycarboxylic acids (EDTA, HEDTA, CDTA and DTPA). As noted by past workers, response behavior is markedly affected by the specific complexing agent used, the concentration of complexing agent present and the pH of the solution. In the present studies titration curves of trien and tetren manifest inflection points corresponding to complexes of unreported stoichiometries. EDTA and its analogs improve the detection limit of the electrode but yield limited stability constant information for measurements made in the presence of a moderate excess of either ligand or metal ion. In the absence of cupric ions, electrode response is very slow. Up to eighty minutes are required for the electrode to reach equilibrium with solutions of various ligands. Accepted literature values for the stability constants of complexes expected in these systems have been employed to generate equivalent titration curves with a computer model for comparison with the experimentally measured curves.

- 247 ANALYTICAL EVALUATION OF CORROSION-INDUCED MICROSTRUCTURAL CHANGES IN A U. S. CORE GRAPHITE. D. A. Lee, W. P. Eatherly,\* J. D. Kintigh. Analytical Chemistry Division, Oak Ridge National Laboratory,† P. O. Box X, Oak Ridge, Tennessee 37830.

Great Lakes-grade graphite for the high-temperature gas-cooled reactor (HTGR) has been submitted to oxidation testing to simulate the effect of an inleakage of moisture in the secondary helium coolant flowing in the HTGR. The analytical techniques used to characterize oxidation effects upon the pore structure of the graphite include BET surface area analyses by nitrogen adsorption at 77°K, helium pycnometry, and mercury porosimetry. Changes in accessible and inaccessible void volumes with oxidation of the graphite by water vapor in helium at 900-1000°C were demonstrated. Significant changes in BET surface areas were also noted as the oxidation increased. Changes in pore-size distributions were determined from gas adsorption and mercury porosimetry isotherms. Evidence of catalytic oxidation was noted. The surface area and helium pycnometer apparatus is a fully automated system controlled by an HP9835A microcomputer. The computer also processes the data, stores it on tape, calculates the surface areas and helium densities with appropriate statistics, prints hardcopy, and plots isotherms using an HP9872A plotter. Mercury porosimetry data are also processed by the computer, and pore distribution curves are charted by the plotter.

\*Metals and Ceramics Division, ORNL.  
†Oak Ridge National Laboratory is operated by Union Carbide Corporation for the U. S. Department of Energy under contract W-7405-eng-26.

- 248 APPLICATIONS OF STABLE ISOTOPE MASS SPECTROMETRY IN CLINICAL MEDICINE. P.V. Fennessey, Department of Pediatrics and Pharmacology, University of Colorado, Boulder, CO 80306.

Stable isotopes, particularly those of hydrogen, carbon and oxygen have found an important place in human research. They offer an attractive alternate to radioisotopes because of the lower risk to children and adults of reproductive age. Because of the sensitivity of radioisotope analyses these risks were set aside as there were no other reasonable alternative methods. GC/MS and selected ion monitoring techniques have recently been proven to be a competitive approach In the diagnosis of many disease states. As more investigators have become involved in these techniques an additional benefit, namely, the price of compounds labeled with stable isotopes have been reduced and the variety of compounds that can be used in this type of research has increased.

We will present examples of the use of stable isotopes in the diagnosis of disease, in the measurement of the kinetics of basic biochemical pathways and in the absorption and distribution of trace metals in the newborn. Comparisons to accepted diagnostic techniques will be made wherever possible.

- 249 FAST ATOM BOMBARDMENT MASS SPECTROMETRY IN BIOMEDICAL RESEARCH. K.L. Clay and R.C. Murphy, Department of Pharmacology, University of Colorado, Boulder, CO 80306.

Fast atom bombardment is a new technique in mass spectrometry involving secondary ion production from a glycerol solution surface following impact of accelerated atoms at almost glazing angles. Already this technique has found wide application in the analysis of nonvolatile, thermally unstable biomolecules of relatively high molecular weight. This technique has been used to verify the covalent structure of leukotriene C<sub>6</sub> as 5-hydroxy-6-(S-glutathionyl)-7,9,11,14-eicosatetraenoic acid.

The results of a study of the relative intensities of ions produced in the FAB experiment from various molecules including phospholipids, sulfuric acid esters, carbohydrates, nucleotides, and peptides has been carried out on eight different FAB mass spectrometers in various laboratories in the United States. The variations in the observed spectra will be presented as well as evaluation of the interlaboratory reproducibility of FAB mass spectra.

- 250 CHEMICAL IONIZATION UTILIZING A SINGLE HIGH VACUUM PUMP. David E. Smith, Donald Remling, Finnigan MAT Corporation, 355 River Oaks Parkway, San Jose, California 95134.

Mass spectrometers usually rely on costly, differential high vacuum pumping when performing chemical ionization (CI). This is necessary because flow rates and ion source pressures required for CI are high relative to the analyzer pressure. A new CI ion source is available that allows for high ion source pressure (~1 torr) and low analyzer pressure (<10<sup>-4</sup> torr) while utilizing a single high vacuum pump. By reducing gas flow rates to the ion source, high sensitivity and good spectral quality chemical ionization can be performed without differential high vacuum pumping. The novel CI ion source design permits analysis by gas chromatography mass spectrometry (GC/MS) using packed or capillary columns, solids probe, direct exposure probe, and batch inlet for gas analysis. There is no limit on the choice of CI reagent gas or combinations of reagent gas for the GC columns or CI ion source other than they be non-oxidizing. Data will be presented on the design of the ion source as well as applications of the different modes of operation utilizing the Finnigan MAT 1020 GC/MS system. Specific analyses include: erythromycin, glucose, adenosine and routine monitoring of biological fluids for drugs and metabolites.

- 251 isotope CLUSTER program used TO selectively characterize mass spectral data. Abrams, Linda, Paul p. Dymerski, O. H. Materials Company, p.o. Box 551, Findlay, OH 45840.

The computer program isotop is a rapid method of sorting GC/MS data of halogenated compounds. It readily identifies the presence of characteristic halogen isotope clusters in their mass spectra. The natural isotope abundance ratios M, M+2, and M+4 at each mass fragment in the mass spectrum is compared to an "Isotope Table" and, if similar, the peak is flagged and placed in a new scan list. Survey parameters are under the complete control of the analyst. These include the scan list searched, mass range of process, minimum intensity of mass to search and allowed tolerance range between mass ratios within each cluster.

With this program, detection of halogenated compounds in a data file containing some 300 scans to be library searched is reduced from several hours of data processing to 10 minutes. Halogenated compounds missed by normal library searches due to overlapping and coeluting non-halogenated compounds are found by isotop as well as those missed by Biller-Biemann searches. Complex matrices, such as environmental samples, can be quickly analyzed for the presence of halogenated compounds.

The full capability of isotop will be discussed, including searching of other compound classes, such as polynuclear aromatics (PNA's).

252 Discharge **onization/Secondary** Ion Mass Spectrometry **Analysis** of Biologically Important **Compounds**. **David E. Smith**, Donald **Remling**, Finnigan MAT **Corporation**, 355 **River Oaks Parkway**, San Jose, **California 95134**.

Most ionization techniques in mass spectrometry (MS) require that the sample be vaporized prior to ionization. The energy required for the **vaporization** is often greater than the energy required for thermal degradation. Thus, thermally labile compounds are not usually amenable to mass **spectrometri** analysis by electron impact or chemical ionization MS or **GC/MS**.

An ionization technique that does not require vaporization of the sample has been developed and received extensive attention in the last few **years**. This technique relies on a beam of fast neutral atoms to bombard the sample and produce ionization prior to volatilization. Volatilization occurs with little heat generation, thus thermally labile **compounds** exhibit little thermal **fragmentation**. Finnigan MAT has adopted this technique to the 4500 and triple stage **uadrupole (TSQ™) GC/MS** systems in the form of discharge **ionization/secondary** ion mass spectrometry (**DISIMS**).

**DISIMS** analysis of peptides, ionic surfactants and other polar biologically important compounds will be discussed. Analysis of compounds in the 1000-1800 molecular weight range with a Finnigan MAT **quadrupole GC/MS** will also be **presented**.

253 **CHARACTERIZATION OF HETEROGENEOUS METAL CHELATE REACTIONS BY GC/MS**. **W.C. Gorman, Jr.** and **R.K. Skogerboe**, Department of Chemistry, Colorado State **University**, Fort **Collins**, CO 80523.

Recent emphasis in the **analysis** of trace metals has focused on reduction on the amount of time **spent** on sample **preparation**. One area of focus has been the use of volatile **metal** chelate reactions. An understanding of the parameters involved in **metal** chelate formation will be developed using an on-column GC reactor with detection by mass spectrometry.

254 **PLASMA DISCHARGE MASS SPECTROMETRY**. **P.J. Turner**, E. Hall, and J. E. **Cantle**. VG Isotopes **Ltd.**, Winsford, Cheshire, England.

An **assessment** of the present state of two types of plasma discharge mass spectrometers will be presented.

In the first **type**, the plasma used to produce sample **ionisation** is an atmospheric inductively coupled argon system, similar to that used in atomic emission spectroscopy. However, in this case, the ions produced are directly sampled by a quadrupole mass spectrometer and ion counting system to give a measure of the concentrations of the components in the sample. Data available indicates that levels down to parts per billion may readily be measured, that relative sensitivity variations are small and sample throughput is rapid.

The other type of plasma which will be considered is the low pressure DC argon discharge. When suitably configured, neutrals sputtered from the cathode are subsequently ionised in the discharge, and these ions may be analyzed in a mass spectrometer, usually a magnetic sector type. This technique may be a simple alternative to the spark source mass spectrometer, offering relatively low sensitivity variation between elements and a capability of looking at the parts per billion level in solid samples.

Both techniques are capable of modest measurements of isotope **ratios**.

255 **ENRICHED STABLE ISOTOPES AS INTERNAL STANDARDS**. **S.H. Cole** and **P.H. Hemberger**, Oak Ridge **Y-12 Plant(a)**, P.O. Box Y, Oak Ridge, Tennessee 37830.

Mass spectrometric **methodology** for the quantitative determination of trace and bulk **substituents** in metal alloys is described. Standard solutions with varying concentrations of an isotopically normal element were spiked with a constant quantity of the isotopically enriched element. An isotopic ratio was measured by HV peak switching with an automated **single-focusing** mcs spectrometer. The dependence of the isotopic ratio upon the concentration of the element in the standard solution was used to quantify the element in a spiked unknown **sample**. Analyses of different elements ranging in concentrations from ppm to bulk **matrix** levels are discussed. Statistical analyses of the results are presented with comparisons to other **methods** of analysis.

256 A CONVERSION AND APPRAISAL OF A THERMAL IONIZATION INSTRUMENT TO A FIELD CONTROL SYSTEM. Vincent E. Connolly, New Brunswick Laboratory, **USDOE**, 9800 So. Cass Avenue, **Argonne**, Illinois 60439.

In older *mass spectrometers*, high voltage, current-controlled magnet systems present problems for peak-stepping analysis schemes **due** to magnet hysteresis, limited relay switching systems and frequent repairs of tube-type magnet supplies. A 30cm, 90° magnet sector **NBL** instrument was converted from a current-controlled system to a low voltage, solid state, field control system. The new **system** is directly interfaced to a minicomputer via a full range digital-to-analog converter. Details of the program control, system performance, and data evaluation will be presented.

257 Abstract not available

258 CONTAMINATION, INTERFERENCES AND MEMORY EFFECTS IN THE DETERMINATION OF ISOTOPIC RATIOS BY VOLATILE METAL CHELATE-MASS SPECTROMETRY TECHNIQUES. S.R. Hill and R.K. Skogerboe, Department of Chemistry, Colorado State University, Fort Collins, CO 80523. F.E. Lichte, U.S.G.S., Denver, CO 80225.

Volatile metal chelates suitable for isotopic ratio determination by mass spectrometric techniques may be formed by the reaction of the metal salt with TFA and HFA ligand. This methodology suffers from three major problems. These are:

1. the contamination of the isotopically enriched sample with naturally occurring metal (i.e. from glassware and handling);
2. the biasing of the isotopic ratio due to mass spectral **interferences**; and,
3. the past history of the instrument influencing each subsequent ratio determination.

A technique will be presented to estimate the contribution to the isotopic ratio from contamination and/or **interferences**. The nature of the "memory effect" will be examined in **detail**. Methods for correcting data and for eliminating the problem will also be discussed.

259 DYNAMIC MASS SPECTROMETRY - A RESIDUAL GAS ANALYSIS METHOD AND SOME APPLICATIONS. Tom L. McFeeters- Rockwell International, Energy Systems Group, Rocky Flats Plant, P.O. Box 464, Golden, Colorado 80401.

A mass **spectrometric** residual gas analysis method based on **flowrate** sensitivities is briefly described. Several industrial process-oriented applications and case histories with emphasis on vacuum brazing processes are briefly presented.

260 Abstract not available

261 Abstract not available

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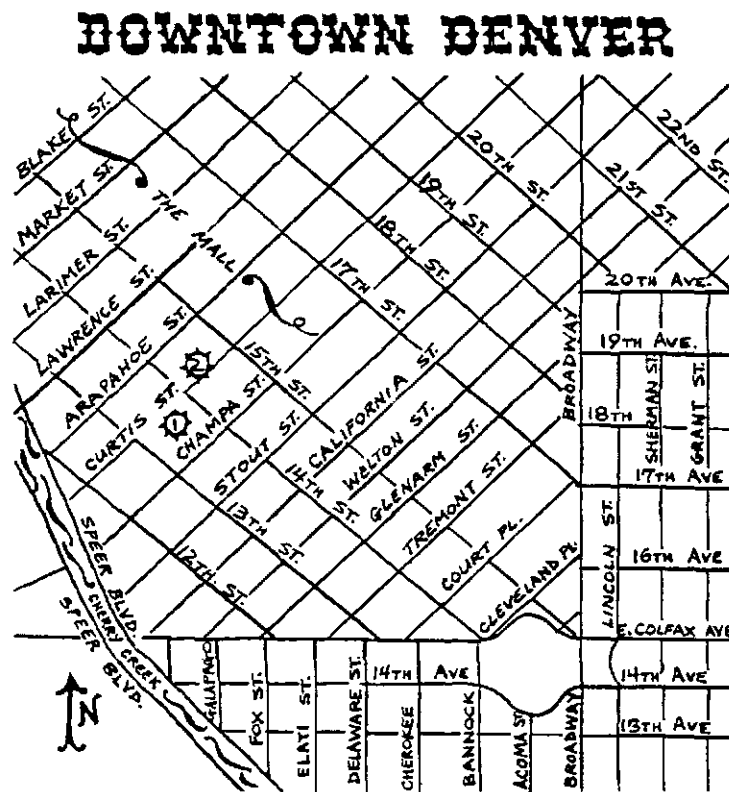
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