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22nd Rocky Mountain Conference on Analytical Chemistry

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22nd Rocky Mountain Conference on Analytical Chemistry

Abstract

Abstracts and meeting program from the 22nd annual meeting of the Rocky Mountain Conference on Analytical Chemistry, 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 10-14, 1980.

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Publication Statement

tracts and Meeting Program

22ND ROCKY MOUNTAIN CONFERENCE ON ANALYTICAL CHEMISTRY

Sponsored jointly by

Rocky Mountain Section Society for Applied Spectroscopy	and	Rocky Mountain Chromatography Discussion Group

DENVER CONVENTION COMPLEX

Denver, Colorado

August 10-14, 1980

ROCKY MOUNTAIN CONFERENCE
WISHES TO THANK THE COMPANIES
WHO PROVIDED FUNDS TOWARD THE
PRINTING OF THIS PROGRAM BOOK.

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WELCOME CONFEREES

I am delighted to welcome you to the 22nd Rocky Mountain Conference on Analytical Chemistry.

The Conference this year has proven to be the largest yet, with over 250 papers to be presented and the Atomic Spectroscopy Symposium has been greatly expanded from the preliminary program. My most humble apology is extended to those authors who we omitted in the preliminary program. Please check this directory for the most up to date information on the talks you wish to attend.

This year we also have over 50 poster paper sessions and you can have one-to-one technical conversations with the authors while they are present. We are also pleased to host the Third Annual International E.P.R. Symposium.

The theme for our Conference banquet is a lighthearted one. Mr. Ron Ruhoff will provide a refreshingly different look at the Colorado wilderness in his presentation of "Colorado Adventure Trails." I hope you are there to enjoy the evening with us.

Thanks to all attendees, presenters and backstage coordinators for helping to make this Conference a success.

We have an added attraction of several energy exhibits. These exhibits are sponsored by the following organizations; Laramie Energy Research Center, Rockwell International, Sandia Laboratories, and Los Alamos Scientific Laboratories.

A great big thanks is also extended to the exhibitors who participated, because without their financial support we could not present such a fine program.

Sincerely,

Jerry R Turbett

Jerry R. Turbett
Conference Chairman

REGISTRATION HOURS AND LOCATION

Sunday	August 10	Executive Tower Inn	4:00 pm - 8:00 pm
Monday	August 11	Denver Convention Complex	7:30 am - 3:30 pm
Tuesday	August 12	Denver Convention Complex	7:30 am - 3:30 pm
Wednesday	August 13	Denver Convention Complex	7:30 am - 3:30 pm
Thursday	August 14	Denver Convention Complex	7:30 am -11:30 am

Registration at the Executive Tower Inn is located in the main lobby. Registration at the Denver Convention Complex is located on the first floor in the lobby on the Champa Street entrance (doorway under the bridge). Plan to register early and avoid the lines.

REGISTRATION FEES

Registration	$30.00
Registration one day only	$15.00
Students	$10.00
Unemployed or retired chemists	No Charge

Badges are required to attend all technical programs and the exhibit area. Those not wishing to attend technical meetings can obtain "exhibit area only" badges. All Conference attendees are invited to a free mixer on Monday, August 11, from 5:30 pm to 8:00 pm at the Executive Tower Inn.

SOCIAL FUNCTIONS

The Conference banquet for Conference attendees will be held Tuesday, August 12 at 7:00 p.m. in the Executive Tower Inn. Conference banquet attendees will be treated to an outstanding after dinner program from Ron Ruhoff's collection of "Photomusical Adventures" titled "Colorado Adventure Trails". Cost is $11.00 per person.

For over 20 years, Ron Ruhoff has been on a "grand tour" of the West. In the process, he has captured on film a monumental assortment of scenes. Many of his photographs have appeared in books and magazines and on calendars and postcards. His shows have been popular with Colorado audiences for many years and include performances on television and with the Denver Symphony Orchestra. The program which he will present is called "Colorado Adventure Trails". Ron leaves the beaten path and travels by Jeep, horse, airplane, rubber raft and narrow gauge railroad. Besides these "conventional" means of transportation, he utilizes a snowmobile, dog sled, and even snowshoes to reach the fascinating places far back in the Colorado Rockies.

The Conference has arranged for group tickets to the Wednesday, August 13th evening performance of "The Best Little Whorehouse in Texas." Reviewers have termed this play the hit musical of the year. Tickets are $12.00 each and must be paid in advance.

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. It will be only for incoming calls. There are numerous pay phones in the Conference complex for outgoing calls.

SOCIETY FOR APPLIED SPECTROSCOPY STUDENT AWARD

The Society for Applied Spectroscopy's annual student award recipient for 1980 is Alan J. Hurd. Alan is a student at the University of Colorado in the Department of Physics. Alan will present an award address Monday, August 11 in Room E on the second floor at 9:00 am. Alan's paper is titled "A Light Scattering Study of Contrained Brownian Motion".

TOURS

A visit to the Regional NMR Facility at Colorado State University, Ft. Collins, CO, is being planned for Thursday, August 14, if there is sufficient interest.

EXHIBITS

Exhibits of new chemical products, instruments, publications and services will be on display in the Auditorium Area. The sponsoring societies of the conference gratefully acknowledge the support of the exhibitors.

EXHIBIT HOURS

Open daily from 9:00 to 4:00 except Thursday when exhibits close at 12:00.

EXHIBITORS

American Monitor
Brinkmann Instruments, Inc.
Carle Instruments
Curtin Matheson Scientific, Inc.
Denver Valve and Fitting Co.
Dionex
Encyclopaedia Britannica
Hach Chemical Co
Hauser Laboratories
IBM
Instrumentation Sales
Instrumentation Specialties, Co,
JEOL USA, Inc.
Kevex Corporation
Micromeritics
Perkin Elmer
Sadtler Research Laboratories, Inc.
Spectra Metrics, Inc.
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Varian Instruments
Wilmad Glass Company, Inc.
Southern Scientific
Spectra Physics
Scientific Products
Beckman Instruments, Inc.
Bruker Instruments
Coulometrics, Inc.
CVC Products Inc.
Digilab
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Finnigan Corporation
Hamilton Company
Hewlett Packard
Instrumentation Laboratory, Inc.
Instruments, S.A.
Jarrell Ash
Johns Manville
McCarthy Scientific Co.
Nicolet Instrument Corp.
R.H. Allen Company
Sargent-Welch Scientific Co.
Ultra Carbon
Van Waters and Rogers
Waters Associates, Inc.
Kearns Group
MCB Manufacturing Chemists, Inc.
Scientech
Balzers

SPECIAL ENERGY EXHIBITS

Laramie Energy Research Center. . . . Shale Oil
Rockwell International. . . . . Wind Energy
Sandia Laboratories . . . . Energy Program
Los Alamos Scientific Laboratory. . . Nuclear

ORGANIZERS OF 22nd ANNUAL ROCKY MOUNTAIN CONFERENCE

Conference Chairman	Jerry R. Turbett UTI 325 N. Mathilda Avenue P.O. Box 519 Sunnyvale, California 94086
Conference Vice-Chairman (Chairman 1981 Conference)	Marvin J. Fishman U.S. Geological Survey
Exhibits Chairperson	Debe Bell Kevex Corporation
Registration/Treasurer	Edward A. Brovsky Rockwell International
Publicity	Keith J. Grossaint Rockwell International
Printing	Fred E. Lichte U.S. Geological Survey
Banquet/Mixer	Bill Wiginton Marathon Oil Company Bill McCarthy Marathon Oil Company
Visitors Information	Ed Huffman Huffman Laboratories
Audio-Visual	Duane I. Hunter Rockwell International
Short Courses	Bill Beard USDA-ARS

Future Conference Dates

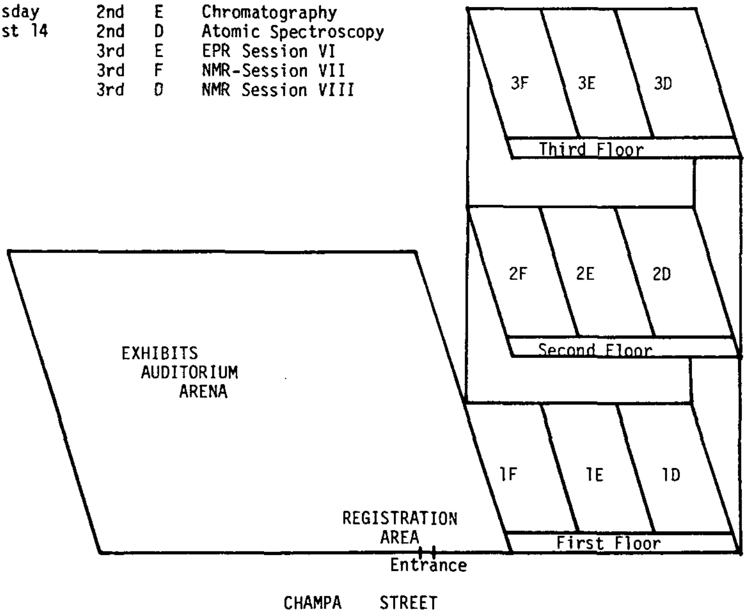
August 2 - 7, 1981
August 1 - 6, 1982
August 14 - 19, 1983
August 5 - 10, 1984
July 14 - 19, 1985

SYMPOSIA CHAIRMAN

Atomic Spectroscopy	Fred Lichte U.S. Geological Survey
Chromatography	Bill Beard USDA-ARS Chuck Andre USDA-ARS
Mass Spectrometry	Jim Franklin Union Carbide Corporation, Oak Ridge
Electron Paramagnetic Resonance	Gareth Eaton University of Denver
NMR of Macromolecules	Fran Miknis Laramie Energy Research Center
Fourier Transform Infrared	Dwight Smith University of Denver
Environmental	Roy Koirtyohann University of Missouri
Ion Chromatography	Marvin Fishman U.S. Geological Survey
Poster Sessions	Bill Beard USDA-ARS

TECHNICAL PROGRAM

	Floor	Rm	MORNING	Floor	Rm	AFTERNOON
Monday	2nd	F	Ion Chromatography	2nd	F	Ion Chromatography
August 11	2nd	D	Fourier Transform Infrared	2nd	D	Fourier Transform Infrared
	3rd	F	NMR-Session I	3rd	F	EPR Session I
	2nd	E	General Session	3rd	E	NMR-Session II
				2nd	E	General Session
Tuesday	2nd	F	Environmental Chemistry	2nd	F	Environmental Chemistry
August 12	2nd	E	Mass Spectrometry	2nd	E	Mass Spectrometry
	2nd	D	Fourier Transform Infrared	3rd	E	EPR Session III
	3rd	E	EPR Session II	3rd	F	NMR-Session IV
	3rd	F	NMR-Session III	1st	F	General Session Posters
	3rd	D	Atomic Spectroscopy	3rd	D	Atomic Spectroscopy
Wednesday	2nd	F	Ion Chromatography	2nd	F	Ion Chromatography
August 13	2nd	E	Chromatography	2nd	E	Chromatography
	3rd	E	EPR Session IV	1st	F	EPR Session V Posters
	3rd	F	NMR-Session V	3rd	F	NMR-Session VI
	2nd	D	Atomic Spectroscopy	2nd	D	Atomic Spectroscopy
				1st	F	NMR Posters
Thursday	2nd	E	Chromatography			
August 14	2nd	D	Atomic Spectroscopy			
	3rd	E	EPR Session VI			
	3rd	F	NMR-Session VII			
	3rd	D	NMR Session VIII			



SYMPOSIUM ON ION CHROMATOGRAPHY

M. J. Fishman, Chairman

MONDAY MORNING, AUGUST 11 - Second Floor, Room F
M. J. Fishman, Presiding

8:30 INTRODUCTORY REMARKS M. J. Fishman

8:35 1. "Use of Ion Chromatography for Analysis of MAP3S Precipitation Samples", J.E. Rothert, Battelle Northwest Laboratory.

9:00 2. "Separation and Analysis of Tungsten and Molybdenum in Natural Waters by Ion Chromatography", W.H. Ficklin, U.S. Geological Survey.

9:25 3. "Ion Chromatographic Determination of Bromide and Sulfate in Geological Brines", R.M. Merrill and R.J. Kottenstette, Sandia National Laboratories.

9:50 BREAK

10:30 4. "Analysis of Inorganic and Organic Arsenic Using Ion Chromatography Coupled with Atomic Absorption", L.S. Shepard, G.R. Ricci, N.H. Hester and G. Colovos, Rockwell International.

10:50 5. "Identification of Unknown Peaks and Observation of Nitrate Wandering in the Ion Chromatographic Analysis of Environmentally Significant Samples", D.R. Jenke, D.R. Kendall and C.M. Falvey, Montana Energy and MHD Research and Development Institute.

11:20 6. "Use of Ion Chromatography as an Analytical Technique for Determining the Environmental Impact of a Test-Scale MHD Facility", C.M. Flavey, D.R. Jenke and D.R. Kendall, Montana Energy and MHD Research Development Institute.

MONDAY AFTERNOON, AUGUST 11 - Second Floor, Room F
M. J. Fishman, Presiding

1:30 7. "Ion Chromatographic Analysis of Contaminants on Zinc and Aluminum Surfaces Exposed to a Range of Urban Environments", J.D. Sinclair, Bell Laboratories.

1:55 8. "Ion Chromatography as a Problem Solving Tool for Electronic Components and Equipment", L.A. Psota, Bell Laboratories.

2:20 9. "Sample Preparation, Handling and Ion Chromatographic Techniques Used in the Analyses of Various Nuclear Wastes", S.J. Johnson, Rockwell Hanford Operations.

2:45 10. "Ion Chromatographic Analyses of Selected Anions Associated with Copper Smelting Operations", J.H. Lowry, K.Wang and R.C. Ross, U.S. Environmental Protection Agency.

3:10 BREAK

3:40 11. "Computerized Analysis of Sulfates and Ammonia in Diesel Samples Using Ion Chromatography", J.M. Clingenpeel and D.E. Seizinger, U.S. Department of Energy.

4:05 12. "IC Analysis of Formaldehyde Stabilized Sulfite Solutions", J.C. Terry and E.E. Ellsworth, Radian Corporation.

4:30 13. Application of Ion Chromatography to Nuclear Technology Development", J.M.Keller, Oak Ridge National Laboratory.

WEDNESDAY MORNING, AUGUST 13 - Second Floor, Room F
W. H. Ficklin, Presiding

8:30 14. "Modification of a Dionex Model 14 Ion Chromatograph to Permit Analyzing Radioactively Contaminated Samples", R.J. Sironen, Rockwell International.

8:55 15. "Automation of an Ion Chromatograph to Increase Throughput", R.C. Graham and J.K. Robertson, U.S. Military Academy.

9:20 16. "Automated Ion Chromatography: A Useful Technique for High Sample Throughput and Process Monitoring", R. Wetzel, Dionex Corporation.

9:45 BREAK

10:30 17. "New Advances in Ion Chromatography", F.C. Smith, Dionex Corporation.

10:55 18. "Mixed Eluent and pH Effects on Retention Times of Polybasic Acids", T.B. Hoover, U.S. Environmental Protection Agency.

11:20 19. "Accuracy and Precision in IC: System Calibration and Standard Additions", C.C. Torquato, S. J. Nagourney and D.C. Bogen, U.S. Department of Energy.

WEDNESDAY AFTERNOON, AUGUST 13 - Second Floor, Room F
W.H. Ficklin, Presiding

1:30 20. "A Rapid Method for the Ion Chromatographic Analysis of Chlorine in Meteorites and Silicate Rocks", K.L. Evans and C.B. Moore, Arizona State University.

1:50 21. "Applications of Ion Chromatography to Geochemical Exploration", A.D. Murray, C.J. Vairo and R.E. Lett, Barringer Magenta Limited.

2:15 22. "A Method for the Ion Chromatographic Determination of Sulfur in Industrial Steels and Iron Meteorites", J.G. Tarter, K.L. Evans and C.B. Moore, Arizona State University.

2:30 23. "Application of Ion Chromatography to the Analysis of Organic Sulfur Compounds", R.J. Williams, Allied Chemical Corporation.

2:55 BREAK

3:25 24. "Low Pressure Chromatograhic Analysis of Benzidine and Congeners", F.E. Butler, D.H. Swanson, D.J. Driscoll, D.R. Scott and R.J. Thompson, U.S. Environmental Protection Agency.

3:50 25. "Cation Analysis by Ion Chromatography: From Cements to Vitamins", R. Posner, E. Patxot and A. Schoffman, United States Testing Company.

4:15 26. "The Determination of Sodium Monofluorophosphate and Sodium Fluoride in Dental Cream Using Ion Chromatography", S.W. Babulak, Colgate-Palmolive Company.

SYMPOSIUM ON FOURIER TRANSFORM INFRARED SEPCTROSCOPY AND ITS APPLICATIONS

D.M. Smith, Chairman

MONDAY MORNING, AUGUST 11 - Second Floor, Room D
D.M. Smith, Presiding

9:00 INTRODUCTORY REMARKS - D. M. Smith

9:05 27. Plenary Lecture
"Some Novel Applications of FTIR Spectrometry", P.R. Griffiths.

9:55 28. "A Direct-Linked GC-Fourier Infrared-Mass Spectrometry Chemical Information System", C.L. Wilkins, G.N. Giss, S. Steiner, G. M. Brissey, R.I. White.

10:20 BREAK

10:45 29. "Optimization of the Signal-To-Noise-Ratio in FTIR Spectroscopy", J.L. Gray.

11:10 30. "Fourier Transform Infrared Photoacoustic Spectroscopy of Solids", M.G. Rockley, J.P. Devlin, D.M. Davis, and H.H. Richardson.

MONDAY AFTERNOON, AUGUST 11 - Second Floor, Room D
P.R. Griffiths., Presiding

1:30 31. Plenary Lecture "Analytical Applications of FTIR", W.G. Fateley

2:20 32. "Recent Developments of GC FTIR Spectroscopy", K. Krishnan.

2:45 33. "FTIR, A Versatile tool for Environmental Analysis", R.L. Barbour, R.M. Genderau, K.H. Shafer, and R.J. Jakobsen

3:10 BREAK

3:45 34. "Infrared Spectroscopic and Related Studies of Metal Ligands Bound via Silylation to Silica Surfaces", D.E. Leyden, D.S. Kendall, L.W. Burggraf, F.J. Pern.

4:10 35. "Phosphate Sorption from Aqueous Solution on FeO (OH) crystals and FeO (OH) Coatings", P.M. Boymel, E.R. Weiner and M.C. Goldberg.

TUESDAY MORNING, AUGUST 12 - Second Floor, Room D
W.G. Fateley, Presiding

9:00 36. "Changes in the Structure of Coals Occurring During Reactions as Measured by Diffuse Reflectance FTIR Spectroscopy", M.P. Fuller and P.R. Griffiths.

9:25 37. "Characterization of the Surface of Elemental Carbon (Soot) Produced During Hexane Combustion", D.M. Smith, J.R. Keifer and N. Novicky.

9:50 38. "The Interaction of Some Oxides of Sulfur and Nitrogen with the Soot Surface as Revealed by FTIR", A.R. Chughtai, N.Novicky, L. Coletta, M.S. Akhter, D. Somerville and D.M. Smith.

10:15 BREAK

10:45 39. "Characterization of Epoxy Resins by LC-FTIR", W.A. Johnson, and J.S. Chen

11:10 40. "A Spectroscopic Method for Determining Photodegradation Mechanisms and Rates in Polymeric Mirror Coatings", D.M. Smith, A.R. Chughtai, J.D. Webb, P.O. Schissel and A.W. Czanderna.

SYMPOSIUM ON NUCLEAR MAGNETIC RESONANCE

F. Miknis, Chairman

MONDAY MORNING, AUGUST 11 - Third Floor, Room F
NMR Session I - Bernard Gerstein, Presiding

8:45 INTRODUCTORY REMARKS - F. Miknis

9:00 41. Plenary Lecture, Robert Vaughan, "Applications of High Resolution NMR to One-Two-and Three Dimensional Solids", M. Mehring, Institut fur Physik, Universitat Dortmund.

9:50 42. "High Resolution NMR in Solids", J.S. Waugh, Massachusetts Institute of Technology.

10:30 BREAK

11:00 43. "Novel Aspects of Selectivity in Multiple Quantum Spectroscopy", A. Pines, University of California, Berkley.

11:30 44. "Double Cross-Polarization NMR in Solids", E.O. Stejskal, J. Schaefer, R.A. McKay, Monsanto Company.

MONDAY AFTERNOON, AUGUST 11 - Third Floor, Room F
NMR Session II - Victor Bartuska, Presiding

1:30 45. "Protonic Species in $H_{1.7}MoO_3$", R.E. Taylor, L.M. Ryan, P.Tindall, B.C. Gerstein, Iowa State University.

2:00 46. "Quantitation in Cross Polarization NMR in Solids: Intensity Distortions in Mixed Systems", W. Earl, D. VanderHart, National Bureau of Standards.

2:40 47. "Chemical Shifts of Spin-½ Nuclei as Bridges Between States of Matter", G.E. Maciel, D.W. Sindorf, M.J. Sullivan, D.J. O'Donnell, L.W. Dennis, M.P. Shathock, P.G. Mennitt, V.J. Bartuska, Colorado State University.

3:30 BREAK

3:35 48. "NMR Studies of Surface States: H_2 on a Suspended Metal Catalyst", C.R. Dybowski, T.M. Apple, P. Gajardo, University of Delaware.

4:05 49. "Spin 1/2 Nuclei in Catalytic Environments", P. Ellis, University of South Carolina.

4:35 50. "Chemical Shielding Studies of Small Molecules Isolated in Argon Matrices", K. Zilm, D. Grant, University of Utah.

TUESDAY MORNING, AUGUST 12 - Third floor Room F
NMR Session III - Bruce Hawkins, Presiding

8:30 51. "Applications of Rotating Frame Polarization Transfer", G.C. Chingas, A.N. Garroway, B.S. Holmes, W.B. Moniz, Naval Research Laboratories.

9:00 52. "Recent Investigations on NMR of Oriented Systems", C.L. Khetrapal, National Institute of Health.

9:30 53. "^{17}O, ^{14}N and ^{2}H NMR Study of Orientation of Urea Molecules in the Magnetic Field Oriented Lyotropic Liquid Crystalline Phase", M.I. Burger, B. Valentine, T. St. Amour, D. Fiat, University of Illinois, Chicago.

10:00 BREAK

10:30 54. "^{23}Na NMR in Ionic Mesophase", J. Bonekamp, T. Eguchi, J. Jonas, University of Illinois, Urbana

11:00 55. "Ion Pairing in Solution by Multinuclear Magnetic Resonance", J.L. Gray, G.E. Maciel, Colorado State Universtiy.

11:30 56. "Solution & Solid State ^{31}P NMR Studies of Polyphosphates", T.M. Carr, W. Veeman, W.R Ritchey, Case Western Reserve University and University of Nijmegen.

TUESDAY AFTERNOON, AUGUST 12 - Third Floor, Room F
NMR Session IV - Sam Kaplan, Presiding

1:30 57. "^{13}C Relaxation Measurements on Solid Polymers Using Variable Temperature Magic-Angle Spinning", W.W. Fleming, J. Lyerla, C. Yannoni, IBM Research Laboratory.

2:00 58. "^{2}H NMR of Polyethylene Terephthalate and Poly-(methylmethacrylate)", A.J. Vega, E. I. DuPont de Nemours & Company.

2:30 59. "Molecular Configurations & Dynamics of Elastomers via Solid State NMR", Y. Lin, R. Pratt, J. Goebel, J.L. Ackerman, University of Cincinnati.

3:00 BREAK

3:30 60. "NMR Chemical Shifts & Polymer Microstructure", A.E. Tonelli, Bell Laboratories.

4:00 61. "Carbon-13 NMR Studies on the Microstructure of Poly (Vinylchloride) and the Mechanism of Vinyl Chloride Polymerization", F.C. Shilling, W.H. Starnes, F.A. Bovey, Bell Laboratories.

4:30 62. "^{13}C NMR and Transistions in Polyethylene", J. Dechter, D. Axelson, L. Mandelkern, Florida State University.

WEDNESDAY MORNING, AUGUST 13 - Third Floor, Room F
NMR Session V - Nick Matwiyoff, Presiding

8:30 63. "Solid State ^{2}H and ^{13}C NMR of Fibrous Collagen", L.S. Batchelder, C.E. Sullivan, L.W. Jelinksi, D.A. Torchia, National Institutes of Health.

8:50 64. "Characterization of the Metal Clusters in Metallothionen by ^{113}Cd NMR", J.D. Otvos, I.M. Armitage, Yale University.

9:20 65. "NMR of Filamentous Viruses", S. Opella, University of Pennsylvania.

10:00 BREAK

10:30 66. "The Nuclear Overhauser Effect in Large Molecules", J.H. Noggle, University of Delaware.

11:15 67. "Internal Motions in Globular Proteins Examined by ^{13}C NMR Off-Resonance Relaxation Experiments", W.J. Goux, T.L. James, University of California, San Francisco.

11:35 68. "Characterization of the Calcium-Induced Conformational Change in Heparin", J.Boyd, P. Gettins, F.B. Williamson, Oxford University, Yale University, and University of Aberdeen.

WEDNESDAY AFTERNOON, AUGUST 13 - Third Floor, Room F
NMR Session VI - Nick Matwiyoff, Presiding

1:30 69. "NMR in Super-Cooled Aqueous Solutions, An Approach to Model Biopolymer Systems", M.B. Ackerman & J.H. Ackerman, Washington University.

1:50 70. "Carbon-13 NMR of Glycoproteins", A. Allerhand, Indiana University.

WEDNESDAY AFTERNOON, AUGUST 13 - First Floor
Poster Session 1:30-5:00

Authors Present 2:30-3:30 for papers labeled B
3:30-4:30 for papers labeled C

B 71. "^{13}C/^{15}N Study of Aldehyde Interaction With Polypeptide Models", J.C. Kertesz, National Institutes of Health.

C 72. "Sequence Analysis of Polyesters", R.C. Newmark, 3 M Company.

B. 73. "NMR Studies of Molecular Motions in Metal Ammonia Compounds", W. Glauwsinger, Arizona State University.

C. 74. "Carbon-13 NMR Spectra of Multifunctional Acrylates", M.A. Pokorney, M.J. Vaickus De Soto, Inc.

B 75. "^{13}C NMR of Tyrosyl -(1-^{13}C) Acetylated-Guanidinated Cytochrome C. De-Naturation by Guanidine HCl", R.A. Nieman, D. Gust, J.R. Cronin, Arizona State University.

C 76. "Carbon-13 NMR Studies of Specifically Labeled Tosylchymotrypsin", J.T.Gerig, E.F. Weigard, University of California, Santa Barbara.

B. 77. "New Binuclear Shift Reagents for Altering NMR Spectra of Aromatic, Olefinic & Halogented Compounds", T.J. Wenzel, R.E. Sievers, University of Colorado.

C 78. High Resolution ^{13}C NMR of Solids at High Magnteic Field" A.D.H. Clague, G.R. Hays, Shell Laboratories, Amsterdam

B 79. "NMR Lanthanide Shift Reagents with Polydentate Cage Ligands", K.C. Brooks, R.E. Sievers, University of Colorado.

C 80. "Aluminum-27 NMR Studies of Room Temperature Molten Salt, 1-n-Butylpyridinium Chloride/Aluminum Chloride", J.L. Gray, G.E. Maciel, Colorado State University.

B 81. Paper withdrawn

C 82. "Carbon-13 Nuclear Magnetic Resonance of Phenolic Resins", S.J. Sojka, R.A. Wolfe, E.A. Dietz, B.F. Dannels, Hooker Chemical & Plastics Corp.

B 83. "High Resolution^{13}C NMR of Solid Fossil Fuel Fractions", M.T. Melchoir, K.D. Rose, Exxon Research and Engineering Company.

THURSDAY MORNING, AUGUST 14 - Third Floor, Room F
NMR Session VII - Joel Ackerman, Presiding

8:30 84. "^{31}P NMR Studies of Rhodopsin-Phospholipid Interactions", N. Zumbulyadis, D.F. O'Brien, Eastman Kodak Research Labs.

9:00 85. "Oligonucleotide Conformation. ^{31}P Relaxation Studies", P. Hart, C. Anderson, University of Wisconsin.

9:30 86. "Cytochrome C553 Heme Environment and Unpaired Electron Distribution as Determined by H NMR Spectroscopy at 360 MH$_3$", E. Ulrich, J. Markely, Purdue University.

10:00 BREAK

10:30 87. "Conformational Changes in Cytochrome C Studies by ^{13}C and ^{2}H NMR Methods", J. Wooten, J. Cohen, A. Schejter, National Institutes of Health and Tel Aviv University.

11:00 88. "^{13}C NMR Studies of ^{13}C Enriched Dihydofolate Reductase", N. Matwiyoff, R. London, R. Blakley, J. Graff, Los Alamos Scientific Laboratory

11:30 89. "Structure Determination of Certain Mold Metabolites of Myrothecium Verrucaria: Roridin J. Trichodermidine, And Certain Trichuverrols and Trichoverrins", E.P. Mazzola, B.B. Jarvis, G.P. Stahly, J. Midiwo, T.D. Silva, G. Pavanasasivan, R. Geohegan, Food & Drug Administration and University of Maryland.

THURSDAY MORNING, AUGUST 14 - Third Floor, Room D
NMR Session VIII - Dan Netzel, Presiding

8:30 90 "Relationship Between Humic Substances & Their Probable Plant Progenitors as Determined by Solid State ^{13}C NMR", P. Hatcher, W. Earl, U.S. Geological Survey and National Bureau of Standards.

9:00 91 "Magnetic Resonance Studies of Coal Metamorphism and Coal Liquefaction Mechanisms", H. Retcofsky, R.G. Lett, R.F. Spricher, D.L. VanderHart, Pittsburgh Energy Technology Center and National Bureau of Standards.

9:30 92 "Special C-13 Chemical Shift Correlations for Characterizing Synthetic Fuels", N. Chamberlain, R. Pabst, Exxon Research and Engineering Company.

10:00 BREAK

10:30 93 "The Characterization of Coal Liquid Heteroatom Functionalities by ^{29}Si NMR Spectroscopy", K.D. Rose, Exxon Research and Engineering Company.

11:00 94 "Flow NMR Studies of Coal & Petroleum Samples", H. Dorn, J. Haw, T. Glass, Virginia Polytechnic Institute.

11:30 95 "Characterization of Residual Carbon in Retorted Oil Shales by Solid State ^{13}C NMR", F.P. Miknis, D. Sindorf, M. Sullivan & G.E. Maciel, Laramie Energy Technology Center and Colorado State University.

11:50 96 "Survey of Spectroscopic Methods for Shale Hydrocarbons", D.M. Wilson, E.J. Gallegos, S.R. Silverman, K.W. Zilm, R.J. Pugmire, D.M. Grant, L.M. Ryan, B.C. Gerstein, P.R. Solomon, Chevron Research Company, Chevron Oil Field Research Company, University of Utah, Iowa State University and United Technology Research Center.

GENERAL SESSIONS

J.R. Turbett, Chairman

MONDAY MORNING, AUGUST 11 - Second Floor, Room E
W.C. Brown, Presiding

9:00 INTRODUCTORY REMARKS - W.C. Brown

9:05 97 Society for Applied Spectroscopy, Rocky Mountain Section Student Award Address " A Light Scattering Study of Contrained Brownian Motion", Alan J. Hurd, W.J. O'Sullivan and R.C. Mockler, Deptartment of Physics, University of Colorado.

9:30 98 "Microwave Measurements of Chemical Shift Tensors", S.G. Kukolich, University of Arizona.

10:00 99 "A Quality Assurance Program For Characterization of Deionized Water Used in a Semiconductor Facility", J.L. Gurnsey, Hewlett Packard.

10:30 BREAK

11:00 100 "Elemental Composition of Aerosol Sample From Low BTU Coal Gasifier Streams", S. Weissman, R.L. Carpenter and G.J. Newton. Inhalation Toxicology Research Insititute, Lovelace Biomedical and Environmental Research Institute.

11:30 101 "A Multi-Instrument Approach to the Control of Coolant Systems Based on Emulsifiable Oils", R. Almen, E. Apel, G. Mantelli, S. Bronstad, T. Osbourn and M. Rasmussen. Coors Container Company.

MONDAY AFTERNOON, AUGUST 11 - Second Floor, Room E
C. Taylor Presiding

2:00 102 "Application of the Mole to Micro-Chemical Analysis", F. Adar, R. E. Grayzel and A. Grillo. Instruments SA, Incorporated

2:30 103 "A High Speed Pulse Amplifier/Discriminator and Counter for Photon Counting", R. A. Borders and J. Birks, Department of Chemistry and Coop Inst. for Research in Environmental Sciences, University of Colorado. J. A. Borders, Naval Ship Weapon Systems Engineering Station.

3:00 BREAK

3:30 104 "Electrochemical Characterization of Vanadium Acetylacetonate Complexes in Aprotic Solvents", M.A. Nawi and T.L. Riechel, Miami University.

4:00 105 "The Coulometric Determination of Carbon Dioxide in Geologic Materials", D. Norton and E. Engleman, U.S. Geological Survey.

GENERAL SESSION POSTERS - B. Beard Presiding

TUESDAY AFTERNOON, AUGUST 12 - First Floor
1:30-5:00
Authors Present 2:30 - 3:30

106 "Survey of Spectroscopic Methods for Shale Hydrocarbons", D.M. Wilson, E.J. Gallegos, S.R. Silverman, K.W. Zilm, R.J. Pugmire, D.M. Grant, L.M. Ryan, B.C. Gerstein, and P.R. Solmon, Chevron Research Company; Chevron Oil Field Research Company, University of Utah, Iowa State University, and United Technology Research Center.

107 "Application of High Performance Liquid Chromatographic Techniques to Component Analysis and Quality Control, for Production of an Organo Metallic Rocket Fuel Catalyst and an Acrylic Adhesive for Dental Applications", D.P. Stull and D.T. Blair. Hauser Laboratories.

108 "A Synoptic Survey of Organic Compounds Extracted from Bed Sediment Using Capillary Gas Chromatogrpahy/Mass Spectrometry/Computer Techniques", W.E. Pereira and T.R. Steinheimer, US Geological Survey.

109 "Acids on I.C.E. - The Analysis of Weak Acids by Ion Chromatography Exclusion", J. Frye and N. Meyer. The Standard Oil Company (Ohio).

110 "Anion Interferences in Laser Enhanced Ionization Spectrometry", T.O. Trask and R.B. Green. University of Arkansas.

111 "Determination of Subicrogram Amounts of Beryllium in Air Filters Samples by Non-Flame Atomic Absorption", J. D. Grooms, Rockwell International.

112 "Inexpensive Automation and Control for the Analytical Laboratory Using a Multipurpose Solid State Set-Point Regulator", C.E. Andre and G.L. Hutchinson. US Department of Agriculture - SEA.

252 "Electro Analysis of Selnoamino Acids" R.W. Andrews, R.A. Grier, R. Graves Department of Chemistry, University of Alabama at Birmingham

THIRD INTERNATIONAL ELECTRON PARAMAGETIC RESONANCE SYMPOSIUM

G. R. Eaton, Chairman

MONDAY, AUGUST 11 - Third Floor, Room E
G. R. Eaton, Presiding
EPR SESSION I

1:30 INTRODUCTORY REMARKS - G.R. Eaton

1:35 113 Plenary Lecture - "Electron-Proton Double Resonance and the Structure of Molecules", C.A. Hutchison, Jr.

2:20 114 "ENDOR of NO-Ligated Heme Systems", C.P. Scholes, R.LoBrutto, Y.H.Wei, and T.E. King.

2:40 115 "Photoreaction in Molecular Single Crystals - EPR Studies of Light Induced Hydrogen Transfer", R. Furrer.

3:00 BREAK

3:30 116 "Applications of ESR to Carbonaceous Materials", L.S. Singer and I.C. Lewis.

4:00 117 "An ESR Investigation of Free Radicals in Coals and Coal Conversion", L. Petrakis and D.W. Grandy.

4:20 118 "Hydrogen Exchange Between Bituminous Coal and Naphthalene or Tetralin: An EPR and NMR Study", J.J. Ratto and I.R. Goldberg.

4:40 119 "Zero-field Splitting Tensor of the Excited Triplet State of Charge Transfer Phanes", M. Bar, K. Hausser.

TUESDAY, AUGUST 12 - Third Floor, Room E
I.B Goldberg, Presiding
EPR SESSION II

8:30 120 Plenary Lecture - "Transient Radical in Liquids. Time Resolved EPR", A.D. Trifunac.

9:20 121 "Picosecond Electron Transfer Kinetic Measurements by Electron Spin Echo Spectroscopy", M.K. Bowman and J.R. Norris.

9:40 122 "Electron Spin Resonance Studies of Metal-Ammonia Compounds", F.Y. Robb and W.S. Glaunsinger.

10:00 BREAK

10:30 123 Plenary Lecture - "Modulated Electron Spin Echoes: A Probe for the Solvation Geometry of Paramagnetic Species in Bulk and on Surfaces", L. Kevan.

11:20 124 "Electron Spin Resonance of Mn $(H_2O)_6^{2+}$ Aqueous Solutions Adsorbed on Silica Gels", G. Martini.

11:40 125 "The Reactions Between DPPH and Surface Active Sites of Metal Oxides - Surface Properties", T. Kawaguchi, S. Hasegawa and K. Yasuda.

TUESDAY, AUGUST 12 - Third Floor, Room E
C.P. Scholes, Presiding
EPR SESSION III

1:30 126 Plenary Lecture - "Electron Spin Echo Envelope Spectroscopy in the Study of Chemical Complexes and Metalloproteins", W.B. Mims and J. Peisach.

2:20 127 "The ENDOR and ESEEM Detection of Nitrogen Couplings in a Model Amide Crystal: A Comparison Study", L.D. Kispert, M. Bowman and J.R. Norris.

2:40 128 "The Temperature-Dependent ESR Linewidths of a Radical Spectrum Detected in X-Irradiated Cyanoguanidine Crystals, M.D. Pace and W.B. Moniz.

3:00 BREAK

3:30 129 "Multiple Frequency EPR Studies on an 'Intermediate' in the Oxidation Reduced Cytochrom c Oxidase", W.R. Dunham, R.H. Sands, R.W. Shaw, and H. Beinert.

3:50 130 "Application of Fast Fourier Transforms to EPR Spectra of Free Radicals in Solution", W.R. Dunham, L.J. Harding, J.A. Fee, and H.J. Grande.

4:10 131 "Unraveling the EPR Spectra of Modified Flavin Free Radical Cations", H.J. Grande, F. Muller, L.J. Harding and W.R. Dunham.

4:30 132 "An ESR Study of a Peroxyl Radical Intermediate in Horseradish Peroxidase (HRP)/t-Butyl Hydroperoxide (t-BuOOH), B. Kalyanaraman, E.Perex-Reyes and R.P. Mason.

WEDNESDAY, AUGUST 13 - Third Floor, Room E
W.S. Glaunsinger, Presiding
EPR SESSION IV

8:30 133 Plenary Lecture - Some Intriguing Observations in the ESR of Partially Oriented Media", J.H. Freed.

9:20 134 "EPR and ENDOR Observations of the 'Central Peak' Phenomenon", N.S. Dalal.

10:00 BREAK

10:30 135 "The Detection of Phase Transitions in $NH_4Ln (SO_4)_2 \cdot 4H_2O$ Single Crystals Using Electron Paramagnetic Resonance of Gd^{3+} Impurity Ions", H. A. Buckmaster and V.M. Malhotra.

10:50 136 "Dynamic and Cooperative Jahn-Teller Distortions in Copper Pyridine N-oxide Complexes", C.P. Keijzers, E. de Boer and J.S. Wood.

11:10 137 "EPR Studies of Thermochemical and Photochemical Decomposition of Nitramines", H.L. Pugh, L.P. Davis, J.S. Wilkes, R.C. Dorey and F.J. Seiler.

11:30 138 "EPR Studies in the Structure of the Active Site of Adrenal Sterol Hydroxylation", J.C. Salerno, J.D. Lambeth, J.R. Lancaster, J.O. Wilkerson, H. Kamin.

11:50 139 "Electrochemical and EPR Studies of Dicarbene Carbonyl Metal Complexes and Arene Tricarbonyl Chromium Complexes" R.D. Rieke, S. Milligan, I. Tucker, G. Zotti and R.B. Willeford.

WEDNESDAY, AUGUST 13 - First Floor
1:30 - 5:00
Authors Present 1:30-2:30 for papers labeled A; 2:30-3:30 for papers labeled B; 3:30-4:30 for papers labeled C;
S.S. Eaton, Presiding

SESSION V POSTERS

A 140 "Proton ENDOR Study of Copper (II) Bis(dithiocarbamate)", C.P. Keijzers, D. Snaathorst, E. de Boer and A. K. Klaassen.

B 141 "EPR and ENDOR Studies of Zn/Cu Superoxide Dismutase", R.A. Lieberman, J.A. Fee, H.L. Van Camp and R.H. Sands.

C 142 "Proton and Nonproton ENDOR Investigations of Novel Galvinoxyls in Different Electron Spin States" H. Kurreck, B. Kirste, W. Gierke, and K. Schubert.

A 143 "EPR Study of Homogentisate Oxygenase from Aspergillus", M. Sonoda and Y. Sakagishi.

B 144 "A Single Crystal EPR Study of Ground State Triplet Trimethylenemethane", O. Claesson, A. Lund, T. Gillbro, T. Ichikawa, O. Edlund, and H. Yoshida.

C 145 "Geometrical Isomerism of Quinolyl Methylenes", R.S. Hutton, H.D. Roth, M.L. Schilling and J.W. Suggs.

A 146 "TMA Dehydrogenase: A Study in Triplet State EPR", R.C. Stevenson, W.R. Dunham, R.H. Sands, and H. Beinert.

B 147 "An Unusual Electron Spin Echo Phase Shift Observed in the Early Reactions of Photosynthesis", M.C. Thurnauer, L.L. Shipman and J.R. Norris.

C 148 "Interaction Between Dysprosium Complexes and Soluble Iron-Sulfur Proteins, H. Blum, J.S. Leigh and T. Ohnishi.

A 149 "A Magnetic Interaction Between Gd^{3+} and Nitroxide Bound to Cys-98 of the Ca^{2+} Binding Protein, Troponin-C", C.-L A. Wang, P.C. Leavis, J.C. Seidel and J. Gergely.

B 150 "Proton Involvement with the Light-Induced Hindrance of Spin Label Motion in the Lumen of Spin Thylakoids", S.P. Berg and D.M. Nesbitt.

C 151 "Spin Labels for Membrane-Water Partition Studies", P.D. Morse, II, R. Clarkson and D. M. Lusczakoski-Nesbitt.

A 152 "Preferential Segregation of Spin Labeled Cardiolipin Within the Boundary Layer of the Membrane Enzyme Cytochrome C Oxidase", G.L. Powell and M.B. Cable.

B 153 "High Frequency (35 GHz) Saturation Transfer EPR: An Approach to Slow Anisotropic Rotational Diffusion", M.E. Johnson.

C 154 "Spin-Label Study of Rabbit Thymocyte Membranes", G. Rakhit.

A 155 "Does Fatty Acyl-CoA Micellize?", G.L. Powell and D. Freeland.

B 156 "Spin Label Assay for Trapped Volume and Lipid Vesicle Fusion", A.I. Vistnes and J.S. Puskin.

C 157 "EPR Spectra of Spin-Labeled Derivatives of Copper Tetraphenylporphyrins", K.M. More, S.S. Eaton and G.R. Eaton.

A 158 "Copper-Nitroxyl Interactions in a Spin-Labeled Copper Porphyrin", B.M. Sawant, G.A. Braden, R.A. Smith, G.R. Eaton and S.S. Eaton.

B 159 "Spin-Spin Interactions in Spin-Lablel Copper Carboxylate Dimers and Related Monomers", D.P. Dalal, S.S. Eaton and G.R. Eaton.

C 160 "Spin-Spin Interactions in Copper Acetate Biogenic Ammine Spin Label Complex", R. Haran, J. Gairin, P. Sharrock, C. Dugounkoff and M. Massol.

A 161 "A Systematic Experimental Attempt to Separate Hydrodynamic and Microscopic Contributions to Molecular Translational Diffusion in Liquids", R. N. Schwartz, M. Patron and B.L. Bales.

B 162 "Electron Spin Resonance Study of the Oxidation of Aromatic Hydrocarbons", I.C. Lewis and L.S. Singer.

C 163 "Spin Correlation of Carbazolyl Radicals", Y. Matsumoto.

A 164 "An ESR-ENDOR Study of Radiation Induced Free Radicals in Citric Acid, From 4.2K to 300K", G.C. Moulton and L.L. Finch.

B 165 "ESR and INDO Studies of Anion Radicals in Acetic Acid and Acetamide; Non-Planarity and Barriers to Hindered Rotation", D. Suryanarayana and M.D. Sevilla.

C 166 "Theory of Proton Hyperfine Interaction in High Spin Five and Six Liganded Iron and Manganese Heme Systems", M. K. Mallick, S.K. Mun, S. Mishra, J.C. Chang and T.P. Das.

A 167 "EPR G-Values for a Quantum Mechanically-Mixed Spin 3/2, 5/2 Species with Rhombic and Axial Symmetry Components", M. Eberhart and M.M. Maltempo.

B 168 "Spectral Evidence for at Least Two-Fold Multiplicity in Two- and Four-Iron Ferredoxins", D.O. Hearshen, W.R. Dunham, R.H. Sands and H.J. Grande.

DOI: https://doi.org/10.56902/RMCMR.1980.22.1

C 169 "Theory of Electronics Structures of Nitrosylhemoglobin in R and T State", S.K. Mun and T.P. Das.

A 170 "ESR, NMR and Moessbauer Studies of the High Spin-Low Spin Transition in $Fe(phen)_2 (NCS)_2$ and $Fe(pic)_3Cl_2$·EtOH", P.S. Rao, A Reuveni, B.R. McGarvey, P.Ganguli and P. Gutlich

B 171 "A New Induction Cavity for High Power Dispersion EPR Experiments", R.B. Clarkson and R. Sneed.

C 254 "ENDOR Studies of Organic Radical Ions in Liquid Crystals", B. Kirste.

THURSDAY, AUGUST 14 - Third Floor, Room E
M.K. Bowman, Presiding

EPR SESSION VI

8:30 172 Plenary Lecture - Rotation Relaxation and Magnetic Resonance "Anomalies", D. Kivelson, J.L. Dote and R.N. Schwartz.

9:20 173 "Electron Spin-Spin Interactions in Biological Systems by EPR", R.H. Sands.

9:50 174 "A Spin-Label Assay for Metal Ion Chelation and Complex Formation", S. J. Wagner, A.D. Keith and W. Snipes.

10:10 BREAK

10:40 175 Plenary Lecture - Saturation-Transfer Spectroscopy of Protein and Lipid Components of Lipid Bilayers", J.S. Hyde.

11:30 176 "Use of Deuterated Spin Labels for Improved Sensitivity and Resolution in ST-EPR Studies", A.H. Beth, S.D. Venkataramu, R.T. Wilder, R.C. Perkins, L.S. Wilkerson, D.E. Pearson, C.R. Park and J.H. Park.

SYMPOSIUM ON ENVIRONMENTAL CHEMISTRY

S.R. Koirtyohann, Chairman

TUESDAY MORNING, AUGUST 12 - Second Floor, Room F
S.R. Koirtyohann, Presiding

INTRODUCTORY REMARKS - S.R. Koirtyohann

9:00 177 "Soil Absorption-Desorption of Phosphate and Anionic Trace Metals", C.L. Grant and S.A. Gasiorowski.

9:30 178 "Investigations of the Interaction of Trace Elements with Organic Ligands in Oil Shale Retort Process Waters", J.S. Stanley, M.A. Caolo, and R.E. Sievers.

9:50 179 "Analytical Approaches to the Characterization of Metal Binding by Organic Ligands", R.K. Skogerboe, H.O. Hayworth, C.R. Gumina, T.C. Huth and S.A. Wilson.

10:10 BREAK

10:25 180 "Characterization of the Redox Properties of Fulvic Acid", R.K. Skogerboe and S.A. Wilson.

10:45 181 "Chemistry of Sequentially Sampled Precipitation Events", J.K. Robertson and R.C. Graham.

11:05 182 "Utilization of Low-Grade Water in Coal Slurry Pipelines: Decontamination of Water by Slurries of Coal and Coal-Derived Solids", S.E. Manahan, R. Gale, D. Schuler, and D. Bornhop.

11:25 183 "Treatment of Acid Mine Drainage by Lime Neutralization-Computer Simulation of an Industrial Process", D. Jenke and F. Diebold.

11:45 184 "An Intercomparison of Simultaneous Multielement Ultratrace Metals Determinations in Natural Waters by ICP Spectrometery and Anodic Stripping Voltammetry", J.E. Bonelli, H.E. Taylor, J.R. Garbarino, and R.K. Skogerboe

TUESDAY AFTERNOON, AUGUST 12 - Second Floor, Room F
S.R. Koirtyohann, Presiding

1:50 186 "Selective Electron Capture Sensitization (SECS) in Environmental Analysis", M.A. Wizner and R.E. Sievers.

2:10 187 "Water Treatment: Effects on Trace Organics in Drinking Water", R.S. Hutte, R.E. Sievers, R.M. Barkley, C.R. Rudkin, and S.S. Ferguson.

2:30 188 "Mass Spectral Characterization of the Thermal Decomposition Products of Kepone", J.A. Mescher.

2:50 189 "An Improved Method for Determination of Dithiocaramate Fungicides", S.M. McCown, R. Strohschein, M.W Hucks, and R.D. Baker.

3:10 BREAK

3:25 190 "Preparation of Glass Capillary Columns for the Separation of Organic Pollutants in the Environment", J.T. Snow and B. Bush.

3:45 191 "Automated Determination of Phenolic Compounds in Water", R.T. Hentschel.

4:05 192 "Assessment of Polynuclear Aromatic Hydrocarbon Pollution in Aquatic Samples, HPLC Methods and Results", J.J. Black and P.P. Dymerski.

4:25 193 "Reduction of Complex Chromatograms, Part I", S.M. McCown, D.R. Pitzer, C.G. Manos, Jr., and C.M. Earnest.

4:45 194 "Reduction of Complex Chromatograms, Part II", S. McCown, D.R. Pitzer, C.G. Manos, Jr., and C.M. Earnest.

SYMPOSIUM ON MASS SPECTROMETRY

W.H. Christie

TUESDAY MORNING, AUGUST 12 - *Second Floor*, Room E
W.H. Christie, Presiding

8:30 INTRODUCTORY REMARKS - W.H. Christie,

8:35 195 Plenary Lecture "Mass Spectrometry-Then and Now", H.J. Svec, Iowa State University.

9:30 196 "GC/MS Analysis of Multifunctional Acrylates", E.M. Saladino, A. J. Widzisz, and M.J. Vaickus, Desoto Inc.

9:55 Break

10:20 197 "Mass Spectra Characteristics of the Sulfur Containing Ketoxime Carbamates Thiofanox and Metabolites", H.G.Corkins, J.J. Mannion, and L. Storace, Diamond Shamrock Corporation.

10:45 198 "A GC-MS Method for Studying Interactions of Other Drugs with Warfarin", C.E. Hignite and D.E. Rollins, Veterans Administration Medical Center, Kansas City, Missouri.

11:10 199 "Positive and Negative Ion Chemical Ionization GC/MS Utilizing Fused Silica Capillary Columns for Equine Drug Analysis, J.D. Henion and G.A. Maylin, Cornell University.

11:35 200 "Negative Ion Mass Spectrometry of Some C-8 to C-12 Alcohols", J.M. Knox, University of Wyoming.

11:55 201 "Quadrupole Mass Spectrometer Applications in Semiconductor Processes", J.D. Burden, UTI.

TUESDAY AFTERNOON, AUGUST 12 - Second Floor, Room E
W.H. Christie, Presiding

1:30 202 "Direct Determination of Cesium in Pilot Plant Effluents by Isotope Dilution Mass Spectrometry" P. Chastagner, E.I. duPont de Nemours & Company.

2:00 203 "Recent Applications of Spark Source Mass Spectrography to Biological Samples", M.L. Jacobs, Commercial Testing and Engineering Company.

2:30 204 "Laser Mass Spectrometry of Solids", R.J. Conzemius and H. J. Svec, Iowa State University.

3:00 BREAK

3:30 205 "Factors Involved in Quantitative Gas Analysis by Mass Spectrometry, R.E. Ellefson, Mound Facility.

4:00 206 "Secondary Ion Mass Spectrometry: Quantification Techniques and Their Application", W.H. Christie, Oak Ridge Laboratory.

4:30 207 "Applications of Dynamic Mass Spectrometry at Rocky Flats", T.L. McFeeters, Rockwell International.

SYMPOSIUM ON CHROMATOGRAPHY

B. Beard and C. Andre, Co-Chairman

WEDNESDAY MORNING, AUGUST 13 - Second Floor, Room E
D. Lawlor, Presiding

8:20 INTRODUCTORY REMARKS - B. Beard

8:30 208 "Purification of Radioactive Steroid Hormones by High Performance Liquid Chromatogrpahy (HPLC)", M.P. Kautsky and D.D. Hagerman. University of Colorado.

9:00 209 "Determination of BHT, Irganox 1076 and Irganox 1010 in Polyethylene by High Performance Liquid Chromatography", J.F. Schabron and L.E. Fenska. Phillips Petroleum Company.

9:30 BREAK

10:00 210 "How to Pack a Chromosorb High Efficiency Column for HPLC", J.L. Medina, S.B. Dave, Johns-Manville

10:30 211 "Chemiluminescence Detectors for Gas and Liquid Chromatography", J.W. Birks, B. Shoemaker, R.H. Getty, E. Hill and K. Kurita, University of Colorado.

WEDNESDAY AFTERNOON, AUGUST 13 - Second Floor, Room E
B. Barkley, Presiding

1:30 212 "Selective Sorption of Nucleophiles Using Lanthanide Metal Complexes", J.E. Picker and R. E. Sievers, University of Colorado.

2:00 213 "O-Alkyloxime Derivatives for the Selective GC and GC-MS Determination of Aldehydes", S.P. Levine and T.M. Harvey. Ford Motor Company and T.J. Waeghe, R.H. Shapiro, University of Colorado.

2:30 214 "A Continuous Extracter-Concentrater and its Application to Nitrosamine Analysis in Beer", H.B. Peterson, Adolph Coors Company.

3:00 BREAK

3:30 215 "Capillary Gas Chromatographic and Gas Chromatographic-Mass Spectrometric Analyses of Nicotine and Metabolites of Nicotine in Mouse Tissue", M.S. Ho, K.M. Simon, D.R. Petersen and J.A. Thompson. University of Colorado.

4:00 216 "Some Applications of Fused Silica Capillary Columns", R. Leibrand", Hewlett Packard.

THURSDAY MORNING, AUGUST 14 - Second Floor, Room E
M Kaiser, Presiding

8:30 217 "A High Pressure Liquid Chromatographic Method for the Determination of Thiamin, Niacin, and Riboflavin in Ready-To-Eat Cereal", D.I. Johnson and S.B. Dave. Johns-Manville.

9:00 218 "Detection of Organic Anionic Ground-Water Tracers at the PPB Level by HPLC Through Pre-Column Enrichment. K. Stetzenbac, S. Jensen, G. Thompson, University of Arizona.

10:00 219 "Combined Liquid Chromatography/Mass Spectrometery Using the Direct Interface", R. Leibrand. Hewlett Packard.

10:30 220 "Application of HPLC to the Study of Microorganisms in Emulsifiable Oils", R. Almen, G. Mantell, P. McTeer, and S. Nakayama. Coors Container Company.

11:00 221 "Reversed Phase HPLC Techniques for the Determination of Aldehydes and Ketones in Gaseous Effluents", T.F. Cole and R.M. Riggin, Battelle Columbus Laboratories.

SYMPOSIUM ON ATOMIC SPECTROSCOPY

F.E. Lichte, Chairman

TUESDAY, MORNING, AUGUST 13 - Third Floor, Room D
F.E. Lichte - Presiding

8:30 INTRODUCTORY REMARKS - F.E. Lichte

8:35 222 "New Techniques in Emission Spectroscopy", T. Niemczyk, University of New Mexico.

9:00 238 "Sampling Effects in Positionally Stable Spark Discharge Trains" David Ekimoff and T.J. Whitaker, University of Wisconsin

9:25 237 "Doppler-Cancelled, Two-Photon Resonant Ionization Spectroscopy", B.A. Bushaw, T.J. Whitaker, Battelle, Pacific Northwest Laboratory.

9:50 Break

10:30 236 "Collisionally Induced Ionization of Rubidium in High Rydberg States", T.J. Whitaker, B.A. Bushaw, Battelle, Pacific Northwest Laboratory.

11:00 239 "Metastable Transfer Emission Spectroscopy of Metal Vapors Produced in a Sputtering Cell" Steven D. Hornung, Henry C. Na, and Thomas M. Niemczyk, University of New Mexico

11:30 227 "Microcomputer Controlled Optical Emission Spectrometer", T.L. Futrell, R.T. Goodpasture, G.F. Larson, Oak Ridge Laboratories.

TUESDAY, AFTERNOON, AUGUST 12 - Third Floor, Room D
F.E. Lichte - Presiding

1:30 233 "Analysis of Barium Titanate Material by DC ARC Spectrography", T. Schmitt, Globe Union.

2:00 234 "An Evauation of Wavelength Selection Parameters for the Direct Reading Emission Spectrometric Analysis of Geological Materials", J.L. Seeley, P.J. Lamothe, T.L. Fries, U.S. Geological Survey.

2:30 240 "Recent Developments in Inductively Coupled Plasma, Plasma Atomic Emission Analysis" Barry Rosovsky, Angelo C. Grillo, and Joseph Katzenberger, Instruments SA, Inc.

3:00 Break

3:30 228 "The Selection of Optimum Parameters for a Sequential Multi-Element ICP Emission Spectrometer", G.F. Wallace and R.D. Ediger, Perkin-Elmer Corporation.

4:00 226 "Evaluation of an Inductively Coupled Plasma-Echelle Spectrometer System For Multielement Analyses", D.L. Dick, W.A. Hanagan, R.K. Skogerboe, Colorado State University.

4:30 241 "Recent Developments in Inductively Coupled Plasma Atomic Emission Analysis" Joseph Katzenberger, Angelo C. Grillo, and Edward M. Clarke, Instruments SA, Inc.

WEDNESDAY, MORNING, AUGUST 13, 1980 - Second Floor, Room D
J.L. Seeley - Presiding

8:30 242 "Flameless AA Matrix Effects: A View Through Time and Space" by J.A. Holcombe, N. Akerlind, Jr., and W.K. Stephenson University of Texas

9:00 243 "Graphite Furnance Atomic Absorption Spectroscopy of Heavy Matrix Samples", by John P. Erspamer and Thomas M. Niemczyk, University of New Mexico

9:30 244 "Use of Microsampling for Flame Atomic Absorption", by A.J. Stratton and T. McKenzie, Varian Associates, Inc.

10:00 Break

10:30 245 "Design Factors for a Modern Electrothermal Atomic Absorption Instrument" by John A. Nichols, Ray Woodriff, Steve Lawson, Gary Dewalt, and Robert Sanks, University of Denver and Montana State University

11:00 246 "The Mechanism for Lead Release from Chemically Altered Graphite Surfaces in Flameless AA", S.G. Salmon and J.A. Holcombe, University of Texas

11:30 235 "The Use of High Speed Data Acquisition and Graphics Display to Study Factors Influencing Signals in the HGA Graphite Furnace", G.F. Wallace, R.D. Ediger, Perkin-Elmer.

WEDNESDAY, AFTERNOON, AUGUST 13, 1980 - Second Floor, Room D
J.L. Seeley - Presiding

1:30 225 "The Use of the Holographic Grating in Emission Spectroscopy", J. Lerner, Instruments SA, Inc.

2:00 247 "Evaluation of Some Commercial Pneumatic Nebulizers with Respect to Memory Effects in ICP-AES Analysis", Dave Dobb, Montana College of Mineral Science and Technology

2:30 232 "Effects of Solution Composition on the Physico-Chemical Characteristics of Aqueous Aerosols", K.G. Kronholm, G.M. Butcher, R.K. Skogerboe, Colorado State University.

3:00 Break

3:30 230 "Investigation of the Properties of a Glass Frit Nebulizer", L.R. Layman and F.E. Lichte, U.S. Geological Survey

4:00 229 "The Ionization Repression Effect; Is it Real?" G.M. Butcher, K.G. Kronholm, R.K. Skogerboe, Colorado State University.

4:30 231 "Nebulizer Spray Chamber Design for an Inductively Coupled Plasma", F.E. Lichte, A.L. Sutton, U.S. Geological Survey.

THURSDAY, MORNING, AUGUST 14, 1980 - Second Floor, Room D
H.E. Taylor - Presiding

8:30	223	"Elemental Analysis of Coal, Fly Ash and Slag Samples", D. Yates, T. Clevenger, D. James, and E. Hinderberger, University of Missouri.
9:00	248	"Analysis of Major, Minor, and Trace Elements in Geologic Samples Dissolved by Various Techniques by Inductively Couple Plasma--Atomic Emission Spectrometer", C.L. Ho, S. Tweedy, and J.R. Calvo University of Texas
9:30	249	"Analysis of As by Distillation of $AsCl_3$--Inductively Coupled Plasma--Atomic Emission Spectrometer" C.L. Ho and S. Tweedy, University of Texas
10:00		Break
10:30	250	"Analysis of Se in gologic Samples by Fluorometric Method and Inductively Coupled Plasma--Atomic Emission Spectrometer" by C.L. Ho and S. Tweedy, University of Texas
11:00	224	"Simultaneous Determination of Volatile Elements Via Hydride Generation ICAP-OES", A.F. Ward, Jarrell-Ash Division.
11:30	251	"Emission Enhancement in a DC Plasma", D.D. Nygaard, Bates College

ABSTRACTS NOT LISTED WERE UNAVAILABLE AT TIME OF PRINTING.

1 USE OF ION CHROMATOGRAPHY FOR ANALYSIS OF MAP3S PRECIPITATION SAMPLES.

J.E. Rothert. Battelle Northwest Laboratory, P.O. Box 999, Richland, Washington 99352

The Multistate Atmospheric Power Production Pollution Study (MAP3S) includes measurement and modeling of fossil-fuel effluent concentrations in precipitation and air in the northeast United States region. To determine precipitation concentrations of sulfur and nitrogen oxides as well as PO_4^{3-}, Cl^-, Na^+, K^+, NH_4^+, Ca^{2+}, Mg^{2+}, pH, and conductivity, an eight-site precipitation network in rural eastern United States has been established.

Ion chromatography is ideally suited for trace analysis of precipitation samples, because several ionic species at various concentrations can be analyzed simultaneously with little or no sample preparation. In the precipitation samples found in the rural eastern United States, seven species (SO_4^{2-}, NO_3^-, Cl^-, PO_4^{3-}, K^+, NH_4^+, and Na^+) are all that are easily separated for trace analysis work using the anion and cation columns.

Two Dionex Model 10 Ion Chromatographs are used to analyze the precipitation network samples. The anion system uses the standard eluent 0.003M $NaCO_3$/0.0024M Na_2CO_3. The cation system uses the eluent 0.005N HCl. The 3 μmho/cm scale with one pen of a dual pen recorder being equal to 0.3 μmho/cm is used for sample analysis. Each anion sample is spiked with $Na_2CO_3/NaHCO_3$ to eliminate the water dip. For cation analysis no sample preparation is needed.

2 SEPARATION AND ANALYSIS OF TUNGSTEN AND MOLYBDENUM IN NATURAL WATERS BY ION CHROMATOGRAPHY.

W. H. Ficklin. U.S. Geological Survey, Branch of Exploration Research, Denver Federal Center, Denver, Colorado 80226.

Most tungsten or molybdenum in natural waters occurs as tungtate or molybdate, and the elements can be measured in natural waters by ion chromatography. Ion chromatographic separation of tungstate and molybdate is achieved using a 3 x 250 mm standard separator column, a 0.006 M sodium carbonate eluent, a standard anion suppressor column, and a flow rate 138 ml/hr. Elution of the peaks for the species tungstate and molybdate occurs at nine and twelve minutes, respectively, and peak heights are distinguishable from the base line at concentrations of 0.1 mg/L, using a full scale deflection of 3 μmho and a dual-pen recorder. Tungstate and molybdate must be concentrated from 1L of water by collecting them on a chelating resin after the pH of the water is adjusted to 4.5. Tungstate and molybdate are eluted with concentrated ammonium hydroxide. The ammonia is evaporated, leaving a water solution containing tungstate and molybdate. About 90% of the tungsten and molybdenum is recovered, with a relative standard deviation of 15% at the 5 μg/L level. Natural concentrations of tungsten or molybdenum as small as 1 μg/L are measured by this technique.

3 ION CHROMATOGRAPHIC DETERMINATION OF BROMIDE AND SULFATE IN GEOLOGICAL BRINES,

R. M. Merrill and R. J. Kottenstette, Sandia National Laboratories, P. O. Box 5800, Albuquerque, New Mexico 87185.

Ion chromatography has been used to determine bromide and sulfate concentrations in ground water brines from rocks of the Delaware Basin in southeastern New Mexico. The chemical composition of ground waters is indicative of the geological and meteorological origins of the water and of rock/water interactions which are important factors in site evaluation for a proposed nuclear waste repository. Total halogens in the brines, determined by argentometric titration, vary from 47,000 mg/L to nearly 200,000 mg/L. Bromide concentrations were found to range from 20 mg/L to 700 mg/L and sulfate concentrations from undetectable to 20,000 mg/L. An ion chromatographic procedure was developed for the simultaneous determination of bromide and sulfate with detection limits for both ions of less than 20 mg/L in the brines and with analysis time of less than 20 minutes. The ion chromatographic results are compared with those obtained from gravimetric sulfate and iodometric bromide analyses.

4 ANALYSIS OF INORGANIC AND ORGANIC ARSENIC USING ION CHROMATOGRAPHY COUPLED WITH ATOMIC ABSORPTION,

L. S. Shepard, G. R. Ricci, N. H. Hester, G. Colovos, Rockwell International, Environmental Monitoring & Services Center, 2421 W. Hillcrest Drive, Newbury Park, California, 91320.

It is becoming increasingly important to know the valence state and the chemical form of arsenic in the environment (both air and water). This paper describes a technique for the speciation and analysis of arsenic III, arsenic V, methylarsonic acid, dimethylarsenic acid, and p-aminophenylarsonic acid. The method developed for this purpose makes use of an automated ion chromatograph coupled with an arsenic specific (hydride system) atomic absorption spectrophotometer. Detection limits of less than 10 ng/ml were obtained for each species.

5 IDENTIFICATION OF UNKNOWN PEAKS AND OBSERVATION OF NITRATE WANDERING IN THE ION CHROMATOGRAPHIC ANALYSIS OF ENVIRONMENTALLY SIGNIFICANT SAMPLES. D. R. Jenke, D. R. Kendall and C. M. Falvey. Montana Energy and MHD Research and Development Institute, Butte, Montana 59701.

The ion chromatographic analysis of samples designed to provide data relevant to the assessment of the environmental impact of a test scale MHD facility results in the generation of data whose significance is not readily apparent. Specifically, the ionic source of peaks observed in the chromatograms produced are not commonly known. Identification of some of the peaks is further hampered by similarities in the elution characteristics of the anions in question with others routinely observed. Separation of the peaks and identification of their anionic source is accomplished through the use of alternate elution techniques, sample spiking, and wet chemical quantitative anion analysis. In addition, the observation of the mobile nature of the nitrate anion peak has been observed. This mobility is characterized as a function of nitrate concentration, sulfate concentration, and eluent strength.

6 USE OF ION CHROMATOGRAPHY AS AN ANALYTICAL TECHNIQUE FOR DETERMINING THE ENVIRONMENTAL IMPACT OF A TEST-SCALE MHD FACILITY. C. M. Falvey, D. R. Jenke, and D. R. Kendall. Montana Energy and MHD Research and Development Institute, Inc., Butte, Montana 59701.

Magnetohydrodynamics (MHD) is a new generation technology designed to more efficiently use coal, an abundant national energy source, to generate electrical power. Essentially, it involves the passage of seeded, superheated gas at high speed through a magnetic field, resulting in the generation of direct current electrical energy. To determine the environmental impact of a test site (50 mw) facility on the Butte Valley, an environmental base line study including air, ambient water, and terrestrial sampling was initiated. Ion chromatography was chosen as potentially being the most effective technique for anion analysis. Data requirements, manpower availability and funding limitations necessitated the generation of an analytical procedure somewhat different than that cited in the literature. The use of a .003 M $NaHCO_3$ and .009 M Na_2CO_3 eluent and moderate flow rates allows for the quantitative determination of Cl^-, NO_3^-, PO_4^{-3}, and $SO_4^=$ in 10 minutes. Instrument response is linear to concentrations in excess of 50 ppm. Working detection limits are .02 ppm for Cl^- and SO_4^{-2}, .04 ppm for PO_4^{-3} and .06 ppm for NO_3^-. Analysis of control samples and spike recovery information indicates the effectiveness of this procedure. Appropriate sampling material for collection of airborne particulate samples destined for anion analysis is determined and a three step extraction mechanism proposed.

7 ION CHROMATOGRAPHIC ANALYSIS OF CONTAMINANTS ON ZINC AND ALUMINUM SURFACES EXPOSED TO A RANGE OF URBAN ENVIRONMENTS. J. D. Sinclair. Bell Laboratories, Crawfords Corner Road, Holmdel, New Jersey 07733.

The effect of environmental pollutants on the kinds and amounts of contaminants that accumulate on indoor equipment surfaces has been studied infrequently at best. Ion chromatography has been used in this study to analyze water soluble contaminants and corrosion products that accumulate on zinc and aluminum electronic equipment surfaces. Particular attention in this study focused on chloride and sulfate concentrations. Nitrate, sodium, ammonium, and potassium have also been examined. Field sampling was accomplished by extracting surfaces with moistened squares of filter paper. The water soluble species from the metal surfaces accumulate in the paper as it dries. Accumulation rates for each ion were based on the average of at least 50 filter paper samples for most locations. Accumulation rates for each ion varied widely from city to city. The ranges of accumulation rates observed to date for chloride and sulfate are 1.2-0.2 μg chloride/cm^2/yr on zinc, 0.8-0.04 μg chloride/cm^2/yr on aluminum, 2.2-0.2 μg sulfate/cm^2/yr on zinc, and 1.0-0.2 μg sulfate/cm^2/yr on aluminum. Cities studied included New York, Cleveland, Houston, Council Bluffs (Iowa), Boulder, Colorado Springs, Denver, and Minneapolis. The rates do not correlate well with atmospheric or rain water concentrations of environmental pollutants in these cities.

8 ION CHROMATOGRAPHY AS A PROBLEM SOLVING TOOL FOR ELECTRONIC COMPONENTS AND EQUIPMENT. L. A. Psota. Bell Laboratories, Crawfords Corner Road, Holmdel, New Jersey 07733.

In investigations of the contamination of electronic components and equipment, it is often necessary to identify and quantify very small concentrations of water soluble cations and anions. These contaminants can be corrosive to metal components and can cause electrical leakage. Some of the contaminants that have been encountered include: (1) substances that are evolved from fires involving the burning of certain plastics; (2) residues from the water involved in floods, roof leaks, and pipe ruptures, in which the water carries along with it any soluble and some insoluble contaminants that happen to be in its pathway; and (3) corrosion products from electrical components and terminals exposed to polluted and humid environments.

Anion and cation (both mono- and divalent) concentrations are determined using standard ion chromatography techniques. Monovalent cation concentrations are less accurate than anion concentrations due to column instabilities and transition metal poisoning of the cation separator column as a result of the nature of the samples. Metal surfaces are usually sampled by immersion in the laboratory and by wet filter paper extraction techniques in the field.

9 SAMPLE PREPARATION, HANDLING AND ION CHROMATOGRAPHIC TECHNIQUES USED IN THE ANALYSES OF VARIOUS NUCLEAR WASTES. S. J. Johnson. Rockwell Hanford Operations, Chemical Sciences Group, 222-S, 200 West, P. O. Box 800, Richland, Washington 99352.

Radioactive wastes produced from the reprocessing of Defense fuel and stored in underground tanks at the Hanford site are present in a number of physical and chemical forms. Processes for waste concentration, radionuclide removal and isolation, and immobilization for long term storage require analytical support to characterize their feeds and products, and to monitor their operations.

Anion analyses are needed for samples which include such diverse types as HCl dissolutions of insolubles, caustic, high-salt solutions, and low ion concentration waters. Ion Chromatography (I.C.) has proven to be a versatile analytical tool in these determinations. These varied matrices present complex I. C. problems, not only in their chemistry, but in sample preparation and safe handling. These techniques and analyses will be discussed.

10 ION CHROMATOGRAPHIC ANALYSES OF SELECTED ANIONS ASSOCIATED WITH COPPER SMELTING OPERATIONS, Lowry, J.H., Wang, K., Ross, R.C., US Environmental Protection Agency, Box 25227, Denver, Colorado, 80225

Air particulates from process emission stack and ore concentrate samples originating from several southwestern copper smelters were analyzed for total sulfur as sulfate and extractable sulfate, chloride, fluoride, and nitrate using ion chromatography (IC). Sulfur compounds were converted to sulfate by an alkaline fusion technique in the determination of total sulfur. The water soluble anion extraction and the total sulfur alkaline fusion procedures were verified by the analyses of NBS standard reference materials and known additions of metallic sulfides. When the IC method was compared to the Ba-MTB colorimetric method for total sulfur (as sulfate) and water soluble sulfate, the IC method was found to be superior. Practical conciderations in applying the IC method are discussed. These include economic conciderations, interferences and column and eluent selection.

11 COMPUTERIZED ANALYSIS OF SULFATES AND AMMONIA IN DIESEL SAMPLES USING ION CHROMATOGRAPHY. J. M. Clingenpeel and D. E. Seizinger. U.S. Department of Energy, Bartlesville Energy Technology Center, P.O. Box 1398, Bartlesville, Oklahoma 74003.

An ion chromatograph has been interfaced with a computer to control the various sampling and analysis operations thereby reducing the manpower requirement for analysis of sulfates in samples collected from diesel exhaust. The various steps in the sample analysis include transferring a sample from an incrementing sampling apparatus via pump through the chromatographic sampling loop prior to sample injection. Upon sample injection, the computer is triggered to start data acquisition of the sample being analyzed. Following a number of analyses, a regeneration cycle of the suppressor column is completed and the computer returns to routine analyses of samples. The programmed control of the ancillary analysis operations, including precautions for automatic shutdown in event of power failure or over-pressure of the mobile phase, will be included in the discussion. Unattended routine analyses of sulfates and ammonia in diesel samples have been performed for several months.

12 IC ANALYSIS OF FORMALDEHYDE STABILIZED SULFITE SOLUTIONS. J.C. Terry and E.E. Ellsworth. Radian Corporation, 8500 Shoal Creek Boulevard, Austin, Texas 78766.

The analysis of sulfite ion in aqueous solutions such as flue gas desulfurization scrubber liquors is freqently desired for process characterization and emissions studies. Usually the analysis of sulfite must be performed by collecting the sulfite solution directly into a standard iodine solution followed by analysis within a short time. It is sometimes undesirable or impossible to perform the analysis quickly or on-site. In these cases a method of stabilizing the sulfite to retard or prevent sulfite oxidation is necessary. The use of formaldehyde to prevent sulfite oxidation has been reported. Its use in this laboratory has shown that interferences are present when formaldehyde stabilized solutions are analyzed by ion chromatography. This paper presents the results of a parametric study of the effects of formaldehyde concentration and solution pH on the extent of sulfite oxidation, signal enhancement of sulfite, sulfate, and other common scrubber ions, and solution shelf life.

13 *APPLICATION OF ION CHROMATOGRAPHY TO NUCLEAR TECHNOLOGY DEVELOPMENT.** J. M. Keller. Consolidated Fuel Reprocessing Program, Oak Ridge National Laboratory, P. O. Box X, Oak Ridge, Tennessee 37830.

There is a need for sensitive and selective methods of analysis for ionic species in the development of nuclear processing technology. In the reprocessing of nuclear fuel, a tributylphosphate (TBP):*n*-paraffinic hydrocarbon is employed to extract uranium. During the process TBP is degraded to dibutyl- and monobutylphosphoric (DBP and MBP) acids. Dibutylphosphate forms a stable complex with uranium which cannot be completely stripped from the organic extractant. The ability to follow the presence or removal of such ionic species can be accomplished by ion chromatography. However, the complex nature of the reprocess solutions can present problems of interference. Trace analysis of DBP in the presence of high levels of carbonate, oxalate, and nitric acid must be obtained. The low levels of DBP prevent dilution as a means of resolving the anion of interest. A discussion of the types of interference and methods for removal of some interferences will be presented.

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*Research sponsored by the Nuclear Power Development Division, U.S. Department of Energy under contract W-7405-eng-26 with Union Carbide Corporation. By acceptance of this article, the publisher or recipient acknowledges the U.S. Government's right to retain a non-exclusive, royalty-free license to and for any copyright covering the article.

14 MODIFICATION OF A DIONEX MODEL 14 ION CHROMATOGRAPH TO PERMIT ANALYZING RADIOACTIVELY CONTAMINATED SAMPLES. R. J. Sironen. Rockwell International, Rocky Flats Plant, Energy Systems Group, P. O. Box 464, Golden, CO 80401.

Analysis of radioactively contaminated solutions for multiple anions and cations is a frequent requirement at the Rocky Flats Plant. The recent introduction of the Ion Chromatograph as an analytical tool has obvious advantages for such analyses. However, control of contamination using an unmodified instrument would require that the total instrument be committed to a glove box. This would complicate instrument usage and servicing to an impractical degree. An alternate solution has been employed which involved removal of injection ports, valves, columns, and conductivity cell from the commercial instrument and isolation of same in a separate chamber located within a glove box. Air, electrical, and liquid lines comprise umbilical connections to the controls on the instrument chassis located on an adjacent laboratory bench.

15 AUTOMATION OF AN ION CHROMATOGRAPHY TO INCREASE THROUGHPUT. Richard C. Graham, and John K. Robertson. Science Research Laboratory, United States Military Academy, West Point, NY 10996.

A Dionex Model 14 Ion Chromatograph has been modified to allow for simultaneous determination of 2 ionic systems. Any combination of anionic-cationic determinations can be accomplished merely by changing columns and elements. Automation has been partially accomplished by addition of a liquid chromatographic auto-injector. This sample is unique as it allows unattended simultaneous injections of sample onto both systems. Effects of carryover will be discussed. Calibration and analysis data will be presented which compares manual and auto-injection. A progress report on the interfacing of a micro-computer to control sample injection and data output from the IC will be given.

16 AUTOMATED ION CHROMATOGRAPHY: A USEFUL TECHNIQUE FOR HIGH SAMPLE THROUGHPUT AND PROCESS MONITORING. Roy Wetzel. Dionex Corporation, 1228 Titan Way, Sunnyvale, California 94086.

Ion Chromatography (IC) is continuously increasing the scope of applications for which it may be used and is continuously expanding its capability for established uses such as air and water pollution analysis and industrial process monitoring. The increased use of IC has resulted in the development of automated instrumentation. Automated IC, in its most straightforward form, includes sample loading, injection and data reduction. This scheme is useful for most laboratory samples. Multi-ion analysis is possible as with normal IC techniques as demonstrated by the determination of NO_3^- and

SO_4^{2-} in high volume filter extracts of air pollution samples. Because the suppressor column may be regenerated by a sub-program during any main analytical program, sample throughput is increased. Ninety-nine samples may be analyzed without operator supervision. In addition to increased sample throughput, IC versatility is increased by automation. Continuous on-line analysis is possible by replacing the auto-sampler with a sample pump. Using this configuration, sample may be continually pumped through a bypass loop except when loading the injection loop. If a concentrator column replaces the injection loop, continuous monitoring at ppb levels is possible. Other advantages of automated IC are discussed.

17 NEW ADVANCES IN ION CHROMATOGRAPHY. Frank C. Smith, Jr., Arthur W. Fitchett and Roger George. Dionex Corporation, 1228 Titan Way, Sunnyvale, CA 94086.

Ion Chromatography (IC) has proven effective in sequentially determining a wide variety of anions and cations in different matrices. A recent review of IC has detailed both the ions presently analyzable by IC and the known IC application areas. This paper details recent advanced methods that have been developed to extend the range of IC. Included are new eluents, new eluent column combinations, and separation of several species that were previously not analyzable by IC. Use of sodium iodide eluent and silver suppression has resulted in improved separation and detection of perchlorate ion in brine and in possible separation of polythionic acids. New column eluent combinations have been used to separate both monovalent and divalent cations in a single injection. Additionally, a method of directly determining trace (1 ppm) levels of calcium and magnesium ions in high concentration brines has been developed. A single injection separation of fluoride, chloride, acetate, formate, nitrate, bromide, sulfate, iodide, and thiocyanate in low concentration (1% NaCl) brines has been shown. This method uses both column and eluent gradients to achieve the anion separations. Some ions have been eluted using variations of existing eluents. These ions include small aliphatic sulfonic acids, halogenated aliphatic sulfonic acids, and fluorinated short chain aliphatic carboxylic acids. Use of sodium carbonate-bicarbonate and sodium citrate eluents has resulted in the separation of some oxyphosphorous species. Included here are phosphite, orthophosphate, pyrophosphate, and tripolyphosphate. Two injections onto different column sets using different eluents are required to separate all these species.

18 MIXED ELUENT AND pH EFFECTS ON RETENTION TIMES OF POLYBASIC ACIDS. Thomas B. Hoover. Environmental Research Laboratory, U.S. Environmental Protection Agency, College Station Rd., Athens, Georgia 30605.

Mixed carbonate-bicarbonate eluents have been used effectively for the separation of common anions in the Dionex ® ion chromatographic system. The empirical shifting of the retention time of orthophosphate in this system by varying the pH of the eluent is a recognized technique for eliminating interferences. A theory of ion exchange separation using multiple eluent ions was derived on the assumption of stoichiometric exchange among ions of different charge types. Based on this theory and the treatment of Beukenkamp et al. (Anal. Chem. 26, 505 (1954)) for the equilibria among the hydrolytic species of anions of polybasic acids, a quantitative treatment of the effect of pH on retention time was derived. The selectivity coefficient for singly- and doubly-charged eluent ions was measured with bromide and with sulfate analytes. This value was used in the analysis of retention times for orthophosphate and for arsenate to obtain measures of the selectivity coefficients for each of the charged anionic species of these acids. Measurements were made over the range pH 8.7 to pH 12.0 and an approximately ten-fold range of retention times.

19 ACCURACY AND PRECISION IN IC: SYSTEM CALIBRATION AND STANDARD ADDITIONS. C. C. Torquato, S. J. Nagourney and D. C. Bogen, Environmental Measurements Laboratory, U.S. Department of Energy, 376 Hudson St., New York, NY 10014.

Loss of separator column capacity, a common problem in ion chromatography, can be seen by loss of resolution between peaks and shortened retention times for the ions eluting later. Since changes in resolution and retention time affect peak height, any loss of column capacity also affects the accurate determination of ionic concentrations from calibration curves. While it is recognized that separator column capacity loss becomes a more serious problem as the age of the column increases, we have found that variations in column conditions also affect the accurate determination of species concentrations from calibration curves. An anion standard (2 ppm Cl^-, 10 ppm PO_4^{-3}, NO_3^-, SO_4^{-2}) was run daily to monitor variations in separator column conditions. While daily precision between peak heights was excellent, anion standard concentrations were found to fluctuate on a day-to-day basis with column conditions. In an effort to eliminate this problem, the method of standard addition was employed to determine daily standard and sample ionic concentrations. The accuracy and precision of the system calibration and the standard addition method were subsequently compared.

20 A RAPID METHOD FOR THE ION CHROMATOGRAPHIC ANALYSIS OF CHLORINE IN METEORITES AND SILICATE ROCKS. K.L. Evans and C.B. Moore. Arizona State University, Tempe Arizona 85281

The analysis of chlorine in solid geochemical samples is not routinely done because of its low concentration which leads to tedious analyses by NAA or XRF. The determination of chlorine in rock samples is important because of the significant role that chlorides play in the geochemical paragenesis. Chlorides are the most important form in which metals are removed from a magma. A rapid combustion-ion chromatographic method for chlorine determination has been applied to meteorites and silicate rocks. Samples are combusted in a LECO induction furnace using oxygen carrier gas. The volatile products are collected in a $NaHCO_3$-Na_2CO_3 eluent and analysed in a DIONEX Model 10 Ion Chromatograph. The analyses compare favorably with superior NAA and XRF results on standard rocks and meteorites. Analyses of different splits of some standard rocks showed significant variations between different bottles indicating inhomogeneities in the samples. Within homogenized splits relative standard deviations ranged from 2 to 7%. The analysis of five rock samples may be made in one hour.

21 APPLICATIONS OF ION CHROMATOGRAPHY TO GEOCHEMICAL EXPLORATION. A.D. Murray, C.J. Vairo and R.E. Lett. Barringer Magenta Ltd., 304 Carlingview Drive, Metropolitan Toronto, Rexdale, Ontario, Canada, M9W 5G2.

The presence of anomalous anion concentrations in rocks, soils and waters, has been known for many years. Until recently although, the applications of anion analysis in mineral exploration has not been utilized on a routine basis due to high analytical costs, basic analytical problems and the absence of information describing the geochemical behaviour of anions. However, recent studies have shown that anion geochemistry can be an important exploration technique especially in the areas of hydrogeochemistry and lithogeochemistry. Ion Chromatography provides an extremely cost effective, precise and rapid method of multi-anion analysis, factors which satisfy the principle requirements of exploration geochemistry. The variation of anion and cation abundance in ground water may often be the only method for detecting deeply concealed mineral deposits. The interpretation of hydrogeochemical anomalies can be improved by the use of chemical modelling techniques based on water chemistry. In this particular application reliable multi-anion data is essential. Also, different anion concentrations of phosphate, sulphate and chloride as found in soils and rocks may serve as indicators of mineralization under certain conditions. This paper describes the application of ion chromatography as a method of multi-anion analysis in geochemical prospecting. Further research requirements of the technique, pertaining in particular to the areas of methodology and digestion techniques will also be reviewed.

22 A METHOD FOR THE ION CHROMATOGRAPHIC DETERMINATION OF SULFUR IN INDUSTRIAL STEELS AND IRON METEORITES. J.G. Tarter, K. L. Evans and C.B. Moore. Arizona State University, Tempe, AZ 85281

The determination of sulfur in iron alloys and steels is of interest due to the dramatic effects that ppm amounts of sulfur can have upon the physical properties of these materials. A combustion-ion chromatographic technique has been applied to the determination of sulfur in NBS standard steels and iron meteorites and compared to the common method of a combustion-iodometric titration. In both techniques the sample is initially combusted in a LECO induction furnace using an oxygen carrier gas. In the iodometric titration method volatile products including SO_2 are bubbled through a solution containing an I_2-starch complex, the SO_2 bleaches the solution and it is automatically spectrophotometrically titrated to a present endpoint with KIO_3. In the ion chromatographic method the combustion products are trapped in a $NaHCO_3$-Na_2CO_3 solution which is subsequently analyzed on a DIONEX Model 10 Ion Chromatograph. The total sulfur may be determined by quantification of the $SO_3^=$ and $SO_4^=$ peaks or by oxidizing all sulfur to $SO_4^=$ using hydrogen peroxide. The IC technique may be the more versatile of the two techniques, because it allows other trace non-metallic components to be determined along with sulfur.

23 APPLICATION OF ION CHROMATOGRAPHY TO THE ANALYSIS OF ORGANIC SULFUR COMPOUNDS. R. J. Williams, Allied Chemical Corp, P.O. Box 1021 R, Morristown, NJ 07960.

Ion Chromatographic (IC) methods have been developed for the separation of aliphatic (RSO_3H), and aromatic sulfonic acids ($ArSO_3H$), aliphatic sulfates ($ROSO_3H$) and aromatic sulfinic acids ($ArSO_2H$). The effect of chemical structure and aromatic substitution on retention time was investigated. The standard, 0.003 M/0.0024 M sodium bicarbonate/sodium carbonate, eluent was used for most of the separations. A 0.001 M sodium bicarbonate eluent was developed for the separation of the aliphatic sulfonic acid homologs. The analytical application of a variable wavelength UV detectorin series with the normal conductivity detector will also be presented. The UV detector is more selective than the conductivity detector and was very useful in the detection of the aromatic sulfinic and sulfonic acids.

24 LOW PRESSURE CHROMATOGRAPHIC ANALYSIS OF BENZIDINE AND CONGENERS.

F. E. Butler, D. H. Swanson, D. J. Driscoll, D. R. Scott, and R. J. Thompson. Environmental Protection Agency, EMSL/RTP, EMD (MD-78), Research Triangle Park, North Carolina 27711.

Benzidine related dyes and pigments and their precursors and degradation products are of interest to this Agency because these compounds are demonstrated or suspected cancer agents. Air concentrations, especially in fenceline monitoring, are proposed. Selected blue and black dyes and yellow pigments, azobenzene, hydrazobenzene, benzidine, and chloro, methyl, and methoxy benzidine compounds will be determined. This paper describes initial separation and analysis of mixtures using a modified commercial ion chromatograph. Separations were made using the anion column supplied with the instrument and using reverse-phase packing materials and paired-ion reagents available for high performance liquid chromatography. Methanol--water solution was used as eluent. Detectors used were conductivity, ultraviolet, refractive index, and fluorescence. Detection sensitivities and separation techniques are reported. Exposed high-volume filters spiked with trace amounts of these compounds were extracted and analyzed.

25 CATION ANALYSIS BY ION CHROMATOGRAPHY: FROM CEMENTS TO VITAMINS.

Richard Posner, Eli Patxot and Alan Schoffman. United States Testing Co., Inc., Hoboken, New Jersey 07030.

For the most part, users of Ion Chromatography have confined their work to Anion Analysis. Moreover, the bulk of all application work by the Dionex Corporation and IC users has been again, on Anion Analysis.

Cation Analysis by Ion Chromatography is a field in which we feel has been neglected. One may attribute the apathy to the availability of the strong analytical competition, Atomic Absorption and Emission Spectroscopy. However, Ion Chromatography has some very real advantages including multiple element analysis which are free of the ionization effects that plague Atomic Absorption.

The thrust of this paper is to demonstrate the utility of Cation Analysis to real world samples and analytical problems. Sample types will include cements, cereals, juices, sodas and other food items, vitamins and corrosion products. Analytes to be determined will include Sodium, Potassium, Magnesium and Calcium.

26 THE DETERMINATION OF SODIUM MONOFLUOROPHOSPHATE AND SODIUM FLUORIDE IN DENTAL CREAM USING ION CHROMATOGRAPHY.

Stephen W. Babulak. Colgate-Palmolive Company, 909 River Road, Piscataway, New Jersey 08854.

The Dionex model 10, ion chromatography, is used routinely to analyze both sodium fluoride (F^-) and sodium monofluorophosphate (MFP) in dental cream. With a carbonate/bicarbonate eluent the above species are eluted and separated on a 500 mm length anion separator column in series with pre-column and a suppressor column. Statistical data have shown that the analyses are comparable to existing methods, a selective fluoride electrode for ionic fluoride and an automated chromatographic - colormetric technique for MPF. The automated procedure used to determine the MFP takes approximately 70 minutes per sample. The Dionex 10 will analyze both MFP and ionic fluoride in approximately 10-18 minutes. Computations can be by peak height measurement, integrator, or using a computer for automatic calculations.

27 SOME NOVEL APPLICATIONS OF FT-IR SPECTROMETRY.

Peter R. Griffiths, Ohio University, Athens, Ohio 45701.

In the past decade, Fourier transform infrared (FT-IR) spectrometry has become an accepted means of measuring high quality infrared spectra. Most users, however, still use the same sampling techniques that are required by conventional spectrometers and few new sampling techniques (with the notable exception of GC/FT-IR) are in common usage. In the past two years, several novel sampling techniques have been reported, and some of these which we are developing at Ohio University will be described in this paper. Among these are several applications of diffuse reflectance spectrometry, including an interface between an FT-IR spectrometer and a high performance liquid chromatograph and a device for studying heterogeneous reactions in situ. Other unusual applications include the development of an optical subtraction system to enable very weakly absorbing materials to be studied and, possibly, to allow vibrational circular dichroism spectra to be measured. Finally the progress towards a method for the remote quantitative analysis of stack gases by infrared emission spectrometry will be reported.

28 A DIRECT-LINKED GAS CHROMATOGRAPHY-FOURIER INFRARED-MASS SPECTROMETRY CHEMICAL INFORMATION SYSTEM. Charles L. Wilkins, Gary N. Giss, Steve Steiner, Greg M.Brissey, and Robert L. White, Department of Chemistry, University of Nebraska-Lincoln, Lincoln, Nebraska, 68588.

A Nicolet 7000 GC-IR system has been directly interfaced with a Kratos MS-5076 high resolution mass spectrometer and is presently serving as the basis of studies directed toward development of an integrated chemical structure information. The joint use of the complementary chemical information provided by this analysis system is intended to simplify the problem of semi-automated structure determination for unknowns. This paper will be devoted to a review of our progress and discussion of some of the preliminary results obtained from a combination of pattern recognition, search, and graph theoretic approaches to the data interpretation problem. Future plans, including a potential link of the GC-IR system to a new Fourier transform mass spectrometer under development in our laboratories, will also be discussed.

29 OPTIMIZATION OF THE SIGNAL-TO-NOISE RATIO IN FTIR SPECTROSCOPY. Joel L. Gray Coors Container Company, 17755 West 32nd Avenue, Golden, Colorado 80401.

Analysts have long been aware of the importance of optimizing instrument sensitivity by improving the signal-to-noise ratio (S/N) of any given spectrometer. Maximizing S/N provides a reduction in instrumental detection limits and a reduction in data acquisition time for techniques having signal averaging capability. Of course the latter situation applies to Fourier transform infrared, FTIR, spectroscopy.

The ultimate S/N observed in a FTIR spectrum to a large part is determined by the number of interferograms co-added before transformation into the frequency domain. Clearly if one can decrease the number of transients required for an appropriate S/N in the spectrum, the time required for data accumulation will be reduced. Several methods we have found important in increasing S/N will be discussed, and in general include sample preparation, minor instrument hardware modifications and judicious selections of values for data acquisition parameters. For example, in specific instances we have observed legitimate two-fold increases in S/N merely by readjusting acquisition parameters.

30 FOURIER TRANSFORM INFRARED PHOTOACOUSTIC SPECTROSCOPY OF SOLIDS. M.G. Rockley, J.P. Devlin, D.M. Davis and H.H. Richardson. Chemistry Dept., Oklahoma State University, Stillwater, Ok.,74074.

Fourier Transform Infrared Photoacoustic Spectroscopy (FTIR-PAS) represents a notable advance in both infrared spectroscopy and photoacoustic spectroscopy since it combines the high energy throughput and multiplexing advantages of FTIR spectroscopy with the advantages of photoacoustic spectroscopy for studying surface species.

A wide selection of infrared photoacoustic absorption spectra of opaque solid samples will be presented to show the versatility of FTIR-PAS. A method for correcting these spectra for incident power variations with respect to wavelength will be shown. The dependence of the photoacoustic signal strength on the incident modulation frequency, sample concentration, surface area, particle size, and weight will be discussed. The utility of this technique for studying coal surfaces, catalysts, oil-bearing rocks, epoxies and semiconductor surfaces will be demonstrated.

31 ANALYTICAL APPLICATIONS OF FTIR. W. G. Fateley, Department of Chemistry, Kansas State University, Manhattan, Kansas 66506 and John Casper, IBM, Box 390, Poughkeepsie, New York 12602

Fourier transform infrared (FTIR) spectroscopy has several well known advantages over dispersive spectroscopy. These include high signal throughput, high speed, and high wavenumber precision. The proper exploitations of these advantages can allow the performance of analyses that would be difficult or impossible with dispersive instruments.

This paper will explore some of the gains that can be expected from the analytical application of FTIR. These will be illustrated with a broad range of general interest examples.

33 FT-IR: A VERSATILE TOOL FOR ENVIRONMENTAL ANALYSES. R. L. Barbour, R. M. Gendreau, K. H. Shafer, and R. J. Jakobsen. Batelle, Columbus Laboratories, 505 King Avenue, Columbus, OH 43201.

Fourier transform infrared spectroscopy (FT-IR) is a versatile tool in that it can be used for both organic and inorganic characterization of a variety of environmental samples. Not only can FT-IR provide both organic and inorganic sample information, but the analyses can be done on samples in a variety of conditions and matrices. With infrared spectroscopy we have been able to identify specific inorganic compounds, greatly expanding the elemental data typically obtained on environmental samples. Pelletizing (in KBr) particulates such as fly ash and ambient air particulates has been a very successful method for us. Other techniques, such as use of the diamond anvil cell, diffuse reflectance and attenuated total reflectance, allow us not only to check for matrix affects due to KBr by looking at the 'neat' sample, but the reflection techniques give surface information as a bonus. We can also look at both inorganics and organics directly on filters, i.e., without removing the sample from the filter, thus minimizing sample losses and/or contamination. Organic class information is of course routine by FT-IR, with subtraction capabilities clarifying overlapping information due to unclean separation techniques such as liquid chromatography. A clear advantage FT-IR offers is the ability to do on the fly GC-IR analysis. This enables actual compound identifications to be made allowing better environmental and health assessments of the sample. This means that GC-FT-IR now offers information both comparable and complementary to GC-MS. Thus FT-IR offers organic and inorganic information as well as a variety of innovative sample handling techniques.

34 Infrared Spectroscopic and Related Studies of Metal Ligands Bound via Silylation to Silica Surfaces

D. E. Leyden, D. S. Kendall, L. W. Burggraf, F.-J. Pern, Department of Chemistry, University of Denver, Denver, CO 80208 and D. Williams, Dow Corning Corporation, Midland, MI 48640

Work at this laboratory and others has shown the utility of complexing reagents bound via silylation to silica or glass surfaces for concentrating metals. Recent progress in understanding some of the detailed chemistry of these materials will be discussed. A bound acetoacetamide and a β-diketone have been prepared and studied. Model compounds with the same functional groups and their iron and copper complexes have been prepared and adsorbed onto silica surfaces. Fourier transform infrared spectroscopy has been used to compare bound species, adsorbed species and dissolved model compounds. In particular, keto-enol equilibria and hydrogen bonding have been studied. FTIR has also been used to follow the course of reactions on surfaces and to study the conformation and coverage of molecules bound to the surface. Photoacoustic spectroscopy, X-ray fluorescence and other techniques have served to complement and extend infrared studies. A combination of spectroscopic and other methods shows promise in elucidating structures on surfaces.

35 PHOSPHATE SORPTION FROM AQUEOUS SOLUTION ON FeOOH CRYSTALS AND ON FeOOH COATINGS.

P. M. Boymel, E. R. Weiner and M. C. Goldberg. U. S. Geological Survey, P.O. Box 25046, M.S. 424, Denver Federal Center, Lakewood, Colorado 80225.

Goethite (α-FeOOH) occurs both as relatively pure crystals and as coatings on sediments in natural water systems. It can influence the chemical composition of natural waters by sorbing or releasing soluble species. In studies of phosphate sorption to Goethite, there is no difference between the Fourier Transform Infrared spectra of surface bound phosphate on pure Goethite crystals or Goethite coated on silica. There is an energy shift of the adsorption bands of phosphate sorbed onto Goethite which is coated on MnO_2. Goethite appears to be physisorbed to silica but chemisorbed to MnO_2. The band shift is due to the influence of chemisorption which changes the crystal growth of Goethite coated on MnO_2 to give a different surface structure.

36 CHANGES IN THE STRUCTURE OF COALS OCCURRING DURING REACTIONS AS MEASURED BY DIFFUSE REFLECTANCE FT-IR SPECTROSCOPY.

Michael P. Fuller and Peter R. Griffiths, Department of Chemistry, Ohio University, Athens, Ohio 45701.

Although some very useful FT-IR measurements on coals pressed into KBr pellets have been reported recently, the infrared spectra of powdered coals may not be measured directly using conventional sampling techniques. We have shown that it is possible to measure the infrared spectrum of powdered coal by diffuse reflectance infrared Fourier transform (DRIFT) spectroscopy. Using this technique, a rapid method for characterizing the organic and mineral components of coals has been devised. The mineral spectrum may be found by treating the coal in a low temperature asher and measuring the DRIFT spectrum of the residue. The spectrum of the organic component is found by subtracting this spectrum from the spectrum of the whole coal.

We have developed and built a heated cell to hold coal samples undergoing reactions such as oxidation and gasification while their DRIFT spectrum is measured. Using this cell we have shown that coal oxidation proceeds by different mechanisms depending on the temperature of the cell. The formation of coke from high volatile coals by destructive distillation has also been monitored, and spectra measured at different times during coke formation will be shown.

37 CHARACTERIZATION OF THE SURFACE OF ELEMENTAL CARBON (SOOT) PRODUCED DURING HEXANE COMBUSTION.

D. M. Smith, John R. Keifer, Nick Novicky, Department of Chemistry, University of Denver, Denver, Colorado 80208.

Fourier transform infrared spectroscopy (FT-IR) and thermal desorption studies have been carried out on the soot produced during the combustion of hexane. Characterization of those surface functionalities present at greater than 1% surface coverage has been accomplished. Values of the integrated absorbance of infrared bands, combined with measurements of gaseous products of thermal desorption (CO, CO_2, H_2O, H_2) allow the assignment of specific absorption frequencies to carbon-oxygen and carbon-hydrogen functional groups on the soot surface. These functionalities include a surface anhydride, two types of carbonyl groups (one in conjugation with an aromatic segment of the bulk structure) and an aryl ether linkage. The appearance and temperature distributions from thermal desorption of H_2O and H_2, whose origin is shown by FT-IR to be surface hydrocarbon, indicate that the hydrogen present in freshly generated soot plays an important role in determining the products of desorption as a function of temperature. The presence of this hydrogen significantly differentiates freshly generated soot, presumably that from all fossil fuel combustion, from the more idealized elemental carbons previously studied.

38 THE INTERACTION OF SOME OXIDES OF SULFUR AND NITROGEN WITH THE SOOT SURFACE AS REVEALED BY FT-IR. A. R. Chughtai, N. Novicky, L. Coletta, M. S. Akhter, D. Somerville, and D. M. Smith, Department of Chemistry, University of Denver, Denver, Colorado 80208.

The interactions of SO_2 and NO with the surface of freshly-generated hexane soot have been separately studied by FT-IR spectroscopy. Changes in the characteristic surface functionalities of soot are observed which can be ascribed to reactions between these functionalities and the oxides of sulfur and nitrogen. In the absence of oxygen and at pressures as low as 30 torr, SO_2 reacts at the surface to produce sulfate species at temperatures much lower than thermal changes in the soot surface functionalities are otherwise observed. Under similar conditions NO produces a surface carboxylate and is reduced in the process. The observation of intermediates and kinetic studies also are reported in this paper.

39 CHARACTERIZATION OF EPOXY RESINS BY LC-FTIR. W. A. Johnson, J. S. Chen. *Boeing Commercial Airplane Company, Boeing Material Technology, P.O. Box 3707,* Seattle, Washington 98124.

In order to characterize and evaluate the epoxy resins used in aerospace composite resin fabrications, LC-FTIR characterizations were undertaken. A Waters 244 high pressure liquid chromatograph with Model 6000A pump and U6K injector were sequentially connected to a BaF_2 flow cell placed in the optical train of a Nicolet 7199 Fourier Transform Infrared Spectrometer. Samples were dissolved and eluted isocratically with aqueous-acetonitrile solvent using a Waters µbondapak/C-18 column. Through Nicolet's real time software "Chemigram" the appearance of the epoxies and hardeners can be followed. The Chemigram denotes saved interferograms which after the separation are coadded, fourier processed, and plotted. LC-FTIR characterizations of tetraglycidyl methylenedianiline epoxy (MY720) mixtures with hardeners, diaminodiphenyl sulfone and dicyanodiamide as well as others will be presented.

40 A SPECTROSCOPIC METHOD FOR DETERMINING PHOTODEGRADATION MECHANISMS AND RATES IN POLYMERIC MIRROR COATINGS. Dwight M. Smith, A. R. Chughtai, Department of Chemistry University of Denver, Denver, Colorado 80208. J. D. Webb, P. O. Schissel and A. W. Czanderna, Solar Energy Research Institute, Golden, Colorado 80401.

A method for determining mechanisms and rates of photo-induced degradation reactions in polymeric coatings on metal surfaces using specular reflection Fourier transform infrared spectroscopy has been developed. The polymer-coated metal specimens are placed in a chamber equipped with temperature control and gas flow inlets permitting the introduction of synthetic gaseous atmospheres. The chamber is fitted with a quartz window to admit simulated solar radiation and is accommodated in the sample compartment of a Digilab FTS-14 spectrometer. Infrared spectra are obtained as a function of exposure time at various temperatures and partial pressures of atmospheric contaminants. Spectral changes in the 5 micron unstabilized polycarbonate films on gold surfaces consistent with the photoFries rearrangement reactions were noted only after 300 second exposure time at ten Air Mass Zero solar constants. Characteristics of the Fourier transform infrared technique make possible the observation of photo-degradation events which conventionally take hours or days of accelerated testing.

42

HIGH RESOLUTION NMR IN SOLIDS By John S. Waugh, Massachusetts Institute of Technology, Cambridge, MA 02139

A hand-waving account will be given of the principles of coherent averaging, and how this notion has led to the development of a number of new NMR techniques, particularly ones useful for the study of solids. Principal techniques will be briefly illustrated. The latter part of the talk will be devoted to new methods for studying very slow molecular motion in solids.

43 SELECTIVITY IN MULTIPLE QUANTUM SPECTROSCOPY,* A. Pines, University of California, Berkeley, California 94720.

In Multiple-Quantum NMR Spectroscopy of N coupled spins one obtains n-quantum Fourier transform spectra, where n=0,1,2,...,N. The spectra of particular interest are often those with high n, which may be analyzable for a complex molecule without the need for isotopic spin labeling. For large n the intensity decreases, so an important question is whether selective excitation of n-quantum transitions is possible. Namely, can one design pulse sequences such that only a particular n or set of n's is excited? This corresponds to the absorption of only groups of n quanta. It will be shown that this can indeed be achieved by employing a combination of time reversal sequences and phase shifts. The principles of the theory will be outlined and examples of experimental results for large n in solids and liquid crystals will be presented. The discussion will include spectra, statistical treatment of intensities, degree of selectivity, and n-quantum relaxation. Extensions to other types of spectroscopy, where time reversal may not be possible, for example infrared multiphoton excitation, will be discussed.

*For a preliminary communication, see W. S. Warren, S. Sinton, D. P. Weitekamp and A. Pines, Phys. Rev. Lett. 43, 1791 (1979)

44 DOUBLE-CROSS-POLARIZATION NMR IN SOLIDS. E. O. Stejskal, Jacob Schaefer, and R. A. McKay; Monsanto Co., 800 N. Lindbergh Blvd., St. Louis, MO 63166.

In our double-cross-polarization NMR experiments we transfer polarization sequentially between three spin systems, usually from ^{1}H to ^{15}N to ^{13}C or from ^{1}H to ^{13}C to ^{15}N. We do this to determine the concentration of ^{13}C-^{15}N bonds in doubly labeled proteins. The method requires that we know the cross-polarization transfer rates between ^{13}C and ^{15}N for each of the various C-N bonds present. To determine directly the strength of the ^{13}C-^{15}N coupling, which is a factor in the cross-polarization transfer rate, we have examined the non-spinning, ^{15}N-line shapes (with proton-dipolar decoupling) of both singly and doubly labeled glycine, $^{15}NH_2CH_2CO_2H$ and $^{15}NH_2{}^{13}CH_2CO_2H$, and asparagine, $^{15}NH_2COCH_2CH(NH_2)CO_2H$ and $^{15}NH_2{}^{13}COCH_2CH(NH_2)CO_2H$. The line-shapes of the singly labeled species are largely determined by the chemical-shift anisotropy (CSA) pattern. For the doubly labeled species, there are other contributions to the line-shape, most prominently the ^{13}C-^{15}N dipolar coupling but also the anisotropic J-coupling between the ^{13}C and ^{15}N spins which combines with the dipolar coupling and either increases it or decreases it. We have employed a moment analysis to study these line-shapes and to separate the CSA contribution from the total spin-spin coupling.

45

PROTONIC SPECIES IN $H_{1.7}MoO_3$

R. E. Taylor, L. M. Ryan, P. Tindall, and B. C. Gerstein, 229 Spedding, Iowa State University, Ames, Iowa 50011

The nature of hydrogen in $H_{1.7}MoO_3$ has been investigated with solid state nuclear magnetic resonance. Samples prepared utilizing wet chemical reduction of MoO_3 in zinc and HCl, and dry hydrogen spillover on platinized MoO_3 have been characterized by proton NMR with and without strong proton decoupling and magic angle spinning. The results of these experiments indicate that there are at least two types of protons in these "hydrogen molybdenum bronzes", with the relative amounts depending upon the method of preparation. The major protonic species in both samples exhibits a shielding anisotropy which negates its identification as a hydroxyl proton in a hydrogen bond, or as a proton belonging to H_2O undergoing rapid rotation at room temperature. The NMR spectra of protons in samples prepared by different methods are in addition distinctly different at 90K. Photoelectron spectroscopy indicates that the molybdenum species in both types of samples are identical, to within the resolution of the experiment.

46 Quantitation in Cross Polarization NMR in Solids - Intensity Distortions in Mixed Systems. William L. Earl and D.L. VanderHart, National Bureau of Standards, Washington, D.C. 20234.

High resolution ^{13}C NMR in solids is being used for the analysis of a variety of solid materials from well defined crystalline solids to complicated organic geochemicals. Cross polarization is not intrinsically a quantitative technique in mixed systems. Variations in cross polarization times, T_{CH}, proton relaxation times, $T_1{}^H$ and $T_{1\rho}$, and spin diffusion can all produce distortions of the ^{13}C NMR spectrum obtained. Examples of these effects and their relationship to molecular properties will be presented.

A subject which has been mentioned but only cursorily investigated is the possibility of ^{13}C spectral distortions due to the presence of free radicals in the sample. This is currently under investigation in our laboratory and data will be shown with special reference to thermal decomposition of natural products.

47 CHEMICAL SHIFTS OF SPIN-½ NUCLEI AS BRIDGES BETWEEN THE STATES OF MATTER. G.E. Maciel, D.W. Sindorf, M.J. Sullivan, D.J. O'Donnell, L.W. Dennis, M.P. Shatlock, P.G. Mennitt and V.J. Bartuska, Department of Chemistry, Colorado State University, Fort Collins, CO 80523.

With the availability of cross polarization and magic-angle spinning (CP/MAS) techniques, high resolution nmr approaches can be used for solid or solid-like samples. This provides an opportunity for structural comparisons of what are nominally the same or related species in more than one state. Some of the ways in which such comparisons are useful are: using x-ray characterized structures as benchmarks for interpreting solution nmr data; using solid-state nmr data or solution nmr data for structural interpretations of surface-adsorbed or surface-attached species; comparing conformational details of a substance in the crystalline and solution states; assessing the analytical reliability of using extract data for inferring the nature of an insoluble residue; structural comparisons of related soluble and insoluble substances. Examples of such approaches are discussed, based on data from various spin-½ nuclides.

48 NMR STUDIES OF SURFACE STATES: H_2 ON A SUSPENDED METAL CATALYST, Cecil Dybowski, T. M. Apple and P. Gajardo, Departments of Chemistry and Chemical Engineering and the Center for Catalytic Science and Technology, University of Delaware, Newark, Delaware 19711.

Rhodium impregnated catalysts are important in the Fischer-Tropsch reaction to produce alkanes from carbon monoxide and hydrogen. Understanding the mechanism of this reaction might be aided by identifying surface species. To this end, we have studied the ^1H NMR spectra and the ESR spectra of catalysts loaded with hydrogen. The spectra show a number of surface species, when the catalyst is pretreated in a variety of ways. The results are consistent with a mechanism for surface adsorption involving association with the metal centers, followed by delocalization of some hydrogen on the surface. Studies of hydrogen adsorbed Rh catalysts on varying supports are under way to determine the effect of support constitution on hydrogen adsorption.

50

CHEMICAL SHIELDING STUDIES OF SMALL ORGANICS IN ARGON MATRICES By Kurt W. Zilm, University of Utah Research Institute, Salt Lake City, UT 84108, and David M. Grant, University of Utah, Salt Lake City, UT 84112

The ^{13}C shift tensors for a variety of small organics taken at 20°K will be presented. Drawing on symmetry arguments and work using dilabled ^{13}C compounds ($^{13}C_2H_4$, $^{13}C_2H_4$, $^{13}CH_3{}^{13}CHO$, $^{13}CH_3F$) the tensor axes can be related to the molecular frame. The observed trends in tensor values can then be explained in terms of structural and electronic effects. The studies using the dilabeled ^{13}C compounds also yield useful geometric information which will be discussed. In addition the effect of anisotropic indirect dipolar coupling will be addressed.

51 APLLICATIONS OF ROTATING FRAME POLARIZATION TRANSFER. G. C. Chingas, A. N. Garroway, *B. S. Holmes and W. B. Moniz. Chemistry Division, Naval Research Laboratory, Code 6120,* Washington, D. C. 20375.

Liquid state NMR signals of low γ nuclei can be enhanced by transferring polarization from a higher γ species when a resolvable J coupling is present. Since the signal enhancement E is equal to the ratio of the γ's, time savings on the order of E^2 ($\simeq 10^2$ to 10^3) are possible. This opens the possibility of observing low γ species which have not been previously studied because of impractically long accumulation times. We have developed several rotating frame polarization transfer methods, and have applied them to ^1H-^{13}C and ^1H-^{15}N systems. Recent applications of this method to low γ nuclei will be presented.

52

RECENT INVESTIGATIONS ON NMR OR ORIENTED SYSTEMS By C. L. Khetrapal, National Institutes of Health, Bethesda, Maryland 20205

NMR spectroscopy of molecules oriented in liquid crystals provides a convenient and relatively new method for the study of structure and conformation in the liquid phase. The application of the method to problems of biological importance has only recently been attempted. Such results will be discussed. The conformation around the nitrogen atom in model peptide systems, structure of some substituted imidazoles and studies on tricyclic molecules containing two nitrogen heteroatoms will be described. The application of 2-dimensional NMR to oriented systems and the use of the NMR spectroscopy to the determination of covalent and van der Waals radii will be demonstrated.

53 ^{17}O, ^{14}H NMR STUDY OF ORIENTATION OF UREA MOLECULES IN THE MAGNETIC FIELD ORIENTED LYOTROPIC LIQUID CRYSTALLINE PHASE

By M.I. Burgar, B. Valentine, T. St. Amour and D. Fiat, Department of Physiology and Biophysics, University of Illinois, Chicago, Illinois

The lyotropic liquid crystalline phase of type II oriented in a magnetic field has been used as an anisotropic media for orientation of urea molecules in the magnetic field. Since the ampliphilic liquid crystalline systems are cylindrically symmetrical around the director and assuming that a dissolved molecule stays within a domain of a given orientation of the director over a time that is long compared with the inverse of the quadrupole interaction one can describe a quadrupolar splitting of O-17, N-14 and H-2 nuclei as

$$\Delta\nu_Q = \frac{3}{2I(2I-1)} \left(\frac{e^2qQ}{\hbar}\right) S \left(\frac{3\cos^2\Theta_{LD} - 1}{2}\right)$$

where S is the order parameter which is a measure of the degree of orientation of particular groups and Θ_{LD} is the angle between the liquid crystal director and the magnetic field for an aligned sample.

We have used O-17 and H-2 quadrupolar splittings of water molecules to demonstrate the differences between two types of mesophases and different order parameters. The quadrupole coupling constant of O-17 in urea enriched to 20% oxygen-17 has been determined in a lyotropic liquid crystalline phase of type II and was found to be 10.2 MHz. The order parameters S of the degree of orientation of different groups has been determined from the quadrupolar splittings of O-17, N-14, and H-2 nuclei of urea.

54 ^{23}Na NMR in IONIC MESOPHASES

J. Bonekamp, T. Eguchi, and J. Jonas: Department of Chemistry, School of Chemical Sciences, University of Illinois, Urbana, Illinois 61801.

Upon melting sodium n-butyrate and sodium isovalerate exhibit liquid-crystalline ionic mesophases before isotropic melting. We report the ^{23}Na T_1 of each compound at 47.605 MHz over a wide range of temperatures including solid, mesophase, and isotropic melt. The temperature variation of the lineshape was also followed by using the Fourier transform technique. The most interesting feature in the lineshape measurements is the observation of the second order quadrupole shift powder pattern of the central line in the mesophase. This splitting is observed in spite of the short translational correlation time (c.a.10^{-10} sec) for the sodium cation. From the T_1 results the activation energy of Na^+ diffusion in the mesophase is determined to be E_a=4.13 kcal mol^{-1} for sodium n-butyrate and E_a=7.49 kcal mol^{-1} for sodium isovalerate. Furthermore, the motional narrowing of the linewidth observed in the solid phase indicates that Na^+ diffusion is fast enough to satisfy the narrowing condition ($\tau_c \simeq 10^{-5}$ sec). These experimental results are explained by a comparison with the characteristic behavior of a fast ionic conductor such as sodium β-alumina. Our discussion focuses upon the transport properties of sodium cation in the two compounds studied.

55 ION PAIRING IN SOLUTION BY MULTINUCLEAR MAGNETIC RESONANCE.

Joel L. Gray, Gary E. Maciel, Colorado State University, Ft. Collins, CO

In the literature concerning metal-ion nmr, ion pairing has been suspected as a prime reason for chemical shift dependences on electrolyte concentration. We felt that a promising approach to this problem would be multinuclear nmr on an electrolyte system where the cation and anion could both be observed directly.

Electrolyte systems of sodium tetraethylaluminate (NaTEA) in m-xylene, and binary mixtures of m-xylene and THF and of m-xylene and pyridine have been studied by sodium-23. aluminum-27 and proton nmr. In m-xylene aggregation was found to be the important influence on the sodium-23 chemical shift and linewidth. In mixtures of m-xylene and THF or m-xylene and pyridine variations in sodium-23 chemical shift, linewidth and spin-lattice relaxation time, aluminum-27 linewidth and spin-lattice relaxation time, and proton chemical shift and line shape were recorded to investigate the nature of and gross structural features of ionic species in solution. Evidence for the existence of discrete sodium tetraethylaluminate complexes with two, four and six THF molecules and one, two and four pyridine molecules was found from the sodium-23 and proton chemical shift data. All complexes involved only direct solvent-to-Na^+ coordination, except for the NaTEA·6THF complex, where two THF molecules were associated with the tetraethylaluminate anion. The proton line shapes of the tetraethylaluminate methylene protons indicated that sodium tetraethylaluminate and its solvent complexes existed as contact ion pairs and various forms of solvent-associated ion pairs, respectively.

SOLUTION AND SOLID ^{31}P NMR STUDIES OF POLYPHOSPHATES

56 T. M. Carr, W. Veeman and W. M. Ritchey, Case Western Reserve University
Cleveland, Ohio 44106 and Univ. of Nijmegen, Nijmegen, Netherlands

Solution state P-31 NMR spectroscopy was performed on vitreous polyphosphate materials derived from melts of various alkali metal and phosphorus containing compounds.

A series of glasses varying in average chain length (designated $\bar{n}$) were prepared ($\bar{n}$ being determined by the mole ratio of alkali metal to phosphorus, according to the relationship, $\bar{n} = 2/(\frac{M}{P}-1)$. Certain significant spectral features were observed to vary in relationship to increasing $\bar{n}$,

The composition of these materials were determined with regard to ring and linear chain components in these glasses with the ultimate goal of being able to characterize the amorphic state.

High resolution solid state ^{31}P NMR spectroscopy has been performed on a number of condensed phosphate, both glassy and crystalline, species. It was found that broadening due to chemical shift anisotropy and dipolar interactions are largely eliminated by magic angle rotation at a rate of 4 KHz. This permitted study of spectral features, that include significant down field shifts of resonances from solution phase values and resonances resulting from orientations of phosphate moieties in the solid.

57

^{13}C RELAXATION MEASUREMENTS ON SOLID POLYMERS USING VARIABLE-TEMPERATURE MAGIC-ANGLE SPINNING

By W. W. Fleming, J. R. Lyerla, and C. S. Yannoni, IBM Research Laboratory, San Jose, CA 95193

Proton-decoupling, variable-temperature magic-angle spinning (VT-MAS), and cross-polarization techniques have been utilized to determine ^{13}C spin-lattice (T_1^C), rotating frame ($T_{1\rho}^C$), and spin-spin (T_2^C) relaxation times for each carbon in the repeat unit of semi-crystalline poly (propylene), PP and PMMA over a temperature range 77°K to 300°K. In addition, proton rotating-frame ($T_{1\rho}^H$) relaxation times and cross-polarization time T_{CH}, have been measured over the temperature interval for the polymer systems. All the carbons in PMMA and PP show minima in T_1^C and $T_{1\rho}^C$ which reflect methyl group reorientational motion at the appropriate measuring frequencies (15 MHz and 57 kHz). An interesting phenomenon observed in both molecules is strong motional broadening of the methyl carbon resonance in the temperature region of the respective $T_{1\rho}^C$ minimum. Other facets of the relaxation behavior of these polymers will be discussed with respect to their implications for insight into polymer chain dynamics in the solid state.

58

DEUTERIUM NMR OF POLYETHELENE TEREPHTHALATE AND POLYMETHYL METHACRYLATE.

A. J. Vega, Central Research and Development Department, E. I. du Pont de Nemours and Company, Experimental Station, Wilmington, Delaware 19898.

Deuterium NMR data will be presented of selectively deuterated samples of polyethylene terephthalate (PET) and polymethyl methacrylate (PMMA). The absence of spin diffusion provides the possibility to utilize T_1 dispersion for the separate observation of distinct molecular environments in the polymer. The combination of line-shape, T_1, and T_2 measurements enables a quantitative determination of the nature, the amplitude, and the rate of various macromolecular motions. The results for PET include vibrations and benzene-ring flips in the crystalline regions and the gradual onset of liquid-type behavior in the amorphous regions above the glass transition temperature. In PMMA, the backbone motions related to the glass transition will be discussed. The results will be compared to dynamic mechanical and dielectric relaxation measurements.

59 MOLECULAR CONFIGURATIONS AND DYNAMICS OF ELASTOMERS VIA SOLID STATE NMR.

Yau-Yam Lin, Ronald Pratt, James Goebel and Jerome Ackerman. Department of Chemistry, University of Cincinnati, Cincinnati, Ohio 45221.

The linear high polymeric phosphazenes $(\text{-PR}_2\text{=N-})_n$ constitute an interesting class of materials. Although the first of these was prepared over eighty years ago, only recently has significant interest arisen in the chemistry and physics of these polymers. We have studied the high resolution ^{31}P NMR of several phosphazene elastomers (R = OCH_3, OCH_2CH_3, OCH_2CF_3, OC_5H_{11}, OC_6H_5/p-OC_6H_4Et) at temperatures above and below their glass transitions.

As a specific case, spectra of the aryl copolymer obtained over the range 150K to 500K displaying a number of interesting features are presented. Motional narrowing to an axially symmetric chemical shift powder pattern (suggestive of the onset of rapid reorientation about the chain axis) occurs only at temperatures well above T_G, while near isotropic spectra are obtained at temperatures well below the presumed melt temperature. However, spin echo measurements of the ^{31}P homonuclear dipolar contribution to the linewidth indicate that some relaxation mechanism is still operative at 150K.

Additionally, in marked contrast to currently accepted theories of phosphazene polymerization, we find evidence for an equilibrium between the substituted cyclic trimer and linear oligomers or high polymer.

Results on our continuing computer studies of the configurational behavior of dilute ^{19}F spin-labeled polymers under bulk deformation, as well as some preliminary experimental findings, will also be presented.

60 NMR CHEMICAL SHIFTS AND POLYMER MICROSTRUCTURE. Alan E. Tonelli, Bell Laboratories, 600 Mountain Avenue, Murray Hill, New Jersey 07974.

^{13}C and ^{19}F chemical shifts are calculated for the various carbon and fluorine atoms contained in synthetic vinyl polymers and the biologically relevant polypeptides (^{13}C NMR chemical shifts only). This is achieved by assuming upfield chemical shifts for those carbons and fluorines in a three-bond gauche arrangement with other carbon or fluorine atoms in the γ position relative to their trans arrangement. From the conformational characteristics of these polymers, we obtain backbone bond rotation probabilities leading directly to the necessary frequencies of the γ gauche effects which determine the relative ^{13}C and ^{19}F NMR chemical shifts. Adoption of $\gamma_{C,C} \approx \gamma_{C,F} \approx -5$ ppm, $\gamma_{F,C} \approx -30$ ppm, and $\gamma_{F,F} \approx -15$ ppm, where $\gamma_{a,b}$ denotes the upfield shift produced at atom a by γ substituent b when in a gauche arrangement with a, leads to calculated chemical shifts in agreement with the observed. This provides us a means for determining the microstructure (stereoregularity, head-to-head:tail-to-tail defect content, sequence of monomers) of synthetic vinyl homo- and copolymers and polypeptides.

61 CARBON-13 NMR STUDIES ON THE MICROSTRUCTURE OF POLY(VINYL CHLORIDE) AND THE MECHANISM OF VINYL CHLORIDE POLYMERIZATION. F. C. Schilling, W. H. Starnes, Jr. and F. A. Bovey, Bell Laboratories, Murray Hill, New Jersey 07974.

^{13}C NMR is a powerful technique for the determination of polymer microstructure. Attempts to determine the microstructure of PVC by this technique have not been successful, however, due to the dispersion of carbon chemical shifts resulting from the different stereoisomers. Recently, it has been shown that this difficulty can be overcome by applying ^{13}C NMR to PVC which has been reductively dehalogenated by $LiAlH_4$, $LiAlD_4$, Bu_3SnH, or Bu_3SnD. The replacement of chlorine by hydrogen or deuterium removes the complexity of stereochemistry and makes possible a detailed analysis of the polymer microstructure. The primary defect in PVC is the chloromethyl branch. It can be shown that all of the chloromethyl branches are formed via a 1,2-chlorine-atom shift following a head-to-head addition of monomer to the growing chain. Long branches occur at a lesser frequency than the chloromethyl branches and result from hydrogen abstraction from the polymer. Tertiary halogen is present at all of the long-branch points of polymers prepared at 100°C. PVC also contains a few 2-chloroethyl branches with tertiary chlorine present at the branch points. Two types of saturated long-chain end are present in PVC prepared at 100°C. The first type, $-CHCl-CH_2-CHCl-CH_2Cl$, represents about 75% of these ends and is formed by reaction of a chlorine atom with monomer to initiate chain growth: $Cl\cdot + CH_2{=}CHCl \rightarrow ClCH_2CHCl$ + monomer $\rightarrow ClCH_2-CHCl-CH_2-CHCl\cdot \rightarrow$ etc. The second type, $-CH_2-CHCl-CH_2-CH_2-Cl$, represents about 25% of the saturated long-chain ends and is formed via hydrogen abstraction from the polymer by the growing-chain carbon radical.

62 CARBON-13 NMR AND TRANSITIONS IN POLYETHYLENE. J. J. Dechter, D. E. Axelson and L. Mandelkern. Department of Chemistry, Florida State University, Tallahassee, Florida 32306.

By probing the non-crystalline regions of linear polyethylene with proton decoupled ^{13}C NMR, we have reported that a conservative upper limit to the glass temperature of this polymer was -40°C. This conclusion was reached because a spectrum could still be observed at this temperature but collapses at lower temperatures; and the correlation time for segmental motion was determined to be about 10^{-8} sec., which is much too small for a glass. This kind of experiment has now been extended to the branched polyethylenes, characterized by a well-defined dynamic-mechanical transition in the vicinity of -20°C (the β transition) which is usually identified with the glass temperature. Two samples, which show dynamic-mechanical transitions at -19 and -6°C, respectively, were studied in detail. For both samples ^{13}C NMR spectra could be obtained within 1° of this temperature; correlation times were the order of 10^{-10} sec. The identification of the β transition with the glass temperature must, therefore, be seriously questioned. A transition definitely exists, as evidenced by the dynamic-mechanical results and temperature dependence of the correlation time. Possible molecular origins for this transition will be discussed.

63 SOLID STATE ^{2}H NMR OF FIBROUS COLLAGEN, Lynne S. Batchelder, C. E. Sullivan, Lynn W. Jelinski, and D. A. Torchia, National Institutes of Health, Bethesda, MD 20205.

The ^{2}H quadrupolar echo technique was used to study the mobility of the peptide backbone and amino acid sidechains of collagen in solution and as fibrils. Samples labeled with [3,3,3-d_3]alanine and [d_{10}]leucine were prepared *via* chick calvaria culture. A 38.8 kHz quadrupolar splitting is observed for powdered deuterated alanine at +18°C. A reduced value of $\Delta\upsilon_q$ to 10 kHz for the alanine labeled collagen in solution indicates that an average angle of 70° is made between the alanine C^{α}-C^{β} bond axis and the long axis of the helix. Near absence of motion in frozen fibrils is indicated by the observed $\Delta\upsilon_q$ of 37.3 kHz for the alanine labeled fibrils at -18°C. At +18°C the apparent qquadrupolar splitting for the same sample is reduced to ~30 kHz and nearly two-thirds of the signal intensity is lost. The homogeneous T_2 determined to be 105 μsec explains the loss of intensity. Analysis of the lineshape of the alanine labeled fibrils at +18°C in terms of a two-site jump model in which the jump rate is rapid compared to $(\Delta\upsilon_q)^{-1}$ indicates that the collagen backbone undergoes an ~30° azimuthal reorientation. Observed quadrupolar splittings for the leucine labeled sample as the powdered amino acid, in solution at +18°C, and as fibrils at -18°C and +18°C are 35.2, 9, 32, and 25 kHz. These values are less than those for the alanine labeled sample. A qualitative analysis suggests that sidechain motion in addition to backbone reorientation is responsible for the further reduction in $\Delta\upsilon_q$.

64 *CHARACTERIZATION OF THE METAL CLUSTERS IN METALLOTHIONEIN BY ^{113}Cd NMR By* James D. Otvos and Ian M. Armitage, Yale University, New Haven, CT 06510

Metallothionein is a small cysteine-rich metal binding protein, found in the kidney and liver of a wide variety of animal species, which has been postulated to play an important role in metal detoxification and/or metabolism. The structural basis for its remarkable metal binding capacity (about 7 g-atoms metal/mole) has been investigated by ^{113}Cd NMR of the Cd, Zn liver protein isolated from rabbits injected with 96%-enriched $^{113}CdCl_2$. The spectrum exhibits extensive ^{113}Cd-^{113}Cd spin coupling which arises from adjacent metal ions linked by bridging cysteine thiolate ligands. The structure of these polynuclear metal clusters has been elucidated by selective homonuclear decoupling and spin echo modulation experiments. The NMR data indicates that pure rabbit liver metallothionein is a mixture of species containing different relative amounts of Cd^{2+} and Zn^{2+}, though the extent of this heterogeneity is quite limited. In contrast to the rabbit protein, $^{113}Cd^{2+}$-induced metallothionein from the crab Scylla serrata contains no Zn^{2+}. The ^{113}Cd NMR properties of the homogeneous crab protein and the structures of its tow 3-metal clusters will also be presented. (Supported by NIH Grants ES 01674 and AM 18778).

65 NMR STUDIES OF THE FILAMENTOUS VIRUSES. S.J. Opella. Department of Chemistry, University of Pennsylvania, Philadelphia, Pennsylvania 19104

The viruses fd and Pf1 from infected Escherichia coli and Pseudomonas aeruginosa, respectively are being studied by NMR. These bacteriophages consist of a single stranded circle of DNA packaged in a tubular shell made of several thousand copies of a 5,000 MW major coat protein. The DNA and the coat protein can be characterized by NMR. Because of the high molecular weight and rigidity of the virus particle, methods of solid state NMR are required to study the intact virion. The isolated virus DNA and coat protein have much smaller size and more motion, thus they can be studied by solution approaches. The ^{31}P NMR chemical shift properties of the DNA of these viruses do not show evidence of structural changes induced by protein-DNA interactions. There is only partial averaging of the phosphodiester chemical shielding tensor of the viruses in solution which is indicative of substantial immobilization of the DNA backbone by the coat proteins. Changes in coat protein structure that result from virus formation and the DNA-protein interactions can be described by comparing NMR properties of the virion to those of the coat protein isolated in solution. NMR spectra of the filamentous viruses in solution are characteristic of a highly ordered system with some aliphatic amino acid sidechains able to rotate independently of the protein backbone. The coat protein in solution has spectral properties of a low molecular weight native folded protein.

66 THE NUCLEAR OVERHAUSER EFFECT IN LARGE MOLECULES. Joseph H. Noggle, Department of Chemistry, University of Delaware, Newark, DE 19711

The effect of spin diffusion and nuclear relaxation in slowly moving molecules will be discussed, particularly as it affects the measurement of nuclear Overhauser effects (NOE) in such circumstances. Theoretical results on effects of rf power and frequency on such experiments will be presented along with theoretical methods for calculating NOE's in model systems.

67 INTERNAL MOTION IN GLOBULAR PROTEINS EXAMINED BY ^{13}C NMR OFF-RESONANCE RELAXATION EXPERIMENTS. W. J. Goux and T. L. James. Dept. of Pharmaceutical Chemistry, School of Pharmacy, UCSF, San Francisco, Ca. 94143.

Off-resonance relaxation measurements have been carried out on three small globular proteins using natural abundance ^{13}C NMR spectroscopy. The experimental observable consists of the ratio (R) of the intensity of a resonance peak in the presense of an rf field applied off-resonance to the intensity in the absense of the applied field. The intensity ratio is related to a relaxation rate ($1/T_{1\rho}^{off}$) produced by the off-resonance radiation. In the present study, R values were acquired for horse myoglobin, bovine ribonuclease A and HEW lysozyme. These values, in addition to conventional relaxation parameters, enabled a comparison of the molecular motions of the various aliphatic sidechains both within and between the three proteins. A more in-depth study has been undertaken to characterize the motions of the sidechains of the six tyrosine residues in ribonuclease A.

68 CHARACTERISATION OF THE CALCIUM-INDUCED CONFORMATIONAL CHANGE IN HEPARIN. J. Boyd*, P. Gettins+ and F.B. Williamson#. *Dept. Biochemistry, Oxford University, Oxford OX1 3QU, U.K.; +Dept. Molecular Biophysics and Biochemistry, Yale University, New Haven 06510; #Dept. Biochemistry, University of Aberdeen, Aberdeen AB9 1AS, U.K.

Heparin is a glycosaminoglycan polysaccharide with a repeating disaccharide unit of D-glucosamine and uronic acid. It has well documented pharmacological properties including anticoagulant activity, lipaemic activity and the ability to induce platelet aggregation.

It is shown by ^{13}C and ^{1}H NMR and physical methods that heparin interacts strongly with calcium ions to form a complex with the stoichiometry of one calcium ion per tetrasaccharide unit. Spin-echo methods and lanthanide ions are used to help characterise the tetrasaccharide-metal complex. It is found to have a well defined rigid structure.

It is proposed that the reason for post-polymerisation epimerisation of D-glucuronate to L-iduronate is the attainment of a configuration which permits binding of calcium ions. This gives rise to a modulation of the flexibility of the tetrasaccharide units within the heparin polymer, which may have functional significance.

70 CARBON-13 NMR OF GLYCOPROTEINS. Adam Allerhand, Department of Chemistry, Indiana University, Bloomington, Indiana 47405.

Natural-abundance ^{13}C NMR spectroscopy yields information about structure and internal motions of glycoproteins. The following topics will be presented: (1) Chemical shifts of glycopeptides (model compounds). (2) A comparison of the unglycosylated bovine ribonuclease A and the glycoprotein ribonuclease B. (3) A study of antifreeze glycoproteins from Antarctic fishes. (4) Determination of anomeric linkages and internal motions of the carbohydrate residues of glucoamylase from *Aspergillus niger* (intact and enzymatically modified; native and denatured). (5) A study of the carbohydrate composition and other properties of laccase from *Rhus vernicifera*.

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CARBON-13 NMR SPECTRA OF MULTIFUNCTIONAL ACRYLATES By M. J. Vaickus and M. A. Pokorney, DeSoto, Inc. 1700 S. Mt. Prospect Road, DesPlaines, IL 60018

Multifunctional acrylates typically encountered in the coatings industry were examined by Carbon-13 spectroscopic methods. The chemical shifts of each carbon, in the various materials, were assigned. This method in addtion to its relative quickness and ease is both qualitatively and quantitatively efficient. Furthermore, this technique can ascertain the presence of impurities and or isomers of the individual multifunctional acrylates. Additionally the method can be used in the analysis of multifunctional acrylate mixtures. Correlations determined for the various homoolgous series are presented in conjunction with the distinctive features between acrylate and methacrylate functionalities.

75 ^{13}C-NMR OF TYROSYL-[1-^{13}C] ACETYLATED-GUANIDINATED CYTOCHROME C. DENATURATION BY GUANIDINE HCl.

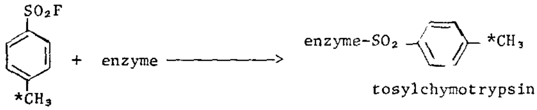
R. A. Nieman, D. Gust, and J. R. Cronin, Arizona State University, Tempe, Arizona 85281

Guanidinated cytochrome c from horse heart can be fully acetylated at tyrosyls 48, 67, 74, and 97 by reaction with N-[1-^{13}C] acetyl imidazole in the presence of 8 M urea. ^{13}C-NMR spectra of the resulting O-[1-^{13}C] acetyl-tyrosyl-guanidinated cytochrome c derivative (ac$_4$-guan cyt c) show distinct and resolved resonances for the four [1-^{13}C] acetyl-tyr groups. The resonances have been assigned to specific tyrosyls in the primary sequence of the protein. We report here the results of ^{13}C-NMR studies of [1-^{13}C] acetylated-guanidinated cyt c derivatives in the absence and presence of guanidine HCl (guan-HCl). Ac$_4$-guan cyt c was titrated with guan-HCL from 0 to 6 M, and the changes in chemical shifts of the [1-^{13}C] acetyl-tyr resonances were observed by ^{13}C-NMR. T_1 studies were performed in the absence and presence of denaturant. These results show that the protein undergoes a conformational rearrangement in the presence of 0.5-1.0 M guan-HCl and a denaturing transition in the presence of 2.5-3.5 M guan-HCl. Denaturation is cooperative in this region, with simultaneous changes in chemical shifts and intensities for the four [1-^{13}C]acetyl-tyr resonances seen. Changes observed in the ^{13}C-NMR spectra of this derivative correlate with alterations observed by other spectrophotometric methods. Results for other [1-^{13}C] acetylated guan cyt c derivatives will also be discussed. Work supported by the American Heart Association, Arizona Affiliate.

76 CARBON-13 NMR STUDIES OF SPECIFICALLY LABELED TOSYLCHYMOTRYPSIN

by J. T. Gerig and E.F. Weigand. Department of Chemistry, University of California, Santa Barbara, California 93106.

Tosylchymotrypsin in which the methyl carbon of the toluenesulfonyl group is enriched with carbon-13 has been prepared by treating the enzyme with labeled compound I. The chemical shift of this carbon is invariant to sample pH or to denaturation of the protein.



When considered in light of the structure of the crystalline enzyme derivative and the effects of solvents on methyl chemical shifts of model compounds, the results suggest that the tosyl methyl group is exposed to solvent when the protein is in solution.

This work was supported by grants from the N.I.H.

77 NEW BINUCLEAR SHIFT REAGENTS FOR ALTERING NMR SPECTRA OF AROMATIC, OLEFINIC, AND HALOGENATED COMPOUNDS.

T. J. Wenzel and R. E. Sievers, Dept. of Chemistry and CIRES, Univ. of Colorado, Boulder, CO 80309.

New nmr shift reagents capable of selectively altering the spectra of soft Lewis bases such as aromatics, olefins, halogens and phosphines will be discussed. The shift reagents are binuclear complexes involving a lanthanide(III) β-diketonate and silver(I) β-diketonate. These shift reagents can be used to measure the relative amounts of cis and trans isomers of alkenes in a mixture. The nmr spectra of mono and polycyclic aromatic compounds are considerably clarified in the presence of these shift reagents. The binuclear shift reagents can also be used to quantitate mixtures of xylenes. Significant shifts have also been observed in the nmr spectra of compounds such as cyclohexyl chloride and 1-bromopentane. The proton nmr spectrum of triphenylphosphine becomes first order in the presence of these binuclear complexes. Also, through the use of chiral lanthanide and silver β-diketonates, certain resonances for the dextro and levo protons of enantiomers exhibit different chemical shifts. This permits determination of enantiomeric composition of olefinic compounds such as terpenes.

78 HIGH RESOLUTION ^{13}C NMR OR SOLIDS AT HIGH MAGNETIC FIELDS

By A.D.H. Clague, KONINKLIJKE/SHELL-LABORATORIUM, AMSTERDAM (Shell Research B.V.)

Some of the important aspects of performing high resolution ^{13}C NMR at a magnetic field of 7.05 T (300 MHz ^{1}H NMR) using high power proton decoupling, cross polarization and magic angle spinning (CPMAS) will be discussed. The advantages of improved sensitivity and greater chemical shift dispersion are to some extent offset by the need to spin the samples at very high speeds. There are, however, many areas for solid state NMR study where the chemical shift anisotropy of the material under study is not excessive and there is no need to spin faster than about 4 kHz which is a readily achievable speed.

By way of example we will show spectra of the solid polymers; polybutadiene, polysioprene and polystyrene/butadiene. These materials display characteristics of both liquids and solids from the point of view of their molecular motion; this is demonstrated by comparing their so-called "conventional" high resolution spectra obtained under liquid state NMR conditions with their high resolution solid-state spectra. It will be shown that as the degree of molecular motion diminishes, the achievable resolution of the "conventional" spectra deteriorates while the CPMAS spectra retain their high resolution characteristics.

Amsterdam, April 8th 1980

79 NMR LANTHANIDE SHIFT REAGENTS WITH POLYDENTATE CAGE LIGANDS. K. C. Brooks and R. E. Sievers. Dept. of Chemistry and CIRES, University of Colorado, Boulder, CO 80309.

Polydentate cage-like ligands have been synthesized by the Schiff's base condensation of tris(2-aminoethyl) amine with a variety of β-diketones (trifluoroacetylacetone, 2,2-dimethyl-6,6,7,7,8,8,8-heptafluoro-3,5-octanedione, and 1-phenyl-4,4,5,5,6,6,6-heptafluoro-1,3-hexanedione). Complexes have been made of these ligands with selected lanthanide and transition metal ions. The complexes of Eu(III) Yb(III), and Pr(III) have been evaluated as nmr shift reagents for substrates with oxygen and nitrogen donor atoms. The structural consequences of the rigid cage-like geometry will be discussed. Particular attention will be paid to the use of these shift reagents in McConnell-Robertson calculations.

80 ALUMINUM-27 NMR STUDIES ON THE ROOM TEMPERATURE MOLTEN SALT, 1-n-BUTYLPYRIDINIUM CHLORIDE/ALUMINUM CHLORIDE, Joel L. Gray, Gary E. Maciel, Colorado State University, Ft. Collins, CO 80523.

Aluminum-27 nmr was used to study room temperature molten salt mixtures of 1-n-butylpyridium chloride and $AlCl_3$. Two overlapping aluminum-27 resonances with vastly different linewidths were resolved by time-resolution nmr experiments. Without using time-resolution techniques only one resonance was observed and the overall linewidth of the resonance was dependent on the formal mole ratio, moles $AlCl_3$:moles 1-n-butylpyridium chloride. The exchange rate between $AlCl_4^-$ and $Al_2Cl_7^-$ was found to be slow and a positive enthalpy change was determined for the equilibrium shown below.

$$2AlCl_4^- \rightleftarrows Al_2Cl_7^- + Cl^-$$

Addition of iodide to a melt with a formal $AlCl_3$:BuPyCl mole ratio of 1.4 produced an aluminum-27 spectrum consisting of four resonances that were assigned to $AlCl_4^-$, $AlCl_3I^-$, $AlCl_2I_2^-$ and $AlClI_3^-$.

82 CARBON-13 NUCLEAR MAGNETIC RESONANCE OF PHENOLIC RESINS. Stanley A. Sojka, Roger A. Wolfe, Edward A. Dietz, Jr., and Bobby F. Dannels. Hooker Chemical & Plastics Corp., Research Center and Durez Division, Grand Island Complex, Niagara Falls, NY 14302.

Carbon-13 FT/NMR has proven to be an important tool in the structural elucidation and compositional analysis of complex phenolic resins. The carbon-13 chemical shifts of the phenoxy carbons are very sensitive to phenolic substituents of penultimate phenol rings. Branching also plays an important role in determining C-13 NMR line positions. The spectra of a number of substituted phenolic resins will be discussed with a view towards establishing chemical shift/structure relationships.

83 HIGH RESOLUTION CARBON-13 NMR OF SOLID FOSSIL FUEL FRACTIONS, M. T. Melchior and K. D. Rose, Exxon Research and Engineering Company, 1900 E. Linden Avenue, Linden, N. J. 07036

The characterization of solid fossil fuel materials by cross polarization (CP) ^{13}C NMR with high speed magic angle sample spinning (MAS) is becoming an important new area for research. This technique has the potential of providing a description of the carbon type distribution in a variety of previously intractable solids such as coals, oil shales, chars, cokes, etc. The purpose of this paper is to assess the quality of and the limitations on this description, especially as regards quantitative reliability and the potential for resolving structural details beyond aromatic/aliphatic differences. In this study solid samples of asphaltenes and pitches from petroleum and coal have proven to be valuable reference points. These solids have spectral characteristics similar to native coals yet they can be well characterized by liquid solution FTNMR. Informative results have also been obtained for chemically modified solid coals into which known structural features have been introduced. Study of the quantitative aspects of cross-polarization using these materials as examples has given very encouraging results. At least for hydrocarbon rich solids, reliable relative intensities (i.e. aromaticities) are obtained for an easily realizable range of operating conditions. Although CP/MAS spectra of carbonaceous solids are generally severely limited in chemical shift resolution, preliminary results indicate that resolution of carbon types can be greatly enhanced by exploiting differences in relaxation behavior.

84 PHOSPHORUS-31 NMR STUDIES OF RHODOPSIN-PHOSPHOLIPID INTERACTIONS. N. Zumbulyadis and D. F. O'Brien. Eastman Kodak Company, Research Laboratories, Rochester, NY, 14650.

The lineshapes of the ^{31}P NMR spectra of unsonicated phospholipid bilayers and lipid-protein complexes are determined by restricted molecular mobility and the dynamics of protein-lipid interactions. The results of lineshape analyses for recombinants of the photochemically active protein rhodopsin with egg phosphatidylcholine will be presented.

The presence of rhodopsin in protein:lipid ratios of 1:200 and 1:100 does not alter significantly the effective chemical shift anisotropy. However, a broadening of the powder pattern is observed. The lineshape is discussed in terms of changes in the rotational diffusion coefficient using the approach of Freed et al. (J. Phys. Chem., 75, 3385(1971); ibid 83, 525(1979)).

Anisotropic T_1 and T_2 values are observed and are shown to be due to angularly restricted motion.

Finally, attention will be drawn to possible NMR artifacts that may arise from an improper preparation of protein-lipid complexes.

85 OLIGONUCLEOTIDE CONFORMATION. P^{31} RELAXATION STUDIES. Phillip A. Hart and Charles F. Anderson. School of Pharmacy, University of Wisconsin, Madison, Wisconsin 53706

We have begun the adaptation of existing NMR relaxation theory to dipolar phosphorus spin-lattice relaxation and phosphorus-proton nuclear Overhauser effects pertinent to the phosphodiester backbone conformation of nucleic acids. The current model includes isotropic overall motion as well as internal motion. The model for internal motion is more general than any of those recently published. It is a discrete model, allowing each bond to assume the classical g^+, g^-, and t conformations independently and randomly. For each bond, it is assumed that all activation barriers are the same, but that occupation probabilities may be different. The model has been used to compute phosphorus relaxation parameters for a POCH system allowing discrete, random and independent rotation about the PO and the OC bonds. The computed T_1's and NOE's are sensitive to rates of overall as well as internal motion and to the distribution of rotamers among the classical positions for each bond. Application of this model to the conformational analysis of the phosphodiester backbone of oligonucleotides will be presented.

86 CYTOCHROME c_{553}. HEME ENVIRONMENT AND UNPAIRED ELECTRON DISTRIBUTION AS DETERMINED BY ^{1}H NMR SPECTROSCOPY AT 360 MHz. Eldon L. Ulrich and John L. Markley, Department of Chemistry, Purdue University, West Lafayette, IN 47907

Nuclear Overhauser enchancement (NOE) measurements have been used to assign resonance peaks to specific heme-ring methyl, meso, methine, and methine-methyl protons in spectra of ferrocytochrome c_{553} from Aphanizomenon flos-aquae. Further NOE experiments indicate that the side chains of Met^{44} and Tyr^{45} are located near pyrrole ring IV of the heme and that the benzyl ring of Phe^{65} is near the heme α-meso proton. The His^{18} C$^{\delta}$ proton exhibits an NOE from the heme α-meso proton; therefore, the plane of the imidazole is aligned perpendicular to the plane of the heme α-meso, Fe, γ-meso axis. From these results cytochrome c_{553} appears to have the same general tertiary structure as other c-type cytochromes. Exchange broadening of the heme proton resonances from partially oxidized samples indicates that the unpaired electron spin density of ferricytochrome c_{553} is somewhat localized on pyrrole rings I and III. We agree with the recent suggestion that the polarization of electron spin density in ferricytochromes c of this type is determined by the chirality of the methionine sulfur ligand to the iron [Senn, H., Keller, R. M., Wüthrich, K., Biochem. Biophys. Res. Commun. 92, 1362 (1980)]. Hence we predict that the methionine sulfur in cytochrome c_{553} is S as found by X-ray crystallography for cytochrome c_{551} [Almassy, R. J., and Dickerson, R. E., Proc. Natl. Acad. Sci. USA 75, 2674 (1978)] rather than R as found for tuna cytochrome c [Takano, T., Trus, B. L., Mandel, N., Mandel, G., Kallai, O. B., Swanson, R., Dickerson, R. E., J. Biol. Chem. 252, 776 (1977)]. (Supported by Grants USDA 5901141080160O and NIH RR 01077.)

87 CONFORMATIONAL TRANSITIONS OF CYTOCHROME C BY ^{13}C AND ^{2}H NMR METHODS. J. B. Wooten and J. S. Cohen, DPB, NICHD, NIH, Bethesda, Maryland 20205 and A. Schejter, Biochemistry Department, Tel Aviv University, Israel.

The conformational transitions of cytochrome c induced by acid and base have been studied by ^{13}C and ^{2}H NMR methods. The two methionyl methyl groups were selectively monitored in samples enriched in ^{13}C and ^{2}H, prepared by substitution with the appropriate isotopically labeled methyl iodide. The novelty of the ^{2}H NMR method is that it is possible to unambiguously monitor the Met 80 residue in both Fe-bound and unbound conformations simultaneously. While the overall transition of ferricytochrome c occurred with an apparent pK of ca. 3.4, as indicated by the ^{13}C natural abundance spectra, the ^{13}C resonance of Met 80 was not observed in [ε-^{13}C]Met 65, Met 80 ferricytochrome c down to even pH 1. This is because of the proximity of this residue to the paramagnetic Fe(III) atom, to which it is bound in the native form. The ^{2}H spectra of [ε-^{2}H]Met 65, Met 80 ferricytochrome c showed that Met 80 is exchanging rapidly between Fe(III)-bound and unbound forms as the pH is lowered. The alkaline transition of ferricytochrome c was followed by measuring the relative areas of the ^{2}H NMR peaks corresponding to bound and unbound [ε-^{2}H]Met 80, and from the reappearance of the ^{13}C signal of [ε-^{13}C]Met 80 as the pH was raised. Titration curves yielded pK values varying from 7.6 to 9.1 and Hill coefficients (n) from 0.75 to 1.0 for different samples, and these values were confirmed by UV measurements. These variations arise from conformational alterations resulting from extended alkaline treatment and/or extensive chromatographic purification.

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STRUCTURE OF METABOLITES OF MYROTHECIUM VERRUCARIA: RORIDIN J. TRICHODERMADIENE, AND CERTAIN TRICHOVERROLS AND TRICHOVERRINS By E. P. Mazzola, Food & Drug Administration, Washington, D C 20204, B. B. Jarvis, G. P. Stahly, J. Midiwo, T. DiSilva, G. Pavanasasivam, and R. Geohegan, University of Maryland, College Park, Maryland 20742

Over the past decade metabolites of Myrothecium verrucaria have been investigated by a number of research groups. These compounds are members of the roridin and verrucarin groups and were, until recently, believed to possess characteristic macrocyclic ring systems. Metabolites have now been isolated which contain either (i) the dienic portion of the previously-characterized macrocyclic rings or (ii) both "halves" of the general macrocyclic ring system but broken near the middle. The carbon-13 NMR chemical shifts of olefinic methyl groups which are situated cis or trans to acrylic lactonic oxygen atoms appear to be diagnostic and may eliminate the dependence on NOE measurements to determine the stereochemistry of these systems.

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RELATIONSHIPS BETWEEN HUMIC SUBSTANCES AND THEIR PROBABLE PROGENITORS AS DETERMINED BY SOLID STATE ^{13}C NMR By P. G. Hatcher, U.S. Geological Survey, Reston, VA 22092, and W. L. Earl, National Bureau of Standards, Washington, D.C. 20234

We have obtained solid-state ^{13}C nuclear magnetic resonance (NMR) spectra by means of cross-polarization with magic-angle sample spinning (CPMASS) for wood, degraded wood, lignin, algae, and chemically degraded algae in an effort to explain the origin of the chemical structures of humic acids and humins. Humic substances, isolated from a variety of depositional environments including soils, peats, and marine sediments, were examined similarly for comparative purposes. The results of these studies suggust that humic acids and humins are composed of chemical structures that are derived primarily from two sources: (1) the remains of vascular plants that contain primarily lignin residues rich in aromatic structures, and (2) algal residues rich in unsubstituted hydrocarbon-like structures. The NMR spectra clearly indicate that the aromatic structures of the lignin components of wood and degraded wood are similar to the aromatic structures observed in humic acids and humins, and that the unsubstituted aliphatic structures of humic acids and humin are similar to those derived from algae and degraded algae. The relative contributions from algal and vascular plant sources vary depending on the type of depositional environment. Estimates of the relative contributions from each source can be made by measuring the aliphatic and aromatic peaks in the NMR spectra of humic acids and humins.

91 MAGNETIC RESONANCE STUDIES OF COAL METAMORPHISM AND COAL LIQUEFACTION MECHANISMS. H. L. Retcofsky, R. G. Lett, R. F. Sprecher, U. S. Department of Energy, Pittsburgh Energy Technology Center, P.O. Box 10940, Pittsburgh, PA 15236, and D. L. VanderHart, U. S. Department of Commerce, National Bureau of Standards, Washington, DC 20234.

Magnetic resonance spectrometries, including high-resolution proton and carbon-13 NMR, cross polarization carbon-13 NMR, ESR and ENDOR, are being used at the Pittsburgh

Energy Technology Center to characterize direct coal liquefaction processes. The work has included characterization of coal, liquefaction products, and "intermediates" in the conversion chemistry. Taken collectively, the resulting data provide insight into the changes in chemical structure occurring during coalification and those that accompany liquefaction. The multi-technique approach is being used to elucidate the chemical mechanisms involved in the liquefaction of coal in small continuous units as well as in larger units such as the Fort Lewis SRC pilot plant and the Trenton H-Coal PDU. In addition to data on United States coals, characterization and liquefaction behavior of several coals from the Peoples Republic of China will be discussed.

92 SPECIAL C-13 CHEMICAL SHIFT CORRELATIONS FOR CHARACTERIZING SYNTHETIC FUELS.
N. F. Chamberlain and R. E. Pabst. Exxon Research & Engineering Company, P. O. Box 4255, Baytown, Texas 77520.

The carbon-13 chemical shifts of hydrocarbons and their oxygen, nitrogen and sulfur derivatives overlap severely in both the aliphatic and aromatic regions, making identification of functional groups in complex mixtures difficult. At first glance, it seems that the only groups which can be clearly identified are substituted aromatic, unsubstituted aromatic and aliphatic carbons. There are, however, some dominant features in the C-13 spectra of synthetic fuels which are observed repeatedly and call for special effort to identify them. When the shifts of these features are combined with data from hydrogen NMR, mass spectrometry and the expected chemistry, it becomes possible to identify many specific functional groups with reasonable confidence. Related carbon-13 spectral features can then be compared more or less quantitatively to confirm the choices. This process leads to a set of carbon-13 chemical shift correlations specifically designed for synthetic fuels characterization. Such a set of correlations will be presented and their application illustrated.

93
THE CHARACTERIZATION OF COAL LIQUID HETEROATOM FUNCTIONALITIES BY ^{29}Si NMR SPECTROSCOPY, By K. D. Rose, Exxon Research & Engineering, Linden, NJ 07036

The nature and quantity of heteroatom functionalities present in the liquid products derived from coal can conveniently be analyzed by selective trimethylsilyl derivitization and ^{29}Si NMR Spectroscopy. Silicon-29 chemical shift data on a variety of compounds which model coal liquid components show that the NMR resonance positions are segregated according to NH, COOH, and OH, SH derivatives. The trimethylsilyl resonances of aromatic OH derivatives are further differentiated by chemical shift so that the major components of coal liquid distillate fractions can be monitored as a function of distillation temperature. Combination of elemental oxygen and quantitative ^{29}Si NMR data permits an estimation of percentage OH of total oxygen for distillation fractions in the range 100-1050°F.

94 FLOW LC-NMR STUDIES OF COAL AND PETROLEUM SAMPLES. H. C. Dorn, J.F. Haw, T.E. Glass, D.W. Hausler, E. Motell, Department of Chemistry, Virginia Polytechnic Institute and State University, Blacksburg, VA 24061

We have recently coupled a flow ^{1}H and ^{19}F NMR detector to a liquid chromatography (LC-NMR). Results achieved for model mixtures, jet fuels and solvent refined coal samples will be discussed. Factors limiting the performance of the LC-NMR approach, such as, NMR sensitivity, chromatographic and NMR linewidths, flow rate and sample load will also be presented. In addition, NMR as a chromatographic detector will be compared with other "classical" detectors (e.g., refractive index). The results to date indicate a significant time advantage for the LC-NMR approach when compared with the normal procedure of chromatographic fraction collection, solvent evaporation and preparation for spectroscopic examination.

95 CHARACTERIZATION OF THE RESIDUAL CARBON IN RETORTED OIL SHALES BY SOLID STATE ^{13}C NMR. F. P. Miknis, Laramie Energy Technology Center, Laramie, WY 82071 and D. Sindorf and G. E. Maciel, Chemistry Department, Colorado State University, Ft. Collins, CO 80503.

Carbon-13 NMR with Cross Polarization (CP) and Magic Angle Spinning (MAS) is an emerging technique that shows great promise for the characterization of residual fuels. One reason is because the CP/MAS techniques provide information about the carbon distribution in intractable solid materials such as oil shales. The distribution of carbon in spent and partially retorted oil shales provides information about the value of spent shales as residual fuels, and provides insight into the nature of the retorting process. A CP/MAS analysis of the carbon distribution in oil shales from an interrupted vertical retorting process has been made. CP/MAS analyses also, have been made on spent shales obtained from different retorting processes and for retorted oil shales from formations, other than the Green River formation. The significance of these results as they relate to oil shale retorting and process control will be discussed.

97 A LIGHT SCATTERING STUDY OF CONSTRAINED BROWNIAN MOTION. Alan J. Hurd, W. J. O'Sullivan, and R. C. Mockler. Department of Physics, University of Colorado, Boulder, CO 80309.

Quasi-elastic light scattering was used to measure the friction factor of non-interacting polystyrene microspheres in an aqueous suspension constrained by parallel glass windows. The scattering geometry was such that only motion parallel to the walls was monitored. Heterodyne detection was used in order to eliminate the effects of stray light scattered by the surface. It was found that as the ratio, m, of sphere diameter to spacing between the walls increases, the friction factor increases according to the well-known theory of Faxen for a sphere centered between two walls, with deviations resulting from slowly diffusing spheres very near the walls. The intensity autocorrelation function is exponential to within the uncertainty of the experiment indicating that most spheres are centered by transverse forces. Since electrical forces were eliminated by using a high ionic strength solution, these transverse forces must be hydrodynamic in nature.

Special techniques developed for intensity autocorrelation spectroscopy of thin fluid samples will be discussed.

98 MICROWAVE MEASUREMENTS OF CHEMICAL SHIFT TENSORS. S. G. Kukolich. Chemistry Dept., University of Arizona, Tucson, AZ 85721.

The paramagnetic contributions to chemical shift tensors can be directly calculated from electronic contributions to the spin-rotation tensor interaction. These paramagnetic contributions are combined with accurate theoretical diamagnetic contributions to yield the total chemical shift tensor. The spin-rotation tensor is obtained from high resolution microwave measurements of hyperfine structure on rotational transitions. The high resolution microwave spectra are measured using a molecular beam maser spectrometer. The chemical shift tensors for ^{19}F and ^{1}H in small molecules will be discussed. Results for the ^{13}C chemical shift tensor in $CH_3{}^{13}CN$ will be presented.

99 A QUALITY ASSURANCE PROGRAM FOR CHARACTERIZATION OF DEIONIZED WATER USED IN A SEMICONDUCTOR FACILITY. J. L. Gurnsey, DCD, Hewlett Packard, Ft. Collins, CO 80525.

Water is the most abundantly used reagent in the fabrication of integrated circuits in our facility. But there is little known about the deionized water's physical and chemical characteristics with relationship to the process.

It is known that the presence of certain elements in any reagent can quickly stop production. These known problem areas seemed to be a logical starting point for investigation.

This paper will outline a Q/A program for such an investigation starting with the selection of sampling points, sampling techniques and describe some of the analytical techniques used for the establishment of deionized water profiles as well as problems incurred. The profiles will then be used as a basis for predicting water quality at a given time.

100 ELEMENTAL COMPOSITION OF AEROSOL SAMPLES FROM LOW BTU COAL GASIFIER STREAMS. S. Heisler Weissman, R. L. Carpenter and G. J. Newton, Inhalation Toxicology Research Institute, Lovelace Biomedical and Environmental Research Institute, P. O. Box 5890, Albuquerque, NM 87115.

Filter and impactor samples from an experimental low Btu coal gasifier located at the Morgantown Energy Technology Center were obtained using an extractive sampling scheme. Samples were analyzed using spark source mass spectrometry and atomic absorption spectroscopy to determine elemental composition. Ash from the gasifier bottom and the cyclone resembled coal combustion ash in concentrations of major inorganic elements, such as Si, Al, Fe, Ca, K and Mg. Aerosols derived from the clean and raw gas streams were considerably different from coal combustion ash. Trace elemental composition of aerosols derived from gas streams varied with particle size, operating parameters and extent of clean up. Toxic elements, such as Cd and Pb, were present at low concentrations in gasifier bottom ash (Cd 0.36 μg/g, Pb 0.60 μg/g) and cyclone ash (Cd 14 μg/g, Pb 23 μg/g). Concentrations of Cd and Pb in aerosols derived from the gas streams varied considerably with gasifier and clean up system operating parameters. Cadmium and lead concentrations in raw gas stream aerosols were < 1 μg/g in all samples. In clean gas stream aerosols Cd concentrations ranged from < 0.36 to 83 μg/g and Pb from 5.6 to 470 μg/g. (Research performed under U. S. Department of Energy Contract Number EY-76-C-04-1013.)

101 A MULTI-INSTRUMENT APPROACH TO THE CONTROL OF COOLANT SYSTEMS BASED ON EMULSIFIABLE OILS. Rick Almen, Eric Apel, Gary Mantelli, Susan Bronstad, Tim Osbourn, and Mark Rasmussen. Coors Container Co., 17755 W. 32nd Ave., Golden, CO 80401.

The first operation in the manufacture of two-piece aluminum cans is the press area where aluminum coil stock is drawn and ironed into can bodies. The cooling and lubrication in the press area are provided by large, central systems consisting of emulsifiable oils in water. There are several types of problems associated with these systems that can cause production down time and/or scrap. These problems vary from those of contamination to those associated with depletion and degradation. We presently use GC, HPLC, FTIR and UV-VIS techniques to characterize these coolant systems. This paper will describe the methods used and the benefits derived from this multi-instrument approach to the control of these systems.

102 APPLICATIONS OF THE MOLE TO MICRO-CHEMICAL ANALYSIS. Fran Adar, Roy E. Grayzel, and Angelo Grillo. Instruments SA, Inc., 173 Essex Avenue, Metuchen, NJ 08840.

Use of the MOLE (Molecular Optical Laser Examiner) for Micro analysis of chemical components and crystalline isomorphs in heterogeneous samples will be presented. By combining a research grade optical microscope and intensified vidicon detector with a novel spectrometer, the MOLE functions as a micro-Raman spectrometer, a Raman spectrograph, and a Raman microscope.

Because of the specificity of Raman bands, it is often possible to differentiate between closely related hydrocarbons and between crystalline solids of identical elemental composition, but differing crystal structure. The 1 micron spatial resolution of the technique is determined by the theoretical limits imposed by the wavelength of the radiation.

Areas of applications of the MOLE include (1) the identification of particulate contaminants that appear during manufacture; (2) failure analysis of co-polymers or polymer blends that can be related to the identification and concentration of the components; (3) identification of the chemical species of uranium present in uranium ore; (4) analysis of geological formations relating to their history and composition. In this area of interest, hydrocarbons have been identified in fluid inclusions incurring in quartz-carbonate minerals.

103 A HIGH SPEED PULSE AMPLIFIER/DISCRIMINATOR AND COUNTER FOR PHOTON COUNTING. Richard A. Borders and John Birks. Dept. of Chemistry and Coop. Inst. for Research in Environmental Sciences, Univ. of Colorado, Boulder, CO 80309 and John A. Borders, Naval Ship Weapon Systems Engineering Station, Port Hueneme, CA 93043.

The design for a Pulse Amplifier/Discriminator (PAD) and high speed counter is given. The PAD is completely self-contained, has complementary Emitter Coupled Logic (ECL) outputs which can drive a 50 Ω load (coaxial cable) to a remote counter, and costs less than $150 to construct. The PAD is typically capable of detecting a single pulse with an amplitude of $\geq$ 200 μV, typically has a Pulse Pair Resolution (PPR) of 10 ns for 350 μV to $\geq$ 40 mV pulses, and can operate to > 250 MHz with periodic input pulses of $\geq$ 8 mV. The front-end of the counter circuit uses high speed ECL flip-flops. The output data from the front-end is converted to TTL and the remainder of the counting is done using slower cascaded TTL counters. The counter is capable of counting at frequencies > 250 MHz and the maximum count is $2^{23}-1$. The counter is interfaced to a 8080-based micro-computer. The PAD and counter were tested using a matched pair of EMI 9658RA Photomultiplier Tubes (PMT's) and the relationship between current and photon counting was found to be linear to > 2 MHz.

104 ELECTROCHEMICAL CHARACTERIZATION OF VANADIUM ACETYLACETONATE COMPLEXES IN APROTIC SOLVENTS. M.A. Nawi and T.L. Riechel. Department of Chemistry, Miami University, Oxford, Ohio 45056.

With increasing evidence for the biological importance of vanadium, fundamental studies of the electrochemistry and spectroscopy of multidentate ligand complexes in aprotic solvents have been undertaken. Complexes of vanadium(III), (IV) and (V) with 2,4-pentanedione (acetylacetone, acac) have been studied by cyclic voltammetry, controlled potential coulometry, and IR and UV-VIS spectroscopy in DMSO. Results from complexes with this ligand, bonding through two oxygen atoms, will be compared to results from 8-hydroxyquinoline compounds (oxygen and nitrogen bonding) and diethyldithiocarbamate compounds (bonding through two sulfur atoms). The cyclic voltammogram of $V(acac)_3$ shows reversible couples at -1.42 and +0.76V *vs* SCE. Coulometry indicates that the couple at -1.42V corresponds to a one electron process and cyclics following electrolysis show that the vanadium(II) product is stable. Although the oxidation process at +0.76V also involves one electron, the initial product is not stable. These results are similar to those of the other ligand systems. Cyclics of $VO(acac)_2$ show a one electron reversible oxidation at +0.81V, but the initial vanadium(V) product is unstable in the electrolysis time frame and gives four additional products. The vanadium(V) compounds $VO(acac)_2Cl$ and $VO(acac)Cl_2$ are unstable and decompose to several products including

$VO(acac)_2$, free ligand, and perhaps Cl_2. Attempts to synthesize $VO(acac)_3$ will be discussed and the instability of vanadium(V) acetylacetonate species will be contrasted with the stability of vanadium(V) 8-hydroxyquinoline and diethyldithiocarbamate complexes.

105 The Coulometric Determination of Carbon Dioxide in Geologic Materials. Daniel R. Norton and Edythe E. Engleman. U.S. Geological Survey, Box 25046, MS 928, Denver Federal Center, Denver, Colorado 80225.

A study is presented of the coulometric determination of carbon dioxide in geologic materials that have a wide range in concentration of carbon dioxide. In the method studied, carbon dioxide is released from an acid solution, absorbed in a solution of monoethanolamine, and the resulting acid derivative is titrated automatically with coulometrically generated base to a photometric end point. The factors studied were air-flow rate, type of acid, sample size and dispersion, rate of release of carbon dioxide, absorption of interfering gases, electrical interference, and calibration of the instrument. A standard method of analysis is presented together with a discussion of accuracy and precision. Comparison between the results of this method with the results of the classical gravimetric method is given. Comparative results are shown for some U.S. Geological Survey rock standards and new data presented on some recently issued standards. The method maintains the theoretical equivalence advantage of the classical method, has high accuracy and precision, and is more rapid.

106 SURVEY OF SPECTROSCOPIC METHODS FOR SHALE HYDROCARBONS. D. M. Wilson[1], E. J. Gallegos[1], S. R. Silverman[2], K. W. Zilm[3], R. J. Pugmire[3], D. M. Grant[3], L. M. Ryan[4], B. C. Gerstein[4], and P. R. Solomon[5], Chevron Research Company[1], Richmond, California 94802; Chevron Oil Field Research Company[2], La Habra, California 90631; University of Utah[3], Salt Lake City, Utah 84112; Iowa State University[4], Ames, Iowa 50011; and United Technology Research Center[5], East Hartford, Connecticut 06108 (present address: Advanced Fuel Research, Inc., East Hartford, Connecticut 06118).

A variety of spectroscopic techniques have been used to characterize bitumen-extracted shales and kerogens of diverse origin and metamorphic state. Methods include high-resolution ^{13}C cross-polarization magic-angle spinning (CP-MAS) NMR, high-resolution ^{1}H NMR combined rotation and multiple-pulse spectroscopy (CRAMPS), ESR, quantitative Fourier Transform infrared (FTIR) spectroscopy, pyrolysis gas-chromatography mass spectrometry (GC-MS), and elemental analysis. Samples were an immature (shallow depth) Green River shale and its laboratory-matured (260°C for 1 yr) counterpart, and naturally-matured Green River and North Sea shales. A combined analytical approach is seen to have value in finding consistent characterizations (e.g. aromatic hydrogen %) in evaluating kerogen isolation procedures, and in targeting new instrumental developments that would be particularly fruitful.

107 APPLICATION OF HIGH PERFORMANCE LIQUID CHROMATOGRAPHIC TECHNIQUES TO COMPONENT ANALYSIS AND QUALITY CONTROL, FOR PRODUCTION OF AN ORGANO METALLIC ROCKET FUEL CATALYST AND AN ACRYLIC ADHESIVE FOR DENTAL APPLICATIONS. D.P. Stull and D.T. Blair. Hauser Laboratories, P.O. Box G, 5680 Central Avenue, Boulder, Colorado, 80306.

Continued development of High Performance Liquid Chromatograph (HPLC) techniques has lead to a variety of separation procedures in new diverse areas of commercial applications. For example, purity requirements for solid fuel catalysts in the aerospace industries are classically determined by wet chemical techniques. These techniques are of questionable reliability considering the high purity requirements. Similarly, new techniques for rapid, simplified quality assurance procedures, for use in Bis-phenol A type acrylic adhesive in dental applications are desired.

We have developed HPLC techniques for evaluation of those two diverse commercial products with remarkably simple technology. Component separation, peak collection and concentrations followed by spectrographic analysis was used to identify key components in both commercial processes. These results have been used to fine tune the processes used in production and are being extended to better understand the synthetic pathways involved. This paper will discuss the separation schemes developed and their application to quality control studies. General application of the procedure will also be discussed as they pertain to chemical characterization of the complex commercial mixtures. Infrared and Nuclear Magnetic Resonance spectroscopic techniques were helpful in component identification.

108 A SYNOPTIC SURVEY OF ORGANIC COMPOUNDS EXTRACTED FROM BED SEDIMENT USING CAPILLARY GAS CHROMATOGRAPHY/MASS SPECTROMETRY/COMPUTER TECHNIQUES. W.E. Pereira and T.R. Steinheimer, U.S. Geological Survey, Box 25046, Denver Federal Center, Denver, Colorado 80225.

A synoptic survey was undertaken in an area impacted by heavy industrial activity to determine the occurrence and environmental significance of organic compounds adsorbed to bed sediment. Extraction was effected on a Soxhlet apparatus using a freeze-dried sample. The organic extract was fractionated using silica gel micro-column adsorption chromatography. Separation and identification of the organic compounds were accomplished by capillary gas chromatography/mass spectrometry techniques. More than 50 compounds have been tentatively identified. These include saturated hydrocarbons, olefins, aromatic hydrocarbons, alkylated polycyclic aromatic hydrocarbons, and oxygenated compounds such as aldehydes and ketones. The role of bed sediments as a source or sink for organic pollutants will be discussed.

109 ACIDS ON I.C.E. - THE ANALYSIS OF WEAK ACIDS BY ION CHROMATOGRAPHY EXCLUSION. Jann Frye and Nan Meyer. The Standard Oil Co. (Ohio), 4440 Warrensville Center Rd., Cleveland, Ohio 44128.

Mixtures of weak acids are difficult to separate quantitatively by conventional analytical methods. The analysis of weak acids is important in foods, industrial plant streams and biological fluids. They are often components of complex matrices. We have successfully used ion chromatography to separate various homologous series of weak acids, using a Dionex Model 16 Ion Chromatograph, in the Ion Chromatography Exclusion (ICE) mode.

Krebs Cycle acids, of interest to biological researchers, were analyzed using the standard ICE column set, and conductivity detector. Detector limits of 1-5 ppm were obtained. Retention times of various mono-, di-, halo-, and keto-acids were also determined.

Ion chromatography has proven to be invaluable for the analysis of low molecular weight weak acids, and in many cases may be the best available technique.

110 ANION INTERFERENCES IN LASER ENHANCED IONIZATION SPECTROMETRY. T.O. Trask and R.B. Green. Dept. of Chemistry, University of Arkansas, Fayetteville, Arkansas 72701

Laser Enhanced Ionization (LEI) is a unique flame spectroscopic method for trace metal analysis. LEI is based upon the change in flame impedance produced by the collisional ionization of laser excited atoms. The change in flame impedance is monitored by electrodes placed outside the flame. Although the electrical nature of the detection method eliminates many of the problems associated with optical detection systems, perturbations in the electrical nature of the flame result in interferences in the LEI signal collection mechanism. The present study is an evaluation of the anionic interferences encountered in LEI spectrometry.

Anionic species which pose significant interferences are those that will modify the electron concentration in the flame. Anions, such as the halogens, with high electron attachment energies demonstrate the most dramatic change in the LEI signal. The magnitude and nature of the interferences will be evaluated for representative analytes. Characterization of the anionic interferences as a function of experimental conditions will be discussed. Analysis of real samples will demonstrate the effectiveness of interference removal techniques for LEI spectrometry.

This work was supported by NSF - CHE - 7918626

111 DETERMINATION OF SUBMICROGRAM AMOUNTS OF BERYLLIUM IN AIR FILTER SAMPLES BY NON-FLAME ATOMIC ABSORPTION. John D. Grooms. Rockwell International, Analytical Laboratories, P.O. Box 464, Golden, CO 80401.

A flowchart illustrates the collection of samples, preparation of filters for analysis and final analysis by flameless atomic absorption spectrometry. Submicrogram quantities of beryllium are detected and related back to total air volume used to collect the samples on the filter media.

112 INEXPENSIVE AUTOMATION AND CONTROL FOR THE ANALYTICAL LABORATORY USING A MULTI-PURPOSE SOLID STATE SET-POINT REGULATOR, C. E. Andre and G. L. Hutchinson. U.S.Dept. of Agriculture - SEA, P. O. Box E, Ft. Collins, Colorado 80522.

Experiments and equipment in the modern laboratory quite often call for periods of unattended operation. During these periods some sort of control must be maintained to ensure the instrument or experiment remains within certain predefined operating parameters or limits. A device will be described which can be interfaced with a variety of common transducers (i.e. level, temperature, pH, pressure, count) to allow for various schemes of automation or control. Details will be given on how to use low cost off-the-shelf components to assemble a versatile system using multiple set points and adjustable hysteresis. Emphasis will be placed on portability, low parts count, battery operation, adaptability, and ease of assembly by non-electronics laboratory personnel.

113 ELECTRON-PROTON DOUBLE RESONANCE AND THE STRUCTURE OF MOLECULES, Clyde A. Hutchison Jr., Department of Chemistry, University of Chicago, Chicago, IL 60637.

The most common tool for the determination of the structure of large organic molecules, in particular those of biological interest, has been x-ray diffraction. For these molecules, however, this technique fails to give precise locations of hydrogen atoms because of their low scattering power. On the other hand, for many such molecules, e.g. organo-metallic complexes and proteins, knowledge of the locations of the hydrogen atoms is very important structural information because these atoms play essential roles in binding the molecules into relatively rigid structures, in fixing the molecular conformations, or in making possible their biological functions.

We have investigated the feasibility of using the EPR absorptions of paramagnetic metal ions attached to organic molecules in crystals to obtain ENDOR spectra of protons in the neighborhood of these ions. Such spectra can afford precise measurements of the anisotropic magnetic dipole-dipole interactions between the ions and the protons and with sufficient understanding of the physics of these interactions, and x-ray information concerning the locations of the metal ions, can give precise hydrogen atom coordinates.

We will discuss such studies made in our laboratory on various types of systems including organo-metallic complex molecules as well as enzyme molecules in crystals.

114 ENDOR OF NO-LIGATED HEME SYSTEMS. C. P. Scholes, R. LoBrutto, Y. H. Wei, and Tsoo E. King. Lab of Bioenergetics and Dept. of Physics, SUNY at Albany, Albany, NY 12222.

Nitric oxide binds as an axial ligand to many ferrous heme proteins in place of molecular oxygen. The paramagnetic NO electron delocalizes to the heme and often to the opposite, axial ligand of heme. Thus, EPR and ENDOR of NO-heme proteins can be used to explore the oxygen binding site. We have used these techniques to probe the environs of NO-ligated cytochrome a_3 in the protein cytochrome c oxidase; at the a_3 site oxygen is normally bound and is then catalytically converted to water. The EPR spectrum from frozen solutions of the NO complex extends from approximately $g = 2.09$ to $g = 1.97$, and EPR-resolved hyperfine structure shows near $g = 2.01$ (Blokzijl-Homan, M.F.J. and Van Gelder, B.F.(1971) BBA 234, 493). The resolved structure indicates unpaired electron density on the NO ligand and on the nitrogen of another axial ligand, probably histidine. We have obtained ENDOR spectra over the entire g-value range, and these spectra have particularly well-resolved hyperfine couplings near the g-value extremes. Initial work at g-value extremes shows hyperfine couplings of about 40 MHz to ^{15}NO, 30 MHz to ^{14}NO, and about 20 MHz to the other axial nitrogeneous ligand. Well-resolved proton couplings with magnitudes $\leq$ 4 MHz are seen. To help in our assignment of proton ENDOR we are presently studying model heme a-NO-nitrogeneous base complexes. We intend to present data from other heme proteins that have different biological functions from cytochrome a_3 in order to show if there exist ENDOR-detectable differences between them near the NO-binding site. (This work supported by NIH Grants No. AM-17884, GM-16767, and HL-12576.)

115 PHOTOREACTION IN MOLECULAR SINGLE CRYSTALS
EPR Studies of a Light Induced Hydrogentransfer
Reinhard Furrer, Department of Chemistry, The University of Chicago, 5735 S. Ellis
Avenue, Chicago, Illinois 60637

Photochemical reactions are extensively studied in the liquid state. The vast literature in this field however gives information about intermediate reaction products at best indirectly and thus an element of uncertainty or ambiguity remains. Spectroscopic investigations in the solid state on the other hand are rather scarce although radical formation from optically excited aromatic molecules has been well established. Detailed knowledge of magnetic resonance properties of primary reaction products are very desirable in order to allocate pathways of photochemical reactions.

In this context light induced complex formation processes in doped fluorene single crystals have been investigated. The reaction product is a radical pair triplet state created with hydrogen abstraction from the acid CH_2-group of a fluorene host molecule by an optical excited state of different hydrogen acceptor molecules. Acridine, phenazine and even anthracene have proven to be suitable acceptors.

A detailed analysis of fine and hyperfine interactions and transient EPR studies lead to a reaction model for this fundamental photochemical reaction.

116 APPLICATIONS OF ESR TO CARBONACEOUS MATERIALS. L. S. Singer and I. C. Lewis. Union Carbide Corporation, Carbon Products Division, Parma Technical Center, P. O. Box 6116, Cleveland, Ohio 44101.

The heat treatment of organic material at temperatures between 300°C and 3000°C can produce a variety of products including tar, pitch, coke, carbon, and ultimately graphite. Each of these products exhibits a unique type of ESR behavior. At the early stages of the transformation, odd-alternate neutral π-radicals seem to be the predominant species. As dehydrogenative polymerization and condensation reactions continue, the radicals become larger, more stable, and the unpaired electrons more delocalized. Carbons and graphites exhibit conduction electron resonances which are quite sensitive to the degree of structural perfection and traces of certain inorganic impurities. Examples of the many different kinds of ESR characteristics will be presented.

Despite the apparent complexity of these systems, their ESR behavior has been extremely useful in establishing thermal history, reaction mechanisms, and structure. In particular, the technique has been useful in studying reaction intermediates at the early stages of carbonization. The present state of understanding of the various ESR phenomena in carbonaceous materials will be summarized.

117 AN ESR INVESTIGATION OF FREE RADICALS IN COALS AND COAL CONVERSION, Leon Petrakis and D. W. Grandy, Gulf Research and Development Co., Pittsburgh, PA 15230.

Free radicals in coals are formed during coalification. They are also known, and they are generally accepted to be, as playing a key role in coal liquefaction processes as well as possibly causing reactor problems during coal conversion. The nature of free radicals depends on the rank of coal, the maceral content of coal, highest temperatures to which coals are exposed, temperatures under which coals are heated, and the presence or absence of hydrogen and/or hydrogen donating solvents. Residual free radicals may not be the same as those during heating at high temperaures. Trade-offs may exist between different processes and composition variables. These questions will be reviewed, recent data obtained under process type conditions will be given and the implications of free radicals for overall conversions will be discussed.

118 HYDROGEN EXCHANGE BETWEEN BITUMINOUS COAL AND NAPHTHALENE OR TETRALIN: AN EPR AND NMR STUDY. Joseph J. Ratto and Ira B. Goldberg, Rockwell International Science Center, 1049 Camino Dos Rios, Thousand Oaks, California 91360.

The mechanism and rates of hydrogen transfer between coal and the solvents naphthalene and tetralin were investigated by nuclear magnetic resonance (NMR) and electron paramagnetic resonance (EPR). Coal was reacted at 400-450°C in a 1:1 mixture with naph*thalene, tetralin, or their perdeutero analogs. EPR measurements were made after cooling.* The change in linewidth was used to evaluate the change of the hydrogen near radical sites while the g-factor and spin concentrations were used to determine, respectively, the change in the types of radicals formed, and the rate of formation of stable radicals. Samples heated with Naphthalene-d_8 exhibit progressively narrower lines than those heated with naphthalene, while in both cases, the number of radicals formed increase with temperature. NMR measurements were made on the spent solvent, in order to determine the formation of solvent products and to assess the incorporation of deuterium into the α- and β-positions. The rate of deuterium incorporation was found to be about 5 times faster in the α-position than the β-position near the start of the reaction. A kinetic model is proposed to explain these results.

119 ZERO FIELD SPLITTING TENSOR OF THE EXCITED TRIPLET STATE OF CHARGE TRANSFER PHANES. M. Bär and K. H. Hausser, Max-Planck-Institut, Abteilung für Molekulare Physik, Jahn-Straße 29, 6900 Heidelberg.

We have succeeded for the first time to grow single crystals and to study the orientation dependence of the zero field splitting of several phanes and CT-phanes. In this paper we report the results for one phane with identical subunits, the pseudo-geminal 4,7,12,15-tetramethoxy[2.2]paracyclophane 1, and for two CT-phanes, the 4,5,7,8-tetracyano[2.2]paracyclophane 2, and the pseudo-ortho-4,7-dicyano-12,15-dimethyoxy[2.2]-paracyclophane 3. In the case of 1 and 2, the ZFS tensor behaves analogous to the monomers, i.e., the microwave transition with the highest frequency occurs when the magnetic field is perpendicular to the aromatic planes. In contrast, the ZFS tensor of 3 shows a different orientation, the orientation of the magnetic field perpendicular to the aromatic planes leads to the microwave transition with the lowest frequency. The consequence of this result for the interpretation of the ODMR measurements in zero field, in particular of the correlation of the ZFS parameter D with the CT-character, will be discussed.

120 TRANSIENT RADICALS IN LIQUIDS: TIME RESOLVED EPR. Alexander D. Trifunac. Chemistry Division, Argonne National Laboratory, Argonne, Illinois 60439.

Transient radicals produced by pulse radiolysis can be studied both directly and indirectly by the methods of magnetic resonance. Two variations of the pulsed time resolved EPR technique will be illustrated.

Time resolved EPR via spin echo allows study of radical dynamics in liquids with excellent time resolution (20-50 nsec). This technique will be illustrated by the quantitative study of radical kinetics, CIDEP and relaxation in simple organic radicals.

The transient radical anions and cations involved in the production of excited states by ion-recombination are studied by optically detected pulsed EPR. This technique is based on the modulation of the fluorescence intensity by the resonance microwave absorption in the magnetic field. Several studies of radiolysis of aromatics in hydrocarbons will illustrate this technique.

121 PICOSECOND ELECTRON TRANSFER KINETIC MEASUREMENTS BY ELECTRON SPIN ECHO SPECTROSCOPY. Michael K. Bowman and James R. Norris, Chemistry Division, Argonne National Laboratory, 9700 S. Cass Avenue, Argonne, IL 60439.

Transfer of an unpaired electron from a free radical to a diamagnetic molecule generally produces a change in the precessional frequency of the spin of the unpaired electron. Frequency changes give rise to phase shifts for individual electron spins in spin echo experiments and produce phase memory decay of the two pulse electron spin echo. This is a special form of motional effects in magnetic resonance.

We find that the oxidized electron donor in photosynthetic organisms is a convenient model system in which to observe the effects of rapid electron transfer as it consists of an unpaired electron (hole) which is transferred rapidly between two chlorophyll or bacteriochlorophyll molecules. EPR measurements place a limit on the transfer of $\leq$ 6 ns. We manipulated the frequency changes of the unpaired electron as it is transferred from one molecule to the other by altering the magnetic nuclear isotopes in the two molecules. In this way, we have determined that the time between electron transfers within the donor complex in a number of organisms is 50 ps or less.

122 ELECTRON SPIN RESONANCE STUDIES OF METAL-AMMONIA COMPOUNDS. F. Y. Robb, Motorola, Inc., 5005 E. McDowell Rd., Phoenix, Arizona 85016 and W. S. Glaunsinger, Department of Chemistry, Arizona State University, Tempe, Arizona 85281.

Electron spin resonance studies of the known metal-ammonia compounds $Li(NH_3)_4$, $Ca(NH_3)_6$, $Ba(NH_3)_6$, $Eu(NH_3)_6$, and $Yb(NH_3)_6$ have been performed in the range 8-300 K at X-band. Conduction electron spin resonance (CESR) has been observed in $Li(NH_3)_4$, $Ca(NH_3)_6$, and $Sr(NH_3)_6$, but CESR signals in $Ba(NH_3)_6$ and $Yb(NH_3)_6$ were too broad to be detected. CESR lineshapes are in excellent agreement with Dyson's theory, which permitted a precise determination of the conduction-electron g-valves, spin-relaxation time (T_2), and spin-diffusion time. In $Ca(NH_3)_6$ and $Sr(NH_3)_6$ a general decrease in peak-to-peak linewidth is interrupted by a minimum near 100 K, which is probably associated with rapid NH_3 diffusion. In both $Ca(NH_3)_6$ and $Sr(NH_3)_6$ the temperature dependence of T_2 is nearly the same as that of the conductivity, which indicates that the dominant relaxation mechanism involves the vibrational modulation of the spin-orbit coupling interaction of the conduction electrons with the metal ions. In agreement with a recent theory of metallic behavior at low electron densities, a partial localization of conduction electrons has been observed in $Li(NH_3)_4$ and $Sr(NH_3)_6$. Only the Eu^{2+} resonance has been observed in $Eu(NH_3)_6$, and this resonance broadens dramatically below 10 K, which is consistent with an ordering temperature

123 MODULATED ELECTRON SPIN ECHOES: A PROBE FOR THE SOLVATION GEOMETRY OF PARAMAGNETIC SPECIES IN BULK AND ON SURFACES. Larry Kevan. Department of Chemistry, Wayne State University, Detroit, Michigan 48202.

Electron spin echoes are produced in pulsed ESR experiments. Two resonant microwave pulses separated by time τ will typically generate an echo signal at time 2τ after the first pulse. The echo intensity generally decreases as τ increases and this echo envelope is sometimes modulated due to weak electron-nuclear hyperfine interactions. Analysis of this spin echo modulation provides a way of determining weaker hyperfine interactions than one can typically detect by ordinary ESR. In general one can analyze the modulation pattern to obtain the number, distance and isotropic coupling of magnetic nuclei surrounding a paramagnetic species between distances of 0.1 to 0.5 nm. With suitable isotopic substitution the orientation of first solvation shell molecules can be deduced. In many cases the analysis of modulated electron echo envelopes has given the first detailed information on actual solvation shell geometries.

Results will be described on the geometry of solvated electrons, small and large anions, atoms, and cations in aqueous and organic bulk media. The geometry of preferential solvation of ions in mixed solvents will be discussed quantitatively. The solvation of cupric ions on silica surfaces will be contrasted with their bulk solvation geometry.

124 ELECTRON SPIN RESONANCE OF $Mn(H_2O)_6^{2+}$ AQUEOUS SOLUTIONS ADSORBED ON SILICA GELS, Giacomo Martini, Istituto di Chimica Fisica, Università di Firenze, 50121 Firenze, Italy.

The state of liquids adsorbed on porous solids may be usefully investigated by electron spin resonance of appropriate paramagnetic probes. Transition metal ions are suitable spin probes since their electron spin relaxation rates are largely influenced by structural changes of the environment and by viscosity alterations of the solvent. In this work the ESR of the $Mn(H_2O)_6^{2+}$ ion in aqueous solution adsorbed on silica gels with narrow and wide pores has been used to investigate the properties of the water filling the pores and of the solid-liquid interaction. The analysis of the electron spin relaxation rate has shown a decreased mobility of water inside narrow pores with respect to water inside wide pores, where it behaves as bulk water. The existence of a distribution of correlation times for the motion of Mn(II) complexes in such systems has been interpreted in terms of a gradient of mobility of water from the surface to the middle of the pores. The ESR line shape at 77 K has made it possible to evaluate the distance from the surface at which secondary interactions are effective on the spin probe. The line shape analysis allowed to investigate the freezing properties of the water in the different regions of the pores. A comparison with other analogous systems is also made.

125 THE REACTIONS BETWEEN DPPH AND SURFACE ACTIVE SITES OF METAL OXIDES - SURFACE PROPERTIES. T. Kawaguchi, S. Hasegawa, and K. Yasuda, Department of Chemistry, Tokyo Gakugei University, 1-1 Nukui Kitamachi 4-chome, Koganei, Tokyo 184, Japan.

EPR spectra of PbO_2 and MnO_2 interacting with isopropanol and DPPH were used to characterize the radical species involved. The surface species active in the dehydrogenation reaction of isopropanol on MnO_2 may be O_2^- or HO_2^-. The radical formed by the reaction between DPPH and PbO_2 is a biradical.

126 ELECTRON SPIN ECHO ENVELOPE SPECTROSCOPY IN THE STUDY OF CHEMICAL COMPLEXES AND METALLOPROTEINS. W. B. Mims* and J. Peisach*+. *Bell Laboratories, Murray Hill, N.J. 07974, and +Einstein College of Medicine, Bronx, N.Y. 10461.

The amplitude envelope of electron spin echoes is commonly observed to be modulated by frequencies which correspond to the superhyperfine splittings associated with nuclei coupled to the electron spin. The envelope can therefore be made to yield information similar to that obtainable in an ENDOR experiment. The method succeeds for frequencies in the low MHz range and remains practicable when the sample is only available as a glass or frozen solution. It has been used to identify ligands and to determine electron-nuclear couplings in a number of Cu(II)- and Fe(III)-containing proteins, including the blue copper proteins and cytochrome P-450. The rapidity of the measurement (requiring typically $\simeq$ 15 min.) renders it suitable where numerous comparisons must be made as in a titration study.

127 THE ENDOR AND ESEEM DETECTION OF NITROGEN COUPLINGS IN A MODEL AMIDE CRYSTAL: A COMPARISON STUDY, L. D. Kispert, Department of Chemistry, The University of Alabama, Tuscaloosa, Alabama, 35486, and M. Bowman and J. R. Norris, Chemistry Division, Argonne National Laboratory, 9700 South Cass Avenue, Argonne, IL. 60439.

Electron-Nuclear double resonance (ENDOR) and electron spin echo envelope modulation (ESEEM) spectra have been obtained from the high field EPR lines of $\cdot CF_2CONH_2$ in irradiated trifluoroacetamide crystals. This radical undergoes in-phase librational motion at 77 K and torsional oscillation about the C-C bond above 77 K. It was thus chosen as a model system to study the effects of molecular motion on the relative difficulty of obtaining nitrogen ENDOR and ESEEM spectra. Nitrogen hyperfine and quadrupole tensors were deduced from ESEEM spectra at $\geq$ 77 K by taking the Fourier transform of the modulation pattern that is superimposed on the stimulated (3-pulse) electron spin echo decay envelope. The ENDOR like spectral lines were assigned and the signs of the couplings deduced by recording ESEEM spectra as a function of two delay pulse times, τ and T, and as a function of angle.

The nitrogen and quadrupole couplings obtained varied from 9.0 and 1.77 MHz perpendicular to the CON plane to −4.8 and −0.70 MHz in the CON plane respectively. In contrast, ENDOR measurements at the same fields were not possible until the temperature was lowered to 8.7 K. In addition the nitrogen ENDOR line-widths obtained were broader (1 MHz vs. ~100 kHz) and it was not possible to record spectral lines that occurred at frequencies less than 0.5 MHz.

128 THE TEMPERATURE-DEPENDENT ESR LINEWIDTHS OF A RADICAL SPECTRUM DETECTED IN X-IRRADIATED CYANOGUANIDINE CRYSTALS.

M. D. Pace and W. B. Moniz, Naval Research Laboratory, Washington, D. C. 20375

Electron spin resonance studies of irradiated cyanoguanidine single crystals have been previously reported by two research groups. Lind and Kewley[1] reported the formation of radicals produced by γ-irradiation of cyanoguanidine at room temperature and studied radical decay by heating the crystal to 150°C, but did not report any investigations below room temperature. Lin and Lau[2] reported two radicals in x-irradiated cyanoguanidine crystals and studied the nitrogen centered radical (Radical I) at 77 K and at room temperature. In addition a second unidentified radical (Radical II) was found. As they reported, Radical I is observed at 77 K to have a spectrum of eighteen lines with equal linewidth, but at room temperature to have a spectrum with twelve of these lines severely broadened and a reduced nitrogen coupling; however, no explanation for this effect was offered. By using variable temperature ESR we have determined that the line broadening occurs over a temperature range from 200 K to room temperature and that this effect is reversible upon recooling below 200 K.

The results of an angular rotation study of Radical I at 200 K will be presented and an explanation of the temperature-dependent line broadening will be discussed.

1. G. Lind and R. Kewley, Canadian Journal of Chemistry, 49, 2514 (1971).

2. P. W. Lau and W. C. Lin, J. Chem. Phys., 54, 823 (1971).

129 Multiple Frequency EPR Studies on an "Intermediate" in the Oxidation of Reduced Cytochrome *c* Oxidase.

W. R. DUNHAM, R. H. SANDS, Biophysics Research Division, Univ. of Michigan, Ann Arbor, MI 48109, R. W. SHAW, H. BEINERT, Institute for Enzyme Research, Univ. of Wisconsin, Madison, WI 53706.

At the University of Wisconsin, Shaw, Hansen and Beinert (J. Biol. Chem 253, 6637 (1978) have reported the presence of a specific EPR signal from reduced cytochrome *c* oxidase samples which have been rapidly reoxidized by O_2. We present EPR spectra from these samples at 3, 8.9, 9.2, 9.4, 15 and 34 GH_z. These data are compared to diagrams for the positions of the principal resonances versus frequency of spin systems with S = 1, 3/2, 2, 5/2, 3 and spin Hamiltonian:

$$H_z = g\beta H S_z + D\left[S_z^2 - \frac{S(S+1)}{3}\right] + \eta\,(S_x^2 - S_y^2)$$

. In this way, the various possibilities of spin coupling between heme a, heme a_3 and the two copper atoms are considered as candidates for the above-mentioned signal. By process of elimination, we have chosen the S = 2 state arising from a copper-heme a_3 spin coupling as most likely.

130 Application of Fast Fourier Transforms to EPR Spectra of Free Radicals in Solution.

W. R. DUNHAM, L. J. HARDING, J. A. FEE, Biophysics Research Division, Univ. of Michigan, Ann Arbor, MI 48109 and H. J. GRANDE, Landbouwhogeschool, Vakgroep Biochemie, De Dreijen 11, Wageningen 6703 BC, The Netherlands.

A method of obtaining the magnetic hyperfine coupling constants from the EPR spectra of free radicals in solution is shown. This method relies heavily on the use of the fast Fourier transform algorithm and curve fitting in the Fourier space via minimization procedures. We compare our work with previously published work on the EPR spectra of methyl viologen.

131 Unravelling the EPR Spectra of Modified Flavin Free Radical Cations.

H. J. GRANDE, F. Muller, Landbouwhogeschool, Vakgroep Biochemie, De Dreijen 11, Wageningen 6703 BC, The Netherlands, L. J. HARDING, Computing Center, University of Michigan, Ann Arbor, MI 48109 and W. R. DUNHAM, Biophysics Research Division, Univ. of Michigan, Ann Arbor, MI 48109

The EPR spectra of alloxazine cation free radicals which have substitutions at the 5, 6, 7, 8, 9 and 10 positions are presented. These EPR spectra are split by magnetic hyperfine interactions with hydrogen, deuterium, nitrogen, fluorine and chlorine nuclei at various places on the alloxazine rings and on the attached groups. Through the use of fast Fourier transforms (see accompanying abstract by Dunham et al.), the a-values of the contributing nuclei are measured and assigned to specific locations on the molecules. The a-values demonstrate a numerical precision less than one milligauss and an accuracy of around 20 milligauss.

132 AN ESR STUDY OF A PEROXYL RADICAL INTERMEDIATE IN HORSERADISH PEROXIDASE (HRP)/t-BUTYL HYDROPEROXIDE (t-BuOOH), B. Kalyanaraman, Edward Perez-Reyes and Ronald P. Mason, National Institutes of Environmental Health Sciences, Research Triangle Park, NC 27709.

A single broad line ESR spectrum was obtained ($g = 2.0140 \pm 0.0002$) upon the addition of HRP to a solution of excess t-BuOOH in tris (150 mM, pH = 7.4) buffer, under either aerobic or anaerobic conditions at room temperature. The ESR spectrum is dependent on both the enzyme and the substrate. Sodium azide, a known inhibitor of HRP at 0.1 M concentrations, diminished the ESR signal intensity. Phenol, a peroxidase substrate as well as a peroxy radical scavenger, completely inhibited the formation of the single line ESR spectrum (at 1 mM concentrations). SOD (superoxide dismutase) did not have any effect on the intensity of the signal. Incubation of HRP with excess H_2O_2 did not yield any ESR spectrum.

In situ UV irradiation of t-BuOOH at room temperature gave rise to a similar single line ESR spectrum having an identical g-value. The ESR spectrum was observable for several minutes depending on the concentration of t-BuOOH on continuous irradiation, but decayed within seconds after the UV light was switched off. Phenol inhibited the signal at 10 mM concentrations.

Based on these results, the enzymatically obtained ESR spectrum was attributed to a tert-butylperoxy (t-BuOO˙) radical. The mechanism for this production of the t-butylperoxy radical will be discussed via the known one- electron oxidation pathway involving compound I and compound II which normally operates in peroxidase reactions.

133 SOME INTRIGUING OBSERVATIONS IN THE ESR OF PARTIALLY ORIENTED MEDIA. Jack H. Freed. Baker Laboratory of Chemistry, Cornell University, Ithaca, New York 14853.

Some recent ESR results of nitroxides (and other paramagnetic species) in partially oriented media are discussed and analyzed. The media include 1) thermotropic liquid crystals in the nematic and various smectic phases; 2) oriented model membranes; 3) solid surfaces. Particular attention will be given to a) the ways in which the ordering is reflected in the microscopic motional dynamics; b) ways in which ESR may be used to determine sample morphology and long-range cooperativity; c) the ways in which probe molecules sense quasi-critical fluctuations near phase transitions. Particular topics will include: magnetic-field-induced reorientations in Smectic A phases; cooperative chain-distortion waves and magnetic-field-induced headgroup reorientations in lipids and related phenomena in thermotropics; the role of local structure on molecular motions; highly anisotropic motions on surfaces; unusual pre-transitional effects on spin probes at the nematic-Smectic A phase transition. Emphasis will be given to the accurate analysis of ESR spectra including a discussion of new and powerful computation methods for simulating slow-motional ESR spectra.

134 EPR AND ENDOR OBSERVATIONS OF THE "CENTRAL PEAK" PHENOMENON, N. S. Dalal, Chemistry Department, West Viginia University, Morgantown, WV.

This presentation will focus on the role of magnetic resonance and, in particular, EPR in elucidating the origin of the so-called central peak (CP), first observed as a quasi-elastic peak in the neutron and light scattering studies of crystals undergoing phase transitions. Thus, CP corresponds to a low frequency lattice or local mode which apparently borrows intensity from other lattice modes, especially the "soft mode", a mode whose frequency $\nu \to 0$ as $T \to T_p$, T_p being the phase transition temperature. Prior to the discovery of CP, most continuous phase transitions were explained in terms of the condensation of the "soft modes". Now, it is believed that the CP mode might be more fundamental than the "soft mode" itself. However, the microscopic origin of the elementary excitations responsible for CP is not yet known, despite several recent theoretical and experimental attempts.

The talk will consist of a critique of the CP phenomenon, and stress the advantages of magnetic resonance for understanding this new development. Examples will be chosen from a variety of compounds, with a primary focus on ferroelectric and antiferroelectric phase transitions, the role of externally applied electric fields and the ENDOR technique.

135 THE DETECTION OF PHASE TRANSITIONS IN $NH_4Ln(SO_4)_2\cdot 4H_2O$ SINGLE CRYSTALS USING ELECTRON PARAMAGNETIC RESONANCE OF Gd^{3+} IMPURITY IONS. H. A. Buckmaster and V. M. Malhotra, Physics Department, University of Calgary, Calgary, Canada.

The 9.4 GHz electron paramagnetic resonance (EPR) of Gd^{3+} impurity ions in $NH_4Ln(SO_4)_2\cdot 4H_2O$ (Ln=Ce, Pr and Sm) single crystals has been studied at 77-300K. The Gd^{3+} impurity ions are found to substitute for the trivalent lanthanide ions in two inequivalent magnetic complexes corresponding to the tetramolecular unit cell. The EPR spectra at 294K have been analyzed using an orthorhombic symmetry spin-Hamiltonian. The observed zero field splittings of Gd^{3+} impurity ions in nine coordinated double sulfates and in other hydrated host lattices indicate the inadequacy of the splittings mechanisms based only on symmetry. The observation of resolved Gd^{3+} impurity ion spectra in the presence of paramagnetic Ln host ions has been interpreted in terms of random modulation of the interaction between the Gd^{3+} impurity and Ln^{3+} host ions due to fast spin-lattice relaxation time of host Ln^{3+} ions. The spin-lattice relaxation time of Ln^{3+} host ions have been estimated at 290K from the impurity ion linewidths and is found to be consistent with an Orbach resonance process. Using the temperature dependence of the EPR zero field splitting, linewidths and intensities it has been shown for the first time that $NH_4Ln(SO_4)_2 \cdot 4H_2O$ single crystals have a sequence of phase transitions at low temperatures.

136 DYNAMIC AND COOPERATIVE JAHN-TELLER DISTORTIONS IN COPPER PYRIDINE N-OXIDE COMPLEXES, C. P. Keijzers and E. de Boer, Department of Physical Chemistry, University of Nijmegen, Toernooiveld, 6525 ED Nijmegen, The Netherlands; and J. S. Wood, Department of Chemistry, University of Massachusetts, Amherst, MA 01003.

The hexapyridine-N-oxide cuprate ion, $Cu(PyO)_6^{2+}$, is subject to Jahn-Teller distortions which are dynamic above ~45 K. At this temperature, phase transitions occur to statically distorted structures, the nature of which being dependent on the anion (perchlorate, fluoborate and nitrate) and on the solvent used. The low temperature phase of the fluoborate complex is based on a cooperative Jahn-Teller ordering of elongated octahedral complexes which is "ferrodistortive", while two different antiferrodistortive orderings are proposed for the perchlorate and the nitrate complexes. These low temperature structures are in accord with the results of previously published magnetic measurements, which indicate two-dimensional magnetic ordering for the fluoborate complex and one-dimensional ordering for the perchlorate complex.

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EPR STUDIES OF THERMOCHEMICAL AND PHOTOCHEMICAL DECOMPOSITION OF NITRAMINES. H. L. Pugh, L. P. Davis, J. S. Wilkes, and R. C. Dorey, Frank J. Seiler Research Laboratory (AFSC), USAF Academy, CO 80840.

Thermochemical and photochemical decomposition of propellants and explosives during transport and storage has been a problem for many years. Electron paramagnetic resonance (EPR) is one of the few experimental methods applied to this problem that provides measurement of kinetic parameters for specific reacting species as well as identification of radicals involved in the decomposition process. We recently reported EPR results which provided reaction kinetic and mechanism information for the thermochemical and photochemical decomposition of nitroaromatic compounds. This paper reports the extension of this work to include the important nitramine propellants, HMX and RDX. The EPR results clearly indicate radical formation in HMX and RDX dissolved in various solvents and irradiated with a Hg-Xe arc source. We will discuss the reaction kinetics and possible radical structures responsible for the observed EPR spectra.

138 EPR STUDIES ON THE STRUCTURE OF THE ACTIVE SITE OF ADRENAL STEROL HYDROXYLATION J.C. Salerno, J.D. Lambeth, J.R. Lancaster, J.O. Wilkerson, H. Kamin. Dept of Biochemistry, Duke University Medical Center, Durham, North Carolina 27710.

The initial reaction in adrenal mitochondrial cholesterol metabolism is a triple hydroxylation and cleavage of the cholesterol side chain catalyzed by cytochrome P-450_{scc} EPR studies, using partially-hydrated oriented multilayers prepared from adrenal mitochondrial membranes or from reconstituted phospholipid vesicles, show that the P-450_{scc} heme is highly oriented in the membrane. In all preparations, $g\sim8.0$ and $g\sim3.6$ features of the high spin spectra and the $g\sim2.24$ and $g\sim1.9$ features of the low spin spectra are maximal when the magnetic field is parallel to the plane of the membrane; the $g=1.8$ and $g=2.4$ high and low spin features are maximal when the field is normal to the membrane. This agrees with recent reports on bulk P-450 orientation in adrenal mitochondria and liver microsomes. By analogy with the relative orientations of hemes and g tensors in crystalline cytochromes c, myoglobin and P-450cam, we conclude that the heme plane of P-450_{scc} is essentially parallel to the membrane plane; computer simulation suggests a disorder parameter of about 30°. Similar results were obtained for P-$450_{11\beta}$ and adrenal microsomal P-450. Broadening of the ESR spectra of h.s. P-450_{scc} by dysprosium-EDTA suggests that the heme site of P-450_{scc} is at least as exposed as that of cytochrome c. The broadening was unaffected by reconstitution into phospholipid vesicles and was also seen in adrenal SMP, but not in mitochondria. Addition of adrenodoxin, the physiological reductant, greatly decreased the Dy induced broadening. Thus, the heme interacts with dy through the ADX binding site, which is essentially unaffected by the membrane.

139 ELECTROCHEMICAL AND EPR STUDIES OF DICARBENE CARBONYL METAL COMPLEXES AND ARENE TRICARBONYL CHROMIUM COMPLEXES. Reuben D. Rieke, Stuart Milligan, Indu Tucker, Gianni Zotti and R. Bennet Willeford, Department of Chemistry, University of Nebraska-Lincoln, Lincoln, Nebraska 68588

Electrochemical and EPR studies were carried out on a series of *cis* and *trans*-dicarbenetetracarbonylmetal complexes and also on a series of dimethyldiphenyltinbis (tricarbonylchromium(0)) complexes. The *cis* and *trans*-dicarbene complexes yielded a single reversible oxidative wave in the region of +0.5V to -0.2V. The trans cations were shown to undergo a rapid isomerization to the cis cations. A simple photoelectric cell using these complexes will be discussed. A series of mono-substituted dicarbenetricarbonylmetal complexes were also prepared and their redox properties were determined. EPR of the cations of all the dicarbene complexes will be discussed.

A new series of mixed valent complexes were prepared by the electrochemical oxidation of substituted dimethyldiphenyltinbis (tricarbonyl-chromium(0)) complexes. In contrast to the electrochemical oxidation of arenetricarbonylchromium(0) complexes, electrochemical oxidation of the appropriately phenyl substituted biscarbonyl complexes yields a very stable cation. The redox properties of these complexes will be discussed as well as the reasons for this unusual stabilization of the mixed valence species.

140 PROTON ENDOR STUDY OF COPPER(II) BIS(DITHIOCARBAMATE). C. P. Keijzers, D. Snaathorst, E. de Boer, and A. A. K. Klaassen. Department of Physical Chemistry, University of Nijmegen, Toernooiveld, 6525 ED Nijmegen, The Netherlands.

In a doped single crystal of methyl-deuterated ^{63}Cu(II) bis(N,N-diethyldithiocarbamate) in the corresponding diamagnetic nickel complex, the methylene proton hyperfine coupling tensors are measured with ENDOR spectroscopie. Two intermolecular and all four intramolecular proton coupling tensors could be determined. Using spin densities which were obtained from extended Huckel-MO calculations, the anisotropic part of the tensors can be reproduced quantitatively, if all two- and three-center contributions are taken into account. Comparison of the transition frequencies which are computed from the theoretical tensors with the experimentally obtained transitions, enabled the tracing of another five (intermolecular) tensors which could not be completely determined experimentally.

141 EPR and ENDOR Studies of Zn/Cu Superoxide Dismutase. R. A. LIEBERMAN, J.A. FEE, H.L. VAN CAMP, R.H. SANDS, Biophysics Research Div., Univ. of Michigan.

Magnetic resonance techniques (ENDOR, and single-crystal EPR) have been used to examine the Cu^{2+} binding site of bovine superoxide dismutase (BSD). Studies of this enzyme in its native state and of its mono-cyano complex indicate a reorientation of the copper ion's magnetic (g and A) tensors upon anion binding. This shift may be interpreted as a rearrangement of the imidazole (histidine) rings which coordinate to the Cu^{2+} ion in BSD, and its presence leads to a detailed hypothesis for the first step (reduction of Cu^{2+} to Cu^{+}) in the protein's catalysis.

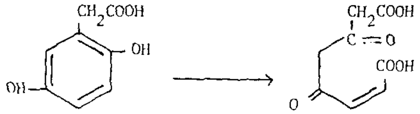
142 PROTON AND NONPROTON ENDOR INVESTIGATIONS OF NOVEL GALVINOXYLS IN DIFFERENT ELECTRON SPIN STATES. H. Kurreck, B. Kirste, W. Gierke, K. Schubert. Freie Universität Berlin, FB 21, WE 02, Takustrasse 3, 1000 Berlin 33.

The synthetic pathways yielding a variety of mono and oligo galvinols, including ^{13}C labeled derivatives, are described. These galvinols are well-known precursors of the galvinoxyl series for free radicals. Two of the latter turned out to be particularly interesting in the field of applied ENDOR spectroscopy and shall be discussed in this context. Partial oxidation of the first one yields a highly overcrowded doublet spin state molecule existing in two different conformations. Careful ENDOR and TRIPLE resonance techniques allow detection and discrimination of these conformations. By performing ENDOR induced ESR experiments, definite assignments of the respective sets of ENDOR lines to the two specific species could be achieved.

The second galvinol, partially ^{13}C labeled, can be oxidized to three different radical species exhibiting doublet, triplet and quartet spin states, respectively. It is shown that the respective spin states can unambiguously be determined from the ENDOR measurements. Moreover, these species offer the potentiality of probing the ENDOR effect within different electron spin (M_s) manifolds. For this purpose detailed proton as well as ^{13}C ENDOR experiments have been performed.

143 EPR STUDY OF HOMOGENTISATE OXYGENASE FROM *ASPERGILLUS* sp. M. Sonoda and Y. Sakagishi, Saitama Medical School, Japan.

The mechanism of the reaction of homogentisate oxygenase (2,5-dihydroxyacetate-1,2-dioxygenase, E.C. 1.99. 25) from *Aspergillus* sp. has been studied by the EPR spectrometer. This enzyme was isolated from *Aspergillus* sp. which was screened from soil of the farm in Saitama Pref. Japan. This fungus produced the homogentisate oxygenase when it was cultivated in a medium containing ferrous iron and L-tyrosine as a sole carbon source. Our fungal homogentisate oxygenase catalyzed the folllowing reaction and required ferrous iron as a cofactor.



EPR experiments on the fungal enzyme demonstrated the involvement of an iron component during the oxidation reaction. An enzyme-specific EPR signal was observed at $g = 4.28$ by the addition of homogentisate and oxygen. And this signal disappeared during incubation for 5 min. at 25°C. From these results, we presumed a new reaction mechanism which associated with paramagnetic change in this oxidation of homgentisate.

144 A SINGLE CRYSTAL EPR STUDY OF GROUND STATE TRIPLET TRIMETHYLENEMETHANE. O. Claesson, A. Lund, T. Gillbro, T. Ichikawa, O. Edlund, and H. Yoshida, The Studsvik Research Laboratory, Nykoping, Sweden.

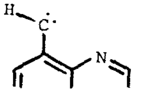
Trimethylenemethane, a ground state triplet, has been generated in a single crystal of methylenecyclopropane by γ-irradiation at 77 K and studied by the electron paramagnetic resonance technique in the temperature range 4.2 - 106 K. From the observed anisotropy of the epr spectra, the zero-field splitting constants can be determined as $D = 0.0246\ \mathrm{cm}^{-1}$ and $|E| \leq 0.0003\ \mathrm{cm}^{-1}$, and the principal values of the proton hyperfine coupling tensor as -14, -38, and -26 MHz with an isotropic coupling of -26 MHz at 77 K. Computer simulations of some of the spectra were performed using a computer program developed for this investigation. The system is described by the spin Hamiltonian

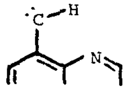
$$H = \beta\underline{B}\cdot\underset{\sim}{g}\cdot\underline{S}+\underline{S}\cdot\underset{\sim}{D}\cdot\underline{S} + \sum_{i=1}^{6} \{\underline{S}\cdot\underset{\sim}{A}_i\cdot I_i - \beta_N g_{Ni}\underline{B}\cdot I_i\}$$

The first two terms are treated exactly and the hyperfine and nuclear terms by perturbation theory. Both the position and the intensity of the spectral lines were reproduced with a good result. The simulations gave a positive sign for the zero-field splitting constant D. The zero-splitting is temperature dependent above *ca* 20 K probably due to an oscillating motion of the molecular plane. The hyperfine structure changes above *ca* 80 K and becomes isotropic at 100 K. This change is attributed to an anisotropic rotation about the threefold symmetry axis of the molecule.

145 GEOMETRICAL ISOMERISM OF QUINOLYLMETHYLENES. R. S. Hutton, H. D. Roth, M. L. Schilling, J. W. Suggs. Bell Laboratories, Murray Hill, NJ 07974.

Triplet esr spectra have been obtained for several isomers of quinolylmethylene (QM) generated by photosensitized decomposition of the respective quinolyldiazomethanes or of triazoloquinoline. For QM's derived from the diazomethanes the spectra indicate the presence of two similar but non-identical triplets, which are assigned to the two rotameric structures with different orientations of the carbene proton.





For 2-QM only one triplet is observed as dictated by the fixed position of the proton in the triazoloquinoline precursor. The particular rotamers were assigned by calculating the zero-field splitting parameter, D, using a simple point-spin model and taking the spin distribution of the corresponding quinolylmethyl radical to represent the π-electron distribution of the triplet. The values of D range from 0.44 to 0.50 cm^{-1}, 2-QM and 3-QM having greater D values than 4-QM and 8-QM. This ordering is the same as that for the analogous naphthylmethylenes. The magnitudes of the D values of the QM's indicate that the presence of the nitrogen in the ring has only a small effect on the spin distribution of the triplet.

146 TMA Dehydrogenase: A Study in Triplet State EPR. R. C. STEVENSON, W. R. DUNHAM, R. H. SANDS, Biophysics Research Division, Univ. of Michigan, Ann Arbor, MI 48109, H. BEINERT, Institute for Enzyme Research, Univ. of Wisconsin, Madison, WI 53706.

Electron paramagnetic resonance (EPR) spectra were obtained on the protein tri-methylamine dehydrogenase (TMA dehydrogenase) at S band ($3GH_z$), X band ($9GH_z$), and P band ($15GH_z$) microwave frequencies. These data include spectra centered about $g = 2$ as well as half-field data. We have mathematically modeled that data as representing two strongly-coupled spin one-half systems; An fe/S center of the protein and an attached free radical giving rise to a triplet (spin one) system. The modeling was aided by a computer program developed to simulate EPR spectra for a Hamiltonian,

$H = (S_1 + S_2)\cdot g\cdot H + S_1{:}D{:}S_2$ projected onto $S = S_1 + S_2 = 1$ subspace. Expressions for the eigenstates and resonant fields were obtained in closed form. Subject to a minimization requirement, the triplet program was used to simultaneously fit the TMA dehydrogenase spectrum (including half-field) at three different microwave frequencies. Data at three frequencies were used to guarantee a unique set of Hamiltonian parameters.

147 AN UNUSUAL ELECTRON SPIN ECHO PHASE SHIFT OBSERVED IN THE EARLY REACTIONS OF PHOTOSYNTHESIS* by Marion C. Thurnauer, Lester L. Shipman and James R. Norris, Argonne National Laboratory, Argonne, IL 60439

In our studies of green plant photosynthesis by time resolved electron spin echo (ESE) spectroscopy we have observed an unusual echo phase shift (EPS) of the signal due to the primary electron donor of photosynthesis (P^{+}_{700}). The EPS decays within approximately 200 nsec of the exciting laser pulse. We can explain this phenomenon as resulting from a short-lived radical pair interaction between P^{+}_{700} and one of the early electron acceptors of photosynthesis. A density matrix treatment of the ESE experiment carried out on a short-lived radical pair can explain key aspects of the observations. We are using this analysis to determine the identity of the early acceptor, the lifetime of the radical pair intermediate, and the exchange interaction between P^{+}_{700} and the early acceptor.

*Work performed under the auspicies of the Office of Basic Energy Sciences, Division of Chemical Sciences, U.S. Department of Energy.

148 INTERACTION BETWEEN DYSPROSIUM COMPLEXES AND SOLUBLE IRON-SULFUR PROTEINS. Haywood Blum, J. S. Leigh, and Tomoko Ohnishi. Dept. of Biochemistry and Biophysics, University of Pennsylvania, School of Medicine, Philadelphia, PA 19104.

Purified iron-sulfur proteins and cytochrome c, when exposed to dysprosium complexes are seen to have reduced spin-lattice relaxation times (T_1) as measured by changes in saturation parameter ($P_{\frac{1}{2}}$) and broadened line widths (ΔH) due to dipole-dipole interactions. We have studied a number of proteins whose structures are similar to those already determined by X-ray crystallography. We find that $Dy(NO_3)_3$ and Dy-EDTA with nominally positive and negative overall charge, respectively, have very different effects, with the EDTA complex usually more effective in soluble systems and the nitrate complex occasionally more effective in membrane-bound systems. Dy-HEDTA, a neutral complex, is not effective at all. The $\Delta P_{\frac{1}{2}}$ and ΔH are proportional to $[Dy]$ in the mM and higher range. These results can be understood in terms of a model in which the complex electrostatically binds to the surface of the protein in a shell, rather than distributing uniformly in space. With this model, $\Delta P_{\frac{1}{2}} \propto 1/T_1 \propto r^{-6}$ and $\Delta H \propto r^{-3}$ where r is the Dy-active iron distance. For Dy-EDTA we find $\Delta P_{\frac{1}{2}} = 1.11 \times 10^8 r^{-6} \exp(-12.5/T)$ mW/mM and $\Delta H = 1.65 \times 10^3 r^{-3}$ mT/mM, where r is in Angstroms, the line broadening is measured below 10 K, and the temperature dependence of $\Delta P_{\frac{1}{2}}$ is due to the intrinsic T_1 of Dy-EDTA.

Supported by NIH Grants GM 25052 and GM 12202 and by NSF Grant PCM 78-16779.

149 A MAGNETIC INTERACTION BETWEEN Gd^{3+} AND NITROXIDE BOUND TO CYS-98 OF THE Ca^{2+} BINDING PROTEIN, TROPONIN-C. C.-L.A. Wang, P.C. Leavis, J.C. Seidel, and J. Gergely. Dept. of Muscle Research, Boston Biomedical Research Institute, 20 Staniford St., Boston, MA 02114.

Troponin-C (TnC), the Ca^{2+} binding protein involved in regulation of contraction of skeletal muscle, contains two low affinity Ca^{2+} binding sites ($K_{app}=5x10^5\ M^{-1}$) and two high affinity sites ($K_{app}=2x10^7\ M^{-1}$). It contains a single cysteine residue (Cys-98) to which we have attached N-(1-oxyl-2,2,6,6-tetramethyl-4-piperidinyl)-maleimide. Binding of Ca^{2+} to the high affinity sites of TnC alters the shape of the EPR spectrum (Ebashi et al., J.Biochem. 75 211 (1974)), indicating decreased mobility of the probe. Gd^{3+} alters the shape of the EPR spectrum in a manner similar to Ca^{2+}, but also decreases the amplitude progressively with the binding up to four Gd^{3+} per mole of TnC, the effect being reversed by addition of EDTA. When Gd^{3+} displaces Ca^{2+} from TnC the change in shape of the EPR spectrum is minimized and the decrease in amplitude predominates. This protein may provide a model to compare distances between the Ca^{2+} binding sites and Cys-98 calculated from the tertiary structure of a homologous protein, parvalbumin (Kretsinger and Barry, Biochim.Biophys.Acta 405 40 (1975)), with those obtained from EPR assuming a dipolar interaction between the paramagnetic ion and the spin probe. (Supported by NIH, AHA and MDA)

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PROTON INVOLVEMENT WITH THE LIGHT-INDUCED HINDRANCE OF SPIN LABEL MOTION IN THE LUMEN OF SPINACH THYLAKOIDS

Steven P. Berg and Donna M. Nesbitt. Department of Biological Science University of Denver, Denver, Colorado 80208.

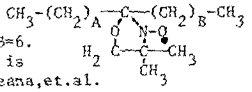
We have measured the motion of the spin label Tempamine (2,2,6,6-tetramethylpiperidine-N-oxyl-4-amine) in the internal aqueous space (lumen) of thylakoids by using $K_3Fe(CN)_6$ [Arch. Biochem. Biophys. 194: 138-148 (1979)] or $K_3Cr(C_2O_4)_3$ [Biochim. Biophys. Acta 548: 608-615(1979)] as membrane impermeable broadening agents for Tempamine not residing in the lumen. We have recently reported [FEBS Letters, March 1980, in press] that illumination of thylakoids imposes a considerable additional hindrance of Tempamine motion. We report here, that this additional light-induced hindrance is related to the acidification (pH8→pH5) of the lumen concomitant with light-driven thylakoid electron transport. Our conclusions are based on studies using uncouplers of photophosphorylation which prevent lumen acidification and on pH studies which mimic the light-induced change.

151 SPIN LABELS FOR MEMBRANE-WATER PARTITION STUDIES

Philip D. Morse, II, Robert Clarkson*, and Donna M. Lusczakoski-Nesbitt**. Department of Biological Sciences, Wayne State University, Detroit, Michigan 48202. *Varian Associates, Palo Alto, California 94303. **University of Denver, Department of Biological Sciences, Denver, Colorado 80208.

Spin label partitioning using the spin label Tempo has been widely used as a measure of membrane fluidity in model membrane systems and bacteria. This measurement is more difficult and sometimes impossible in more complex membrane systems such as red blood cells, spinach thylakoids, and mitochondrial membranes. The purpose of this presentation is to introduce spin labels which will partition into these membranes.

These labels are of the general structure:



$CH_3-(CH_2)_A-C-(CH_2)_B-CH_3$

When A=0,B=1,3,5,7,9, or 11; when A=3,B=4; and when A=5,B=6. We use the shorthand notation (A+2)N(A+B+3),i.e. A=5,B=6 is 7N14. These labels are synthesized from the methods of Keana,et.al. [J.A.C.S. 89 (1967) p.3055]. The syntheses and purifications will be described in detail. Gas chromatography serves to separate the spin labels from their precursors.

At a spin label to lipid ratio of 1:50, partitioning of the labels in dipalmitoyl lecithin occurs to varying degrees both below and above the phase transition of the lecithin. X-band and Q-band spectra will be shown along with plots of the highfield line height ratios of the spin labels in both the phospholipid and aqueous phases. Line height plots will be compared to quantitative evaluations of the actual spin label concentrations in both phases. Partitioning and rotational motion of some of the labels in red blood cell membranes will also be presented.

152 PREFERENTIAL SEGREGATION OF SPIN LABELED CARDIOLIPIN WITHIN THE BOUNDARY LAYER OF THE MEMBRANE ENZYME CYTOCHROME C OXIDASE

G. L. Powell & M. B. Cable, Dept. of Biochem., Clemson University, Clemson, S. C. 29631.

Membrane proteins decrease the segmental motion of a fraction of labeled lipid analogues intercalated into the membrane bilayer. The fraction immobilized (on the ESR time scale) is proportional to the total lipid content down to a limiting value. This limiting value called the boundary layer, corresponds with the amount of lipid which could form a shell or annulus one molecule wide around the protein (Griffith, et al., Ann. NY Acad. Sci. 222 (1973)561). A variety of evidence has suggested that cardiolipin (found in higher organisms almost exclusively within the inner mitochondrial membrane) associates with a membrane enzyme like cytochrome c oxidase. We have tested this hypothesis by comparing the segregation of a spin labeled cardiolipin analogue (1-(3-sn-phosphatidyl)-3-(1-acyl-2-(16-doxylstearoyl)glycerol(3)phosphocholine)) with the corresponding spin labeled phosphatidylcholine (1-acyl-2-(16-doxylstearoyl)glycerol(3)phosphocholine). The boundary layer observed using spin labeled cardiolipin appeared larger using spin labeled cardiolipin when the membrane lipid was phosphatidylcholine; otherwise the boundary layers were the same. Scatchard-type analysis of this data (Jost and Griffith in the Proceedings of the Japanese and American Symposium on Cytochrome Oxidase (B. Chance, et al., eds) Elsevier, Amsterdam, 1979, pp.207) suggested that the cardiolipin boundary layer was actually the same size but had a partition coefficient twice that of other lipids. Several interpretations for the observations will be offered. This work was supported by the National Science Foundation (BMS 75-14983) and the Americal Heart Association (78778).

153 HIGH FREQUENCY (35 GHz) SATURATION TRANSFER EPR: AN APPROACH TO SLOW ANISOTROPIC ROTATIONAL DIFFUSION

M. E. Johnson. Medicinal Chemistry Department, University of Illinois Medical Center, Chicago, Illinois 60680.

Many biomolecular systems undergo substantially anisotropic rotational diffusion. In developing an understanding of anisotropic motion in the saturation transfer time domain, we have extended its use to an EPR observational frequency of 35 GHz (Q Band). At this frequency spectral resolution is greatly enhanced due to increased *g* anisotropy. This permits an improved correlation between spectral changes, and the rates and orientations of rotational diffusion. Two lipid bilayer model systems have been used to investigate axial anisotropic rotational motion: dipalmitoylphosphatidylcholine (DPPC) with an incorporated nitroxide fatty acid analog in which rotational diffusion is primarily around the nitroxide principal *z*-axis, and DPPC with an incorporated nitroxide cholestane analog in which diffusion is primarily around the nitroxide principal *y*-axis.

The behavior of these model systems has been used to interpret motional behavior of sickle hemoglobin (HbS) upon aggregating into the gel state. The results indicate that HbS rotational motion is greatly restricted along an axis corresponding closely to the principal *z*-axis of the nitroxide label, but that motion around this axis remains relatively free. This information, along with the orientation of the nitroxide with respect to the Hb molecule, then provides information on the location of some of the essential intermolecular binding sites.

(Supported by grants from Research Corporation and the NIH; MEJ is an Established Investigator of the American Heart Association.)

154 SPIN-LABEL STUDY OF RABBIT THYMOCYTE MEMBRANES.

Gopa Rakhit. Food and Drug Administration, Washington, D. C. 20204.

Rabbit thymocytes were isolated and prepared according to published procedures. The fluidity of thymocyte membrane was studied using fatty acid spin labels. The viability of these cells were checked before and after spin-labelling procedure by Trypan-Blue dye exclusion experiment. ESR spectra of 5-doxyl stearic acid spin label incorporated into the membrane were indicative of moderate viscosity near nitroxide radical. No significant change in the membrane fluidity could be detected from ESR spectra of these cells after challenge by Concanavalin A (Con A).

The interaction of rabbit thymocytes with Con A and certain anti-tumor drugs were also studied using NEM spin-label technique.

155 DOES FATTY ACYL-CoA MICELLIZE?

G. L. Powell and D. Freeland. Dept. of Biochemistry Clemson University,Clemson,S. C. 29631.

Fatty acyl-CoA are amphipathic nucleotides,probably membrane-associated *in vivo*, and they are important intermediates and regulatory effectors (Caggiano & Powell,*J. Biol. Chem.* 254(1979)2800) in lipid metabolism. Solution properties of fatty acyl-CoA have only been parti ally characterized,but a critical micelle concentration in the μM range has been regarded as an important feature of the biochemistry of these compounds (Zahler, *et al. Biochim. Biophys. Acta* 164(1968)1. Apparent intensity changes in the visible specta of low concentrations of dyes in the presence of fatty acyl-CoA have been ascribed to micellization (3-4 μM). We are employing a spin-labeled fatty acyl-CoA (S-(2-(5-carboxybutyl)-2-dodecyl-4,4-dimethyl-3-oxazolidinyl-N-oxyl)CoA) to detect micellization. Experiments have been done two ways: using 6-doxylstearoyl-CoA as a label at low concentration (1.5 μM) in the presence of increasing concentrations of palmitoyl-CoA and by observing the spectra of increasing concentrations of 6-doxylstearoyl-CoA. No changes are seen in the former spectra; in the latter experiments the spectral intensities increase linearly with concentration. At 200 μM spin exchange effects are apparent. The absense of effects may be interpreted in two ways: micellization does not occur within the concentration range studied (0.8-200 μM) or the spin label is not an appropriate analogue. 6-Doxylstearoyl-CoA partitions into phospholipid vesicles and provides distinctive changes in line shape upon intercalation; the analogue also detects Triton X-100 micellization very efficively. We are using the analogue to search for some specfic interaction between fatty acyl-CoA and dye. This work was supported by the National Institutes of Health Grant 2 R01 GM 22788-04. C.A.Evans has contributed to this project.

156 SPIN LABEL ASSAY FOR TRAPPED VOLUME AND LIPID VESICLE FUSION,

A.I. Vistnes and J.S. Puskin, University of Rochester, Rochester, NY 14642.

The neutral spin label TEMPONE rapidly equilibrates across lipid bilayers. Addition of TEMPONE plus a nonpermeable paramagnetic quencher, $K_3Cr(C_2O_4)_3$, to preformed lipid vesicles produces an EPR spectrum consisting of 3 components: (a) a broadened signal due to TEMPONE molecules in the external medium, (b) a signal from label partitioned into the lipid, and (c) a narrow signal arising from TEMPONE in the trapped aqueous compartment. After subtracting contributions from the first two components, the intensity of the third can be estimated. From this intensity the trapped volume can be calculated.

Internal volumes of several kinds of vesicles were measured in this way, yielding values close to those determined by independent means. Trapped volume determinations, as a function of varying salt concentration, on large vesicles prepared by reverse phase evaporation indicated that these structures are nearly perfect osmometers.

Vesicle fusion can be followed by monitoring concomitant increases in trapped volume. Thus, more than 20-fold increases in trapped volume were observed following incubation of phosphatidylserine vesicles with Ca^{2+}. The final trapped volume depended on the incubation temperature, showing a sudden increase upon heating to ≈11°C. (Supported by DOE and NIH; A.I.V. was supported in part also by a fellowship from the Norwegian government).

157 EPR SPECTRA OF SPIN-LABELED DERIVATIVES OF COPPER TETRAPHENYLPORPHYRINS.

K. M. More, S. S. Eaton, and G. R. Eaton, Department of Chemistry, University of Denver, Denver, Colorado 80208.

Nitroxyl spin labels have been attached to the cis and trans isomers of copper meso-tetraphenyl-1-[3-acrylic acid]porphyrin and to copper (5-(2-R-phenyl)-10,15,20-tritolyl-porphyrin) ($R=NH_2$, COOH, and OH) by ester and amide linkages. The values of the electron spin-electron spin splitting constant, J, were obtained from the EPR spectra. The magnitude of J is dependent on the nature of the porphyrin-nitroxyl linkage and on solvent.

158 COPPER-NITROXYL INTERACTIONS IN A SPIN-LABELED COPPER PORPHYRIN.

B. M. Sawant, G. A. Braden, R. A. Smith, G. R. Eaton, and S. S. Eaton, Department of Chemistry, University of Denver, Denver, Colorado 80208.

Copper(2-carboxy-7,12-diethyl-3,8,13,17,18-pentamethyl)porphyrin has been spin-labeled at the carboxy group by reaction with 4-hydroxy-2,2,6,6-tetramethylpiperine-N-oxyl, 4-amino-2,2,6,6-tetramethylpiperidine-N-oxyl, and 3-amino-2,2,5,5-tetramethyl-pyrrolidine-N-oxyl. The magnitude of the electron spin-electron spin coupling constant, J, was obtained from the EPR spectra. The effects of the porphyrin-nitroxyl linkage on the EPR spectra and visible spectra will be compared.

159 SPIN-SPIN INTERACTIONS IN SPIN-LABELED COPPER CARBOXYLATE DIMERS AND RELATED MONOMERS.

D. P. Dalal, S. S. Eaton, and G. R. Eaton, Department of Chemistry, University of Denver, Denver, Colorado 80208.

The EPR spectra of the monomeric and dimeric copper(II) complexes of 3-carboxy-2,2,5,5-tetramethylpyrroline-1-oxyl and 3-carboxy-2,2,5,5-tetramethylpyrrolidine-1-oxyl have been examined in solution and in frozen glasses. The effects of the spin-spin interactions in the two classes of compounds will be compared.

160 SPIN-SPIN INTERACTIONS IN COPPER ACETATE BIOGENIC AMMINE SPIN LABEL COMPLEX.

R. Haran, J. Gairin, P. Sharrock, C. Dogounkoff, M. Massol. Laboratoire de chimie de coordination du CNRS et Laboratoire de chimie bioinorganique, Université Paul Sabatier, Toulouse, France, 31400 et Département de chimie, Université de Sherbrooke, Québec J1K 2R1.

Various spin probes have been synthesized incorporating the amino alcohol function, for use as building blocks for spin labels of biological relevance. These include aliphatic and aromatic ammines coupled *via* an amide function to various five and six membered ring nitroxydes. These spin probes are weak complexing agents and little but line broadening can be seen in the presence of $CuCl_2$. However, addition of methanolic copper acetate to these spin probes causes a line broadening which can be reduced by introduction of spin-free ammine. This suggests that the spin probes are weakly bonded in the axial positions of copper acetate molecules. Addition of ammines to methanolic copper acetate dissociates the dimers to form monomeric adducts with resolved hyperfine structure. Frozen solution spectra show triplet state features which allow us to conclude that the spin-spin interaction between the nitroxyde and the metal atom is weak compared to the metal-metal. The effect of added ligands on the rhombic distortion of copper acetate dimers will also be discussed. These results should help in the interpretation of spin-label spectra obtained in metal ion containing biological fluids (blood) where peptide hormones are to be determined by Spin Label Immuno Assay.

161 A SYSTEMATIC EXPERIMENTAL ATTEMPT TO SEPARATE HYDRODYNAMIC AND MICROSCOPIC CONTRIBUTIONS TO MOLECULAR TRANSLATIONAL DIFFUSION IN LIQUIDS.

R. N. Schwartz and Marco Patrón, UCLA, Los Angeles 90024 and Barney L. Bales, California State University, Northridge 91330.

Translational diffusion of nitroxide free radicals in a wide variety of liquids was measured using Heisenberg Spin Exchange. Radicals and solvents of various sizes and shapes were chosen to yield a systematic variation of solute to solvent size. After correcting for inhomogenous line broadening and dipolar coupling, the data were interpretable in terms of a hydrodynamic model except that, invariably, the exchange frequency did not extrapolate to zero as $T/\eta \rightarrow 0$ as predicted by the Stokes-Einstein equation. Deviations from strong-exchange behavior were also noted in many cases. The results were interpreted in terms of various modified hydrodynamic models and correlations between the model parameters and the solute to size ratio were sought.

162 ELECTRON SPIN RESONANCE STUDY OF THE OXIDATION OF AROMATIC HYDROCARBONS.

I. C. Lewis and L. S. Singer. Union Carbide Corporation, Carbon Products Division, Parma Technical Center, P. O. Box 6116, Cleveland, Ohio 44101.

Electron spin resonance was used to study the free radical intermediates formed during the reaction of polynuclear aromatic hydrocarbons with oxygen. The treatment of 25 hydrocarbons with O_2 at 275°C in an inert solvent gave rise to colored solutions which generally exhibited intense ESR signals. Proton hyperfine spectra could be resolved for approximately one-half the radicals. The high g-values of between 2.0032 and 2.0040 confirmed the presence of chemically-bound oxygen in the radical structure. The g-values show a linear relation when plotted against either the energy of the lowest vacant molecular orbital or the polarographic half-wave reduction potential of the parent hydrocarbon. Preliminary analysis of some of the hyperfine spectra indicate that the radicals are stable aryloxyradicals produced by substitution of hydrogen by oxygen at a reactive site in the molecule.

163 *SPIN CORRELATION OF CARBAZOLYL RADICALS.*

Y. *Matsumoto, Department of Natural Science,* Kyushu Institute of Technology, Kitakyushu, Japan

9-Ethylcarbazole was complexed with antimony(V) chloride in cooperation with trichloromethane. Complexes consisted of cations for bis-(9-ethyl-3-carbazolyl) methine, or 9-ethyl-3-carbazolyl chloromethine, and anions for antimony hexachloride. The aryl-cations seem to be neutral by charge transfer from the diaryl-dye. ESR and other studies show that these radicals, in the presence of excess ethylcarbazole, form dimers of ground singlet spin-state in the disperison medium, or build up a one-dimensional antiferomagnet in the powder at temperature below 200K. Diaryl-cations also show Curie-Weiss' law with antimony hexachloride, having paramagnetic Curie temperature -40K.

The conclusion was confirmed by adsorption of oxygen gas to the powdered specimen at various low temperature. Formation of dimers was strongly concerned with the disappearance of initial paramagnetism and another paramagnetism appeared at about 200K. Both of paramagnetism show ESR spectra having a linewidth about 2.5G for ΔH_{msl}. The reason of such narrowing is not understood by means of any interaction theories for the low-dimensional magnetic column. Aryl-cations, in the powder of 1:1 complexes, show almost amorphous paramagnetism with the same linewidth as described above. In addition, polymeric complexes have linewidth not more than 2.5G too.

164 AN ESR-ENDOR STUDY OF RADIATION INDUCED FREE RADICALS IN CITRIC ACID, FROM 4.2K TO 300K,

Grace C. Moulton and Leon L. Finch, Florida State University, Tallahassee, Florida, 32306.

Single crystals of anhydrous citric acid and citric acid monohydrate, as well as partially deuterated anhydrous citric acid, were irradiated at 4.2K with x-rays from a 3 MeV electron Van de Graaff accelerator. The free radicals produced by the x-rays were studied from their EPR and ENDOR spectra from 4.2K to room temperature. The ESR spectra are quite complex and the ENDOR data were necessary in order to obtain hyperfine tensors. Twenty-four hyperfine tensors were obtained, and using these along with the ESR data, we were able to identify a number of radicals. The free radicals appear to be essentially the same in all three crystal forms except for one case. At low temperature there is one oxidation radical which is present in the monohydrate which does not seem to be present in the two anhydrous crystals. The radicals which have been identified and the radiation damage pathways will be presented.

165 ESR AND INDO STUDIES OF ANION RADICALS IN ACETIC ACID AND ACETAMIDE; NON-PLANARITY AND BARRIERS TO HINDERED ROTATION.

D. Suryanarayana and M. D. Sevilla, Department of Chemistry, Oakland University, Rochester, Michigan 48063

Reactions of electrons at 77K with acetic acid and acetamide in 12M $LiCl(D_2O)$ as well as in 8M NaOD glasses have produced the anion radicals of type $H_3C\text{-}\dot{C}(X)(\dot{Y})$, with $X=O^-$, OD and $Y=OD$, ND_2. ESR studies of these radicals have revealed characteristic spectra due to hindered internal rotation of methyl group. INDO calculations, on the protonated forms, suggest that the radical center in $H_3C\text{-}\dot{C}<$ is pyramidal rather than planar. A comparison of the INDO calculated and ESR experimental β-proton and carbon-13 hyperfine splittings (hfs) suggest a nonplanar angle $\phi = 35^o$. A nonplanar radical geometry results in diminution of the average methyl proton hfs from 23.0G (planar) to 13.5G (nonplanar), in the case of acetate anion radical. For the same radical, the angular dependence of the INDO β-proton hfs can be represented by a relation $a(\theta) = 9.0\cos\theta + 26.0\cos^2\theta$. Using the INDO β-proton hfs, the time-dependent effects in the ESR spectra were simulated employing a computer program making use of the theory of modified Bloch equations for the three jump process. Our present analysis yields 2.5 - 2.7 kcal/mol as the activation energy for the hindered rotation in the case of acetate as well as acetamide radicals. The presence of a three-fold barrier to rotation is a consequence of pyramidal geometry. This research work was supported by the U.S. Army Natick Development center and the U.S. Department of Energy.

166 THEORY OF PROTON HYPERFINE INTERACTION IN HIGH SPIN FIVE AND SIX LIGANDED IRON AND MANGANESE HEME SYSTEMS.

M.K. Mallick, S.K. Mun, S. Mishra, J.C. Chang and T.P. Das, Department of Physics, State University of New York, Albany, New York 12222.

Proton hyperfine interactions provide valuable information regarding the nature of the unpaired spin population distributions over the peripheral regions of the heme unit of hemoglobin derivatives. With this feature in mind we have analyzed the contributions to the hyperfine interactions of protons in a number of high spin five-liganded (F-, Cl-, Br-, I- and OH-FeP) and six-liganded (Met- and F-Mb, H_2O-Mn and Cl-Mn(III)P) heme compounds, data on the hyperfine interactions for a number of these protons being available from ENDOR measurements. Unpaired spin populations over the atoms, obtained from self-consistant-charge extended Huckel calculations, are utilized in this investigation of proton hyperfine constants.

Our results show that the electron-nuclear magnetic dipolar interactions make a major contribution to the hyperfine fields at the protons in high spin heme and hemoglobin systems, and that it is important to consider the actual unpaired spin population-distribution over the entire molecule in question. It is also shown that while the direct and exchange contributions are both smaller than the dipolar contributions, they nevertheless have important influence on the net hyperfine constants in most of the cases considered. For those cases where experimental results are available, in addition to reasonable agreement between individual theoretical and experimental values, the experimental trend of variation among the different protons is well reproduced by the theoretical results.

167 EPR G-VALUES FOR A QUANTUM MECHANICALLY-MIXED SPIN 3/2, 5/2 SPECIES WITH RHOMBIC AND AXIAL SYMMETRY COMPONENTS.

M. Eberhart, M. M. Maltempo, University of Colorado at Denver, 1100 14th Street, Denver, CO 80202.

We have undertaken a calculation of EPR-related parameters for a $3d^5$ spin system involving the low-lying multiplets $^6A_1$, $^4T_1$, and $^2T_2$, coupled by the spin-orbit interaction, in sites with varying degrees of axial and rhombic symmetry. A 24 x 24 Hamiltonian matrix, involving crystal field, electrostatic, spin-orbit, and Zeeman terms, was diagonalized, yielding eigenfunctions, eigenvalues, and EPR g-values. We present our results for a spin species in which the spin-orbit interaction strongly mixes the close-lying $^6A_1$ and $^4T_1$ multiplets yielding a ground state in which the charge density of the iron 3d electrons is a hydridization of mid-spin and high-spin wave functions, and the spin expectation value is intermediate between 3/2 and 5/2. As distinguished from previously published work, this calculation includes consideration of spin-mixed species with rhombic symmetries. In the special cases of pure high-spin and pure mid-spin species, our results are compared with the common spin Hamiltonian approach.

168 Spectral Evidence for at least Two-fold Multiplicity in Two- and Four-Iron Ferredoxins.

D. O. HEARSHEN, W. R. DUNHAM, and R. H. SANDS, Biophysics Research Division, Univ. of Michigan, Ann Arbor, MI 48109 and H. J. GRANDE, Landbouwhogeschool, Vakgroep Biochemie, De Dreijen 11, Wageningen 6703 BC, The Netherlands.

The EPR lineshapes of a reduced fully deuterated 56 Fe exchanged algal ferredoxin from *Synecoccus lividus** and of a four-iron ferredoxin from *Bacillus polymyxa* cannot be fit using one-center models. The next least complicated model would be to envision two different configurations for the active center resulting in two different g-tensors ^{13}C and ^{14}N hfs, such a model including g-strain can account for the spectra observed. One obvious explanation in the case of the two-iron ferredoxins would be for the reducing electron to be on either one or the other of the two non-equivalent iron atoms with equal probability, thus resulting in two slightly different configurations. Spectra and the simulations will be displayed for S, X and K_a band frequencies. Attempts are made to interpret the resulting parameters for g-strain.

169 THEORY OF ELECTRONIC STRUCTURES OF NITROSYLHEMOGLOBIN IN R AND T STATE,

S.K. Mun+ and T.P. Das, Department of Physics, State University of New York, Albany, New York 12222.

Theoretical investigation of electronic distribution in eight different structural forms of nitrosylhemoglobin were carried out to study the changes in electronic structures associated with R to T transition under the influence of inositol hexophosphate or changing pH. We have calculated hyperfine and quadrupole interaction coupling constant of ^{14}N and hyperfine coupling constant of ^{57}Fe in NOHB by use of electronic wave functions obtained through self-consistant extended Huckel procedure. The analysis of ^{14}N hyperfine interaction supports the Fe-NO bond extension model to explain the observed changes in ^{14}N ESR spectra going 9- to 3-line pattern representing R to T transition. The ^{14}N quadrupole coupling constants show significant changes in charge distribution influenced by various structural changes. The calculated ^{57}Fe hyperfine coupling constants provide satisfactory complimentary information in understanding the interactions of nitrosylhemoglobin.

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170 ESR, NMR AND MOESSBAUER STUDIES OF THE HIGH SPIN-LOW SPIN TRANSITION IN $\mathrm{Fe(phen)_2(NCS)_2}$ AND $\mathrm{Fe(pic)_3Cl_2 \cdot EtOH}$. P.S. Rao, A. Reuveni and B.R. McGarvey, Department of Chemistry, University of Windsor, Windsor, Ontario N9B 3P4 and P. Ganguli, and P. Gütlich, Institüt für Anorganische und Analytische Chemie, Johannes Gutenberg-Universität, Saarstrasse 21, D-6500 Mainz, BRD.

ESR studies of Fe(II)(1,10 phenanthroline)$_2$(NCS)$_2$, Fe(II)(2-amino-methylpyridine)$_3$Cl$_2$·EtOH and Zn(II)(2-amino-methylpyridine)$_3$Cl$_2$·EtOH doped with 1 mol % $\mathrm{Mn^{2+}}$ have been done from 77K to 300K. The zero field parameters D and E decrease steadily with increasing temperature but no change associated with the high spin-low spin transition of the iron compounds could be found. Moessbauer studies of the same compounds showed that the presence of $\mathrm{Mn^{2+}}$ had no effect on the transition. The line widths of the ESR spectrum did broaden markedly in the transition region, however. Proton NMR studies on the same iron compounds revealed large changes in the line width and line shape as the system went from diamagnetic to paramagnetic. In the case of $\mathrm{Fe(phen)_2(NCS)_2}$ the change from diamagnetic to paramagnetic was slow enough to allow us to measure its rate. The ESR and NMR studies reveal that the lifetime of a given spin state of paramagnetic $\mathrm{Fe^{2+}}$, τ_{el}, is much shorter than 3nsec at temperatures well above the transition temperature but is in the range of 15μsec $>> \tau_{el} >>$ 3nsec in the transition region.

171 A NEW INDUCTION CAVITY FOR HIGH POWER DISPERSION EPR EXPERIMENTS. R.B. Clarkson and Robert Sneed. Varian Associates, 611 Hansen Way, Palo Alto, CA. 94303

The observation of $d\chi'/dx$ (dispersion) by conventional reflection-type EPR spectrometers has always been more difficult at moderate-to-high microwave powers due to fm noise. This noise (phase noise) has, in many instances, seriously reduced the signal-to-noise (S/N) ratio of dispersion experiments in the power region above 10 milliwatts. Since many of the useful applications of dispersion EPR depend upon a combination of good S/N and high microwave power, (e.g. adiabatic rapid passage, ST-EPR), several techniques capable of producing good S/N dispersion EPR spectra at high microwave powers have been suggested.[1-3] The theory of such techniques is outlined by Conciauro and Randazzo.[4]

We have developed a TM 110 induction cavity which significantly reduces the source noise problem in dispersion EPR work. In a microwave analog of the Bloch induction (crossed-coil) NMR approach, our technique uses a bimodal resonant cavity structure. The principal features of this cavity will be discussed, as well as recent applications of it to dispersion EPR experiments in aqueous and non-aqueous systems.

[1] D.T. Teaney, W.E. Blumberg, and A.M. Portis, Phys. Rev., 119, 1851(1960).

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[3] J.S. Hyde, J.C.W. Chien, and J.H. Freed, J. Chem. Phys., 48, 4211(1968).

[4] G. Conciauro and E. Randazzo, RSI, 44, 1087(1973).

172 ROTATIONAL RELAXATION AND MAGNETIC RESONANCE "ANOMALIES"[†] D. Kivelson, J. L. Dote, and R. N. Schwartz[+] Department of Chemistry, University of California, Los Angeles, CA 90024

Analysis of magnetic resonance spectra of liquids has provided useful information concerning the rotational and translational motions of molecules. The data obtained from magnetic resonance can be combined with those collected by other techniques such as Raman and IR spectroscopy, and, in principle, one should then be able to use this array of results to characterize the molecular motions in great detail. Furthermore, recent careful magnetic resonance studies have identified deviations from relaxation effects predicted from simple theories based on isotropic molecular rotational diffusion; these "anomalies" have been ascribed to anisotropic and non-diffusional motions and, therefore, also used to characterize the motions. We shall discuss the intercomparison of results obtained by various techniques and of magnetic relaxation "anomalies" to study molecular motions. There is some ambiguity in the picture of the rotational motions so obtained because of the neglect of relaxation mechanisms which though not important in studies of correlation times may be significant in the more refined studies of correlation functions. We shall discuss rotational correlation times with the usual inclusion of slip-stick boundaries, correlation functions with comments concerning non-diffusional behavior, and the interpretation of "relaxation anomalies" in the spin resonance spectra.

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173 Electron Spin-Spin Interactions in Biological Systems by EPR. R. H. SANDS, Bio-Physics Research Division. University of Michigan, Ann Arbor, MI 48109

Due presumably to the need for electron transfer (or transport) electron spin-spin interactions are ubiquitous in biological systems. One observes virtually all extremes of dipole-dipole and exchange interactions. These extremes are easily recognized from previous experience in wide-line and high-resolution NMR: the classic "Gutowsky-Pake" dipole-dipole spectra and the high-resolution Type AB spectra occur often. In addition, triplet states resulting from strongly coupled spin one-half species are also observed as are multiple spin-spin couplings. It is possible in principle to obtain distances from the dipolar interactions (when the pseudodipolar interaction can be shown to be negligible) and physical exchange rates from the spin exchange interactions. Several examples of each of the extremes will be given with appropriate references to the relative magnitudes of the various interactions and the methods (including ELDOR) of determining them.

174 A SPIN-LABEL ASSAY FOR METAL ION CHELATION AND COMPLEX FORMATION. Stephen J. Wagner, Alec D. Keith and Wallace Snipes. Biophysics Program, 618 Mueller Laboratory, The Pennsylvania State University, University Park, PA 16802.

The electron spin resonance lines of nitroxide spin labels are broadened by electron spin exchange reactions that take place during collisions with paramagnetic ions. The degree of line broadening is greatly reduced when the paramagnetic ion forms a coordination bond with certain functional groups on organic molecules. These observations form the basis for a spin-label assay for metal ion chelation and complex formation. In addition to monitoring interactions of paramagnetic ions, the assay also allows the detection of non-paramagnetic ions that compete with paramagnetic ions for binding sites. The concentration of various non-paramagnetic ions required to displace paramagnetic Ni^{++} ions from vesicles containing phosphatidyletanolamine and phosphatidylglycerol was used to order the ions with respect to their binding to the vesicles. The line-broadening assay was also used to study the effects of two proteins, ribonuclease and cytochrome C, on the availability of Ni^{++} binding sites on the vesicles. There are several advantages of the line-broadening assay compared to other conventional assays for metal chelation and complexation. The line-broadening assay does not require that the sample be optically clear or chemically defined, it can detect as little as 0.4 to 1 μmole of complexing agent, and it may be utilized in complex biological systems including subcellular organelles and macromolecules.

175 SATURATION-TRANSFER SPECTROSCOPY OF PROTEIN AND LIPID COMPONENTS OF LIPID BILAYERS, James S. Hyde, Department of Biochemistry, The Medical College of Wisconsin, Inc., Wauwatosa, Wisconsin.

Rotational diffusion of spin-labeled lipid components in lipid bilayers can be characterized by two diffusion constants: $D_{\parallel}$ for diffusion about the normal to the bilayer and $D_{\perp}$ for diffusion about axes perpendicular to the normal. $D_{\parallel}$ will often correspond to free diffusion, while $D_{\perp}$ will be highly restricted and often zero. For spin-labeled lipids, the principal magnetic axis is usually an angle θ with respect to the normal of either 0 or 90°, while for proteins θ may be anything and its determination is an experimental problem. Saturation-transfer experiments on the following membrane proteins: Ca^{2+}-ATPase of sarcoplasmic reticulum, rhodopsin, cytochrome oxidase, acetyl choline receptors, and ADP carriers in mitrochondria will be reviewed. In addition, experiments on lipid components will be reviewed.

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USE OF DEUTERATED SPIN LABELS FOR IMPROVED SENSITIVITY AND RESOLUTION IN ST-EPR STUDIES. A.H. Beth, S.D. Venkataramu, R.T. Wilder, R.C. Perkins, L.S. Wilkerson, D.E. Pearson, C.R. Park and J.H. Park. Vanderbilt University, Nashville, TN 37232.

We have synthesized the perdeuterated spin label N-(1-oxyl-2,2,6,6-tetramethyl-4-piperidinyl-d_{17}) maleimide (DMSL) and described the substantial improvements in spectral resolution and sensitivity in the slow tumbling regime characteristic of many biological systems (Chemical Physics Letters, 69, 24-28, 1980). The increase in resolution allows full characterization of the magnetic anisotropy at X-band since spectral characteristics of all major and minor tensor interactions are apparent even in aqueous media. Sensitivity is increased by 50% to 80% in the correlation time range 10^{-7} to 10^{-3} sec. making ST-EPR measurements on many biological systems more feasible. We utilized DMSL to study the reversible association of glyceraldehyde-3-phosphate dehydrogenase (GAPDH) with the Band 3 protein of the red blood cell membrane. Comparison of C'/C and L"/L with model system parameters indicated effective isotropic correlation times of $2x10^{-7}$ and $2x10^{-5}$ sec. for soluble and membrane-bound enzyme respectively. Addition of glycerol resulted in an increase in correlation time suggesting that the mobility of the external segment of Band 3 was dependent on the viscosity of the aqueous phase. The correlation time of $2x10^{-5}$ sec., the isotropic appearing spectrum, and the glycerol effect all indicated considerable mobility of the GAPDH-Band 3 complex relative to the red blood cell membrane.

177 SOIL ADSORPTION-DESORPTION OF PHOSPHATE AND ANIONIC TRACE METALS. C. L. Grant and S. A. Casiorowski, University of New Hampshire, Department of Chemistry, Parsons Hall, Durham, NH 03824.

The effects of varying pH and phosphate content of a typical municipal wastewater on adsorption and desorption rates were determined using two soils; a typical acid soil being used in experimental wastewater treatment, and a soil from a wastewater treatment facility in Manteca, California which is known to leak phosphate to groundwater. Phosphate was monitored using P-32 and spectrophotometric analysis. Suspensions were equilibrated for 46 hours with constant agitation; periodic samples were removed. After 46 hours, the soil samples were separated from the suspensions, treated to remove interstitial solution, and dried at room temperature. The dried soil was then equilibrated with either fresh effluent or a 5×10^{-3} M NaCl solution. The complementary use of P-32 and non-radioactive phosphate enabled us to evaluate the adsorption and desorption of freshly sorbed and native phosphate as well as the role of exchange reactions. The behavior of Manteca soil was dramatically different from Charlton soil. The capacity for phosphate was much lower and sorbed phosphate was subject to a large amount of exchange as well as net desorption. There is strong evidence for dissolution of native phosphate. The sorption process decreased in efficiency with a decrease in pH - opposite to the trend observed for the Charlton soil. The behavior of both soils will be discussed with respect to possible solubility properties of reaction products and relative phosphate saturation of reactive constituents in the soils. Competitive reactions involving arsenate will also be discussed.

178 INVESTIGATIONS OF THE INTERACTION OF TRACE ELEMENTS WITH ORGANIC LIGANDS IN OIL SHALE RETORT PROCESS WATERS. J. S. Stanley, M. A. Caolo, and R. E. Sievers, Dept. of Chemistry and CIRES, Univ. of Colorado, Boulder, CO 80309.

The great amounts of retorted shale and wastewater produced by the various operations of shale oil recovery give rise to many questions concerning the impact upon the quality of the water supply in areas that may be potentially affected by the massive new industry. Organic compounds present in these wastes that could promote the mobilization of toxic trace elements through complexation or chelation are of special interest. Specifically, we are concerned with the separation and identification of nitrogen- and sulfur-containing compounds that may form complexes with trace elements. Investigations have been conducted using the techniques of liquid-liquid extraction, steam distillation, gas chromatography/mass spectrometry and atomic absorption spectrometry. In addition, wet chemical methods have been applied to determine the complexing capacity of the wastewater throughout the separation schemes.

179 ANALYTICAL APPROACHES TO THE CHARACTERIZATION OF METAL BINDING BY ORGANIC LIGANDS. R. K. Skogerboe, H. O. Hayworth, C. R. Gumina, Department of Chemistry, Colorado State University, Fort Collins, Colorado 80523, T. C. Huth, Department of Chemistry, University of Arizona, Tucson, Arizona 85724, and S. A. Wilson, U.S. Geological Survey, 5293 Ward Road, Arvada, Colorado 80002.

The present lack of knowledge regarding the significance of metal binding by organic ligands of natural origins exists, to a large extent, because adequate analytical protocols for differentiating between metal species have not been developed. The development and utilization of two unique approaches to the characterization of metal complexation by organic ligands will be discussed with specific reference to metal interactions with fulvic acid. The first involves the use of a dialysis method in which metal ion passes freely through the membrane while the organic ligands do not. The second involves the use of macroreticular resins which selectively "sorb" neutral organo-metallic species from aqueous solutions. Thus, controlled complexation equilibria can be established to permit differentiation between free and bound forms of metal ions, estimation of metal species distributions in natural aqueous systems, and determination of appropriate thermodynamic parameters. The operational features, the capabilities, and the limitations of these protocols will be described.

180 CHARACTERIZATION OF THE REDOX PROPERTIES OF FULVIC ACID. R. K. Skogerboe, Department of Chemistry, Colorado State University, Fort Collins, Colorado 80523 and S. A. Wilson, U.S. Geological Survey, 5293 Ward Road, Arvada, Colorado 80002.

The role of fulvic acid in complexation of metal ions has received considerable attention. Few investigations have attempted to define the possible significance of redox reactions between metal ions and fulvic acid. The present discussion will summarize the results of experiments which have shown that fulvic acid is capable of reducing a number of significant metal ions under conditions representative of various environmental systems. It has been shown, for example, that Hg(II) can be reduced to the metallic state by fulvic acid while Fe(III) is reduced to Fe(II). The mechanistic aspects of such reactions will be discussed and their significance will be considered with reference to environmental problems.

181 CHEMISTRY OF SEQUENTIALLY SAMPLED PRECIPITATION EVENTS. John K. Robertson and Richard C. Graham. Science Research Laboratory, U.S. Military Academy, West Point, NY 10996.

Sequential sampling techniques and application to collect precipitation are reviewed. Selected chemical data for samples collected by an intensity-weighted sequential sampling device in operation at the U.S. Military Academy, West Point, New York from October 1976 to January 1980 are presented.

The experiments have shown that intensity-weighted sequential sampling is a viable technique for monitoring the rapid changes in precipitation chemistry with a storm. Complete chemical data from individual storms are used to evaluate intensity related scavenging.

182 UTILIZATION OF LOW-GRADE WATER IN COAL SLURRY PIPELINES: DECONTAMINATION OF WATER BY SLURRIES OF COAL AND COAL-DERIVED SOLIDS. Stanley E. Manahan, Robert Gale, Dale Schuler, and Darryl Bornhop, Department of Chemistry, 123 Chemistry Bldg., University of Missouri, Columbia, MO 65211

Questions of water used in coal slurry pipelines usually involve considerations of water supply and potential detrimental effects of coal on water quality. Actually, slurries of coal and coal-derived products can be used for the partial purification of low-grade water that might be available for use in a slurry pipeline, including contaminated byproduct water from synthetic fuels manufacture. This paper reports the results of research on the removal of heavy metals, chromate, and organics from water by slurries of subbituminous coal, coal char, activated coal char, and simulated coal conversion ash. The organic water contaminants studied were produced as byproducts of a laboratory-scale coal conversion process. Rates of the removal of selected contaminants were determined. In general, a number of hours may be required for equilibrium to be attained. In the case of chromate, it appears that reduction to chromium(III) is required prior to sorption by coal. It is concluded that there is a substantial potential for the purification of water by slurries of coal and coal-derived products.

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TREATMENT OF ACID MINE DRAINAGE BY LIME NEUTRALIZATION - COMPUTER SIMULATION OF AN INDUSTRIAL PROCESS

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Abstract

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The Anaconda Mining Company encounters, as a result of the development of its porphyry copper deposit at Butte, Montana, approximately 6000 gallons per minute of acidic, highly dissolved metal solutions (mine drainage and secondary recovery solutions) whose disposal presents environmental problems. These solutions are presently treated in a batch process whereby pH control and heavy metal removal is accomplished by mixing with lime-enriched tailings underflow from the flotation concentrator system. In order to obtain information concerning the treatment mechanism and provide information leading to the more efficient operation of the treatment process, a computer program was created that chemically simulates the mixing of the acid flows with a basic source. This program predicts speciation of the influent streams, creates a dilution model, and then calculates the equilibrium composition of the mixed solution. Precipitation reactions that are allowed to occur are limited by the thermodynamic output. Computer output includes speciation and pH and ionic strength of the effluent solution and the amount and type of precipitate formed. With the appropriate option, the computer program will calculate the amount of lime required to produce a desired effluent chemistry for given influent conditions.

184 AN INTERCOMPARISON OF SIMULTANEOUS MULTIELEMENT ULTRATRACE METALS DETERMINATIONS IN NATURAL WATERS BY ICP SPECTROMETRY AND ANODIC STRIPPING VOLTAMMETRY. J. E. Bonelli, H. E. Taylor, J. R. Garbarino, and R. K. Skogerboe. U.S. Geological Survey, 5293 Ward Rd, Arvada, CO 80002.

Inductively-Coupled Plasma Atomic Emission Spectrometry (ICP-AES) is widely applied to the routine, simultaneous, multielement analysis of natural waters. While the accuracy, precision, and detection limits obtained with this technique are more than adequate for most applications, a few problem areas for water-resource quality monitoring remain. For example, without preconcentration, the detection limit for the environmentally important element lead is marginal for many monitoring projects. In comparison to ICP-AES, Anodic Stripping Voltammetry (ASV) is very limited in scope; however, it possesses many attractive analytical features including: (a) the required instrumentation is relatively simple and inexpensive; (b) the obtainable detection limits for certain elements are dramatically superior to ICP-AES; (c) it offers at least equivalent accuracy and precision; and (d) it is capable of giving information on chemical speciation. A detailed intercomparison of direct determinations of zinc, cadmium, lead, and copper by the two techniques in 10 U.S. Geological Survey Standard Reference Water Samples, and in a suite of 25 natural water samples, demonstrates essential equivalence. Simultaneous, multielement determinations of these elements were successfully obtained with both techniques in these samples up to concentrations of 100 µg/l (ppb). The validity of the intercomparison is supported with parallel determinations of the same four elements by direct aspiration and/or chelation-solvent extraction atomic absorption spectrometry. The relative merits of the ICP-AES and ASV techniques are assessed in the context of application to a routine water analysis laboratory.

187 WATER TREATMENT: EFFECTS ON TRACE ORGANICS IN DRINKING WATER. R. S. Hutte, R. E. Sievers, and R. M. Barkley, Dept. of Chemistry and CIRES, Univ. of Colorado, Boulder, CO 80309; and C. R. Rudkin and S. S. Ferguson, Water Quality Laboratory, City of Boulder, P. O. Box 791, Boulder, CO 80306.

A joint project between the City of Boulder and the Univ. of Colo. was established to identify and quantify organic compounds in the source water, at various stages in the treatment process and in the finished drinking water at the Betasso Water Treatment Plant in Boulder, Colo. The overall goal of the project is the reduction of organics in drinking water through optimization of the treatment process. Volatile organics are analyzed by the purge and trap technique with detection by FID, ECD and mass spectrometry. The levels of trihalomethanes in the finished water are determined routinely at the treatment plant. Seasonal variations in trihalomethane levels and the effects of different treatment processes will be discussed. Less volatile organics are determined by a resin technique. Organics are concentrated on XAD-2 resin by passing large volumes of water through the resin. The organics are eluted from the resin by solvent extraction and concentrated by evaporation of the solvent. G.C. analysis using fused silica capillary columns allows for direct analysis of acids and phenols without derivatization.

188 MASS SPECTRAL CHARACTERIZATION OF THE THERMAL DECOMPOSITION PRODUCTS OF KEPONE. Judith A. Mescher, University of Dayton Research Institute, 300 College Park Avenue, Dayton, OH 45469.

The thermal decomposition process of the organochlorine pesticide Kepone (decachloro-octahydro-1,3,4-metheno-2H-cyclobuta [c,d] pentalen-2-one) has been studied at temperatures up to 900°C in a quartz-tube reactor. Gaseous and major decomposition products were trapped and chromatographically separated for examination through the direct inlet system of the mass spectrometer. Mass spectra were also obtained through high resolution gas chromatography-mass spectrometry (GCMS) techniques. Data from these tests will be presented and the probable thermal degradation pattern of Kepone will be discussed.

An Improved Method for Determination of Dithiocarbamate Fungicides

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189 The tentative E.P.A. method for determination of dithiocarbamate in aqueous samples involves acid hydrolysis of the fungicide to yield carbon disulfide. The carbon disulfide is then determined, and the results are taken to be an indication of the total dithiocarbamate concentration. The method is only class-specific.

A more elaborate method is proposed, whereby more specificity is obtained. The acid hydrolysis is followed by determination of bound metals and amines, which are the unique fragments of dithiocarbamates, but which are useless without the determination of CS_2. A more efficient apparatus was designed and manufactured for the hydrolysis step. Data obtained from wastewater samples, as well as from fortified solutions will be presented.

191 AUTOMATED DETERMINATION OF PHENOLIC COMPOUNDS IN WATER. R. T. Hentschel. U.S. Geological Survey, 5293 Ward Road, Arvada, Colorado 80002.

The standard manual method for determination of phenolic compounds in water was automated to eliminate the inherent lack of precision, and to allow faster screening of samples prior to more expensive gas-chromatographic analysis. Determination of phenolic compounds in water by the manual 4-aminoantipyrine method is slow: one technician analyzes 10 to 15 samples per day, and precision is dependent on the analyst's skill. Both the manual and automated method react steam-distillable phenols with 4-aminoantipyrine at pH 10.0 ±0.2 in the presence of potassium ferricyanide to form a colored complex. This complex is extracted into chloroform, and the absorbance is measured at 460 nanometers.

The automated method has the following advantages: analysis of 20 samples per hour at a detection limit of 1 microgram per liter (μg/L) phenol, as compared to 10 to 15 samples per day by the normal method. The required sample volume is 10 ml. The upper limit of the analytical range is extended from 40 μg/L phenol for the manual method to 200 μg/L for the automated method. The calculated percent relative standard deviations (RSD) were 27 for the range 1-10 μg/L, 8.7 for the range 10-50 μg/L, and 2.5 for sample concentrations greater than 50 μg/L phenol. The automated method compares well with the standard manual method, producing a linear correlation coefficient of 0.995. Average percent recovery of additions of known concentrations of phenol to natural water samples was 98 percent over the concentration range up to 200 μg/L.

192 ASSESSMENT OF POLYNUCLEAR AROMATIC HYDROCARBON POLLUTION IN AQUATIC SAMPLES, HPLC METHODS AND RESULTS. J. J. Black and P. P. Dymerski. Roswell Park Memorial Institute, Buffalo, NY 14263, Division of Laboratories and Research, Albany, NY 12201.

Because some polynuclear aromatic hydrocarbons (PAH) are carcinogenic, the presence of these compounds in the aquatic environment may pose a health hazard.

To support studies of environmental carcinogenesis in aquatic systems we found it useful to develop a method for routine quantitation of PAH in aquatic samples. Methods for sample preparation entailed extraction in alcoholic-KOH, liquid-liquid partitioning of the hydrocarbons into cyclohexane, and adsorbtion chromatography to isolate a PAH containing fraction analyzed for its PAH content by means of reversed phase high pressure liquid chromatography. Ultraviolet adsorbtion and monochromatic fluorescence emission were employed as sequential modes of peak detection. Compounds identified on the basis of retention time were confirmed by trace enrichment experiments and by comparison with fluorescence spectra of authentic PAH standards.

The distribution of PAH pollution in the near shore area of Lake Erie-Niagara River aquatic environment was determined by analysis of sediment samples collected near suspected sources of these compounds. Variations in the distribution patterns indicated likely contribution via point sources.

Analysis of representative biota indicated that fish living in the polluted area had elevated body burdens of PAH.

193 REDUCTION OF COMPLEX CHROMATOGRAMS, PART I. S. Michael McCown, Water and Air Research, Gainesville, FL, Darrell R. Pitzer, Chemistry Purdue University, Charles G. Manos, Jr., Department of Crop and Soli Sciences, Michigan State University, Charles M. Earnest, Perkin-Elmer Corporation.

Pattern recognition has many applications in chromatography. Determinations of petroleumhydrocarbons, essential oils, flavours, fragrances, and pesticide residues find use for methods involving pattern recognition.

The PATR system is one in which the chromatographic parameters "retention time", and "peak intensity" are used to describe chromatograms. Previous work had allowed reduction of only those chromatograms of unknowns which had the same number of peaks as those of reference material. A more advanced algorithm will be presented, which will allow comparison of any chromatogram with any other obtained under the same conditions.

194 REDUCTION OF COMPLEX CHROMATOGRAMS, PART II. [illegible] Water and Air Research, Gainesville, FL, Darrell R. Pitzer, Chemistry Department, Purdue University, Charles G. Manos, Jr., Department of Crop and Soil Sciences, Michigan State University, Charles M. Earnest, Perkin-Elmer Corporation.

The advanced PATR algorithm has been applied to the reduction of chromatograms of extracts of fish tissue. The chromatograms revealed a patterned residue resembling toxaphane, on which another residue was superimposed.

Replicate analyses of the fish tissue homogenate indicated the ability of PATR to reveal peaks which were completely superimposed upon toxaphene peaks. After mathematical removal of the toxaphene pattern, peaks corresponding to DDT-R and several other pesticides were revealed, quantitated, and subsequently confirmed by GC/MS. Fortification experiments and comparisons of other methods led to a statistical comparison of PATR and other methods. This summary indicates that the PATR schemes mean, plus or minus two standard deviation intervals will fall within the interval of one standard deviation from the mean when determined by other methods.

195 MASS SPECTROMETRY - THEN AND NOW. H. J. Svec, Ames Laboratory-USDOE and Dept. of Chemistry, Iowa State University, Ames, Iowa 50011 U.S.A.

A historical overview of mass spectroscopy will be discussed. Emphasis will be on those "landmark" developments which initiated new advances in the use of mass spectroscopes. An attempt will be made to trace the evolution in the field from the discovery of "kanalstrahlen" by Goldstein and their characterization by Wien to modern applications as a tool for studying a wide variety of problems in chemistry. Examples of work with deflection and dynamic instruments which caused "quantum jumps" in our understanding of these problems will be cited.

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GC/MS ANALYSIS OF MULTIFUNCTIONAL ACRYLATES. E.M.Saladino, A.J. Widzisz, M.J. Vaickus, DeSoto, Inc., Des Plaines, IL

A method for the rapid analysis of common multifunctional acrylates was developed using Gas Chromatography - Mass Spectrometry. Gas chromatographic separation of the multifunctional acrylates facilitated identification using mass spectrometry. Electron impact and chemical ionization modes were used to determine the fragmentation products and decomposition mechanisms. The correlations observed between several homologous series and the differences between acrylates and methacrylates are discussed. Impurities encountered in individual multifunctional acrylates are also discussed. The resulting procedure permits rapid qualitative analysis of complex mixtures of multifunctional acrylates as encountered in the coating industry.

198 A GC-MS METHOD FOR STUDYING INTERACTIONS OF OTHER DRUGS WITH WARFARIN. C.E. Hignite and D.E. Rollins. Veterans Administration Medical Center, Research Service 151, Kansas City, Missouri, 64128.

Warfarin is the most widely used oral anticoagulant in man. Unfortunantly, many drugs potentiate its anticoagulant effect when they are administered concomitantly, and some of these interactions are potentially life threatening. Some of the interactions due to altered metabolism are stereoselective, since the rate of elimination from the plasma of one of the enantiomers of warfarin, which is administered as a racemic mixture, is changed to a greater extent than the other. We have developed a GC-MS method for simultaneously determining the pharmacokinetics of both enantiomers such that these interactions can be studied. Because of a report that the antiarrhythmic drug disopyramide potentiated the effect of warfarin we investigated this possible interaction. Pseudoracemic warfarin was prepared which contained one enantiomer unlabeled and one enantiomer pentadeuterated. This material was administered to six healthy volunteers either alone or with disopyramide. Plasma concentrations of the two enantiomers were determined by acidic extraction, methylation with diazomethane, and mass fragmentography of the methylated extracts. Ions at m/z 279 for unlabeled enantiomer, m/z 284 for the labeled enantiomer, and m/z 313 for chlorowarfarin (internal standard) were used for quantitation. The coadministration of disopyramide caused no significant change in the volume of distribution, half-life, or clearance of either enantiomer.

200 NEGATIVE ION MASS SPECTROMETRY OF SOME C_8-C_{12} ALCOHOLS. John M. Knox. Department of Physics and Astronomy, University of Wyoming, Laramie, WY 82071. Research performed under contract with the Laramie Energy Technology Center of US DOE.

The data acquisition system for a Bendix Model 14-107 time-of-flight mass spectrometer has been modified for pulse counting and Negative Ion Mass Spectroscopy (NIMS). It is found that varying the applied potential on the plates leading to the dynode strip electron multiplier significantly changes the detector sensitivity and ability to resolve neutral components of the ion beam. The system has been tested by comparison with published spectra of SF_6 and isopropanol. The goal of the research is to quantitatively identify the alkene components of shale oils as their alcohol derivatives. The proposed process is to use the NIMS of alcohols to obtain data for alkenes present in shale oil. To this end, negative ion spectra of various C_8-C_{12} alcohols will be discussed.

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QUADRUPOLE MASS SPECTROMETER APPLICATIONS IN SEMICONDUCTOR PROCESSES.
J. D. Burden UTI, 325 N. Mathilda Avenue, Sunnyvale, CA.

Gas analysis is a useful tool in many phases of semiconductor processes. These processes are often highly sensitive to the absolute quantities and relative proportions of the gases present during processing. Gases to be analyzed or monitored may range in pressure from 10^{-9} torr, such as an e-beam evaporator, to one atmosphere, such as regulated-cylinder gases or during Chemical Vapor Deposition. The high sensitivity and reproducibility of quadrupole mass spectrometry (QMS) allows gas analysis down to these very low pressures, while careful gas sampling allows analysis of gases at the higher pressures. Some specific examples of the value of QMS in semiconductor process applications will be reviewed.

202 DIRECT DETERMINATION OF CESIUM IN PILOT PLANT EFFLUENTS BY ISOTOPE DILUTION MASS SPECTROMETRY. P. Chastagner. E. I. du Pont de Nemours & Co. (Inc.), Savannah River Laboratory, Aiken, South Carolina 29801

Cesium is routinely determined at part per billion levels in simulated defense waste solutions by isotope dilution mass spectrometry. The analytical work is in support of pilot plant studies of waste immobilization at the Savannah River Laboratory. The stream sampled is a supernate solution of simulated waste containing about 5M Na ion. A 10 µL sample is spiked with a solution that contains a known amount of ^{137}Cs (in the range of 3 to 30 pg). A portion of the mixture is loaded directly on the sample filaments of a multiple filament arrangement, and the 133/137 Cs ratio is determined by thermal ionization mass spectrometry. Computer-controlled magnetic and quadrupole thermal ionization mass spectrometers are used for the analyses. A gentle filament preheating cycle causes the cesium to diffuse thermally to form an enriched layer on the surface of the waste deposits. Subsequently, the sample filament temperature is increased to distill the cesium selectively to the ionizing filament. Sodium and other gross impurities remain on the filament. Barium interference is minimized by adjusting the temperature of the ionizing filament. Cesium blank values are about 0.7 ±0.8 ppb (95% confidence limits). The analytical rate is about 60 minutes per sample with the magnetic instrument and about 45 minutes per sample with the quadrupole instrument. A glove box around the pilot plant sample points, and clean hoods and downflow clean air zones around the ion sources, are used to control environmental contamination.

204 LASER MASS SPECTROMETRY OF SOLIDS. R. J. Conzemius, Ames Laboratory-USDOE, Iowa State University, Ames, Iowa 50011 U.S.A.

The talk will cover the current status of work regarding the use of the laser ion source in solids mass spectrometry. Pertinent historical aspects will be indicated. A panorama of current work will be covered: worldwide geographical distribution of laboratories using the technique; diversity of applications; and instrumental types used in the studies. Basic experimental observations which have led to the development of different models for ion formation will be covered briefly.

Analytical considerations will be given which indicate sensitivity and ability for quantification. The relation of these considerations to the type of laser and mass spectrometer will be noted. Several current but greatly different approaches to the application of the laser to the characterization of solids will be described. Advantages and disadvantages of the different approaches will be covered. This should indicate the power of the technique as well as the potential for future growth.

Description of work at the Ames Laboratory will include: difficulties associated with the laser ion source; specific applications where the technique has provided unique support necessary for solid state studies; the adaptability of the technique to computerization; and some unique instrumentation developed for the laser ion source.

205 FACTORS INVOLVED IN QUANTITATIVE GAS ANALYSIS BY MASS SPECTROMETRY, R. E. Ellefson, Mound Facility,* Miamisburg, Ohio 45342

A number of important factors for achieving quantitative gas analysis by mass spectrometry are reviewed. Three sampling methods used at Mound are presented: single and double ended sample containers and process monitoring by capillary sampling. The advantages of a molecular leak for introduction of gas into the mass spectrometer are discussed in detail. Calibration methods used at Mound are given with sensitivity factors and multicharged or fragment species data for noble gases and inorganic gases presented to demonstrate calibration stability. Techniques for measuring ion intensity and two methods for calculating mixture composition are discussed. Data on the effects of instrument non-linearities, background fluctuations, hot surface reactions, and mixture biases are also presented. A systems approach to accuracy evaluation is used to measure the response of the total analytical system to known standard mixtures simulating samples to be analyzed.

*Mound Facility is operated by Monsanto Research Corporation for the U. S. Department of Energy under Contract No. DE-AC04-76-DP00053.

207 APPLICATIONS OF DYNAMIC MASS SPECTROMETRY AT ROCKY FLATS. Tom L. McFeeters. Rockwell International, Rocky Flats Plant, P.O. Box 464, Golden, Colorado 80401.

Dynamic Mass Spectrometry techniques present unique advantages for the solution of a wide variety of problems. Brief descriptions of the method, instrumentation, and a novel calibration method using vacuum service permeation tubes are presented. The wide variety of applications is demonstrated by a series of brief project descriptions. Applications discussed, with analytical data obtained, include:

1. Teflon® Contamination of Metal Surfaces
2. Surface Defects in Plutonium Castings
3. Cleaning Procedure Development
4. Coating Chamber Monitoring
5. Permeation Rate Determinations

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PURIFICATION OF RADIOACTIVE STEROID HORMONES BY HIGH PERFORMANCE LIQUID CHROMATOGRAPHY (HPLC). Marie P. Kautsky and Dwain D. Hagerman. Dept. of Biochemistry, Biophysics and Genetics and Dept. of Obstetrics and Gynecology, University of Colorado School of Medicine, 4200 E. 9th Ave., Denver, CO, 80262.

The specific activity of commercially available carbon-14 and tritium labeled steroid hormones has increased steadily in recent years. These highly radioactive steroids are well suited for use in radioimmunoassay and in hormone receptor studies, but they are difficult to store because of their tendency to undergo radiodecomposition. In the case of estrogens, the decomposition process is autocatalytic, necessitating frequent purification to remove breakdown products as soon as they are formed. HPLC is useful for this task. The three most common estrogens, estrone, estradiol-17β and estriol, may be purified on Chromegabond® diol columns (ES Industries, Marlton, NJ) using mixtures of 1,2-dichloroethane and chloroform containing traces of ethanol as mobile phase. Androgens such as testosterone or androstenedione may be purified on μPorasil® columns (Waters Assoc., Milford, MA) with similar solvent mixtures or on μBondapak C_{18}® (Waters Assoc.) with aqueous methanol as mobile phase. Estrogens are readily separated from androgens by the addition of tetrahydrofuran to the aqueous methanol system. Columns and other HPLC equipment employed in these separations frequently become contaminated with radioactivity. Special procedures for removing such radioactive residues will be described.

209 DETERMINATION OF BHT, IRGANOX 1076 AND IRGANOX 1010 IN POLYETHYLENE BY HIGH-PERFORMANCE LIQUID CHROMATOGRAPHY. John F. Schabron and Lyle E. Fenska. Phillips Petroleum Co., 258 RB-1, PRC, Bartlesville, OK 74004.

A method was developed for the rapid extraction and determination of the additives 2,6-di-tert-butyl-4-methylphenol (BHT), octadecyl-3,5-di-tert-butyl-4-hydroxyhydrocinnamate (Irganox 1076) and tetrakis [methylene (3,5-di-tert-butyl-4-hydroxyhydrocinnamate)] methane (Irganox 1010) in polyethylene pellets. The pellets were dissolved in decalin at 110° followed by cooling to precipitate the polymer. The concentrations of the additives were determined by normal-phase high-performance liquid chromatography (HPLC) of a portion of filtered extract. The HPLC stationary phase was u-Porasil and the mobile phase was a heptane to methylene chloride gradient. The relative standard deviations were 1.2% for BHT, 1.3% for Irganox 1076, and 2.0% for Irganox 1010. The limits of detection were 0.0006% for BHT, 0.002% for Irganox 1076 and 0.004% for Irganox 1010 in polyethylene.

210 HOW TO PACK A CHROMOSORB* HIGH EFFICIENCY COLUMN FOR HPLC, J. L. Medina, S. B. Davé, Johns-Manville R&D Center, Box 5108, Denver, CO 80217

Packing HPLC columns has always been thought of as very difficult, somewhat costly, and time consuming. An easy, inexpensive, and fairly quick method for slurry packing CHROMOSORB materials will be discussed. This method can be used to pack 5 and 10 micron silica and bonded-phase CHROMOSORB materials with a high degree of reproducibility.

*CHROMOSORB is a registered trade name of Johns-Manville

211 CHEMILUMINESCENCE DETECTORS FOR GAS AND LIQUID CHROMATOGRAPHY, J.W. Birks, B. Shoemaker, R.H. Getty, E. Hill and K. Kurita, Department of Chemistry and Cooperative Institute for Research in Environmental Sciences, University of Colorado, Boulder, Colorado, 80309.

A detector for liquid chromatography based on the observation of chemiluminescence (CL) when the LC effluent is nebulized by a high velocity stream of reagent gas will be described. The CL produced is detected by a photomultiplier tube with an extended red response using the photon counting method. When ozone is used as the reagent gas, this chemiluminescent aerosol spray (CLAS) detector responds selectively to highly fluorescent compounds, olefins, sulfur compounds, and certain nitrogen compounds such as hydrazines, azides and nitrogen heterocycles. The species $O_2(^1\Delta_g)$ may be generated as a CL reagent *in situ* by use of the reaction, $ClO^- + H_2O_2 \rightarrow H_2O + Cl^- + O_2(^1\Delta_g)$. Response of a variety of organic compounds to singlet oxygen as a reagent is currently being investigated, and current results will be described.

A detector for gas chromatography based on the observation of chemiluminescence produced upon reaction of the GC effluent with atoms, radicals or metastable species created in a microwave discharge will also be described. Using SF_6 as a reagent gas, for example, the F atoms produced in the microwave discharge react with iodinated hydrocarbons to produce IF in the $^3\Pi_{0+}$ excited electronic state. Observation of banded emission from this state provides the basis of a selective detector for iodine. Other CL reagents currently being investigated include O, H, N, OH, $O_2(^1\Delta_g)$ and $N_2(^3\Sigma_u^+)$. Using these species, it is expected that other selectivies may be achieved.

212 SELECTIVE SORPTION OF NUCLEOPHILES USING LANTHANIDE METAL COMPLEXES. J. E. Picker and R. E. Sievers. Dept. of Chemistry and CIRES, Univ. of Colorado, Boulder, CO 80309.

Metal complexation inside gas chromatographic columns can be used to selectively separate compounds based upon functional class differences. Lanthanide complexes containing fluorinated β-diketonate ligands can be unsaturated with respect to coordination number and strong Lewis acids. Consequently, they can accept within the coordination sphere additional donors, in particular oxygen-containing compounds. When incorporated into a gas chromatographic precolumn, these metal chelates can strongly retain compounds that can form complexes. Separation of compounds into nucleophilic and non-nucleophilic groups is achieved, which simplifies later chromatographic separations. Previously synthesized fluorinated tris β-diketonates of lanthanides have been used for this purpose. However, due to the volatility of these chelates (a particularly useful feature for other applications) they are not very suitable for use as stationary phases because they tend to bleed from the column. Some novel bis-bidentate β-diketones, which have the ability to form less volatile coordination polymers of the lanthanides, have been synthesized and the polymers of these show promise for facilitating selective separations. Illustrations of simplified class separations of compounds in environmental samples will be discussed.

213 O-ALKYLOXIME DERIVATIVES FOR THE SELECTIVE GC AND GC-MS DETERMINATION OF ALDEHYDES. S.P. Levine and T. M. Harvey. Ford Motor Company, Analytical Division, Dearborn, Michigan. T. J. Waeghe and R. H. Shapiro, Department of Chemistry, University of Colorado, Boulder, Colorado. 80309.

Incomplete combustion of hydrocarbon fuels leads to the formation of aldehydes as well as other carbonyl compounds. Since aldehydes have been implicated as precursors of photochemical smog, as mucous membrane irritants, and as bacterial mutagens, it is desirable to be able to identify and quantitate aldehydes present in contaminated air samples. Methods currently available suffer from the drawbacks of non-selectivity and/or instability of derivatives. A method in which aldehydes are converted to their O-methyl- and O-benzyloximes has been developed. The procedures for quantitative preparation of these derivatives will be presented and typical conditions for collection of airborne samples will be given. These derivatives can be easily separated, selectively detected, and quantitated in the presence of hydrocarbons using a gas chromatograph equipped with a nitrogen-selective detector or gas chromatography-chemical ionization mass spectrometry using ammonia as the reagent gas.

214 A CONINUOUS EXTRACTER-CONCENTRATER AND ITS APPLICATION TO NITROSAMINE ANALYSIS IN BEER.

Harney B. Peterson, Adolph Coors Co., Golden CO 80401.

Nitrosamines, which are known carcinogens, occur in a variety of food products, cutting oils, and cosmetics. They have been detected in some malt, wort, and beer, the last mostly at low parts per billion levels. Usual methods of sample preparation for subsequent chromatographic detection include distillation from under an oil layer, separatory funnel extraction, and elution from proprietary packings in preparation tubes. Large amounts of solvent in relation to sample size are used with separatory funnel extraction, and intractable emulsions form. An all-glass continuous extracter has been made, accommodating larger sample size (100 ml) and less than 40 ml of heavier-than-water solvent. The sidearm boiler includes the Kuderna-Danish function of concentrating the solvent to the desired final sample size of 1 ml, with no transferring or drying steps needed. A repeated extraction to check for completeness of the first extraction may be easily done using less than 5 ml of additional solvent. A simple method is described for coalescing the solvent droplets as they collect after falling through the sample. So little solvent is lost that a fume hood is not necessary. Examples of detection of nitrosamines at less than 1 ppb are shown, as detected by gas chromatography and the Hall Electrolytic Conductivity Detector.

215 CAPILLARY GAS CHROMATOGRAPHIC AND GAS CHROMATOGRAPHIC-MASS SPECTROMETRIC ANALYSES OF NICOTINE AND METABOLITES OF NICOTINE IN MOUSE TISSUE.

M.S. Ho, K.M. Simon, D.R. Petersen and J.A. Thompson. School of Pharmacy, University of Colorado, Boulder, Colorado 80309.

Other investigators have identified inbred strains of mice which demonstrate significantly different behavioral responses to nicotine administration. In order to determine if these differences are related to metabolism of the alkaloid, we have developed sensitive and specific techniques for analyzing nicotine and several of it's major biotransformation products in mouse tissues. Following tissue homogenization and solvent extraction, analyses were performed by GC with a specific nitrogen-phosphorous detector and by GC/MS with selected ion monitoring. Several types of columns were evaluated, including packed, glass capillary and fused silica capillary columns. The latter, deactivated with Carbowax 20M and coated with SP-2100, gave superior results with regard to peak shape, resolution and reproducibility. This was especially important for analyses of cotinine (a major metabolite), which is a γ-lactam giving broad peaks on other columns. Sensitivity in the splitless injection mode is approximately 1 picomole for each compound. With this GC system using N-methylanabosine and 3-(N,N-diethylaminomethyl) pyridine as internal standards, quantitative linearity was established from 0.1 to 50 ng of nicotine. Both electron impact and chemical ionization GC/MS have been used to analyze tissue extracts. Deuterated analogs of the compounds were synthesized and employed as internal standards. Sensitivity and quantitative results were comparable to the capillary GC technique.

216 SOME APPLICATIONS OF FUSED SILICA CAPILLARY COLUMNS.

Roger Leibrand. Hewlett Packard, Neely Sales Region, 3003 Scott Blvd., Santa Clara, CA 95050.

This paper describes the results of several studies of fused silica open tubular columns. Their chromatographic performance is illustrated with the analysis of a variety of samples. Their use, construction, and operational characteristics are also discussed.

217 A HIGH PRESSURE LIQUID CHROMATOGRAPHIC METHOD FOR THE DETERMINATION OF THIAMIN, NIACIN, AND RIBOFLAVIN IN READY-TO-EAT CEREAL.

D. I. Johnson and S. B. Davé. Johns-Manville Research and Development Center, Denver, CO 80217

Since vitamins are necessary for the human body to maintain good health, it is often desirable to know the amounts of each type of vitamin present in foods. The thirteen vitamins are a diverse group of organic compounds which are normally classified as either fat or water soluble. The anlysis of water-soluble vitamins has been done by a wide range of methods including chemical, physical, microbiological and animal assays. A high pressure liquid chromatographic method has now been developed for the analysis of several water-soluble vitamins in ready-to-eat cereal.

Breakfast cereals are usually fortified with both fat and water-soluble vitamins. The amounts of riboflavin, thiamin and niacin present in cereals usually range from 25 to 100 percent of the U.S. Recommended Daily Allowances. The chromatographic determination of these three water-soluble vitamins involves an extraction with dilute acid and methanol followed by a separation and determination by paired ion chromatography using a CHROMOSORB* LC-7 column.

218 DETECTION OF ORGANIC ANIONIC GROUND-WATER TRACERS AT THE PPB LEVEL BY HPLC THROUGH PRE-COLUMN ENRICHMENT.

Klaus Stetzenbach, Steven Jensen, Glenn Thompson, Department of Hydrology and Water Resources, University of Arizona, Tucson, AZ 85721.

A simple, rapid concentration method has been developed for the quantitative analysis of some organic acids that are used as ground-water tracers. By replacing the sample loop of the injection valve with a short (3 cm long x 4 mm ID) pre-column packed with a C_{18} hydrocarbon bonded phase or a bonded anion exchanger, samples can be concentrated with the valve in the load position and eluted onto the analytical column by switching the valve to the inject position. Acids having a pK_a as low as 1 can be quantitatively concentrated out of 35 ml of water, whereas acids having a pK_a of 3.5 or greater can be quantitatively removed from volumes as large as 500 ml. The technique is preferable to on-column concentration methods because the sample solution can be pumped more rapidly through the shorter pre-column at moderate pressures. In addition, the various problems associated with rapid mobile phase changes in the analytical column are avoided.

219 COMBINED LIQUID CHROMATOGRAPHY/MASS SPECTROMETRY USING THE DIRECT INTERFACE.

Roger Leibrand. Hewlett Packard, Neely Sales Region, 3003 Scott Blvd., Santa Clara, CA 95050.

This paper describes the Baldwin/McLafferty/Hewlett-Packard direct chemical ionization split technique for LC/MS. The hardware interface considerations are discussed and the performance illustrated with a variety of difficult samples.

220 APPLICATION OF HPLC TO THE STUDY OF MICROORGANISMS IN EMULSIFIABLE OILS.

Rick Almen, Gary Mantelli, Patrick McTeer, and Stan Nakayama. Coors Container Co., 17755 W. 32nd Ave., Golden, CO 80401.

The presence of microorganisms (bacteria, mold and fungi) in emulsifiable oil systems is well known and their effect is deleterious in systems we are familiar with. The standard method used to measure their presence requires a 48 hour incubation period. This prevents an immediate reaction to a microbial problem except those based on historical trend analysis. In order to provide faster answers to potential microbial problems, an analytical technique has been developed utilizing HPLC. By using this method, the effect of microbial action on one particular emulsifiable oil system has been determined. This technique is applied both to control and trouble shooting aspects of three 10,000 gallon coolant systems based on this emulsifiable oil.

221 REVERSED PHASE HPLC TECHNIQUES FOR THE DETERMINATION OF ALDEHYDES AND KETONES IN GASEOUS EFFLUENTS.

T. F. Cole and R. M. Riggin, Battelle Columbus Laboratories.

The application of reversed phase HPLC techniques to the determination of aldehydes and ketones in gaseous effluents (e.g. engine exhaust) is described. The carbonyl compounds are collected from the gas streams as their dinitrophenylhydrazine (DNPH) derivatives using liquid impingers. The DNPH derivatives are extracted from the impingers solution with methylene chloride which is concentrated, exchanged with methanol, and analyzed by reversed phase HPLC.

Reversed phase HPLC parameters are studied in detail and retention data are provided using various 5 micron bonded phases (e.g. Lichrosorb RP-18, Sperisorb ODS, and Lichrosorb RP-2) and mobile phase compositions, including water/methanol and methanol/acetonitrile mixtures. Sensitivities using ultraviolet detection are also discussed.

222 NEW TECHNIQUES IN EMISSION SPECTROSCOPY.

T. M. Niemczyk, Department of Chemistry, University of New Mexico, Albuquerque, NM 87131.

This talk will survey several new areas of emission spectroscopy. Recent developments in the author's laboratory, as well as examples from other researchers, will be discussed. One technique that will be covered is schlieren photography. An apparatus capable of recording index of refraction gradients in self-luminous discharges such as arcs, sparks and inductively coupled plasmas will be described. This apparatus is capable of better than 50 μm spacial resolution and submicrosecond time resolution. Another area to be discussed is that of metastable energy transfer spectroscopy. In this technique, a gas-phase sample is mixed with active nitrogen. Excitation occurs by an efficient energy transfer process between excited state nitrogen and the analyte species. This process is simple, has multielement capabilities and has been shown to be very sensitive. Some recent developments in this field will be outlined.

223 ELEMENTAL ANALYSIS OF COAL, FLY ASH, AND SLAG SAMPLES. Dennis Yates, Tom Clevenger, Dennis James, and Ed Hinderberger. Environmental Trace Substances Research Center and Research Reactor of the University of Missouri, Columbia, MO 65201.

Energy related samples such as coal, fly ash, and slag provide interesting analytical problems. In particular, interest in the element content is broad and arises for several reasons. The elements of general interest include: a) Toxic Trace Elements: Lead Cadmium, Nickel, Magnesium, Beryllium, Bisumuth, Arsenic, Antimony, and Tin. b) Essential Trace Elements: Chromium, Manganese, Cobalt, Copper, Zinc, Selenium, Molybdenum, Boron, and Vanadium. c) Major Constituents: Silicon, Aluminum, Iron, Calcium, Sodium, and Potassium. Rapid and comprehensive preparation and analysis methods have been developed to analyze Coal, Fly Ash, and Slag Samples for these elements. The multi-element techniques of Nuclear Activation Analysis (NAA) and Inductively Coupled Plasma Optical Emission Spectroscopy (ICPOES) were used in the analysis. To evaluate the methods NBS standard reference materials (No. 1632-coal, No. 1632a-coal, No. 1633-fly ash, and No. 1635-coal) were analyzed. A total digestion method using $HClO_4$ and HF acids in Teflon ware was employed prior to ICPOES analysis. Approximately 17 elements were determined by ICPOES and 12 were determined by NAA. Eight elements were found to be equivalent by both techniques. Two elements (Hg and Pb) were determined by atomic absorption spectroscopy. In general we were able to obtain results which were within 10% of certified published values. Agreement between NAA and ICPOES was good averaging about 7% difference. The precision of the methods employed was on the order 5% RSD when 10 aliquots of sample were analyzed. In this presentation data will be presented summarizing the accuracy and precision studies conducted on the SRM's and outlining the sample handling methods.

224 SIMULTANEOUS DETERMINATION OF VOLATILE ELEMENTS VIA HYDRIDE GENERATION ICAP-OES. Arthur F. Ward. Jarrell-Ash Division, Fisher Scientific Co., 590 Lincoln Street, Waltham, MA 02154.

A compact continuous-flow hydride generation apparatus was designed for use with ICAP direct reading spectrometers. Operating parameters for the plasma and hydride generation chemistry were optimized for As, Bi, Ge, Hg, Sb, Se, Sn, and Te on single element basis. Compromise conditions for multi-elemental determinations were adopted for routine use for these elements over the range from 5ng/ml to 1000ng/ml in solution. The effect of chemical interferences on the hydride generation efficiency was studies and corrected for in real samples by use of masking agents, computerized corrections or use of the method of standard additions. The analysis of samples such as steels, brasses, manganese dioxide, waste water, rocks, plants, and biologicals using this multi-element approach have been successfully accomplished. Data pertaining to these types of determinations will be presented.

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THE USE OF HOLOGRAPHIC GRATINGS IN EMISSION SPECTROSCOPY. J.M.Lerner, Instruments SA, Inc. J. Flamand, G. Passereau, Jobin Yvon, France

Emission Spectroscopy has seen a giant leap forward as techniques using inductively coupled plasmas, dye lasers and molecular lasers become refined.

In all these techniques the diffraction grating is one of the most critical components.

This paper describes how new blazed holographic gratings can help reduce "Interferences", and background emission levels.

The use of new concave aberration-corrected gratings are also reviewed in the context of new generations of instruments establishing themselves in the laboratory.

226 EVALUATION OF AN INDUCTIVELY COUPLED PLASMA-ECHELLE SPECTROMETER SYSTEM FOR MULTI-ELEMENT ANALYSES. D. L. Dick, W. A. Hanagan, and R. K. Skogerboe. Department of Chemistry, Colorado State University, Fort Collins, Colorado 80523.

An ICP system has been coupled to an echelle spectrometer and the system evaluated for the simultaneous determination of 18 elements. The results will be discussed and comparisons will be made between this system and those which rely on conventional direct reading spectrometers.

227 MICROCOMPUTER CONTROLLED OPTICAL EMISSION SPECTROMETER. T. L. Futrell, R. T. Goodpasture, and G. F. Larson. Oak Ridge Y-12 Plant[1], P. O. Box Y, Oak Ridge, Tennessee 37830.

A microcomputer based data acquisition and control system has been added to a Jarrell-Ash Model 750 AtomComp spectrometer to provide automated analysis of beryllium air and smear samples within the concentration range of 0.01 to 1000 micrograms beryllium. The microcomputer utilizes a versatile single user floppy disk based operating system and supports the BASIC language. A video display and keyboard provide operator interaction with the system, and spectrometer alignment is greatly enhanced by a real-time graphical display of any selected channel intensity. The microcomputer controls channel integrators provided within the spectrometer, provides data acquisition with automatic ranging, and interacts with a set of automated electrode changers. A quartz refractor plate, under computer control, provides for background correction adjacent to each spectral line as well as automatic profiling between samples. While presently used only for beryllium, the system is quite versatile and its use in other environmental programs is being investigated. [1]Operated for the Department of Energy by Union Carbide Corporation's Nuclear Division under Contract W-7405-eng-26.

228 THE SELECTION OF OPTIMUM PARAMETERS FOR A SEQUENTIAL MULTI-ELEMENT ICP EMISSION SPECTROMETER

G. F. Wallace and R. D. Ediger. Perkin-Elmer Corporation, Main Ave., Norwalk, Connecticut, 06856.

Most existing inductively coupled plasma (ICP) emission spectrometers are based on polychromators which allow the simultaneous determination of as many as 61 elements. This type of instrumentation is well suited for the routine determination of the same set of elements in matrices quite similar in composition such as might be encountered in quality control analyses on finished products. However, if samples are less homogeneous, such as those encountered in mining and other geochemical exploration activities, different demands are placed on analytical instrumentation. The sequential scanning type of ICP emission spectrometer allows the analyst to determine a broader range of elements in samples of widely varying composition. Different wavelengths can be utilized for a given element in different sample matrices, thus allowing the analyst to avoid the age-old foe of emission spectroscopists, spectral line interferences. Several types of spectral interferences will be discussed, and examples of the utilization of alternate emission wavelengths in order to avoid serious spectral interferences will be presented.

229 THE IONIZATION REPRESSION EFFECT; IS IT REAL?

G. M. Butcher, K. G. Kronholm and R. K. Skogerboe. Department of Chemistry, Colorado State University, Fort Collins, Colorado 80523.

The presence of an easily ionized element often causes increases in the neutral atom populations of other easily ionized elements. This phenomenon is typically explained on the basis of ionization repression. Recent publications, however, have presented data that are not consistent with this mechanism. The present discussion will critically evaluate other possible explanations for the effect observed utilizing experimental data obtained with an atomic absorption flame system.

230 INVESTIGATION OF THE PROPERTIES OF A GLASS FRIT NEBULIZER.

L. R. Layman and F. E. Lichte. U.S. Geological Survey, Box 25046, MS 928, DFC, Denver, Colorado 80225.

Current nebulization systems can be a limiting factor in the performance of both flame and plasma atomic spectrometric methods. Popular pneumatic nebulizers, both cross-flow and concentric, suffer from short-term noise, long-term drift, and sample transport inefficiency. Erratic performance due to nebulizer clogging frequently results during aspiration of samples with either a high dissolved salt content or suspended particulates. The wide range of droplet sizes produced by these nebulizers results in inefficient sample delivery, as larger droplets are lost in transport to the atom cell. Droplet size also appears to be related to desolvation and atomization processes in the atom cell. Ultrasonic nebulizers have overcome some of the problems caused by wide droplet size distribution and clogging. However, the ultrasonic nebulizer system is more complex and expensive than a pneumatic nebulizer, and coupling efficiency appears to be dependent on salt content. The recently introduced Babington nebulizer has been successful in reducing problems due to nebulizer clogging, but it still produces a wide droplet size distribution and poor sample transport efficiency. To overcome these limitations, many alternate nebulization systems are being investigated. This paper will present the results of our studies of the glass frit nebulizer. The optimization of this nebulizer involves choices of frit porosity and diameter, carrier gas flow rate, and sample delivery rate. A study of performance criteria will also be reported. This includes nebulization efficiency, drift, noise, and ease of operation. The discussion will also include studies of possible problem areas such as sample contamination, memory effects, and solute adsorption onto the glass surface.

231 NEBULIZER SPRAY CHAMBER DESIGN FOR AN INDUCTIVELY COUPLED PLASMA.

Frederick E. Lichte and Arthur L. Sutton. U.S. Geological Survey, Box 25046, MS 928, DFC, Denver, Colorado 80225.

The induction-coupled argon plasma (ICP) used in emission spectroscopy is noted for its high temperatures and thus for its freedom from several interferences that are found in cooler sources such as actylene-air flames. However, a review of the literature shows that despite its high temperature, interferences have been noted in some laboratories. In fact, the presence of certain concomitant elements may suppress the signal, enhance, or have no effect, on the signal depending on several conditions external to the plasma itself. We have found one of the major factors affecting interferences in the ICP is the size distribution of droplets of sample entering the plasma. Large droplets entering the plasma require more time to evaporate and dissipate. This effect can be observed qualitatively in the spatially discreet emission from sodium atoms at wavelengths of 588.9 and 589.5 nm. When very large droplets containing sodium enter the plasma a yellow streak can be seen up through the center of the plasma. When the droplets are small, the streak of sodium atom emission disappears and is replaced by a bullet-shaped configuration. Ionization and solute vaporization effects have been noted when this visible streak was present. The absence of large droplets appears to be necessary if interferences are to be minimized. Experimentally, that condition can be produced through the nebulization process, or through discrimination during transport to the plasma. The double spray chamber described by Scott (1974) gives excellent droplet size discrimination. However, its memory effect is severe, therefore the chamber requires several minutes of flushing between samples. A properly designed droplet transport system must exhibit a short memory effect while producing an aerosol that minimizes ionization and vaporization interferences. Different chamber designs are associated with various types of interference effects in the plasma. Reference: Scott, R. H., Fassel, V. A., Kinseley, R. N., Nixon, D. E., Anal. Chem., v. 46, p. 75, (1974).

232 EFFECTS OF SOLUTION COMPOSITION ON THE PHYSICO-CHEMICAL CHARACTERISTICS OF AQUEOUS AEROSOLS. K. G. Kronholm, G. M. Butcher and R. K. Skogerboe. Department of Chemistry, Colorado State University, Fort Collins, Colorado 80523.

The composition of aqueous solutions being nebulized affect the physical and chemical characteristics of the aerosols produced. The nature(s) and extent(s) of changes in these characteristics may be reflected as interference effects occurring in flames and plasmas. This discussion will present results indicative of the changes observed and present a model descriptive of the mechanisms which effect the changes.

233 ANALYSIS OF BARIUM TITANATE MATERIAL BY D. C. ARC SPECTROGRAPHY. Tim J. Schmitt. Globe-Union Inc., a subsidiary of Johnson Controls Inc., 5757 North Green Bay Ave., Milwaukee, Wisconsin 53201.

Barium titanate is an important constituent of ceramic capacitors. The performance of these capacitors can be directly related to the concentration of certain trace impurities. The inherent speed of a one meter Czerny-Turner monochrometer allowed us to use third order spectra. This resulted in a reciprocal linear dispersion equivalent to or better than for the more expensive conventional three meter spectrographs. This procedure was necessitated by the complex spectra emitted by titanate materials. Other modifications of our normal spectrographic operating procedures included the use of order sorting filters and of ion exchange concentration techniques. Overall these modifications resulted in the ability to analyze barium titanate for fifteen trace elements with relatively inexpensive spectrographic equipment. Description of the equipment, line choices and detection limits for fifteen elements will be given. Sample preparation techniques will also be discussed.

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AN EVALUATION OF WAVELENGTH SELECTION PARAMETERS FOR THE DIRECT READING EMISSION SPECTROMETRIC ANALYSIS OF GEOLOGIC MATERIALS, J. L. Seeley, U.S. Geological Survey, Branch of Analytical Laboratories, Denver Federal Center, MS-928, Denver, CO 80225, P. J. Lamothe and T. L. Fries, U.S. Geological Survey, Branch of Analytical Laboratories, 345 Middlefield Road, MS-18, Menlo Park, CA 94025.

A 60 channel, 1.5m, mini-computer controlled direct reading emission spectrometer has been adapted for the DC-Arc semi-quantitative determination of 43 elements in a wide variety of geologic materials. The large number of analytical channels located on a fixed length focal curve makes wavelength selection extemely complex. Parameters used in the selection process and techniques for obtaining additional spectral information from beyond the focal curve will be discussed.

235 THE USE OF HIGH SPEED DATA AQUISITION AND GRAPHICS DISPLAY TO STUDY FACTORS INFLUENCING SIGNALS IN THE HGA GRAPHITE FURNACE G. F. Wallace and R. D. Ediger. Perkin-Elmer Corporation, Main Avenue, Norwalk, Connecticut, 06856.

When analyzing samples via graphite furnace atomic absorption, a microcomputer-controlled furnace coupled with high speed data collection and graphics display can be a powerful combination for optimizing analytical conditions. Microcomputer-controlled graphite furnaces allow great flexibility in thermal programming and in the choice of purge gases. High-speed data collection and graphics display allow the analyst to display and compare the effects of different thermal programs and purge gases on the shape and appearance times of peaks. Data will be presented on the use of oxygen as an internal purge gas during the char cycle. In addition to reducing background, oxygen can also cause changes in the amplitude and appearance times of some element peaks.

236 COLLISIONALLY INDUCED IONIZATION OF RUBIDIUM IN HIGH RYDBERG STATES. T. J. Whitaker and B. A. Bushaw. Battelle, Pacific Northwest Laboratory, Box 999, Richland, WA 99352.

The relative efficiency of collisionally induced ionization of high Rydberg states of rubidium is compared to direct photoionization. A nitrogen-laser pumped dye laser is used to excite the $5^2P_{3/2}$ state at approximately 780 nm. A second dye laser is then scanned from 480-515 nm to populate high S and D states in a sample of $\sim 10^{-6}$ torr rubidium in 4 torr krypton. The ionization produced by collisions of Rb*-Kr is then detected on a wire charged to about 200 V above the body of the cell. A comparison of relative ionization intensities from the excited states suggests that an associative ionization process is the dominant source of ions detected. A comparison of the relative ion yield from associative ionization of the 20^2D state and photoionization suggests that two orders of magnitude improvement in ionization efficiency is possible using this method over normal single frequency resonance ionization techniques.

237 DOPPLER-CANCELLED, TWO-PHOTON RESONANT IONIZATION SPECTROSCOPY. B. A. Bushaw and T. J. Whitaker. Battelle, Pacific Northwest Laboratory, Box 999, Richland, WA 99352.

A technique is demonstrated which allows high-resolution spectroscopy of high excited states. A pulse amplified cw dye laser is frequency doubled in a nonlinear crystal and directed into an ionization chamber containing the sample. When a two-photon resonance occurs, the multiphoton ionization spectrum shows a large enhancement. By reflecting the laser radiation back on itself in the cell, Doppler-free resonances may be observed. Results are given for the $6P[3/2]_2$, $6P[5/2]_2$ and $6P[1/2]_0$ resonances from the ground state in xenon. Hyperfine splitting constants are determined for the odd isotopes in the case of the $6P[3/2]_2$ and the $6P[5/2]_2$ states.

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SAMPLE EFFECTS IN POSITIONALLY STABLE SPARK DISCHARGE TRAINS. David Ekimoff, John P. Walters, Department of Chemistry, University of Wisconsin Madison, WI 53706.

The process of obtaining a representative sample is critical step in any analytical technique. This step is especially significant in the spectrochemical analysis of solid alloys using a high voltage spark discharge for sampling and excitation. In this case, the excitation (or signal-generating) step is strongly influenced by the sampling step. Therefore, a change in sampling efficiency will be directly reflected in the analytical signal.

The inseparable nature of these two basic steps has made the actual effects of sampling processes difficult to categorize and study. When the discharge is positionally stabilized though, strong effects related to the sample system can be observed. In this paper, we will present time-resolved emission data and surface microscopic studies characterizing these effects. New analytical applications based on the unique emission and erosion characteristics of a positionally stable spark discharge train will also be discussed.

239 METASTABLE TRANSFER EMISSION SPECTROSCOPY OF METAL VAPORS PRODUCED IN A SPUTTERING CELL. Steven D. Hornung, Henry C. Na and Thomas M. Niemczyk, Department of Chemistry, University of New Mexico, Albuquerque, NM 87131.

Metastable transfer emission spectroscopy has been shown to be very sensitive for the determination of trace levels of several elements. In this technique the atomic vapor is mixed with active nitrogen and is excited by energy transfer from the $N_2(A^3\Sigma_u^+)$ electronic level providing relatively efficient, nonthermal excitation. The active nitrogen can be produced by either a microwave discharge or an alternating high voltage field upstream from the mixing and observation zone of the flow cell. The resulting glow from the active nitrogen itself has very little background in the near ultraviolet and visible regions of the spectrum; the regions of interest for trace metal determination.

The analyte used in this study was produced by the sputtering process. The design and construction of a flow cell in which flat metal cathodes can be mounted will be discussed. This allows for the direct analysis of trace elements in various metals. Solutions can be analyzed by drying the sample onto an aluminum flat and sputtering the sample from the surface. These results will be compared to results obtained using a tungsten filament atomizer

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RECENT DEVELOPMENTS IN INDUCTIVELY COUPLED PLASMA, PLASMA ATOMIC EMISSION ANALYSIS. Joseph Katzenberger, Angelo C. Grillo, Edward M. Clarke, Instruments SA, Inc.

For some time it has been realized that if a stable inductively coupled plasma source (ICP) could be mated with a high resolution spectrometer, many of the disadvantages of atomic absorption could be eliminated and many additional advantages introduced. In addition, such a spectrometer could be used as a lower priced alternative to direct reading spectrometers. This has now been made possible by the mating of a specteromter utilizing a holographic diffraction grating producing extremely low stray light levels with a new generation of ICP sources.

The overwhelming advantage of this partnership is readily observed in the ability of the user to test for parts per billion of most elements and parts per trillion of some elements. No hollow cathode is necessary; the particular element under consideration need only demonstrate an emission spectrum at 10,000°C. Matrix effects are minimal and the dynamic range is around 10^6.

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RECENT DEVELOPMENTS IN INDUCTIVELY COUPLED PLASMA ATOMIC EMISSION ANALYSIS. Joseph Katzenberger, Angelo C. Grillo, Edward M. Clarke, Instruments SA, Inc.

Instrumentation for inductively coupled plasma (ICP) emission analysis has primarily been developed to exploit the multi-element capabilities of the ICP source. However, one of the significant attributes of the ICP is its stability. This stability, when matched with a computer controlled scanning monochromator, provides the small laboratory with an economical entry into this important analytical field.

The analytical performance in both multi-element and sequential ICP systems will be discussed. Topics such as speed of analysis, sample throughput, stability, sensitivity and flexibility will be discussed.

242 FLAMELESS AA MATRIX EFFECTS: A VIEW THROUGH TIME AND SPACE. J. A. Holcombe, N. Akerlind Jr., and W.K. Stephenson. Department of Chemistry, University of Texas, Austin, Texas 78712.

An optical system will be described which produces time and spatial absorbance data within a 3 mm diameter Varian CRA-90 furnace atomizer with a resolution of better than 250 µm. The often assumed uniform atom distribution was not found for several elements, and the free atom density gradient present will be considered in light of interference effects observed for these elements. The entrainment of O_2 in the sheath gas as well as oxidants generated by the thermal decomposition of matrix salts, e.g., NO_3^- and $SO_4^=$, will be examined and their contribution to "matrix effects" discussed. The unique temporal and spatial distribution of Pb in different matrices will also be presented. The mechanistic implication of free atom generation and the gas phase recombinations leading to analytical problems will be emphasized.

243 GRAPHITE FURNACE ATOMIC ABSORPTION SPECTROSCOPY OF HEAVY MATRIX SAMPLES. John P. Erspamer and Thomas M. Niemczyk, Department of Chemistry, University of New Mexico, Albuquerque, NM 87131.

Flameless atomic absorption spectroscopy has been shown to be very sensitive for trace metal analysis. As the sample matrix becomes more complex, however, the utility of the technique may be diminished due to various matrix interferences. These matrix effects include both chemical and physical interactions between the analyte and the matrix. Physical interactions, such as occlusion, can change the shape of the absorbance vs. time profile thus altering the peak height while leaving the integrated absorbance unaffected. Chemical interferences, on the other hand, may or may not affect the peak height but will reduce the integrated absorbance due to a depletion in the atomic population. We have investigated the effect of heavy matrices on Cu and Pb. Comparison of the appearance times and peak shapes have proven useful in the interpretation of the data. The results indicate that physical interactions, as well as chemical, are important. We have also studied the role the atomizer surface assumes in the atomization process. The results of these investigations, which elucidate some of the interference mechanisms as well as methods to reduce the effects of the matrix, will be discussed.

244 USE of MICROSAMPLING for FLAME ATOMIC ABSORPTION. A. J. Stratton, Varian Instrument Group, 611 Hansen Way, Palo Alto, CA 94303. T. McKenzie, Varian Techtron Pty. Ltd., 679 Springvale Road, Springvale, Victoria, Australia, 3171.

Flame atomic absorption (FAA) is an established analytical technique for 67 elements. However, the relatively large sample size requirement, the necessity to dilute high dissolved solids content solutions, and the consumption of large reagent volumes and much operator time are all limitations on the overall efficiency and cost of an FAA analysis. Utilization of a microsampling accessory offers the analyst a solution to these limitations.

Flame microsampling applies to situations where only a small amount of sample is available or where burner clogging results from continuous aspiration of samples such as sea water, serum, or metallurgical and geological digests. It also allows greater versatility in sample preparation and preconcentration. Digestions of smaller amounts of material (about a half to a third of the normal sample size) and smaller initial samples for solvent extraction or ion exchange are possible.

Two common microsampling methods of introducing sample to the flame are direct injection and dipping. Analytical data will be presented indicating the factors affecting measurements utilizing these two methods. This includes response characteristics involving calibration curves, reproducibility, carry-over, and sample volume for both methods. In addition, the effects of nebulizer uptake rate as well as probe residence time and depth of penetration in the sample solution will be considered for the dipping method.

245 DESIGN FACTORS FOR A MODERN ELECTROTHERMAL ATOMIC ABSORPTION INSTRUMENT.
John A. Nichols*, Ray Woodriff, Steve Lawson, F.G. Dewalt, R.L. Sanks,
Montana State University Dept. of Chem., Bozeman, MT 59717.

A long-tube, constant temperature furnace appears to provide an ideal atomizer from the standpoint of efficiently and ruggedly producing reliable data, i.e. analyte results which are not sensitive to variations in matrix composition.
Certain design factors are of greater importance than others in attaining this ideal. For example, our data show some variations which can occur when the flow of inert gas inside the atomizer chamber is not directed in the proper fashion. Other design factors are important for convenient, rugged operation of the atomizer.

A computerized spectrophotometric readout can add a great deal of flexibility if it is capable of providing results against a calibration curve based on any of three parameters: peak height, peak area, or peak width at fixed height (PWAFH). This last calibration parameter allows high concentration samples to be analyzed, even at 1000-fold higher levels than the upper limit of the linear range for peak height.

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THE MECHANISMS FOR LEAD RELEASE FROM CHEMICALLY ALTERED GRAPHITE SURFACES IN FLAMELESS AA. S.G. Salmon and J.A. Holcombe. Department of Chemistry, University of Texas, Austin, Texas 78712.

The determination of the more volatile elements, such as Pb and Zn, by flameless atomic absorption spectroscopy presents a problem due to the occurence of multiple peaks and appearance temperature shifts. To explain some of these phenomena the surface of the graphite atomizer can be altered in such a way that the relative sizes and positions of the atomic absorption peaks change. By this manipulation of the atomic signal a reasonable model for the release of atoms from the surface can be constructed. This surface alteration is accomplished by the addition of hydrogen, oxygen, oxidizing and reducing conmitants, and metals which form carbide coatings. The presence of oxygen due to oxygen mixed with the sheath gas or oxygen generated by the thermal decomposition of added salts causes an increase in the appearance temperature of Pb. The relative sites of two distinct peaks for Pb are changed by increased oxygen concentrations. The formation of a calcium carbide surface on the atomizer gives rise to a third peak for Pb with a higher appearance temperature than that obtained with graphite. Some mechanisms for Pb release which account for the observed multiple peaks and appearance temperature shifts will be discussed.

247 EVALUATION OF SOME COMMERCIAL PNEUMATIC NEBULIZERS WITH RESPECT TO MEMORY EFFECTS IN ICP-AES ANALYSIS. Dave Dobb, Department of Chemistry and Geochemistry, Montana College of Mineral Science & Technology, Butte, Montana 59701.

When a sample is introduced into an ICP torch-spray chamber system,that system becomes contaminated by the elements in the sample with respect to succeeding determinations. This contamination or memory effect is time dependent in that an increasing washout time yields lower and lower residual signals from previous samples. In some applications of ICP work such as routine analysis of samples of widely varying concentrations or determinations of interelement corrections, the washout times may be undesireably long before residual signals decrease to insignificant levels.

It appears that the nebulizer used has a major influence on the rapidity with which the residual signals drop off. This paper will present an evaluation of several routinely used commercially available pneumatic nebulizers for memory effects. The several types of nebulizers studied were two glass concentric nebulizers of different sizes, a cross-flow nebulizer with homemade glass needles, and an adjustment concentric PT-Ir needled Zr block nebulizer. The cooling gas rate, power, viewing height, and nebulizer properties were optimized for each type using the same spray chamber and torch. When the best detection limits were achieved for each nebulizer, the memory effects were quntified by a rapid and simple method.

Recommendations can be made for a particular nebulizer used in this study based on relative freedom of memory effects without sacrifice to detection limits and stability. A model for possible computer correction of matrix effects was also studied and will be reported.

248 ANALYSIS OF MAJOR, MINOR, AND TRACE ELEMENTS IN GEOLOGIC SAMPLES DISSOLVED BY VARIOUS TECHNIQUES BY INDUCTIVELY COUPLED PLASMA - ATOMIC EMISSION SPECTROMETER.* C. L. Ho, S. Tweedy, and J. R. Calvo. Bureau of Economic Geology, The University of Texas at Austin, Austin, Texas 78712.

Successful application of ICP-AES to the analyses of multiple elements in geologic samples depends on (1) accurate determination of interelement interference correction factors in identical matrices used in samples dissolution and preparation of standards and blanks, (2) proper technique used to dissolve all elements in samples of diversified mineral composition. Such technique must be sufficiently simple, rapid, and economical for handling a large number of samples to justify the operation of an ICP-AES, which is capable of analyzing samples at a rate of less than 3 minutes per sample. Many dissolution techniques have been tested. Among those tested are: (1) fusion with Li-tetraborate followed by HNO_3 dissolution, (2) fusion with Li-tetraborate-HNO_3 dissolution and subsequent removal of hydrous silica with HF, (3) aqua regia-HF, (4) $HNO_3 + H_2SO_4 + HF$, (5) pre-treatment of calcareous samples with $HNO_3 + HCl$ and subsequent dissolution using $HNO_3 + H_2SO_4 + HF$, (6) pre-treatment of samples with $HNO_3 + HCl$ and subsequent treatment with perchloric acid + HF. Our evidence showed that none of these techniques can universally be applied for satisfactory dissolution of all elements in samples of all types. A specific technique may have to be used for a certain group of elements; another technique may be more suitable for another group of elements.

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249 ANALYSIS OF As BY DISTILLATION AS $AsCl_3$ -- INDUCTIVELY COUPLED PLASMA - ATOMIC EMISSION SPECTROMETER.* C. L. Ho, and S. Tweedy. Bureau of Economic Geology, The University of Texas at Austin, Austin, Texas 78712.

Current methods of measuring As in geologic materials and natural waters involve separation of As as AsH_3 prior to its measurement by flameless atomic absorption, by spectrophotometry, or possibly by ICP-AES. $NaBH_4$ is mostly used for reducing As^{+3} to AsH_3. NO_3^- and Ni, and possibly other elements, interfere with arsine generation using $NaBH_4$. Since Ni is invariably present in geologic samples and NO_3^- is usually found in natural waters, successful measurement of As as AsH_3 requires their effective removal. A rapid and simple method of separating As as $AsCl_3$ by distillation has been adapted. A sample is fused with a mixture of $MgO + K_2CO_3$ (1:3 by weight) at 900°C. The flux is dissolved in 6N HCl. Water samples are evaporated in presence of HNO_3 to dryness followed by dissolution in 6N HCl. In an aliquot of the HCl extract, As is distilled as $AsCl_3$ with hydrazine$\cdot SO_4$ and HBr. $AsCl_3$ in distillate is trapped in dilute HNO_3 and analyzed on ICP-AES. No elaborate apparatus is required for the distillation, and less than 1 minute distillation time is needed for complete recovery of As in 10 ml of sample solution.

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250 ANALYSIS OF Se IN GEOLOGIC SAMPLES BY FLUOROMETRIC METHOD AND INDUCTIVELY COUPLED PLASMA - ATOMIC EMISSION SPECTROMETER.* C. L. Ho, S. Tweedy, and J. R. Calvo. Bureau of Economic Geology, The University of Texas at Austin, Austin, Texas 78712.

The oxide and sulfide forms of selenium in geologic samples can be dissolved in a mixture of $H_2SO_4 + HNO_3$ at 150°C. A small fraction of residual Se in silicate minerals can be released by decomposing the silicates using HF. The present technique requires digesting samples with a $H_2SO_4 + HNO_3$ mixture (1:2 by volume) at 150° to 160°C until excess HNO_3 is removed. The digestion is then treated with 6N HCl at 100°C. The acid-soluble fraction is separated on centrifuge; the residue is decomposed with HF in presence of HNO_3 followed by evaporation to dryness in a Teflon beaker. The residue is dissolved in HCl at 100°C and combined with the first acid extract. An aliquot of the solution is analyzed for Se by fluorometric method using 2, 3-naphthalene diamine as complexing agent in a buffered medium of pH 2.0. The Se-DAN complex is extracted into cyclohexane and measured on a Farran Mark I spectrofluorometer at an excitation wavelength of 373 nm and an emission wavelength of 516 nm. Concentration of Se higher than 5 μg per sample in cyclohexane may be brought into 10 ml aqueous solution upon removal of organic matrix using concentrated HNO_3 and then analyzed on inductively coupled plasma - atomic emission spectrometer.

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EMISSION ENHANCEMENT IN A DC PLASMA. D.D. Nygaard, Chemistry Department, Bates College, Lewiston, Maine 04240.

Elemental emission line enhancements in a DC plasma seeded with an easily ionizable element are discussed. Enhancement is shown to be inversely related to the ionization potential of the ionizable matrix element. The temperature of the plasma core is shown to decrease in the presence of easily ionizable elements, whereas the effective temperature experienced by the emitting element is shown to increase under the same conditions. The emission of the plasma is spatially profiled with and without easily ionizable matrix elements.

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ELECTRO ANALYSIS OF SELENOAMINO ACIDS. R.W.Andrews, R.A. Grier, R.Graves, Department of Chemistry, University of Alabama at Birmingham

The electro analysis of selenocystine and selenomethionine is described. Cathodic stripping voltammetry of selenocystine has a detection limit of 5×10^{-10}M when differential pulse voltammetry is used in the measurment step. A single well formed cathodic stripping peak is observed for sub-micromolar quantities of selanocystine in 0.1M mineral assets with E_p of -0.50V vs. SCE. Cystine does not interfere with the determination of selenocystine when present in up to 500-fold molar excess. Selenomethionine is not reducable at Hg electrodes in aqueous solutions; it can be reversably oxidized at carbon (glassy carbon or carbon paste) electrodes with an $E_{1/2}$ of +0.90V vs. SCE in 0.1M mineral acids. The influence of pH upon limiting current and $E_{1/2}$ for the selenomethionine oxidation is described. The analysis of selenocystine and selenomethionine in aqueous extracts of seleniferous grains is described. Differential pulse cathodic stripping voltammetry is used for the assay of selenocystine and LCEC with a glassy carbon walljet electrode detector is used for the assay of selenomethionine.