

# Rocky Mountain Conference on Magnetic Resonance

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Volume 23 *23rd Rocky Mountain Conference*

Article 1

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8-2-1981

## 23rd Rocky Mountain Conference

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## 23rd Rocky Mountain Conference

### Abstract

Abstracts and meeting program from the 23rd annual meeting of the Rocky Mountain Conference, co-sponsored by the Rocky Mountain Section of the Society for Applied Spectroscopy and the Rocky Mountain Chromatography Discussion Group. Held in Denver, Colorado, August 2-6, 1981.

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## ABSTRACTS & MEETING PROGRAM

Sponsored jointly by

Rocky Mountain Section  
Society for Applied  
Spectroscopy

and

Rocky Mountain Chroma-  
tography Discussion Group

DENVER CONVENTION COMPLEX

Denver, Colorado

August 2-6, 1981

THE ROCKY MOUNTAIN CONFERENCE  
WISHES TO THANK THE FOLLOWING COMPANY  
WHO PROVIDED SOME FUNDS TOWARD THE  
PRINTING OF THIS PROGRAM



Analytical Development Corporation

1875 Willow Park Way P O Box 429 Monument, Colorado 80132 (303)488-2777

WELCOME

I am very pleased to welcome you to the 23rd Rocky Mountain Conference. To those conferees who have traveled both near and far, I hope that your stay in the Denver area will be enjoyable.

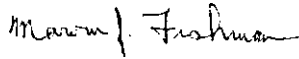
This Conference has become one of the most prominent summer scientific meetings in the United States. In each of the past few years, attendance has grown. Last year we had more than 700 registrants. We anticipate the number will be surpassed this year. More than 260 papers and posters are to be presented. Three of the symposia have attracted well-known scientists from a number of other countries, truly making this an international meeting.

The Conference banquet promises to be extremely interesting. Representatives from the Denver Museum of Natural History will present a program which will focus on the behind-the-scenes look in the preparation of life size ecological habitat dioramas that show animals in their natural environment. Please join us for this enjoyable evening.

Thanks is extended to the more than 50 exhibitors. Without their financial support we could not present this expanded program. The exhibitors will welcome your inquiries in our arena exhibit area from Monday morning until Wednesday evening.

Finally, I wish to thank all the people who have participated in planning the Conference. Only through your support have we been able to make this one of the outstanding technical meetings in the United States.

Sincerely,

A handwritten signature in dark ink, appearing to read "Marvin J. Fishman". The signature is fluid and cursive, with the first name "Marvin" and last name "Fishman" clearly distinguishable.

Marvin J. Fishman  
Conference Chairman

REGISTRATION HOURS AND LOCATION

Sunday,	August 2, Executive Tower Inn	<1:00 p.m. - 8:00 p.m.
Monday,	August 3, Denver Convention Complex	7:30 a.m. - 3:30 p.m.
Tuesday,	August 4, Denver Convention Complex	7:30 a.m. - 3:30 p.m.
Wednesday,	August 5, Denver Convention Complex	7:30 a.m. - 3:30 p.m.
Thursday,	August 6, Denver Convention Complex	7:30 a.m. - 11:30 a.m.

REGISTRATION FEES

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

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

VISITOR INFORMATION

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

SOCIAL FUNCTIONS

MIXER

All conference attendees and spouses are invited to a mixer on Monday, August 3, from 5:30 p.m. to 8:00 p.m. at the Executive Tower Inn.

CONFERENCE BANQUET

The Conference banquet will be held on Tuesday, August 4, at 7:00 p.m. at the Executive Tower Inn. Tickets are \$12.00 each. The social hour (cash bar) will be at 6:00 p.m.

Banquet speakers will be representatives of the Denver Museum of Natural History. The museum is internationally renowned, especially for 66 life size ecological habitat dioramas that show animals from four continents in their natural environments. Hundreds of thousands of man-hours on field expeditions or at the museum have been devoted to producing the unique curved painted backgrounds of these dioramas, their superb mounted specimens and realistic vegetation. This program will focus on a behind-the-scenes look at how these unique exhibits are prepared, and why the museum is the largest cultural attraction in the State of Colorado.

#### DINNER - MUSICAL

The Conference has arranged for a limited number of tickets to the Wednesday, August 5, evening performance of "The Sound of Music" at the Country Dinner Playhouse. This theater "in the round" is one of the better known entertainment places in the Denver area. An excellent buffet dinner is served prior to the performance. Tickets for the dinner and musical are \$13.00 each. Transportation is optional. For those requiring transportation, buses have been reserved. Cost is \$6.00 per person. Payment for the playhouse tickets and transportation must be included with your preregistration. The buffet dinner is served at 6:45 p.m. and buses will leave from the Executive Tower Inn at 6:00 p.m.

#### MESSAGE CENTER

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

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

#### SEMINAR

Thursday, 9:00 a.m., August 6, 2nd Floor, Room D,

Orion Research Inc. will present a seminar entitled, "Advances in pH and ISE Technology". A unique new pH measuring system that eliminates many of the problems caused by temperature will be described. In addition, a review of current applications for ion-selective electrodes will be presented. Speakers will be Mr John Constanineau and Mr. John Osumn.

#### CONFERENCE EXHIBITION

Exhibits of new chemical products, instruments, publications, and services will be on display in the Denver Convention Complex. The sponsoring societies of the Conference gratefully acknowledge the support of the exhibitors.

#### EXHIBIT HOURS

Open daily from 9:30 a.m. to 5:00 p.m. on Monday, August 3; Tuesday, August 4; and Wednesday, August 5.

#### Future Conference Dates

August 1 - 6, 1982

August 14 - 19, 1983

August 5 - 10, 1984

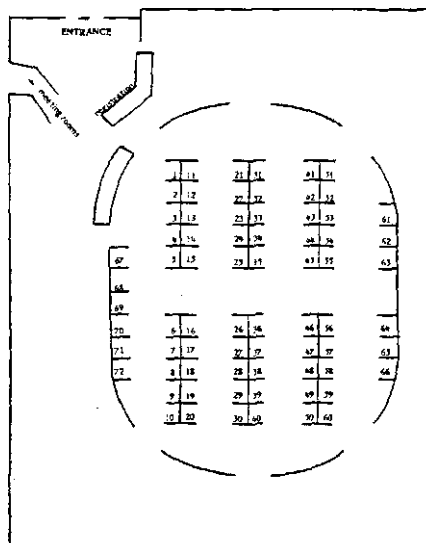
July 14 - 19, 1985

August 3 - 8, 1986

CONFERENCE EXHIBITORS  
(as of May 22)

Booth No.

Air-Row Instruments	41-43
American Monitor Corp.	31
American Scientific Products	60
Antek Instruments	27
Baird Corporation	69-70
Beckman Instruments, Inc.	67
Brinkmann Instruments, Inc.	12
Bruker Instruments	53
Carle Instruments, Inc.	7
Coulometrics, Inc.	15
Dionex Corporation	1-2
EG&G Ortec	64
Finnigan Corporation	16
Gow-Mac Instrument Co.	56
Hauser Laboratories	5
Hewlett-Packard	45
IBM Corporation	61-63
Instrumentation Laboratory	17
Instruments SA Inc.	36
ISCO	68
Jarrell-Ash	
3EOL USA Inc.	51
3ohns-Manville	35
Lachat Instrument Div.	13
LECO Corporation	33-34
MCB Manufacturing Chemists	44
Mettler Instrument Corp.	37
Micromeritics Instrument Corp.	55
Micro-Now Instrument Co., Inc.	52
Nicolet Instrument Corp.	46
Perkin-Elmer Corp.	22-24
R. H. Allen Co.	65
Rocky Mountain Analytical Laboratory	32
Sadtler Research Laboratories	20
SCT Sales, Inc.	21
SpectraMetrics	6
Spectra-Physics	57
Tracor Instruments	4
Ultra Carbon Corp	3
UTI	26
Varian Instruments	14
VWR Scientific, Inc.	54
Waters Associates, Inc.	66
Wescan Instruments, Inc.	25
Wilmad Glass Co. Inc.	11





ORGANIZERS OF 23rd ROCKY MOUNTAIN CONFERENCE

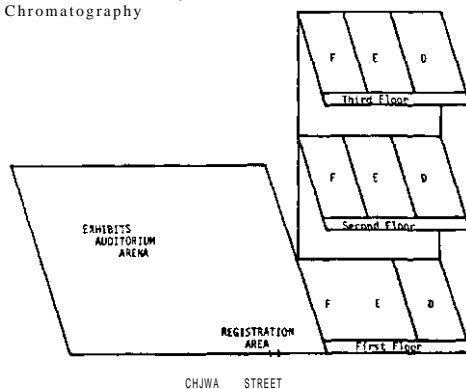
Conference Chairman	M. 3. Fishman U.S. Geological Survey
Conference Vice Chairman Exhibits/Facility	B. Beard U.S. Dept. of Agriculture - ARS
Registration/Treasurer	E. A. Brovsky Rockwell International
Publicity	H. E. Taylor U.S. Geological Survey
	K. 3. Grossaint Rockwell International
Printing	3. D. Grooms Rockwell International
Banquet/Mixer	B. McCarthy Marathon Oil Company
	B. Wiginton Marathon Oil Company
Short Courses	3. Gurnsey Loveland, Colorado
Visitor Information	E. Huffman Huffman Laboratories
Audio-Visual	D. Rains Huffman Laboratories

SYMPOSIA CHAIRMAN

Atomic Emission Spectroscopy	F. E. Lichte U.S. Geological Survey
Atomic Absorption Spectroscopy	T. Niemczyk University of New Mexico
Chromatography	R. Barkley University of Colorado
Environmental Chemistry	3. Bonelli U.S. Geological Survey
EPR	G. R. Eaton S. S. Eaton University of Denver
Ion Chromatography	A- Fitchett Dionex Corp.
NMR	F. Miknis Laramie Energy Technology Center
Raman Spectroscopy	M. C. Goldberg U.S. Geological Survey
Poster Sessions	3. Gurnsey Loveland, Colorado

## TECHNICAL PROGRAM

	Floor	Rm	Morning	Floor	Rm	Afternoon
Monday August 3	2nd	F	Ion Chromatography	2nd	F	Ion Chromatography
	3rd	F	NMR Session I	3rd	F	NMR Session II
	2nd	E	Chromatography	2nd	E	Chromatography
	2nd	D	General Session	2nd	D	General Session
				3rd	E	EPR Session I
Tuesday August 4	2nd	F	Ion Chromatography	2nd	F	Ion Chromatography
	3rd	F	NMR Session III	3rd	F	NMR Session IV
	2nd	E	Chromatography	1st	F	General Session Posters
	3rd	E	EPR Session II	3rd	E	EPR Session III
	2nd	D	Atomic Emission Spect.	3rd	D	Raman Spectroscopy
	3rd	D	Raman Spectroscopy	2nd	D	Atomic Emission Spect.
Wednesday August 5	3rd	F	NMR Session V	3rd	F	NMR Session VI
	3rd	E	EPR Session IV	1st	F	NMR Posters
	2nd	D	Atomic Absorption Spect.	1st	F	EPR Session V Posters
	2nd	E	Environmental Chemistry	2nd	D	Atomic Absorption Spect.
				2nd	E	Environmental Chemistry
				2nd	F	Ion Chromatography
Thursday August 6	3rd	F	NMR Session VII			
	3rd	E	EPR Session VI			
	2nd	E	Environmental Chemistry			
	2nd	F	Ion Chromatography			



SYMPOSIUM ON ION CHROMATOGRAPHY

MONDAY MORNING, AUGUST 3 - Second Floor, Room F  
T. S. Stevens, Presiding

- 8:30 INTRODUCTORY REMARKS and INTRODUCTION OF SESSION CHAIRMAN -  
A. W. Fitchett
- 8:35 1. "Sulfate Assay in Biological Fluids by Ion Chromatography", D. E. C. Cole  
and C. R. Scriver, Montreal Childrens Hospital and McGill University.
- 9:00 2. "Ion Chromatographic Determination of Nonmetallic Elements in Geological  
Materials", J. M. Baldwin and P. R. Klock, U.S. Geological Survey, and C.  
Pohl, Dionex Corp.
- 9:25 3. "Anion Analysis by Ion Chromatography at the National Bureau of  
Standards", W. F. Koch, National Bureau of Standards.
- 9:50 BREAK
- 10:15 4. "Analysis of Boron by Ion Chromatography in Power Production", M. G.  
Mahnke and S. M. Gray, Arizona Public Service.
- 10:40 5. "Impact of Ion Chromatography on the Water Treatment Industry", J. Rawa,  
Calgon Corp.
- 11:05 6. "Ion Chromatography in the Microelectronics Industry", D. R. Anderson and  
S. A. Shear, IBM.
- 11:30 7. "Development of High Speed Ion Chromatography", J. Slanina and F. P.  
Bakker, Netherlands Energy Research Foundation.

SYMPOSIUM ON NUCLEAR MAGNETIC RESONANCE

MONDAY MORNING, AUGUST 3 - Third Floor, Room F  
NMR Session I - Solids - D. Netzel, Presiding

- 8:50 OPENING REMARKS
- 9:00 44. Robert Vaughan Plenary Lecture, "NMR in Solids: A Study in Anisotropy", J.  
S. Waugh, Massachusetts Institute of Technology.
- 9:50 45. "Recent Developments in Multiple Quantum NMR", A. Pines, University of  
California, Berkeley.
- 10:30 BREAK
- 11:00 46. "Geometry of Molecules in the Amorphous State by NMR Nutation Spectros-  
copy", C. S. Yannoni and R. D. Kendrick, IBM Research Labs.
- 11:30 47. "<sup>13</sup>C NMR in Oriented Polymeric Solids", D. L. VanderHart, G. G. A. Bohm,  
and V. O. Mochel, National Bureau of Standards and Firestone Tire and  
Rubber Co.

SYMPOSIUM ON CHROMATOGRAPHY

MONDAY MORNING, August 3 - Second Floor, Room E  
R. M. Barkley, Presiding

- 8:30 90. Plenary Lecture "Trace Analysis of Volatile Organic Compounds in  
Biological and Environmental Problems", Albert Zlatkis, University of  
Houston.
- 9:25 91. "Gas Chromatographic Study of Modified Pyrolytically Coated Graphite  
Supports", O. A. Ogunkeye and J. A. Holcombe, University of Texas, Austin.

- 9:50 92. "Some Factors Influencing Reproducibility in Fused Silica Columns", T. 3. Stark, P. Larson, and R. Dandeneau, Hewlett-Packard Company.

10:15 BREAK

- 10:45 93. "Dynamic Headspace Techniques for Gas Chromatographic Analysis of Enzymatic Dechlorination Reactions", B. Ho, G. Schlickeiser and 3. A. Thompson, University of Colorado.

- 11:10 94. "Quantitative Determination of 1,2-Dibromo-3-chloropropane in Whole Rat Blood at part per trillion Levels", P. E. Kastl, E. A. Hermann and W. H. Braun, Dow Chemical Co.

- 11:35 95. "On-Column Injection with WCOT Columns: Quantitative Analysis of Carbamate Pesticides, Steroids, and Volatile Organics", T. 3. Stark, R. R. Freeman and K. Augenblick, Hewlett-Packard Company.

#### GENERAL SESSION

MONDAY MORNING - AUGUST 3 - Second Floor, Room D  
F. Ryan, Presiding

- 8:30 111. "Differential Pulse Polarographic Determination of Bromide in Brine Solutions", L. Jackson and S. Wilson, U.S. Geological Survey.

- 8:55 112. "High Precision Complexometric Titration of Cadmium in the Presence of Uranium", 3. R. Delmastro, Exxon Nuclear Idaho Company.

- 9:20 113. "Vacuum Ultraviolet Circular Dichroism: Applications to Polysaccharides", E. S. Stevens, University of New York at Binghamton.

9:45 BREAK

- 10:15 114. "Macroencapsulated XAD-2 Extraction Technique for a Rapid Quantitation of Acidic and Neutral Drugs in Whole Blood", N. Eiahi, Chief Medical Examiner Office, New York.

- 10:40 115. "Reactivity of Substituted Phenylhydrazides", R. W. Lauver and W. B. Alston, NASA Lewis Research Center.

- 11:05 116. "Automatic Flow Injection Analysis - A New Technique for High Speed Wet Chemical Analysis", C. Ranger, Lachat Instrument Div.

- 11:30 117. "Separation of Inorganic and Organic Anions on a HPLC Reversed-Phase Column", N. Skelly, The Dow Chemical Company.

#### SYMPOSIUM ON ION CHROMATOGRAPHY

MONDAY AFTERNOON, AUGUST 3 - Second Floor, Room F  
T. S. Stevens, Presiding

- 1:30 8. "Identification of Explosives and Explosive Residues by Ion Chromatography", D. 3. Reutter, R. C. Buechele, T. L. Rudolph, and E. C. Bender, Federal Bureau of Investigation.

- 1:55 9. "Analysis of Boron by Ion Chromatography Exclusion", 3. P. Wilshire, U.S. Borax Research Corporation.

- 2:20 10. "Analysis of Fluoride in Nylon", 3. P. Price, N. W. Stacy, and 3. R. Hawkins, American Enka Company.

- 2:45 11. "Oxalate Quantitation by Ion Chromatography: Clinical Applications", C<sup>^</sup> Mahle and M. Menon, Washington University School of Medicine.

3:10 BREAK

- 3:35 12. "Mobile Phase Ion Chromatography (MPIC)", C. A. Pohl and M. Ebenhahn, Dionex Corp. R&D Dept.
- 4:00 13. "Ion Chromatographic Analysis of Gaseous and Particulate Fluoride Emissions from Brickworks and Aluminium Smelters", C. J. Jackson, D. Bussan, and C. Neuberger, Health and Safety Executive, London.
- 4:25 14. "Temperature Effects in Ion Chromatography", D. R. Baker and C. A. Burgett, Hewlett-Packard.

#### SYMPOSIUM ON NUCLEAR MAGNETIC RESONANCE

MONDAY AFTERNOON, AUGUST 3 - Third Floor, Room F  
NMR Session II - Solids - D. Netzel, Presiding

- 1:30 48. "Elimination of Severe Magnetic Susceptibility Broadening in Solid State NMR", M. Stoll, Sandia National Labs.
- 2:00 49. "<sup>27</sup>Al NMR Characterization of Aluminum Sites in Amorphous and Crystalline Silica-Aluminas", E. G. Derouane, J. B. Nagy, J. P. Gilson, and Z. Gabelica, Facultes Universitaires De Namur, Belgium.
- 2:30 50. "CP/MAS Studies of Surface Adsorbed and Surface Attached Species", G. E. Maciel and I. S. Chuang, Colorado State University.
- 3:00 BREAK
- 3:30 51. "Characterization of Zeolite Molecular Sieves by Magic Angle Silicon-29 NMR", M. J. Melchior, Exxon Research and Engineering Company.
- 4:00 52. "Spin 1/2 Nuclei in Catalytic Environments", W. Dawson, R. Inners, and P. Ellis, University of South Carolina.
- 4:30 53. "Solid State High Resolution <sup>13</sup>C NMR of Organometallics; Correlations with X-Ray Crystallography", N. Zumbulyadis, D. L. Smith and S. Gross, Eastman Kodak Research Labs.

#### SYMPOSIUM ON CHROMATOGRAPHY

MONDAY AFTERNOON, AUGUST 3 - Second Floor, Room E  
D. B. Blair, Presiding

- 1:30 96. "Fluorometric Postcolumn Reaction Detector for Determination of the Anions NO<sub>2</sub><sup>-</sup> S<sub>2</sub>O<sub>3</sub><sup>2-</sup> ..<j f .. „PLC", L. R. Field and Sun Haing Lee, University of Washington.
- 1:55 97. "Autoxidation Chemiluminescence Detector (AOCL) for Liquid Chromatography", M. S. Gandelman and J. W. Birks, University of Colorado.
- 2:20 98. Multidimensional Liquid Chromatography for the Analysis of Complex Samples", K. Ogan and E. Katz, Perkin-Elmer Corp.
- 2:45 BREAK
- 3:15 99. "Optimization of Resin Based Column Packing for Rapid HPLC Carbohydrate Analysis", M. J. Gray, Bio-Rad Laboratories.
- 3:40 100. "Selectivity of Packings and Solvents", T. Hanai and J. Hubert, Universite de Montreal.
- 4:05 101. "Importance of Solvent Choice and Solvent Handling in Chromatography", J. W. Hubert and J. T. Przybytek, Burdick and Jackson Laboratories, Inc.,
- 4:30 102. "The Three Micron Column - A System Consideration", M. Bensinger and T. Meyers, Laboratory Data Control.

GENERAL SESSION

MONDAY AFTERNOON, August 3 - Second Floor, Room D

3. L. Seeley, Presiding

- 1:30 118. "Determination of Pyrrolizidine Alkaloids in Plant Extracts by GC-CIMS", 3. W. McCoy, F. R. Stermitz, and R. K. Skogerboe, Colorado State University.
- 1:55 119. "The Generation and Determination of Volatile Metal Chelates by Analytical Reaction Gas Chromatography", S. R. Hill and R. K. Skogerboe, Colorado State University.
- 2:20 120. "Electrochemical Determination of Copper Species Toxic to Rainbow Trout", C. R. Gumina, R. K. Skogerboe, and P. H. Davies, Colorado State University.
- 2:45 121. "An Investigation of the Mechanisms Involved in Pneumatic Nebulization and Their Effect on the Aerosol Produced", K. G. Kronholm and R. K. Skogerboe, Colorado State University.
- 3:15 BREAK
- 3:40 122. "The Determination of Isotope Ratios in Mercury by Atomic Absorption Spectroscopy", M. D. VanArendonk and R. K. Skogerboe, Colorado State University.
- 4:05 123. "Investigations of Matrix Interference Effects in Graphite furnace Atomic Absorption by Multiple Wavelength Spectrometry", 3. M. Shekiri, 3r. and R. K. Skogerboe, Colorado State University.
- 4:30 124. "Extending the Linear Dynamic Range in Graphite Furnace Atomic Absorption using a Photodiode Array", 3. L. Maglaty and R. K. Skogerboe, Colorado State University.

SYMPOSIUM ON ELECTRON PARAMAGNETIC RESONANCE

MONDAY AFTERNOON, AUGUST 3 - Third Floor, Room E

EPR SESSION I - G. R. Eaton, Presiding

- 1:30 INTRODUCTORY REMARKS - G. R. Eaton
- 1:35 140. Plenary Lecture "EPR Studies of Multi-Protein Complexes", B. 3. Gaffney, The Johns Hopkins University.
- 2:20 141. "Advantages of and Deuterium Substituted Spin Labels for Quantitative Simulation of EPR and ST-EPR Spectra in Biological Studies", A. H. Beth, K. Balasubramanian, R. T. Wilder, S. D. Venkataramu, B. H. Robinson, L. R. Dalton, D. E. Pearson, C. R. Park, and 3. H. Park, Vanderbilt University.
- 2:40 142. "Anisotropic Motional Models in ST-EPR at 9 and 35 GHz", L. Lee, L. Fung, Wayne State University, and M. E. Johnson, University of Illinois at the Medical Center.
- 3:00 BREAK
- 3:30 143. Ca(II) and Mn(II) Binding to -Lactalbumin", K. Murakami, H. Nishikawa, P. 3. Andree, and L. 3. Berliner, Ohio State University.
- 4:00 144. "A Probe of Differential Covalency of Metal-Ligand Bonds in Metalloenzymes", M. W. Makinen, A. C. Kuo, and M. B. Yim, University of Chicago.
- 4:30 145. "Use of Methylmercury as a Spin-Orbit Probe in Optically Detected Magnetic Resonance to Distinguish Between Single-Stranded and Duplex DNA", C. K. Ott and A. H. Maki, University of California at Davis.
- 4:45 146. "The Synthesis and EPR Spectra of Three Novel Spin Labeled Crown Ethers", M. Eastman, University of Texas at El Paso.

SYMPOSIUM ON ION CHROMATOGRAPHY

TUESDAY MORNING, AUGUST 4 - Second Floor, Room F

3. Slanina, Presiding

- 8:30 INTRODUCTION OF SESSION CHAIRMAN - A. W. Fitchett
- 8:35 15. "Further Work in the Use of Ion Chromatography as a Problem-Solving Tool for Electronic Components and Equipment", L. A. Psota, Bell Laboratories.
- 9:00 16. "Automation of an Ion Chromatograph for Precipitation Analysis with Computerized Data Reduction", A. Hedley and M. Fishman, U.S. Geological Survey.
- 9:25 17. "Determination of Hydrogen Cyanide in Environmental Samples by Ion Chromatography", T. W. Dolzine, G. C. Esposito, R. 3. Gaffney, U.S. Army Environmental Hygiene Agency.
- 9:50 BREAK
- 10:15 18. "A Novel Suppression Means for Ion Chromatography", T. S. Stevens, 3. C. Davis, and H. Small, Dow Chemical.
- 10:40 19. "Single Column Ion Chromatography for the Determination of PPB Levels of Chloride and Sulfate in Condensate Waters", J. S. Fritz and D. T. Gjerda, Ames Laboratory, and K. M. Roberts, Republic of South Africa.
- 11:05 20. "High Performance Ion Chromatography (HPIC)", C. A. Pohl and A. Woodruff, Dionex Corp. R&D Dept.
- 11:30 21. "Some Applications of IC and ICE in the Pharmaceutical Industry", I. A. Lindberg, Pharmacia AB, Sweden.

SYMPOSIUM ON NUCLEAR MAGNETIC RESONANCE

TUESDAY MORNING, AUGUST 4 - Third Floor, Room F

NMR Session III - Biopolymers - N. Zumbulyadis, Presiding

- 8:30 54. "<sup>13</sup>C NMR Studies of Lipid-Lipid and Lipid Protein Interactions in Phospholipid Vesicles", J. H. Prestegard, Li-da Ony, and M. A. Fuson, Yale University.
- 9:00 55. "1H NMR Study of the Location and Motion of Ubiquinones in Perdeuterated Phosphatidylcholine Bilayers", P. B. Kingsley and G. W. Feigenson, Cornell University.
- 9:30 56. "<sup>31</sup>P NMR Studies of the Phospholipid-Protein Interface in Cell Membranes", P. L. Yeagle, SUNY at Buffalo.
- 10:00 BREAK
- 10:30 57. "C-<sup>13</sup> Bond Order Parameter Distributions for Partially Ordered Systems with Axial Symmetry", J. H. Davis, University of Guelph.
- 11:00 58. "NMR Studies of Bilayer Membranes at 500 MHz", S. Chan, California Institute of Technology
- 11:30 59. "Studies of Molecular Dynamics Using <sup>13</sup>C NMR", R. E. London, R. L. Blakley, 3. P. Groff, L. Cocco, 3. M. Stewart, M. H. Phillippi, and G. Kwei, Los Alamos National Lab, University of Iowa and University of Colorado Medical Center.

SYMPOSIUM ON CHROMATOGRAPHY

TUESDAY MORNING, AUGUST 4 - Second Floor, Room E  
C. E. Andre, Presiding

- 8:30 103. "High Speed Separation of Ultraviolet Absorbing Constituents in Urine by Liquid Chromatographies", T. Hanai and J. Hubert, Universite de Montreal.
- 8:55 104. "Very High-Speed Liquid Chromatography for Energy and Environmental Research", M. W. Dong, K. Ogan, J. L. DiCesare, Perkin-Elmer Corp.
- 9:20 105. "Chloramphenicol Analysis by HPLC", D. L. Swafford, Laboratory Data Control, Riviera Beach, FL, and J. Trueting, University of Texas Medical School.
- 9:45 106. "The Determination of Calcium Pantothenate in Nutritional Supplements by High Performance Liquid Chromatography Using a Variable Wavelength UV Detector", T. J. Hudson, Shaklee Corp.
- 10:10 BREAK
- 10:25 107. "An HPLC Method for the Determination of Quinidine in Serum", C. P. Patel, Miles Laboratories, Inc.
- 10:50 108. "Separation of Adenosine Monophosphates by Reverse-Phase HPLC", D. Ramos, University of Colorado, Colorado Springs.
- 11:15 109. "Use of HPLC in the Detection of Phenols in Industrial Aqueous Effluents", G. Rehagen, K. Thomas and J. Going, Midwest Research Institute.
- 11:40 110. "Liquid Chromatographic Separation of Shale Oils and Syncrudes by Hydrocarbon Type", R. L. Miller, K. Ogan, and L. Hellinger, Perkin-Elmer Corp.

SYMPOSIUM ON ELECTRON PARAMAGNETIC RESONANCE

TUESDAY MORNING, AUGUST 4 - Third Floor, Room E  
EPR SESSION II - I. B. Goldberg, Presiding

- 8:30 147. Plenary Lecture "Paramagnetic Defect Species in Silicon Dioxide", J. A. Weil, R. H. D. Nuttall and J. Isoya, University of Saskatchewan.
- 9:15 148. "Photochemical Studies of Defect States in Inorganic Solids by EPR", R. S. Eachus, Eastman Kodak Company.
- 9:45 149. "Optically Detected Magnetic Resonance of the Triplet States of Thiouracils", M. R. Taherian, and A. H. Maki, University of California at Davis.
- 10:00 BREAK
- 10:30 150. "EPR Investigation of U.V.-irradiated RDX Single Crystals at 77 K", M. D. Pace and W. B. Moniz, Naval Research Laboratory.
- 10:50 151. "The Varied Guises of Alkoxy Radicals", H. C. Box, Roswell Park Memorial Institute.
- 11:15 152. "Spin Diffusion in Single Crystals of Alkali Biphenyls", E. de Boer and O. Takizawa, University of Nijmegen.
- 11:35 153. "An EPR Study of the Free Radical Processes Occurring in the Reaction of AsF<sub>5</sub> with a p-Terphenyl Single Crystal", L. D. Kispert and K. Ezell, The University of Alabama.



SYMPOSIUM ON ATOMIC EMISSION SPECTROSCOPY

TUESDAY MORNING, AUGUST 4 - Second Floor, Room D  
F. E. Lichte, Presiding

- 8:30 202. Invited Speaker - "Current Trends and New Directions in Atomic Spectroscopy", G. M. Hieftje, Indiana University.
- 9:15 203. "Using an Integrated, Microcomputer-Controlled, Adjustable-Waveform Spark Source for Spectrochemical Analysis with Synchronously-Gated Detection", S. G. Barnhart and 3. P. Walters, University of Wisconsin-Madison.
- 9:35 204. "Observations on the Interfacing of the ICP to Chromatographs for Element Specific Detection", D. A. Yates, D. Fraley, S. Manahan, D. Duebelbise, and 5. Kapila, University of Missouri.
- 9:50 BREAK
- 10:20 205. "Accurate Analysis of High Solids Containing Solutions by ICAP-OE5", A. F. Ward, R. K. Brown, L. Carrara, S. Colosimo, V. Luciano, and L. Marciello, 3arrell-Ash Division Fisher Scientific Company.
- 10:40 206. "Characterization of Effects from High Dissolved Solids on Trace Element Determinations by Inductively Coupled Plasma Spectrometry", 3. R. Garbarino, G. Kimber, and H. E. Taylor, U.S. Geological Survey.
- 11:00 207. "A Modular Approach to Inductively Coupled Plasma Analysis", 3. Katzenberger, R. Randazzo and S. Berman, Instruments SA, Inc.
- 11:20 208. "Optimization Studies of a Sputtering Atomization — Metastable Transfer Emission Source", S. D. Hornung and T. M. Niemczyk, University of New Mexico.

SYMPOSIUM ON RAMAN SPECTROSCOPY

TUESDAY MORNING, AUGUST 4 - Third Floor, Room D

- 8:15 INTRODUCTION - M. C. Goldberg, Presiding
- 8:20 251. Keynote Speaker - "Conformational and Dynamical Properties of Biological Membranes by Raman Spectroscopy", I. W. Levin, National Institutes of Health.
- 9:05 252. "Determination of -Turn Conformation by Laser Raman Spectroscopy", H. Ishizaki, P. Balaram, R. Nagaraj, Y. V. Venkatachalapathi, and A. T. Tu, Indian Institute of Science, Bangalore, and Colorado State University.
- 9:30 253. "Resonance Raman Studies of Molecular Oxygen Adducts of Co(II) Chelates in Solution Equilibria", K. Nakamoto, M. W. Urban, Y. Nonaka, and T. Ishiguro, Marquette University.
- 9:55 BREAK
- 10:25 254. "Resonance Raman Spectra, Excitation Profiles and Normal Coordinate Analysis of Potassium Bis(Dithiooxalato)Nickel(II)", R. Czernuszewicz, D. P. Strommen, and K. Nakamoto, Marquette University.
- 10:50 255. "Extended-Range Resonance Raman Including UV-Laser Excitation", P. 3. Trotter, Eastman Kodak Company.
- 11:15 256. "Objective Considerations in the Measurement of Polarized Raman Spectra with the MOLE", M. E. Andersen, Walter C. McCrone Associates, Inc.
- 11:40 257. "Mechanisms of Aqueous Sorption onto Gibbsite Measured by Raman Spectroscopy", K. M. Cunningham and M. C. Goldberg, U.S. Geological Survey.

SYMPOSIUM ON ION CHROMATOGRAPHY

TUESDAY AFTERNOON, AUGUST 4 - Second Floor, Room F

3. Slanina, Presiding

- 1:30 22. "Ion Chromatographic Analysis of Animal Feeds", A. MacDonald, R. Saperstein, F. Scheidl, E. Hargroves, and A. Love, Hoffmann-LaRoche Inc.
- 1:55 23. "Computerized Acquisition and Reduction of Ion Chromatographic Data", C. C. Torquato, N. Latner, and D. C. Bogen, U.S. Department of Energy.
- 2:20 21. "Low Level Bromide Determination in Drinking Waters by Ion Chromatography", A. Eaton, D. Pietz, A. Trussel, and L. Leong, James M. Montgomery Environmental Research Lab.
- 2:45 25. "The Removal of Iron Interference in IC Analysis by Complexation", N. S. Simon, U. S. Geological Survey.
- 3:10 BREAK
- 3:35 26. "Application of Simultaneous Detection in IC", E. L. Johnson, and E. Carriers, Dionex Corp., and R. Williams, Allied Chemical.
- 4:00 27. "Resistivity Detection of Weak Acids: Carbamates and Carbonates", R. K. Pinschmidt, Jr., and M. 3. Fasolka, Air Products and Chemicals.
- 4:25 28. "Determination of Boron and Phosphorous in Silicate Glasses by ICE", R. M. Merrill, Sandia National Labs.

SYMPOSIUM ON NUCLEAR MAGNETIC RESONANCE

TUESDAY AFTERNOON, AUGUST 4 - Third Floor, Room F

NMR Session IV - Biopolymers - N. Zumbulyadis, Presiding

- 1:30 60. "Solid State NMR Studies of Protein and DNA Dynamics", S. 3. Opella, University of Pennsylvania.
- 2:00 61. "Structure and Interaction of Specifically Carbon-13 Labeled Transfer RNA's", M. P. Schweizer, University of Utah.
- 2:30 62. "CP-MAS <sup>13</sup>C NMR of Carbohydrates Containing Glucose", W. L. Earl and P. E. Pfeffer, National Bureau of Standards, Los Alamos National Lab and U.S. Department of Agriculture.
- 3:00 BREAK
- 3:30 63. "Laser Photo CIDNP Studies of Alpha-Lactalbumins", L. 3. Berliner, Ohio State University.
- 4:00 64. "<sup>3</sup>H and <sup>31</sup>P NMR of Metallo-Alkaline Phosphatase", P. Gettins and J. E. Coleman, Yale University.
- 4:30 65. "Application of <sup>15</sup>N NMR Spectroscopy to Biological Systems", K. Kanamori, W. W. Bachovchin, T. L. Legerton, B. L. Vallee, R. L. Weiss, and J. D. Roberts, California Institute of Technology, Tufts University, UCLA, and Harvard University.

GENERAL SESSION - POSTERS

TUESDAY AFTERNOON, AUGUST <math>t</math> - First Floor, Rooms E-F

3. Gurnsey, Presiding

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.

125. "Quality Control of Commercial Products as Viewed by the Analytical Chemist", P. A. Hyman, Rockwell International.
126. "Characterization of Organic Compounds Associated with Weathered Surface-Retorted Spent Shale Using Capillary Gas Chromatography/Mass Spectrometry/Computer Techniques", W. E. Pereira, C. E. Rostad, T. R. Steinheimer, and S. M. Johnson, U.S. Geological Survey.
127. "Organic Contaminants in Ash, Water, and Sediment Samples Associated with Mount St. Helens, 1980 Volcanic Eruption", C. E. Rostad, W. E. Pereira, H. E. Taylor, U.S. Geological Survey.
128. "An Automatic Solid State Gas Analyzer", 3. Salsgiver, United Technical Corp.
129. "Optical Absorption of Semiconducting KTN (KTaf.,Nb.03) Single Crystals", M. Tsukioka, 3. Tanaka and B. Okai, National Institute for Researches in Inorganic Materials.
130. "Impact of Micro Raman Analysis on Molecular Identification and Micro Structure Characterization", F. Adar, Instruments SA.
131. "Determination of Weak Acids by Ion Chromatography with Conductimetric Detection", T. Sundén and M. Lindgren, Dept. of Analytical Chemistry, Umeå, Sweden.
- B 132. "Use of a Dionex Anion Separator Column for Cation Separations", 3. W. Wimberley, Conoco.
- C 133. "New Eluent for the Ion Chromatographic Separation of Alkaline Earth Metals", 3. W. Wimberley, Conoco.
- A 134. "Techniques for the Routine Analysis of Ambient Sulfur Dioxide by Ion Chromatography", M. 3. Zimmerman, 3. M. Jenks, G. Dean, Texas Air Control Board.
- B 135. "Determination of Bromide in Geologic Materials of High Chloride Content by Ion Chromatography", S. Wilson and L. Jackson, U.S. Geological Survey.
- C 136. "Determination of Dissolved Boron in Natural Waters by D.C. Argon Plasma Emission Spectrometry", A. M. Nefcy, U. S. Geological Survey.
- A 137. "Effects of Street Salting on Ambient Air Monitoring of Particulate Pollutants in Detroit", P. O. Warner, 3. O. Kermoshchuk, Wayne County Health Dept., and 3. O. Jackson, Los Alamos Scientific Lab.
- B 138. "Standard Reference Materials", R. K. Kirby, National Bureau of Standards.
- C 139. "Characterization of Polymeric Plasticizers by Size Exclusion Chromatography and High Performance Liquid Chromatography", C. E. Kurachi, K. L. Wong, and D. D. Solomon, American McGraw.

SYMPOSIUM ON ELECTRON PARAMAGNETIC RESONANCE

TUESDAY AFTERNOON, AUGUST 4 - Third Floor, Room E  
EPR SESSION III - 3. R. Pilbrow, Presiding

- 1:30 154. Plenary Lecture "Structure and Reactivity of Simple Alkane Cations and Characterization of Hydrogen Atom Reactions with Alkanes in Low Temperature Solids", M. Iwasaki, Government Industrial Research, Nagoya.
- 2:15 155. "ENDOR Studies of Coal and its Protiated and Deuterated Products", I. Goldberg, Science Center, Thousand Oaks, California, L. Dalton and H. Tomann, SUNY at Stony Brook.
- 2:40 156. "Electron Paramagnetic Resonance of Whole P.R. Spring Tar Sand and Its Various Fractions", V. M. Malhotra and W. R. M. Graham, Texas Christian University.
- 2:55 157. "An EPR Study of a Bituminous and a Sub-bituminous Coal and Their in Situ Oxidation", V. M. Malhotra and W. R. M. Graham, Texas Christian University.
- 3:05 BREAK
- 3:35 158. "EPR Spectra of Stable Free Radicals Adsorbed on Metal Surfaces", R. D. Allendoerfer and 3. B. Carroll, 3r., SUNY at Buffalo.
- 3:50 159. "Spin-Trapping of Phosphorus Centered Free Radicals", R. Sridhar, Oklahoma Medical Research Foundation.
- 4:05 160. "NMR and ESR Evidence of Molecular Aggregates in Sodium Dibutylphosphate Aqueous Solutions", S. Belaid and C. Chachaty, C.E.N. de Saclay.
- 4:25 161. "Electron Transfer Between Distant Weakly Interacting Functional Groups - Evidence for a Non-adiabatic Process", S. Mazur, V. M. Dixit, and F. Gerson, The University of Chicago and the University of Basel.

SYMPOSIUM ON RAMAN SPECTROSCOPY

TUESDAY AFTERNOON, AUGUST 4 - Third Floor, Room D  
S. M. Klainer, Presiding

- 1:15 258. "Remote Raman Spectroscopy - Its Successes and Failures", S. M. Klainer, Lawrence Berkeley Laboratory, University of California.
- 1:40 259. "Solar Blind Raman Lidar", J. A. Cooney, Drexel University.
- 2:10 260. "High Resolution Raman Lidar for Water Vapor Studies", S. H. Melfi, M. 2. Hansen, 3. D. Spinhirne, and D. Clem, NASA/Goddard Space Flight Center.
- 2:40 261. "Laser Measurements in Flames and the Atmosphere", C. M. Penney, G. E. Research and Development.
- 3:10 BREAK
- 3:25 262. "Remote Raman Spectroscopy in the Ocean", D. A. Leonard, Computer Genetics Corporation.
- 3:55 263. "High Resolution Effects in Remote Sensing with Laser Backscatter", R. L. Schwiesow and V. E. Derr, NO A A Environmental Research Laboratories.
- 4:25 264. "The Effects of Raman and Rayleigh-Brillouin Scattering on Fraunhofer Lines as Seen in Scattered Light", G. W. Kattawar, Texas A&M University.

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SYMPOSIUM ON ATOMIC EMISSION SPECTROSCOPY

TUESDAY AFTERNOON, AUGUST \* - Second Floor, Room D

L. R. Layman, Presiding

- 1:30 209. "Rapid Dissolution Technique for Multielement Analysis of Crop Samples by ICP-AES", R. W. Kuennen and J. A. Caruso, University of Cincinnati, K. A. Wolnik and F. L. Fricke, Food and Drug Administration.
- 1:50 210. "Analysis by Induction Coupled Plasma Spectrometry Using Phosphoric Acid as Solvent", L. Morgenthaler, Applied Research Laboratories.
- 2:10 211. "Automated Simultaneous Multielement Determination of the Hydride Forming Elements and Mercury by Continuous Hydride Evaluation/ICP - PES", J. E. Goulter and D. M. Painchaud, Applied Research Laboratories.
- 2:30 212. "Methods Development for ICP Spectroscopy", H. L. Kahn, 3. 3. Sotera, and A. L. Rattionetti, Instrumentation Lab., Inc.
- 3:00 BREAK
- 3:20 213. "Samarium Metal Analysis by DC Plasma Spectrometry", G. W. Johnson and T. E. Sisneros, Molycorp, Inc.
- 3:40 214. "The Determination of the Rare Earth Elements in Geological Materials by ICAP-OES", J. G. Crock and F. E. Lichte, U.S. Geological Survey.
- 4:00 215. "Application of a Sequential Scanning ICP to the Analysis of Geological Materials", G. F. Wallace, The Perkin-Elmer Corporation.
- 4:20 216. "Simultaneous Multielement Analysis of Difficult Samples with an ICP-Atomic Fluorescence Spectrometer", D. Demer and D. A. Busch, Baird Corp.

SYMPOSIUM ON NUCLEAR MAGNETIC RESONANCE

WEDNESDAY MORNING, AUGUST 5 - Third Floor, Room F  
NMR Session V - Polymers - F. Miknis, Presiding

- 8:30 66. "Structurally Specific Proton Relaxation Studies on Solid Polycarbonates", A. A. Jones, J. F. O'Gara and P. T. Inglefield, Clark University and College of the Holy Cross.
- 9:00 67. "Solid State NMR of Polycarbonates", D. R. Holoccek, Shell Development Co.
- 9:30 68. "Molecular Motion in Substituted Polystyrene", M. Sefcik, Monsanto Company.
- 10:00 BREAK
- 10:30 69. "A <sup>13</sup>C NMR Investigation of Polymers Prepared by Glow Discharge Techniques", S. Kaplan and A. Dilks, Xerox Corporation.
- 11:00 70. "31p Shift Anisotropies and Molecular Motion in Polyphosphazene Elastomers", J. Ackerman, University of Cincinnati.
- 11:30 71. "Determination of Dihedral Angles in Substituted Polybiphenyls by <sup>13</sup>C NMR Spectroscopy", J. R. DeMember, Polaroid Corporation.

SYMPOSIUM ON ELECTRON PARAMAGNETIC RESONANCE

WEDNESDAY MORNING, AUGUST 5 - Third Floor, Room E  
EPR SESSION IV - L. Kevan, Presiding

- 8:30 162. Plenary Lecture "Contemporary Issues in Field-Swept EPR in some High and Low Symmetry Systems", J. R. Pilbrow, Monash University.
- 9:15 163. "EPR and Chemistry in Single Crystals of Nitrosylhemoglobin", D. C. Doetschman and S. G. Utterback, SUNY at Binghamton.
- 9:35 164. "EPR Study of Fe<sup>2+</sup> and Cr<sup>3+</sup> in Different Forsterite Crystals", J. M. Gaite, Universite d'Orleans, S. S. Hafner and H. Rager, Universitat Marburg, and L. V. Bershov, IGEM, USSR.
- 9:55 BREAK
- 10:30 165. "Superposition-Model Analysis of Gd<sup>3+</sup> Spin Hamiltonian Parameters Doping Rare-earth Trifluoride Single Crystals", S. K. Misra, P. Mikolajczak, and N. R. Lewis, Concordia University.
- 10:55 166. "A 9.3 GHz EPR Study of Dynamical Interactions in Gd<sup>3+</sup>: Eu(OH)<sub>3</sub> Single Crystals at 10-300 K", V. M. Malhotra, W. R. M. Graham, Texas Christian University, and H. A. Buckmaster, the University of Calgary.
- 11:15 167. "An EPR Investigation of Gd<sup>3+</sup> in Single Crystal and Powder Specimens of Y(OH)<sub>3</sub> at 10-300 K", J. M. Boteler, V. M. Malhotra, and W. R. M. Graham, Texas Christian University, and H. A. Buckmaster, The University of Calgary.
- 11:30 169. "EPR Spectroscopy at Zero Magnetic Field", S. J. Strach and R. Bramley, Australian National University.

SYMPOSIUM ON ATOMIC ABSORPTION SPECTROMETRY

WEDNESDAY MORNING, AUGUST 5 - Second Floor, Room D

- 8:30 INTRODUCTION - T. V. Niemczyk, Presiding
- 8:35 217. Keynote Speaker - "Absolute Atomization Efficiency of the Graphite Furnace", R. Sturgeon, National Research Council, Canada, Division of Chemistry.
- 9:15 218. "Graphite Furnace Techniques Using The Zeeman/5000 Atomic Absorption Spectrophotometer", K. W. Olson, Perkin-Elmer Corporation.
- 9:35 219. "Second Surface Atomization: A New Approach to Electrothermal Atomizers", M. Sheehan and J. A. Holcombe, University of Texas.
- 9:55 BREAK
- 10:20 220. "Implications of Radially Non-uniform Absorbance Profiles Within Graphite Furnace Atomizers", G. Rayson and J. A. Holcombe, University of Texas.
- 10:40 221. "Progress Towards Making The Graphite Furnace Free of Interferences", W. Slavin and G. Wallace, The Perkin-Elmer Corp.
- 11:00 222. "Reduction of Analytical Interferences by Furnace Atomic Absorption", R. N. Savage, H. L. Kahn, J. J. Sotera, A. L. Rattionetti, Instrumentation Laboratory, Inc.
- 11:20 223. "The Rapid Determination of Selenium in Nutritional Supplements by a Flameless Atomic Absorption Technique Using A Novel Sample Preparation", D. D. Thompson and R. J. Allen, Forrest C. Shaklee Research Center.

SYMPOSIUM ON ENVIRONMENTAL CHEMISTRY

WEDNESDAY MORNING, AUGUST 5 - Second Floor, Room E

- 8:30 INTRODUCTORY REMARKS - J. E. Bonelli, Presiding
- 8:35 230. "Environmental Chemical Characterization of Water Contaminated by in-situ Synthetic Fuels Technologies", D. J. Bornhop, S. E. Manahan, and D. C. Sheesley, University of Missouri and U.S. Department of Energy.
- 9:00 231. "The Effect of Steam Stripping Treatment on the Quality of Oil Shale Wastewater", R. E. Sievers, M. K. Conditt, and R. S. Hutte, University of Colorado.
- 9:25 232. "The Utilization of Gas Chromatography/Fourier Transform Infrared Spectroscopy (GC/FTIR) to Identify Toxic Environmental Contaminants", D. F. Gurka, P. R. Laska, and R. Titus, and K. Shafer, U.S. Environmental Protection Agency, and Battelle - Columbus Laboratories.
- 9:50 BREAK
- 10:10 233. "The Analysis of Hazardous Waste Extracts by Combined GC/FTIR and GC/MS", D. F. Gurka, A. D. Sauter, L. D. Betowski, and H. Webb, U.S. Environmental Protection Agency.
- 10:35 234. "Environmental Applications of Series PID/FID Detection in Gas Chromatography", G. F. Hewitt and J. N. Driscoll, H-Nu Systems, Inc.
- 11:00 235. "Determination of PCBs, PAHs and Aza-Arenes in Lake Sediment Samples", T. M. Engel and J. S. Warner, Battelle Columbus Laboratories.
- 11:25 236. "Isomer-Specific Determination of 2,3,7,8-Tetrachlorodibenzo-P-Dioxin Via Fused Silica GC Combined with Atmospheric Pressure Ionization Mass Spectrometry", W. A. Korfmacher, R. K. Mitchum and G. F. Moler, National Center for Toxicological Research.

SYMPOSIUM ON NUCLEAR MAGNETIC RESONANCE

WEDNESDAY AFTERNOON, AUGUST 5 - Third Floor, Room F

NMR Session VI - Polymers - F. Miknis, Presiding

- 1:30 72. <sup>13</sup>C NMR Studies at Poly (vinylchloride): New Information on Structural Defects and the Mechanism of Vinyl Chloride Polymerization", W. A. Starnes, Jr., F. C. Schilling, I. M. Plitz, R. E. Cais, F. A. Bovey, G. S. Park, and A. H. Saremi, Bell Laboratories and University of Wales Institute of Science and Technology.
- 2:00 73. "Sequence Distribution in Ethylene-1-Butene Linear Low Density Polyethylenes", E. T. Hsieh and J. C. Randall, Phillips Petroleum Company.
- 2:30 74. "Quantitative Analysis of the Microstructure of Dicyclopentadiene/Cyclopentene Copolymers using 20 MHz <sup>13</sup>C NMR Spectroscopy", D. H. Beebe and R. C. Hirst, Goodyear Tire and Rubber Co.
- 3:00 75. <sup>13</sup>C, <sup>29</sup>Si and <sup>199</sup>Hg NMR of Polymers and Model Systems", E. A. Williams, P. E. Donahue and J. D. Cargioli, General Electric Corporate R&D Company.

WEDNESDAY AFTERNOON, AUGUST 5 - First Floor, Room E-F

NMR Poster Session 1:30 - 5:00

Authors Present 3:30 - 4:30

76. <sup>1</sup>H NMR of Paramagnetic Complexes", M. Luciano, University of Milan, Italy.
77. <sup>27</sup>Al NMR Studies of Concentrate Basic Aluminum Chlorides", 3<sup>rd</sup> Fitzgerald, South Dakota School of Mines.
78. "Hydrogen NMR Spin Diffusion in Epoxy Polymers", A. Lind, McDonnell Douglas Corporation.
79. "Carbon-13 NMR Study of Syn-Anti Isomerism in 2-Phenylimino-1,3 Dioxolanes", 3<sup>rd</sup> E. Over, Mobay Chemical Corporation.
80. "Carbon-13 NMR and Other Spectroscopic Studies of Chemically Modified Silica Surfaces", D. S. Kendall and D. E. Leyden, University of Denver.
81. "Determination of the Relative Concentration of Carbohydrate Groups in Fulvic Acid by <sup>13</sup>C NMR", R. L. Wershaw, C. Steelink, K. Thorn, D. 3. Pinckney, and M. A. Mikita II, U.S. Geological Survey and University of Arizona.
82. "Aqueous Relaxation Reagents for Carbon-13 and Nitrogen-15 Nuclear Magnetic Resonance Spectroscopy", T. 3. Wenzel, M. E. Ashley and R. E. Sievers, University of Colorado.
83. "Silicon-29 NMR Chemical Shifts: Additive Relation in Alkylhalo Silanes", D. Cory, A. Wong, and W. M. Ritchey, Case Western Reserve University.
265. "High Pressure <sup>1</sup>H NMR Investigations of Phase Transitions in Double Propionates", S. Arumugam, S. V. Bhat and R. Srinivasan, Indian Institute of Science, India.



SYMPOSIUM ON ELECTRON PARAMAGNETIC RESONANCE

WEDNESDAY AFTERNOON, AUGUST 5 - First Floor, Room E-F  
EPR SESSION V 1:30-5:00 - S. S. Eaton, Presiding

POSTER SESSION - 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

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| A | 170. "EPR Study of the Binding of CuL' to Cat and Normal Human Hemoglobins", <u>W. E. Antholine</u> and F. Taketa, The Medical College of Wisconsin.   |
| B | 171. "EPR and Quantum Chemistry Studies of Adenosylcobalamin", <u>R. E. Coffman</u> and V. O. Ghanekar, University of Iowa.  |
| C | 172. "A Comparative Study of the Active Sites of Atropinesterase and Other Esterases by using Spin Labeling Techniques", B. A. C. Rousseeuw, <u>E. van der Drift</u> , Technical University of Delft, and A. C. M. van der Drift, T.N.O. Rijswijk. |
| A | 173. "High Resolution ENDOR Studies of Flavin and Flavin Analog Free Radicals", <u>H. Kurreck</u> , M. Bock and W. Lubitz, Freie Universitat Berlin.   |
| B | 174. "ENDOR Investigations of an Organic Quintet State Tetradical", <u>B. Kirste</u> , H. Kurreck, and W. Harrer, Freie Universitat Berlin.  |
| C | 175. "EPR Studies on the Effects of Ethanol on Phospholipid Bilayer Membranes", <u>3. D. Zimbrick</u> and 3. A. McFaul, University of Kansas.  |
| A | 176. "Light-Induced Transients of Spin Label Signal Amplitude in Spinach Thylakoids", <u>S. P. Berg</u> , University of Denver.  |
| B | 177. "Examination of Epoxy Morphology Using Nitroxide Free Radicals", <u>T. C. Sandreczki</u> and I. M. Brown, McDonnell Douglas Research Laboratories.  |
| C | 178. "ENDOR on Biradicals Randomly Oriented in Frozen Solution", <u>H. van Willigen</u> and C. F. Mulks, University of Massachusetts at Boston.  |
| A | 179. "Effect of an Added Electron upon the Viability of a Hydrogen Bond Acceptor: an EPR and NMR Study", <u>G. R. Stevenson</u> and M. Pourian, Illinois State University.   |
| B | 180. "EPR Studies of the Photophysics of Silver Chloride and Silver Bromide", <u>R. S. Eachus</u> and M. T. Olm, Eastman Kodak Co.   |
| C | 181. "CIDEP and Heisenberg Spin Exchange in Two Mixed Radical Systems", <u>3. P. Hornak</u> and R. W. Fessenden, University of Notre Dame.   |
| A | 182. "The Reactions Between DPPH and Surface Active Sites of Metal Oxides - Surface Properties", <u>T. Kawaguchi</u> , S. Hasegawa, and K. Yasuda, Tokyo Gakugei University.   |
| B | 183. "EPR Studies of Surface Mobility", 3. Lopata, W. Timmer, S. Abdo, and R. F. <u>Howe</u> , University of Wisconsin-Milwaukee.  |
| C | 184. "Location and Movement on Dehydration of Cations in Zeolites from Electron Spin Echo Modulation Analysis", <u>M. Narayana</u> and L. Kevan, University of Houston.  |
| A | 185. "Superparamagnetic Effects in the EPR Investigation of a Silica Supported Ni-catalyst", <u>V. K. Sharma</u> , ETH-Zentrum, Zurich.  |
| B | 186. "Spin-Spin Interaction Through Saturated and Unsaturated Linkages", <u>K. M. More</u> , G. R. Eaton, University of Denver, and S. S. Eaton, University of Colorado at Denver.   |

- C 187. "Spin-Labeled Pyridine Adducts of Copper and Vanadyl 0-Diketonates", B. M. Sawant, A. L. W. Shroyer, G. R. Eaton, University of Denver, and S. S. Eaton, University of Colorado at Denver.
- A 188. "Collision Broadening of Nitroxyl Radical EPR Spectra by Transition Metals", G. R. Eaton, D. Reddy, D. Dalai, University of Denver, and S. S. Eaton, University of Colorado at Denver.
- B 189. "Exchange Interactions in tropylium bis 11,2-dicyanoethylenedithiolato] nickelate(III){ C7H7>+ {Ni(mnt>2l- } ", E. de Boer, P. T. Manoharan, 3. H. Noordik, and C. P. Keijzers, University of Nijmegen.
- C 190. "The Electric Quadrupole Moment of Niobium-93", D. Attanasio, C. Bellitto, and A. Flamini, ITSE, Italy.
- A 191. "Superposition Analysis of Zero Field Splittings (ZFS) for Mn<sup>2+</sup>. Results and Applications", M. Heming and G. Lehmann, Institut fur Physikalische Chemie, Munster.
- B 192. "EPR of Binuclear Vanadyl(IV) Complexes", R. E. Tapscott, E. Duesler and R. Ortega, University of New Mexico.
- C 193. "Computer Simulations of Quantum Mixed-Spin and High-Spin EPR Signals of Ferric Heme", T. Lutton and M. M. Maltempo, University of Colorado at Denver.
- A 194. "Generalized EPR Parameter Refinement for S = 5/2 Ions in Low Symmetry Sites", W. C. Tennant, DSIR, Petone.
- B 195. "High Spin Fe<sup>2+</sup> in Low Symmetry Sites: Analysis of Polycrystalline EPR Spectra", W. C. Tennant, DSIR, Petone.
- C 196. "Triplet-State Spin Coherence in Photoexcited Benzil Crystals at 77 K: Optically Detected Transient Nutation and Adiabatic Rapid Passage", R. Gillies and A. M. Ponte Goncalves, Department of Chemistry, Temple University.

#### SYMPOSIUM ON ATOMIC ABSORPTION SPECTROSCOPY

WEDNESDAY AFTERNOON, AUGUST 5 - Second Floor, Room D

3. Holcombe, Presiding

- 1:30 224. "The Determination of Priority Pollutants in Waters and Wastes by Furnace Atomic Absorption", M. A. Cunliffe, D. E. Shrader, Varian Instrument Group.
- 1:50 225. "Determination of Cadmium in Whole Blood and Placental Tissues by Graphite Furnace Atomic Absorption Spectroscopy", P. M. Kuhnert, B. R. Kuhnert, P. Erhard, Prenatal Clinical Research Center, Cleveland Metropolitan General Hospital, Case Western Reserve University.
- 2:10 226. "The Interference of Aluminum on Titanium and Uranium in Flame Atomic Spectrometry", C. B. Boss, North Carolina State University.
- 2:30 BREAK
- 3:00 227. "Chemistry on a Graphite Surface", I-Hsiung Yin and T. M. Niemczyk, University of New Mexico.
- 3:20 228. "Trace Selenium Analysis in New Mexico Waters", M. W. Tikkanen, Health and Environment Department, Scientific Laboratory Division, and L. Brandvold, New Mexico Bureau of Mines and Minerals Resources.
229. "Automated Hydride Determination by Atomic Absorption", 3. 3. Sotera, H. L. Kahn, A. L. Ratttonetti, Instrumentation Laboratory, Inc.

SYMPOSIUM ON ENVIRONMENTAL CHEMISTRY

WEDNESDAY AFTERNOON, AUGUST 5 - Second Floor, Room E

3. E. Bonelli, Presiding

- 1:30 237. "Removal of Metal Ions from Aqueous Solution by Ion Exchange on Sulfuric Acid-Treated Peat", 3. P. Ansted and P. MacCarthy, Colorado School of Mines.
- 1:55 238. "Monitoring Mine Tailings in New Mexico for Trace Metals", M. W. Tikkanen, New Mexico Health and Environment Dept. .
- 2:20 239. "Evaluation of Sample Preparation Procedures for the Analysis of POTW Sludges for Be, Cd, Cr, Cu, Pb, Ni, Ag, and Zn", M. Williams, L. Petrie, 3. Frank, 3. Hurt, B. 3ones, S. Swanson, and E. Hansen, Midwest Research Institute.
- 2:\*5 BREAK
- 3:05 2\*0. "Effects of Street Salting on Ambient Air Monitoring of Particulate Pollutants in Detroit", P. O. Warner, 3. O. Kermoshchuk, and 3. O. Jackson, Wayne County, Michigan Health Dept., and Los Alamos Scientific Laboratory.
- 3:30 241. "Acceptance Testing Criteria and Procedures for Hi-Volume Filters Used in Monitoring Networks", C. F. Turlington, Northrop Services, Inc.
- 3:55 2\*2. "Analysis of Toxic Organic Compounds in Ambient Air by Gas Chromatography/Mass Spectrometry", D. E. Smith, W. C. Schnute, Finnigan Corporation.
- \*:20 2\*3. "Optical Design of U.V. Second Derivative Environmental Gas Analyzers", D. E. Osten, Lear Siegler Inc.

SYMPOSIUM ON ION CHROMATOGRAPHY

WEDNESDAY AFTERNOON, AUGUST 6 - Second Floor, Room F

3. D. Mulik, Presiding

- 1:30 INTRODUCTION OF SESSION CHAIRMAN - A. W. Fitchett
- 1:35 29. "ICE Analysis of Adipic Acid Degradation Products in Limestone FGD Scrubber Solutions", 3. C. Terry, E. E. Ellsworth, and D. L. Utley, Radian Corp.
- 2:00 30. "Ion Chromatographic Analysis of Formaldehyde: An Evaluation of Proprietary Solid Adsorber Sampling Tubes Under Laboratory and Field Conditions", C. 3. Jackson and D. Bussan Health and Safety Executive, London.
- 2:25 31. "The Determination of Acids in Coffee by Ion Chromatography (IC) and Ion Chromatography with Exclusion (ICE)", L. D. Davis and A. K. Foltz, General Foods.
- 2:50 BREAK
- 3:15 32. "Practical Experience on the Use of Coupled ICE/IC Systems for the Determination of Anions in Hazardous Waste Samples", 3. H. Lowry, R. C. Ross and K. Wang, U.S. Environmental Protection Agency.
- 3:\*0 33. "Care and Feeding of IC Columns", E. L. Johnson, Dionex Corp.
- \*:05 3\*. "A Rapid Method for the Ion Chromatographic Determination of Fluorine, Chlorine, and Sulfur", C. B. Moore, K. L. Evans, and 3. G. Tarter, Arizona State University.
- \*:30 35. "Analysis of Mount St. Helens Samples Using Ion Chromatography", S. A. Wilson, C. A. Gent, and T. K. Hinkley, U.S. Geological Survey.

SYMPOSIUM ON NUCLEAR MAGNETIC RESONANCE

THURSDAY MORNING, AUGUST 6 - Third Floor, Room F  
NMR Session VII - Fossil Fuels - N. Szeverenyi, Presiding

- 8:30 84. "Solid State  $^{13}\text{C}$  NMR Studies of Coalified Logs and Sapropelic Coals", P. Hatcher, L. W. Dennis, N. A. Szeverenyi, and G. E. Maciel, U.S. Geological Survey and Colorado State University.
- 9:00 85. "Characterization of Carbon Deposits in Coal Conversion Catalysts", H. R. Retcofsky, S. S. Pollack, and G. E. Maciel, Pittsburgh Energy Technical Center and Colorado State University.
- 9:30 86. "Quantitative Aspects of  $^{13}\text{C}$  CPMAS Spectroscopy in Coals: Relaxation Effects and Experimental Requirements", 3. Lee and K. Zilm, University of Utah.
- 10:00 BREAK
- 10:30 87. "Spin Dynamics and CP/MAS Experiments on Fossil Fuels", G. E. Maciel, M. Sullivan and N. A. Szeverenyi, Colorado State University.
- 11:00 88. "High Resolution NMR and Selective Derivatization of Solid Fossil Fuels", K. D. Rose and M. 3- Melchior, Exxon Research and Engineering Company.
- 11:30 89. "An NMR Investigation of Eastern and Western Shale Oils", D. A. Netzel and F. P. Miknis, Laramie Energy Technical Center.

SYMPOSIUM ON ELECTRON PARAMAGNETIC RESONANCE

THURSDAY MORNING, AUGUST 6 - Third Floor, Room E  
EPR SESSION VI - M. Eastman, Presiding

- 8:30 197. Plenary Lecture "Measurement of Electron and Nuclear Spin Lattice Relaxation Times by Magic Angle Spin Locking", 3. M. McNally and R. Kreilick, University of Rochester.
- 9:15 198. "Digitally Controlled ENDOR Spectrometer", R. B. Clarkson, Varian Associates.
- 9:35 199. "ENDOR Detected NMR (EDNMR) Studies in Single Crystals", A. Reuveni and A. L. Kwiram, University of Washington.
- 9:55 BREAK
- 10:30 200. "Pulsed EPR of Electron Dynamics in Organic Conductors", L. Dalton, SUNY at Stony Brook.
- 11:00 201. "Application of Combined Fourier Transform and Time Domain Simulation of Electron Spin Echo Modulation Data to Ion Solvation Geometry", P. A-Narayana and L. Kevan, University of Houston.

SYMPOSIUM ON ENVIRONMENTAL CHEMISTRY

THURSDAY MORNING, AUGUST 6 - Second Floor, Room E  
3. E. Bonelli, Presiding

- 8:35 2\*\*. "Vapor Pressure Measurements of Toxic and Carcinogenic Materials of Interest in Industrial Hygiene", D. C. Sterling and G. M. Breuer, National Institute for Occupational Safety and Health.
- 9:00 245. "Dosimetry in the Workplace", 3. K. Samuels, Republic Steel Corporation.

- 9:25 2hb. "Improved Measurement Techniques for Asbestos Fibres in Workplace Atmospheres", J. C. Meranger and E. J. Chatfield, National Health and Welfare-Canada, and Ontario Research Foundation.
- 9:50 BREAK
- 10:10 2\*7. "Measurement of Airborne Glass Fibres in Residences Due to Insulating Materials", J. C. Meranger and E. J. Chatfield, National Health and Welfare-Canada, and Ontario Research Foundation.
- 10:35 2\*8. "Three-Dimensional Fluorescent Spectra of Humic Acids", M. C. Goldberg, E. R. Weiner, and R. L. Wershaw, U.S. Geological Survey.
- 11:00 2\*9. "An Automated Procedure for Simultaneously Determining Total Cyanide and Thiocyanate in Industrial Wastewaters", J. H. Lowry, T. J. Meszaros, and R. C. Ross, U.S. Environmental Protection Agency.
- 11:25 250. "Determination of Total Nitrogen in Water by Pyrolysis and Chemiluminescence Detection", C. E. Arozarena and V. C. Marti, U.S. Geological Survey.

#### SYMPOSIUM ON ION CHROMATOGRAPHY

THURSDAY MORNING, AUGUST 6 - Second Floor, Room F,  
J. D. Mulik, Presiding

- 8:30 36. "Determination of Spark-Induced By-Products of Sulfur Hexafluoride", J. M. Keller, Oak Ridge National Labs.
- 8:55 37. "Determination of Sulfate in Brine", J. P. Price, N. W. Stacy, and J. R. Hawkins, American Enka Company.
- 9:20 38. "Automated Coupled Liquid Chromatography/Ion Chromatography", T. L. Craven, Monsanto Chemical Intermediates Company.
- 9:45 39. "Determination and Identification of Sulfite in Some Pharmaceutical Compositions Using Ion Chromatography", J. Lindberg, Pharmacia AB, Sweden.
- 10:10 BREAK
- 10:25 40. "The Analysis of Barium Sulfate by Ion Chromatography", R. D. Posner, United States Testing Company, Inc.
- 10:50 11. "Inorganic Anion and Cation Chromatography Applied to Steam Generator Circuit Chemistry Studies", J. T. Brunet, A. Heres, and C. Poletiko, C.E.A.-C.E.N., France.
- 11:15 02. "Some Applications of Ion Chromatography to Oil Well Cement Research and Analysis", W. J. Caveny and J. D. Childs, Halliburton Services.
- 11:W) i\*3. "New Eluents for Non-Suppressed Ion Chromatography", J. Girard and J. A. Glatz, American University.

1 SULFATE ASSAY IN BIOLOGICAL FLUIDS BY ION CHROMATOGRAPHY. D.E.C. Cole and C.R. Scriver. Montreal Children's Hospital Research Institute and McGill University Montreal, Quebec, Canada H3H 1P3.

Traditional methods for inorganic sulfate determination in biological fluids have been based on the relative insolubility of barium or benzidine sulfate salts. These methods suffer from limitations of sensitivity and interference from other physiological constituents, notably organic sulfoesters. Ion chromatography (D-10<sup>+</sup>, Dionex Corp.), measures sulfate accurately in urine, serum or plasma, cerebrospinal fluid, and hepatic tissue extracts. Samples containing 6-60 nmol sulfate, diluted to 1.5 ml in 1 mM NaOH, are chromatographed and quantitated by comparing peak conductances with a series of standards. We saw no interference from other anions in serum (bromide, nitrate, malate, succinate, phosphate, urate, oxalate, chloride) or from organic sulfoesters such as chondroitin sulfate, heparin or steroid sulfates. Ion chromatography of serum sulfate gave values that were 101±4% (x±SEM, n=22) of those determined by our barium-133 precipitation method (Anal. Biochem. 100: 339, 1979) (correlation coefficient 0.87 {p<.001}). The coefficient of variance for the chromatographic method was less than half that of the barium method (3.4% vs 7.6%). The average recovery of sulfate added to CSF, serum and tissue extracts was 101±3% and was complete at all physiological ranges. Tailing was occasionally seen in serum samples and very frequently in tissue extracts; this did not affect sulfate quantitation by peak height. We conclude that ion chromatography is a useful and accurate method for sulfate assay in biological fluids.

2

ION CHROMATOGRAPHIC DETERMINATION OF NONMETALLIC ELEMENTS IN GEOLOGICAL MATERIALS. Jon M. Baldwin and Paul R. Kloek, U.S. Geological Survey, 345 Midalefiela Road, Menlo Park, California 94025; and Christopher Pohl, Dionex Corporation, R&D Department, 1228 Titan Way, Sunnyvale, California 94086.

Among species of geochemical interest, some of the most challenging analytical problems arise in attempting the accurate determination of nonmetallic elements in rocks and minerals. The challenges arise from several quarters: 1) The samples themselves are complex in composition, often leading to serious matrix problems. 2) Sample dissolution is often achieved only by rigorous means, leading to further complication of the matrix. 3) The species of interest often are present in the solid sample at low concentrations and are further diluted during sample preparation, making extreme demands for analytical sensitivity. 4) Multielement techniques for nonmetals are typically nonexistent. 5) Existing wet chemical techniques are generally time-consuming. We have found a viable approach to this problem in a combination of fusion, particularly with lithium metaborate flux, dissolution of the melt in dilute nitric acid, followed by ion chromatography of the resulting anions. Judicious choice of elution conditions, combined with a separator resin specifically formulated to strongly retain nitrate are important to the success of the analysis. Chloride, fluoride, phosphate, and sulfate are readily determined in a single preparation of a rock sample.

ANION ANALYSIS BY ION CHROMATOGRAPHY AT THE NATIONAL BUREAU OF STANDARDS. W. F. Koch, Center for Analytical Chemistry, National Bureau of Standards, Washington, DC 20234.

In the Center for Analytical Chemistry, National Bureau of Standards, ion chromatography is being used extensively for the quantitative determination of inorganic anionic species in a myriad of matrices and samples. The type samples analyzed to date include such diversity as fuel oil, bovine liver, rainwater, and cadmium sulfide. Sample preparation procedures must often be custom-tailored for each sample type to meet the strict requirements of ion chromatography and to take full advantage of its capability for multi-anion analysis. Digestion with sodium alcoholate and dissolution with alkaline hydrogen peroxide are two such techniques. Unique pre-treatment schemes must sometimes be devised to remove interferences. For the highest accuracy, standards prepared from coulometrically assayed stock solutions are used and strict calibration procedures employed. Matrix effects and systematic errors, often quite subtle, must be recognized and compensated for. With sufficient care, analyses with uncertainties of less than one percent relative can be achieved.

Analysis of Boron by Ion Chromatography in Power Production. M.G. Hahnke and J. M. Gray. Arizona Public Service, Four Corners Power Plant, Fruitland, New Mexico 87416

The analysis of selected anions and cations in power production has become increasingly important due to the effect that these species have on the production of electrical energy. At Arizona Public Service, the problem of boron in our boiler feed water has become a concern because of the increased buffer capacity of the feed water and the potential corrosion and pitting due to steam carryover of boric acid. A specific problem found at our Four Corners Power Plant is the presence of both simple and polymeric species of boron found in our water. Since a fast and sensitive analytical procedure for the detection of boron is needed, ion chromatography was chosen for this determination.

The various boron species are first converted to borates and then to tetrafluoroborates. Refining earlier techniques and operating procedures such as eluent concentration and instrumentation sensitivities has produced detection limits down to 0.02 mg/l. Variations in the types of sample preparation for the conversion of the forms of boron to tetrafluoroborates will be discussed along with the interferences observed at different operating conditions.

-> **IMPACT OF ION CHROMATOGRAPHY ON THE WATER TREATMENT INDUSTRY.** Judith A. Rawa. Calgon Corporation, Subsidiary of Merck & Co., Inc., P.O. Box 1346, Pittsburgh, Pennsylvania 15230.

The introduction of ion chromatography (IC) in 1975 and its subsequent commercialization in 1976 has had a significant impact on the water treatment business and the industries they serve. Water conditioning, control of water chemistry through various industrial process water systems, is critical in maintaining efficient production levels, in manufacturing high quality finished products and preventing costly equipment failures. Ion chromatography provides analysis of several anions or cations at the mg/l (ppm) or ug/l (ppb) level on a single aliquot of sample. This feature provides an improved method of characterizing untreated waters and those which are mechanically and/or chemically treated for industrial use.

The power generation industry has been one of the first to realize the benefits afforded by the improved detectability of ions at the ug/l (ppb) level. Various contaminants even when present at ug/l (ppb) levels may have deleterious effects, scale and corrosion, in the steam/water cycle. Identification of these contaminants increases the probability of locating the source and eliminating the problem. Turbine failures, such as stress corrosion cracking of blading, have been linked to impurities in the steam. As a result, turbine manufacturers have set stringent standards for steam purity. The burden of maintaining these standards falls on the user. Ion chromatography has become an essential tool for determining contaminants in the steam/water cycle.

The IC technique has proven to be applicable to the analysis of water and steam samples as well as water-soluble fractions of deposits. Data is being collected throughout the industry to attempt to correlate specific equipment failures using this technique.

Ion chromatographic analysis of various types of industrial process waters and water treatment chemicals will be discussed.

**6 ION CHROMATOGRAPHY IN THE MICROELECTRONICS INDUSTRY.** David R. Anderson and Steven A. Shear, International Business Machines Corporation, P.O. Box 390, Poughkeepsie, New York 12602

The presence of undesirable ionic species in microelectronic devices and packages is a serious concern to the integrated circuits industry. In addition to the common problem of metallurgical corrosion, ionic contamination generally has deleterious effects on the electrical performance and overall reliability of microelectronic components. The recently developed method of ion chromatography, owing to its remarkably better sensitivity and selectivity, has proven to be a very powerful tool for the analysis of ionics in these components. This paper describes a number of sample preparation techniques, extraction methods, and ion chromatograph conditions useful for the analysis of various materials encountered in the microelectronics industry. Application of ion chromatography to the analysis of ionics in device encapsulants, printed circuit board materials, organic thin films, surface contaminants and process waters, and to the determination of changes in ionic content due to environmental stressing, are also described. In general, ion chromatography has provided a much more precise quantitation and more detailed speciation of ionics than was previously possible in the industry.

7 DEVELOPMENT OF HIGH SPEED ION CHROMATOGRAPHY. J. Slanina and F.P. Bakker.  
Netherlands Energy Research Foundation (ECN), Petten (N.H.), The Netherlands.

High speed Ion Chromatography is possible if the following adaptations are made.  
- Thermostating (at  $\sim 40^\circ\text{C}$ ) of columns  
- Minimizing void volume by the use of very small suppressor columns and minimal tubing.  
A modified Dionex model 10 can perform 12 analyses per hour, a specially designed apparatus up to 18.

Accurate results are obtained in the case of simple samples such as rain-water. Complex matrices can be analyzed if multiple detector systems such as a UV monitor at 220 nm (for  $\text{NO}_3^-$  and  $\text{NO}_2^-$ ), flow injection systems (for  $\text{Cl}^-$  and  $\text{Br}^-$ ) and ion-selective electrodes (for  $\text{F}^-$  and  $\text{Cl}^-$ ) are used.

For samples containing more than 0.5 ppm of the ions of interest a sample loop is used. The accuracy is typically 2 - 5 %

A concentrator column is employed for sample volumes of up to 4 ml, resulting in detection limits of 1 to 6 ppb for  $\text{Br}^-$ ,  $\text{Cl}^-$ ,  $\text{NO}_3^-$  and  $\text{SO}_4^{2-}$ .

The computerized system is capable of analyzing large series of samples by means of an automatic recalibration procedure.

**IDENTIFICATION OF EXPLOSIVES AND EXPLOSIVE RESIDUES BY ION CHROMATOGRAPHY. D. J. Reutter, R. C. Buechele, T. L. Rudolph, and E. C. Bender. Federal Bureau of Investigation, Laboratory, 9th A Pennsylvania Avenue, N. W., Washington, D. C. 20535**

Explosives with water soluble constituents were involved in approximately 60% of the bombing incidents in the United States during the last year. These explosives include such high explosives as dynamites and watergels as well as low explosives such as black powder and a variety of commercial and homemade pyrotechnics. Ion chromatography has been demonstrated in the FBI Laboratory as a valuable technique to aid in the analysis of these explosives and their combustion and detonation residues.

The ability of the I.C. to both identify and quantitate several ions in a single run offers an excellent way to differentiate between homemade and commercial explosive formulations. Also, the inherent sensitivity and specificity of I. C. can be used to aid in the detection and identification of very small quantities of explosive residues in comparably high amounts of water soluble bombing debris. From the identity of the residues recovered from the scene of a bombing, the forensic examiner can then characterize the nature of the original explosive used in the bomb.

ANALYSIS OF BORON BY ION CHROMATOGRAPHIC EXCLUSION. J. P. Wilshire. U.S. Borax Research Corporation, U12 Crescent Way, Anaheim, California 92801.

Using ion chromatographic exclusion (ICE) techniques, and a mannitol-HCl eluent, borate analyses can be performed directly, without prior conversion to the tetrafluoroborate or any other anion. Instead, a 1:2 borate-mannitol complex is formed upon injection, in the ion chromatography. With a  $\text{pK}_a=5.1$ , the species is easily detectable by conductivity. Under standard ICE conditions, the peak due to the borate-mannitol complex is observed after approximately 11 minutes, with an estimated minimum detection limit of 0.050 ppm, as boron. The technique has been employed successfully in the analysis of a wide variety of samples: blood, urine, geological materials, and commercial products, e.g., borax, boric acid and ammonium pentaborate. The principal advantages of the method are its simplicity, accuracy, and reproducibility, and its wide range of application, from trace (ppb) analysis to the determination of large (percent) concentrations. The technique, its applications and a comparison with other methods of boron analysis will be discussed.



ANALYSIS OF FLUORIDE IN NYLON. J. P. Price, N. W. Stacy, and J. R. Hawkins  
Research Department, American Erika Co., Enka, NC 23728

In order to meet market demands for greater serviceability, various additives may be incorporated into synthetic fibers which make them more desirable to the consumer. One such area where a contribution toward meeting this goal is to incorporate a fluorochemical into nylon carpet yarn which will increase water and soil repellency.

Ion Chromatography has good sensitivity for the fluoride ion and does afford a quick and accurate method for the quantitation of the levels of fluorocarbon in the fiber. Using the classical SchBniger Oxygen Combustion Technique, up to 80 milligrams of nylon can be burned and the fluoride ion absorbed in water. After a suitable standing period the sample is injected into the ion chromatograph.

Data will be presented to demonstrate the precision of the analysis, sources of error and results of efforts to reduce fluoride levels in blanks.

11 OXALATE QUANTITATION BY ION CHROMATOGRAPHY: CLINICAL APPLICATIONS C. Mahle and M. Menon. Division of Urology, Dept. of Surgery, Washington University School of Medicine, 4960 Audubon Ave., St. Louis, MO 63110.

Fast, sensitive and reliable measurements of oxalates are possible by using a modified technique of the Dionex ion chromatography system. Two 3 x 500 mm standard anion separator columns were connected in series and operated at 20% flow rate and 500 psi pressure using 6mM Na<sup>+</sup>CO<sup>3</sup> eluent. Conductive measurements at 3 - 100 v: mhos full scale revealed a distinct oxalic acid peak following sulfuric acid when .5ml samples of a Na<sup>+</sup>oxalate and Na<sup>+</sup>SO<sup>4</sup> solution were chromatographed. Na-oxalate is detectable down to 0.5 ppm and is linear with peak height up to 50 ppm. The peak was proved to be oxalate by two criteria: 1) addition of Na<sup>+</sup> C-oxalate and quantitation of C activity in collected fractions of eluent passing out of the conductivity cell, and 2) elimination of the oxalate peak after pre-treatment with the enzyme oxalate decarboxylase which specifically cleaves oxalate into formate. This technique was applied to analysis of oxalate in whole urine and found to be faster and requiring less sample preparation than other methods of oxalate analysis. A chromatograph of .5ml of 1:10 diluted urine results in a series of peaks that correspond to Cl<sup>-</sup>, HPO<sup>4</sup> and uric acid followed at 24 minutes by oxalic acid. Day to day imprecision over 21 days of a single urine sample was 4.4 with-in run imprecision was 2.3%, and minimal detection level is 1.0 ppm.

MOBILE PHASE ION CHROMATOGRAPHY (MPIC) C. A. Pohl, M. Ebenhahn  
Dionex Corp., Research and Development Department, 1228 Titan Way,  
Sunnyvale, CA. 94086.

Mobile Phase Ion Chromatography (MPIC) is a new Ion Chromatographic technique which compliments conventional Ion Chromatography. The separation of ions in MPIC is achieved through the use of a carbon based macroporous column in conjunction with specially prepared reagents. The MPIC column is combined in series with a high capacity ion-exchange column (suppressor column) which removes the reagent from the eluent. Following the suppressor column, the sample ions are detected by means of a conductivity detector. While MPIC can be used for the analysis of inorganic ions such as fluoride, chloride, phosphate, bromide, nitrate, nitrite, sulfate, sodium, potassium, ammonia, lithium it is also well suited to the analysis of hydrophobic ions such as perchlorate, tetrafluoroborate, and thiocyanate. MPIC is also useful for the analysis of organic ions such as amines, quaternary ammonium compounds, and anionic surfactants.

<sup>10</sup> ION CHROMATOGRAPHIC ANALYSIS OF GASEOUS AND PARTICULATE FLUORIDE EMISSIONS FROM BRICKWORKS AND ALUMINIUM SMELTERS. C. J. Jackson. D. Bussan, C. Neuberger. Health and Safety Executive, Occupational Hygiene Laboratory, 403 Edgware Road, LONDON NW2 6LN, United Kingdom.

In the United Kingdom, sampling and analysis of gaseous and particulate fluoride emissions from factory stacks is undertaken by the Health and Safety Executive to enable environmental standards to be enforced. From such processes as brickworks and primary aluminium smelters these emissions are dry and include both gaseous (HF, SiF<sub>4</sub>, H<sup>+</sup>SiF<sup>-</sup>) and particulate (AlF<sub>3</sub> hydrate, CaF<sup>+</sup>) fluorides. For many years HSE have used an Ion Selective Electrode (ISE) analysis procedure but to gain the cost benefits of automation there is now considerable pressure to change over to Ion Chromatographic (IC) analysis where possible. Preliminary investigations indicated that IC would be an ideal technique for the determination of fluoride but that it would not be possible to directly use the sampling and sample preparation procedures currently in use since this led to peak overlaps, both from the humectant (glycerol) used in the alkali-trapping of gaseous fluorides and from the HCl used in the dissolution of particulate fluorides. Revision of the sampling, sample preparation and chromatographic procedures to enable IC to be successfully used is described and statistical data from a field comparison of the ISE and IC procedures presented. The cost-benefits of automated IC will be briefly discussed.

<sup>11</sup> TEMPERATURE EFFECTS IN ION CHROMATOGRAPHY. D.R. Baker. Hewlett-Packard, Rt. 41, Avondale, PA 19311. C.A. Burgett. Hewlett-Packard, 24 Inverness Place, Englewood, CO 80112.

A conductivity detector and an ion chromatography column were used with a high performance liquid chromatograph to measure concentrations of anions. Excellent temperature control of the detector cell and column was achieved by placing them in the heated column compartment of the liquid chromatograph. The effect of oven temperature on retention times, peak areas, peak heights and quantitation was examined.

15 FURTHER WORK IN THE USE OF ION CHROMATOGRAPHY AS A PROBLEM-SOLVING TOOL FOR ELECTRONIC COMPONENTS AND EQUIPMENT. L. A. Psota. Bell Laboratories, Crawfords Corner Road, Holmdel, N.J. 07733.

In our continuing efforts to analyze the sources of corrosion and contamination of Bell System equipment, ion chromatography has proven to be a useful tool. The contaminants studied come from a variety of sources: 1) field problems caused by unusual circumstances, such as floods through roof leaks and pipe ruptures, 2) manufacturing problems, 3) atmospheric interactions. We also analyze samples collected from surfaces in telephone company central offices, using a wet filter paper technique, to determine the effects of indoor atmospheres on equipment. In many cases, samples are analyzed using an automated setup, including a sample changer and a computing integrator along with the ion chromatograph. Throughput has been increased by this method, though some disadvantages have been noted and in some cases the "direct-inject" method remains preferable. The sample handling procedures that have been developed are discussed and the analytical results of several studies are interpreted.

<sup>14</sup> AUTOMATION OF AN ION CHROMATOGRAPH FOR PRECIPITATION ANALYSIS WITH COMPUTERIZED DATA REDUCTION. Arthur Hedley and Marvin Fishman. U.S Geological Survey, Water Resources Division, P.O. Box 250\*6, Denver Federal Center, Mail Stop »07, Denver, Colorado 80225

Interconnection of an ion chromatograph, autosampler, and computing integrator to form an analytical system for the simultaneous determination of fluoride, chloride, orthophosphate, bromide, nitrate, and sulfate in precipitation samples is described. Computer programs associated with the integrator are modified for use in ion chromatographic data reduction and data storage. The liquid flow scheme for the ion chromatograph is changed by addition of a second suppressor column to enable greater sample throughput. An additional valve enables selection of either suppressor column for analysis while the other is regenerated and stabilized with concentrated

eluent. Minimum levels of detection and sensitivities for each anion are calculated. These levels are a function of suppressor exhaustion. Precision for replicate analyses of five precipitation samples for fluoride, chloride, phosphate, nitrate, and sulfate varied from 0.005 to 0.025 mg/L. To determine accuracy of results, the same samples were spiked with known levels of the above mentioned anions. Average recovery was 108 percent.

17 DETERMINATION OF HYDROGEN CYANIDE IN ENVIRONMENTAL SAMPLES BY ION CHROMATOGRAPHY. Theodore W. Dolzine, George G. Esposito, and Rosemary J. Gaffney. US Army Environmental Hygiene Agency, Aberdeen Proving Ground) MD 21010.

A new method for the collection and analysis of hydrogen cyanide in the industrial atmosphere is reported. Known concentrations of hydrogen cyanide were generated in a static chamber and collected by pumping the sample through an aqueous sodium hydroxide impinger. Hydrogen cyanide is entrained in the impinger and is irreversibly converted to sodium formate and ammonia when heated in an oven overnight. The analysis was performed using ion chromatography. Three different chromatographic methods were investigated.

The collection, reaction conditions and analytical methods are presented. Recoveries of 103 ± 5% were obtained from spiked laboratory samples over the concentration range investigated. The overall precision and accuracy of the collection and analytical method were tested by sampling known concentrations of hydrogen cyanide. Interferences and the use of ion exchange resins for sample clean-up were also investigated.

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A NOVEL SUPPRESSION MEANS FOR ION CHROMATOGRAPHY, Timothy S. Stevens, James C. Davis, and Hamish Small. Dow Chemical, USA, Midland, MI 48640

Conventional Ion Chromatography benefits by the use of a suppressor column because the separated anions are converted to highly responsive acids while the eluent electrolyte, usually carbonate, is removed or converted to a feebly conducting moiety such as carbonic acid. However, the use of a suppressor column also results in complications. These complications include the need to periodically replace or regenerate the stripper column, varying elution time of weak acid anions, due to ion-exclusion effects in the unexhausted portion of the suppressor column, apparent reaction of some ions such as nitrite with the unexhausted portion of the suppressor column resulting in varying response depending on the percent exhaustion of the suppressor column, and interference from the varying elution time of a characteristic baseline upset, known as the carbonate dip. We have discovered that the use of continuously regenerated ion-exchange hollow fibers in a suppressor device eliminates the above complications.

This paper will describe the characteristics and fabrication of hollow fiber suppressors and present data comparing this new approach with the conventional resin bed suppressor.

19 SINGLE COLUMN ION CHROMATOGRAPHY FOR THE DETERMINATION OF PPB LEVELS OF CHLORIDE AND SULFATE IN CONDENSATE WATER. James S. Fritz and Douglas T. Gjerde. Ames Laboratory and Department of Chemistry, Iowa State University, Ames, Iowa 50011. Kim M. Roberts. AECI Ltd, North Rand, Transvaal, Republic of South Africa.

An effective analytical method is described for the determination of ppb concentrations of chloride and sulfate in very pure water such as steam condensate. Sample anions are concentrated from 10-50 ml samples on a short precolumn column. The precolumn is then placed in an eluent stream and the sample ions are eluted onto a separator column. The eluent and separator columns are chosen so that no "suppressor" column is needed (1-2). The separated ions are detected directly with an electrical conductivity detector. Chloride and sulfate can be determined at concentrations as low as 1-2 ppb in water samples. Design and use of the precolumn and the sample preparation is discussed. Several real water samples have been analyzed successfully by the new procedure. The chromatographic system can be run indefinitely with no "down" time. This makes the method attractive for on-line analysis.

1. Gjerde, D. T.; Fritz, J. S.; Schmuckler, G. J. Chromatogr. 1979, 186, 509.
2. Gjerde, D. T.; Schmuckler, G.; Fritz, J. S. J. Chromatogr. 1980, 186, 35.

\*° HIGH PERFORMANCE ION CHROMATOGRAPHY (HPIC) C. A. Pohl, A. Woodruff  
Dionex Corp., Research and Development Department, ±"228 Titan Way,  
Sunnyvale, CA. 94086.

Ion-Exchange chromatography is a highly selective form of liquid chromatography. Because of this high selectivity Ion Chromatography has been performed primarily on moderate efficiency pellicular ion-exchange resins. However, the increasing demand for high throughput analyses in Ion Chromatography have necessitated the development of high performance Ion Chromatography (HPIC) resins. To meet this need, we have developed a new class of high performance micropellicular ion-exchange resins. These resins exhibit the high efficiencies of silica based microparticulate ion-exchange materials while retaining the excellent chemical stability and low capacity of conventional pellicular ion-exchange materials. Use of the new HPIC resins for high throughput Ion Chromatography analyses will be shown.

21 SOME APPLICATIONS OF IC AND ICE IN THE PHARMACEUTICAL INDUSTRY. J. Lindberg.  
Pharmacia AB, Analytical Research, Box 181, S-751 OA Uppsala, Sweden.

Ion Chromatography has successfully been used for three years to solve problems in the following fields.

1. Analysis of pharmaceutical compositions, mainly infusion solutions.
2. Mapping of production processes.
3. Trouble shooting.

The lecture will give a survey of the merits and drawbacks of ion chromatography in the IC- and ICE-mode.

Some applications have been chosen, each illustrating a certain feature of the IC-technique.

1. Determination of F in an infusion solution, comparison with a fluoride ion selective electrode. (The general problem is: very unequal concentrations of two ions with similar retention times.)
2. Determination of SO<sub>4</sub><sup>2-</sup> in substituted polyglucose, comparison with an LH 20 column. (A number of substances exist, which will poison the separator column, particularly polyanions.)
3. Determination of weak acid anions with ICE eg acetate in routine analysis. (Evaluation of the ICE-mode)
4. Determination of borate with ICE columns. (Weak acids cannot be determined by IC. If pKa can be changed, a determination is possible.)
5. Comparison of IC and official methods notably from different pharmacopeias.

ION CHROMATOGRAPHIC ANALYSIS OF ANIMAL FEEDS. Alexander MacDonald, Robert Saperstein, Franz Scheidl, Edythe Hargroves and Arthur Love. Hoffmann-La Roche Inc., Chemical Research Division, Nutley, NJ 07110.

Ion Chromatography has been utilized to determine minimum available concentrations of ionic components in finished feeds and feed components. A simple water extraction is used and the filtered extract used directly for the assay of anions and cations. Applicable cation concentrations were validated with Atomic Absorption Spectrometry and the anions such as chlorides via micro-titration. Minimum available concentrations of these ions are useful to know, since their absorption would not be dependent on the digestive process. Percent available ions for a wide variety of feeds and feed ingredients have been determined.

23 COMPUTERIZED AQUISITION AND REDUCTION OF ION CHROMATOGRAPHIC DATA. C. C. Torquato.  
N. Latner and D. C. Bogen. Environmental Measurements Laboratory, U. S. Department of Energy, 376 Hudson St., New York, NY 10014.

A Dionex Model 10 Ion Chromatograph has been interfaced with Commodore PET micro-processor, dual drive floppy disk and tractor printer units. A program, written in the BASIC computer language, has been developed which enables the operator to acquire, reduce and store ion chromatographic data. The program's data reduction capability includes the determination of integral and average voltage readings for specified time intervals and data scanning for maximum peak height and retention time values. Chroma to grams can be

displayed on the video display unit. The acquired data is stored on mini-floppy disks. Copies of both chromatograms and data can be obtained from the printer. In this paper peak height and retention time data obtained from the microprocessor will be compared with data obtained from a strip chart recorder.

24 LOW LEVEL BROMIDE DETERMINATION IN DRINKING WATERS BY ION CHROMATOGRAPHY

A. Eaton, D. Pietz, A. Trussell, and L. Leong. James M. Montgomery  
Environmental Research Lab, 555 E. Walnut St. Pasadena, CA 91101

Bromide levels are of direct concern for drinking waters because of the role Br may play in trihalomethane formation (eg. Bromoform) which is regulated at 100 ug/l total THM. Traditional colorimetric methods of analysis have insufficient sensitivity for most drinking waters (DL=100ug/l). We have developed a method for routinely quantifying bromide in natural waters down to levels of 10 ug/l (DL=3ug/l) using ion-chromatography coupled with cadmium reduction of nitrate to remove this interference. The method is rapid (12 minutes/sample), accurate (recoveries of 97% at the 50ug/l level), and precise (4% at 25 ug/l). It is being applied routinely to samples from a number of sources and we are currently examining the role of Br in THM formation using this method along with GC analysis of individual THM's. We will describe the method and present results of our investigations.

25 THE REMOVAL OF IRON INTERFERENCES IN IC ANALYSES BY COMPLEXATION. Nancy S. Simon.  
F.T.S. Geological Purvey, National Center, Vail Stop 472, Weston, Virginia 22092.

The working pH range is 9 to 10.5 for the anion separator system in the Dionex IC ion chromatography instrument. At this hydrogen ion concentration, dissolved iron forms hydroxide precipitates. To analyze riverine pore-water samples, which contain from 0.02 to 2 mmol/l (1 to 112 mg/l) total iron, a procedure for complexing the dissolved iron has been developed. Cyanide is the choice as the complexing agent because it has both a high pK<sub>a</sub> and a low affinity for the anion resin. Sodium cyanide is added to pore-water samples to produce a final concentration of 5 mmol CN<sup>-</sup>/l. The ferro- or ferricyanide complex requires six cyanide ions per one ferrous or ferric ion. The ratio of cyanide to iron in samples with the highest iron concentrations is more than 12 to 1. Inflections in the sample chromatogram occur as a result of the addition of the cyanide complexer.

i/ The use of brand names in this report is for identification purposes only and does not imply endorsement by the U.S. Geological Survey.

26 APPLICATIONS OF SIMULTANEOUS DETECTION IN IC. E.L. Johnson and C. J. Threlkeld.  
Dionex Corporation, 1228 Titan Way, Sunnyvale, California 94086. R. Williams,  
Allied Chemical, P.O. Box 1021 R, Morristown, NJ 07960.

Conductimetric detection has proven to be very sensitive for ions with pK<sub>a</sub>'s less than 7. However, a large number of species such as cyanide, sulfide, hydrazine, hypochlorite, and alkyl mercaptans can not be adequately detected using conductivity. This paper will describe uses of an electrochemical or UV detector which permits routine detection of these species while also determining such species as sulfate, phosphate, and nitrate. Emphasis will be given to the use of multiple detectors to obtain maximum information with only one injection. Illustrations from a wide range of applications will be given.

27 RESISTIVITY DETECTION OF WEAK ACIDS: CARBAMATES AND CARBONATES.

R. K. Pinschmidt, Jr. and M. J. Fasolka. Air Products and Chemicals, Inc.,  
P.O. Box 538, Allentown, PA 18105

The sensitive measurement of simple anions at the ppm level by Ion Chromatography can be extended without instrument modifications to weak acid anions (pK<sub>a</sub> 5-12) using high pH eluent mixtures containing strong acid salts (e.g., nitrate/hydroxide). The weak acid sample ions are quantitatively detected as negative, or resistivity, peaks resulting from a reduction in the strong acid anion flux at the elution time of the weak acid sample component.

This method, previously applied to cyanide, carbonate and tetraborate, has been extended to carbamates ( $\text{RNHCO}_2$ ) of lower alkylamines. The paper discusses: 1) suppression of alkyl ammonium counterion perturbations by the addition of a small high capacity sodium form cation exchange precolumn, 2) eluent selection and chromatogram interpretation, 3) the major influence of carbon dioxide contamination on chromatogram geometry and eluent strength, 4) pH adjustment and tracer pulse concepts in eliminating the interference of the "eluent peak", and 5) the influence of solution agitation on the partition of  $\text{CO}_2$  to carbonate and carbamate in aqueous amine.

28 THE DETERMINATION OF BORON AND PHOSPHORUS IN SILICATE GLASSES USING ION CHROMATOGRAPHY EXCLUSION\* R. M. Merrill. Sandia National Laboratories! P. O. Box 5800, Albuquerque, New Mexico 87185.

Phosphorus and boron have been simultaneously determined in silicate glasses using Ion Chromatography Exclusion. The analyses were accomplished using commercially available instrumentation and columns. A mixed hydrochloric acid/mannitol eluent was used, and the effect of varying HCl concentration was studied. Calibration curves for the technique were found to be linear for solutions containing from 1 - 150 ppm phosphorus, and from 1 - 100 ppm boron. Glass samples were prepared for analysis by fusion at 950°C in sodium carbonate followed by HCl dissolution. Comparison of fused samples which contained known phosphorus and boron concentrations with calibration curves have shown that neither constituent is lost using this fusion technique. The analytical results for phosphorus and boron using ion chromatography exclusion compare very well with results from more classical approaches, and are obtained with considerable time savings.

\*This work was supported by the U. S. Department of Energy(DOE) under contract number DE-AC04-76-DP00789.  
TA U.S. DOE facility.

29 ICE ANALYSIS OF ADIPIC ACID DEGRADATION PRODUCTS IN LIMESTONE FGD SCRUBBER SOLUTIONS. J. C. Terry, E. E. Ellsworth, and D. L. Utley. Radian Corporation, 8500 Shoal Creek Boulevard, Austin, Texas 78766.

The addition of adipic acid to FGD scrubber liquor results in improved limestone utilization and enhanced  $\text{SO}_2$  sorption kinetics. During scrubber operation, however, adipic acid is lost from the system in the liquid and solid phase purge streams and by chemical degradation. In order to provide process control data and to monitor the various mechanisms for adipic acid loss a method for selective organic acid analysis is needed. IC analysis techniques do not separate most dicarboxylic acids or monocarboxylic acids for identification or quantification. ICE is capable of separating and quantifying fairly complex mixtures of these acids. This paper presents results of IC and ICE analyses of scrubber solids and liquor samples from several FGD systems.

30 ION CHROMATOGRAPHIC ANALYSIS OF FORMALDEHYDE. AN EVALUATION OF PROPRIETARY SOLID-ADSORBER SAMPLING TUBES UNDER LABORATORY AND FIELD CONDITIONS. C. J. Jackson and D. Bussan. Health and Safety Executive, Occupational Hygiene Laboratory, 4-03 Edgware Road, LONDON NW2 6LN, United Kingdom.

In the United Kingdom the concentration of formaldehyde in workplace atmospheres is closely controlled, to comply with the ACGIH Threshold Limit Value of 3 mg/m<sup>3</sup>, through inspection and enforcement by the Health and Safety Executive. Enforcement involves the sampling and analysis of this highly irritant gas and problems exist due to the lack of suitable shift sampling and associated analysis procedures. The use of a proprietary impregnated charcoal solid-adsorber tube for sampling together with Ion Chromatographic analysis of the resultant desorbed formate (as described by W. S. Kim, C. L. Geraci and R. E. Kupel, Am. Ind. Hyg. Assoc. J., 334- (1980)) appeared to offer the desired shift sampling capability. Before introducing this procedure, ruggedness testing was undertaken to evaluate the performance of these tubes using laboratory generated standard atmospheres to permit a statistical evaluation of the effect of sampling rate and time, atmospheric level, and the level of a range of potential interferents. Results of these studies are reported together with a field evaluation at locations such as foundries.

- 31 The Determination of Acids in Coffee by Ion Chromatography(IC) and Ion Chromatography with Exclusion (ICE). L. D. Davis and A. K. Foltz, Technical Center, General Foods, 555 S. Broadway, Tarrytown, N.Y. 10591.

Methodology has been developed for the direct, quantitative determination of acids in coffee using IC and ICE in both independent and coupled modes. Diluted and filtered coffee brew samples are chromatographed directly for acids with pKa's up to 7 without interference from the complex sample matrix. This approach avoids problems arising from the preliminary isolation and derivitization steps: utilized by previous methods reported in the literature. The levels of coffee acids found by the latter methods vary greatly, indicating a wide range of variability in coffee acids levels and/or variable degrees of recovery. The recovery levels obtained with IC and ICE (typically 100+ 15%) largely eliminate the latter possibility. The IC and ICE results are compared with previously reported results in order to establish more accurate data on acids present in coffee.

- 32 Practical Experience on the Use of Coupled ICE/IC Systems for the Determination of Anions in Hazardous Waste Samples. J. H. Lowry, R. C. Ross and K. Wang, Environmental Protection Agency, National Enforcement Investigations Center, Box 25227, Bldg. 53, Denver Federal Center, Denver, CO 80225

Samples of leachate, disposal pits, and barrel materials collected on and near sites of the disposal of hazardous wastes have been analyzed for strong and weak acid anions by a combination of coupled ICE/IC systems. Discussion of the pragmatics of obtaining useful data in terms of procedure, interferences and second and third system verification in samples containing complex mixtures of anions are presented. Procedures for individual anion verification are recommended.

- 33 CARE AND FEEDING OF IC COLUMNS. E.L. Johnson. Dionex Corporation, 1228 Titan Way, Sunnyvale, California 94086.

With the increased popularity of Ion Chromatography, there has been a concurrent increase in "abnormal column behavior," while the resins employed in IC are extremely durable and the resulting columns can withstand a variety of abuses, there are certain do's and don'ts which should be observed to maintain good performance. Proper column storage and clean-up techniques will be described. Procedures for establishing routine maintenance programs to assure continued high performance will be illustrated.

- 3\* A RAPID METHOD FOR THE ION CHROMATOGRAPHIC DETERMINATION OF FLUORINE, CHLORINE AND SULFUR. C. B. Moore, K. L. Evans and J. G. Tarter. Department of Chemistry, Arizona State University, Tempe, Arizona 85287

A method for the determination of chlorine in silicate rocks and meteorites has been extended to include fluorine and sulfur. Samples are combusted in a LECO induction furnace using a water saturated oxygen carrier gas. The volatile products are collected in a NaHCO<sub>3</sub>-Na<sub>2</sub>CO<sub>3</sub> eluent and analyzed in a DIONEX Model 10 Ion Chromatograph. The analyses for all three elements compare well with accepted values for standard rock and meteorite samples. Analyses of selected splits of some of the standards showed small but significant differences between the splits of the same sample for chlorine and fluorine -

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Analysis of Mount St. Helens Samples Using Ion Chromatography.  
S. Wilson, C. Gent, and T. Hinkley. U.S. Geological Survey, Box 25046, MS 928, Denver, CO. 80225

The May 18, 1980 eruption of Mount St. Helens resulted in the deposition of substantial amounts of ash throughout the northwest United States. Samples were submitted to the U.S. Geological Survey for the analysis of anions and cations.

Investigations pertaining to the concentrations of fluoride, chloride, nitrate, phosphate and sulfate were performed using a Dionex 12S ion chromatograph. Removal of anions from the ash samples was accomplished using water and 0.01M sulfuric acid leachs. Leachable anion concentrations ranged from tens to several hundred parts per million in the sample. Higher anion concentrations were observed in the acid leachs. Total anion concentrations in the ash samples were estimated using various fusion methods. Leachable anion concentrations are compared to total anion concentrations in the ash. Information is presented which examines the concentrations of anions in the samples as they relate to distance from the volcano.

(Use of brand or manufacturer's name is for descriptive purposes only and does not constitute endorsement by the U. S. Geological Survey)

\* DETERMINATION OF SPARK-INDUCED BY-PRODUCTS OF SULFUR HEXAFLUORIDE. J. M. Keller. Analytical Chemistry Division, Oak Ridge National Laboratory,\* P. O. Box X, Oak Ridge, Tennessee 37830.

The 25-MV tandem accelerator of the ORNL Holifield Heavy-Ion Research Facility employs sulfur hexafluoride as an insulating gas to prevent uncontrolled discharge or arcing. SF<sub>6</sub> is ordinarily very stable; however, it can decompose into very reactive gases when exposed to high-voltage arcs such as found in accelerators. The spark-induced by-products may degrade performance of the accelerator and cause severe corrosion. It is therefore desirable to monitor the SF<sub>6</sub> for the presence of by-products. By allowing the by-products to hydrolyze in a borate buffer, followed by ion chromatographic analysis of the resulting solution, one may obtain a measurement of the decomposition of the SF<sub>6</sub>.

\*Oak Ridge National Laboratory is operated by Union Carbide Corporation for the U. S. Department of Energy under contract W-7405-eng-26. 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.

37 DETERMINATION OF SULFATE IN BRINE. J. P. Price, N. W. Stacy, and J. R. Hawkins Research Department, American Enka Company, Enka, NC 28728

It is important in the production of NaCl for certain applications that the level of sulfate be less than 100 ppm. Heretofore, the classical BaSO<sub>4</sub> precipitation method has been used. While this procedure may be reasonably accurate, if good care is exercised, it is very time consuming.

Using conventional ion chromatographic columns, the extremely high levels of chloride in the presence of low concentrations of sulfate, often as low as 10 ppm, were just not separated. A method has been devised to volatilize the chloride and subsequently inject a chloride free matrix onto the column.

Actual operator time required for a single analysis is 15-20 minutes and a series of 6-10 samples can be handles simultaneously, increasing analysis time by approximately 20 minutes for duplicate injections.

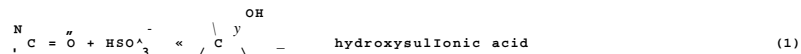
38 AUTOMATED COUPLED LIQUID CHROMATOGRAPHY/ION CHROMATOGRAPHY T. L. Craven. Monsanto Chemical Intermediates Company, Pensacola, Florida 32575

An automated system coupling reversed phase liquid chromatography (LC) and ion chromatography (IC) has been developed for the quantification of inorganic ions, such as chloride, in the presence of organics. The system has been used to determine sulfate and sub ppm levels of chloride in process streams containing 302 total carbon. Inexpensive modification of a Dionex Model 14 ion chromatograph resulted in a system capable of coupled chromatographic operation. Automation via minicomputer event control provided the timing precision necessary for coupled chromatographic operation. Utilization of reversed phase LC coupled to IC is advantageous in that chloride concentrations can be obtained and that shorter cycle times are possible.



- 39 DETERMINATION AND IDENTIFICATION OF SULFITE IN SOME PHARMACEUTICAL COMPOSITIONS USING ION CHROMATOGRAPHY. J. Lindberg. Analytical Research, Pharmacia Co., S-751 04 Uppsala, Sweden.

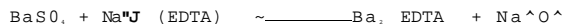
Sulfur dioxide, acting as a preservative agent, is a common additive to food, drinks and to certain pharmaceutical preparations. It is well known that sulfite forms different compounds with aldehydes, ketones, (of reaction 0)).



Reactions similar to reaction (1) may also occur for different types of sugars and certain polymers. This means that sulfite forms more or less labile compounds. As a consequence, depending upon the analytical technique used, more or less sulfite is found. The suitability of using ion chromatography for the analysis of sulfite in the presence of different types of stabilizers and pharmaceutical matrices has been tested. A comparison has also been done with a modified West-Gaeke method (CO. Bjorling and D. Fransson, Pharmacia Co.. personal communication). The agreement between the two methods is acceptable though part of the added sulfite could not be accounted for.

- 40 THE ANALYSIS OF BARIUM SULFATE BY ION CHROMATOGRAPHY. Richard D. Posner, United States Testing Company, Inc., 1415 Park Avenue; Hoboken, NJ 07030.

Barium Sulfate may be dissolved in the Sodium salt of Ethylene Diamine Tetraacetic Acid (0.1% solution adjusted to pH 10.0 \* .2 with NaOH) and injected directly into an anion separator column of an Ion Chromatograph. The EDTA chelates the Barium while displacing a Sodium. In turn the Sodium latches onto the Sulfate forming Soluble Sodium Sulfate. The amount of Sulfate formed is directly proportional to the amount of Barium Sulfate in the original sample.



Direct injection yields a sulfate peak that has a retention time approximately 10% less than that of Aqueous Sodium Sulfate. This is accounted for by the NaOH in the sample and the EDTA acting to increase the strength of the eluent. Furthermore the identity of the Sulfate is confirmed by spiking and by collection and precipitation with BaCl<sub>2</sub>. It is corrected by the use of a one point standard addition followed by extrapolation.

The Sulfate response is linear within a 200 ppm range and thus a sample size of 50 mg diluted to 500ml is used. Results to date have precision relative & absolute errors  $\pm 0.2\%$  **BaSO<sub>4</sub>**.

- 41 INORGANIC ANION AND CATION CHROMATOGRAPHY APPLIED TO STEAM GENERATOR SECONDARY CIRCUIT CHEMISTRY STUDIES by J.P. Brunet - A. Heres and C. Poletiko - C.E.A. - C.E.N. Cadarache, 13115 Saint Paul lez Durance, France.

This work has two objectives :

1 - Chemistry studies of PWR secondary circuit steam generators chemistry and mainly possible effect of sea water and river water pollution. Tests have been performed using the Clarinette loop model boilers. Monitoring of experiments, hide out and hide out return of species is performed leading to accurate measurement of anions (Cl<sup>-</sup>, SO<sub>4</sub><sup>2-</sup>, PO<sub>4</sub><sup>3-</sup>) and cations (Na<sup>+</sup>, K<sup>+</sup>, NH<sub>4</sub><sup>+</sup>, Ca<sup>2+</sup>, Mg<sup>2+</sup>) concentrations. According to experience two measurements ranges used : from 1 to 10 ppm in steam generator blow down and in the field of 1 ppb for the feed water.

Some possible additions (morpholine, hydrazine, boric acid) give rise to chromatogram interferences.

2 - Accurate and precise experimental method studies, using "Dionex" chromatography apparatus.

The goal is to obtain an analysis method for Cl<sup>-</sup>, PO<sub>4</sub><sup>3-</sup>, NO<sub>3</sub><sup>-</sup>, SO<sub>4</sub><sup>2-</sup>, using concentrating column. Minimum possible level is up to now .1 ppb. Methods are given to solve additives interferences problems and in bottle samples evolutions.

SOME APPLICATIONS OF ION CHROMATOGRAPHY TO OIL WELL CEMENT RESEARCH AND ANALYSIS.  
W. J. Caveny and J. D. Childs. Halliburton Services, CRD, Duncan, OK 73536.

The search for oil throughout the world has increasingly placed greater demands on the oil well service industry for quality oil well cements and special application cements. Various chemical aids, such as set time accelerators, set time retarders, friction reducers, and high temperature strength stabilizers are used in cement blends to fulfill the specialized needs of the oil industry. The increased sophistication of chemical systems used in oil well cementing has created the need for more precise analysis.

This paper deals with the use of ion chromatography to examine the large anions present as additives in these cement blends. Several unique extraction methods have been evaluated for the removal of different ionic species from the cement solids.

\* NEW ELUENTS FOR NON-SUPPRESSED ION CHROMATOGRAPHY. O. E. Girard and O. A. Glatz.  
Department of Chemistry, The American University, Washington, D.C. 20016

Recent reports by the authors have shown non-suppressed ion chromatography, which uses conventional high pressure liquid chromatography (HPLC) instrumentation, to be a low cost analytical technique for the analysis of inorganic anions. A Varian Model 5000 HPLC was coupled with a Wescan Conductivity Detector. All separations were achieved on a Vydac 302 IC Column at a controlled temperature of 30°C. This system is designed to work without a suppressor column, thus achieving better chromatographic efficiency and saving time in regenerating the suppressor column. Very efficient separations of anions such as  $\text{Cl}^-$ ,  $\text{NO}_3^-$  and  $\text{SO}_4^{2-}$  are easily achieved with this system. The sensitivity we have observed for  $\text{Cl}^-$  ions (0.5 PPM) is comparable to conventional suppressed IC. Sensitivity for nitrate (1.25 PPM) and sulfate (1.25 PPM) is only slightly less than that which is observed for the conventional suppressed IC method. Linearity is very good over a wide concentration range. By changing the eluting species, its concentration or the pH, improved sensitivity, chromatographic efficiency, selectivity and resolution may be achieved.

M NMR IN SOLIDS: A STUDY IN ANISOTROPY BY John S. Waugh, Massachusetts Institute of Technology

The interactions of nuclear spins with their surroundings and with one another are all anisotropic. The exploitation of this fact is one of the principal motivations for the study of solids. Two kinds of studies will be outlined which make use of the anisotropies in two different ways.

(1) In magic angle sampling spinning, which in its simplest form is designed to remove the anisotropies, the existence of slow random molecular rotations can be conveniently studied. This possibility arises because the random motions tend to destroy the coherent averaging which would otherwise result in perfect rotational echoes and sharp spectra. The same statement can be made about the competition between random motions and coherent averaging methods of other kinds, e.g. spin decoupling. The result is that experimental conditions can often be tuned so as to make accessible for study random motions covering quite a wide range of correlation times. When this is possible, line broadening measurements often provide a more economical way of studying random motions than do spin lattice relaxation methods.

(2) Surprisingly little experimental work has been done on the anisotropy of electron-coupled spin interactions (J coupling). A recent determination will be discussed and some remarks made about the signs of such couplings and possible ways for determining them.

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RECENT DEVELOPMENTS IN MULTIPLE QUANTUM NMR. A. Pines, University of California, Berkeley, California 94720.

Some recent topics in multiple quantum NMR will be discussed from amongst the following:

1. High resolution NMR in inhomogeneous magnetic fields.
2. High resolution proton local field spectra of carbon-13.
3. Conformation of aliphatic chains from high n-quantum spectra.
4. Magic angle spinning with double quantum transitions.
5. Wideband homonuclear decoupling of strongly coupled spins.
6. Selective n-quantum excitation in liquids.

46 GEOMETRY OF MOLECULES IN THE AMORPHOUS STATE BY NMR NUTATION SPECTROSCOPY BY  
R. D. Kendrick and C. S. Yannoni, IBM Research Laboratory, San Jose, California  
95193

There are no readily available methods for determining the carbon skeletal geometry of organic molecules in an amorphous solid phase. This includes matrix-isolated molecules, materials from which a single crystal cannot be made, and most polymers. NMR spectroscopy has the potential for measuring internuclear distances in amorphous solids, although this potential had not been thoroughly explored. Since dipolar coupling between carbon-13 nuclei depends on the inverse third power of the internuclear distance, a measurement of the splitting due to this coupling can yield the carbon-carbon distance. We have developed a relatively simple NMR method designed to directly observe and measure these splittings, which are normally masked by chemical shift effects. A typical sample will consist of a material which has been doubly labeled in carbon-13. No information about the carbon chemical shifts (magnitude or orientation) is required. Thus, the method is applicable to all molecules, even those with no symmetry or with overlapping chemical shift powder patterns.

The utility of the technique depends especially on rf field strength and rf coil inhomogeneity. We have made a comprehensive experimental and theoretical study of doubly labeled acetic acid, which has low symmetry and a large (260 ppm) chemical shift dispersion, and for which the C-C distance is known. This was done to gauge the capability of our spectrometer to make bond length measurements in "unknown" materials. A description of the method, the results for acetic acid, and conclusions regarding its generality will be given.

J. Chem. Phys. 74, 747 (1981)

\*<sup>13</sup>C NMR IN ORIENTED POLYMERIC SOLIDS BY D. L. VanderHart, Structure and Properties Group, Polymer Science and Standards Division, National Bureau of Standards; and G. G. A. Bohm and V. D. Mochel, Firestone Tire and Rubber Co., Central Research Laboratories, Akron, Ohio.

13

Under conditions of high power proton decoupling, <sup>13</sup>C lineshapes are determined by an anisotropic chemical shift interaction. In certain circumstances isolated C - C dipole-dipole interactions may also be present. In unoriented materials with even a few chemically inequivalent carbons, there is usually strong overlap of the various resonances. Use of oriented samples is both simplifying in terms of spectral overlap and informative because the lineshapes reflects the distribution of orientation. For oriented polymers, anisotropic motions can also be studied, particularly those motions occurring in well-oriented "crystalline" regions of the sample. Some insight can also be obtained into the relationship of orientation and mobility where the latter concept should, in turn, be useful in understanding the concept of crystallinity.

Two polymeric systems will be discussed, namely, linear polyethylene (PE) and polyethylene terephthalate (PET). Particular attention will be paid to the flip-flop motion in PE and the aromatic ring rotation in PET. The usefulness of the distinction between crystalline and non-crystalline phases will also be considered.

48 ELIMINATION OF SEVERE MAGNETIC SUSCEPTIBILITY BROADENING IN SOLID-STATE NMR\*.  
M. E. Stoll. Theoretical Division, Sandia National Laboratories, Livermore, CA 94550.

High resolution NMR of hydrogen in strongly paramagnetic metals and hydrides is demonstrated by suppression of severe magnetic susceptibility broadening in powdered samples. The hydrogen-niobium system is investigated using two techniques to narrow the spectral lines which are susceptibility-broadened. The first method of eliminating susceptibility broadening involves matching the susceptibility of a surrounding fluid to that of the sample. The second method involves magic angle sample spinning. Underlying chemical shifts characteristic of different sites and material phases are revealed. Chemical shifts of hydrogen in a and 3 phases of the NbH<sub>3</sub> system are given.

\*This work was supported by the U. S. Dept. of Energy.

\*9 <sup>27</sup>Al-NMR CHARACTERIZATION OF ALUMINIUM SITES IN AMORPHOUS AND CRYSTALLINE SILICA-ALUMINAS BY Z. Gabelica, J. B. Nagy, J. P. Gilson, and E. G. Derouane, Facultes Universitaires de Namur, Laboratoire de Catalyse, Rue de Bruxelles, 61, B-5000 Namur, Belgium.

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Al solid state NMR has been used to characterize aluminum sites in amorphous and crystalline (zeolitic) silica-aluminas of various origins. The technique has been applied to three systems of catalytic interests, ie.:

- i. amorphous silica-aluminas, with Al content varying from 0 to 100% (the end members hence being respectively pure silica and pure alumina),
- ii. classical zeolites, such as type Y, offretite, and mordenite, in the sodium and protonated forms,
- iii. novel zeolites of the ZSM-5 family with varying aluminum content and degree of crystallinity.

The parameters which characterize the Al resonance, its chemical shift(s), its linewidth, and its intensity, depend very strongly not only on the Al content of the materials but also on the concentration of Na counterions as a result of Al-Na dipolar interactions. Chemical shifts are very sensitive to the environment (coordination type) of the aluminum sites. The NMR technique hence provides a quick and reliable means of determination of the number of equivalent T-sites in a given silica-alumina, either amorphous (in which case different chemical shifts may indicate the existence of different phases) or crystalline (in which case evidence for distinct structural sites is gained).

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Because of differences in chemical shifts, <sup>27</sup>Al NMR offers also the possibility to measure quantitatively the amount of amorphous material in semi-crystalline silica-aluminas obtained by terminating the crystallization of synthetic zeolites (in the particular case under investigation, ZSM-5) at various synthesis time. It provides evidence for the presence of zeolitic domains in materials for which no characteristic X-ray diffraction lines are observed (because of line broadening as a result of the small size of these domains).

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It is concluded that <sup>27</sup>Al NMR offers a great potential for future investigation in this particular area of catalysis; even more as complementary information can in principle be obtained from Na and Si solid state NMR.

50 CP/MAS STUDIES OF SURFACE-ADSORBED AND SURFACE-ATTACHED SPECIES. G. E. Maciel, D. W. Sindorf, I-Ssuer Chuang, and W. Kolodziejewski, Department of Chemistry, Colorado State University, Fort Collins, Colorado 80523.

<sup>29</sup>Si and <sup>13</sup>C CP/MAS NMR spectra with a high degree of structural resolution have been obtained on solid samples of silica gels that have been derivatized at the surface by silylating agents. Separate signals are seen for at least two types of Si atoms at the silica gel surface and additional peaks occur in another spectral region, characteristic of the attached silyl groups. Characteristic <sup>13</sup>C resonances can be seen for the attached silyl groups. Experiments have been carried out with a series of silylating agents under a variety of conditions. The <sup>29</sup>Si spectra have been especially useful in characterizing the nature of the silylation products. Changes in the intensities of resonances associated with reacted and unreacted surface segments can be interpreted in terms of specific changes, and suggest applications in quantitative analysis. The nature of adsorption of pyridine on silica, alumina and silica-alumina has been studied by CP/MAS NMR. Small <sup>13</sup>C shifts, which depend upon the composition and method of preparation of the sample, are observed, and related to adsorption models. Preliminary <sup>13</sup>C CP/MAS data on the surface of carbon and derivatized carbon will also be presented.

52 SPIN-1/2 NUCLEI IN CATALYTIC ENVIRONMENTS. Ruth R. Ingers, and Paul D. Ellis, Department of Chemistry, University of South Carolina, Columbia, South Carolina 29208. William H. Dawson, Union Carbide Corporation, Research and Development Department, South Charleston, West Virginia 25202.

To examine the NMR parameters of spin-1/2 nuclides in a catalytic environment (CP-MAS methods), one must design an NMR probe for solids which takes into account the following objectives: (a) sample volume versus spinning speed considerations, (b) the potential problem of carbon background, and (c) the possible inclusion of variable temperature operation.

We have designed a probe that addresses points a and b and have utilized it in studying two representative nuclei ( $^{13}\text{C}$  and  $^{113}\text{Cd}$ ) in catalytic systems. The  $^{13}\text{C}$  NMR research involves small organic molecules (nitrogen bases) adsorbed on an alumina surface ( $\text{SA} = 200 \text{ m}^2/\text{g}$ ). In selected cases, substantial differences can be seen between chemi- and physisorbed species on the surface. The  $^{113}\text{Cd}$  system consists of cadmium substituted into a biological system where the cadmium has replaced the catalytic metal. Results on both of the systems will be presented.

This research was supported in part by the University of South Carolina's regional NMR facility, CHE 7818723, and the NIH grant #GM 26295.

" SOLID-STATE HIGH-RESOLUTION  $^{13}\text{C}$  NMR OF ORGANOMETALLICS; CORRELATIONS WITH X-RAY CRYSTALLOGRAPHY. N. Zutihulyadis, D. L. Smith and S. Gross. Eastman Kodak Company, Research Laboratories, Building 82, Rochester, NY 14650.

The chemical shifts and multiplicities of various carbons in organometallic solids reflect the reduced symmetry of the crystalline environment rather than the (usually higher) molecular symmetry. Methyl moieties are particularly sensitive to crystal packing effects and can serve as reporter groups of the local environment. The spectra of several organotellurium complexes of known crystal structure will be discussed in terms of dimer formation in the solid state. In addition, some features of the home-built solid-state NMR instrumentation will be described.

54  $^{13}\text{C}$  NMR STUDIES OF LIPID-LIPID AND LIPID PROTEIN INTERACTIONS IN PHOSPHOLIPID VESICLES. J. H. Prestegard, Li-da Ong and M. M. Fuson, Chemistry Department, Yale University, P. O. Box 6666, 225 Prospect Street, New Haven, Connecticut 06511

The interaction of glycophorin A with phospholipids in reconstituted small unilamellar vesicles has been investigated using a variety of nuclear spin probes including specifically  $^{13}\text{C}$  enriched phospholipids. Solubilization of protein and lipid in sodium cholate followed by rapid removal of cholate on a gel permeation column leads to small unilamellar vesicles. These vesicles have high levels of protein (40:1 lipid:protein ratio) incorporated in an asymmetric fashion and are of a size comparable to vesicles prepared without protein. Direct comparison of  $^1\text{H}$ ,  $^{13}\text{C}$ ,  $^{31}\text{P}$ , and  $^{19}\text{F}$  spin relaxation parameters is, therefore, possible, in this system. In mixed phosphatidylcholine, phosphatidylethanolamine vesicles  $^{13}\text{C}$  experiments indicate some preference for interaction with phosphatidylethanolamine. Perturbations to lipid motions extend throughout the hydrophobic region of the membrane, but seen most pronounced on the inner half of the bilayer.  $^{13}\text{C}$  relaxation times are interpreted on the basis of a model in which interactions are weak and relatively non specific. Analysis which includes cross correlation spectral densities is used to improve definition of a motional model for lipid hydrocarbon chains.

55  $^1\text{H}$  NMR STUDY OF THE LOCATION AND MOTION OF UBIQUINONES IN PERDEUTERATED PHOSPHATIDYLCHOLINE BILAYERS. P.B. Kingsley and G.W. Feigenson. Section of Biochemistry, Molecular and Cell Biology, Clark Hall, Cornell University, Ithaca, New York 14853.

Ubiquinones ( $n = 1,2,3,4,7,9,10$ ) and ubiquinol ( $n=1,2,3,4,10$ ) were incorporated into ordinary (protonated) or perdeuterated dimyristoyl phosphatidylcholine vesicles and were found to have significant local molecular motion. The motion of the quinone ring, as judged from the linewidth of the OCH<sub>3</sub> proton resonances, decreased in longer-chain ubiquinones. Minimum values for the transverse mobility (flip-flop rates) of ubiquinones-1,2,3,4,10, measured with the aid of lanthanide shift reagents, suggest that they are all able to function in a protonmotive "Q cycle" during electron transport. As the length of the side chain increases beyond 1 isoprenoid unit, the quinone/quinol ring tends to be deeper in the outer monolayer of small sonicated vesicles and in both monolayers of larger freeze-thaw vesicles, but little or no change in depth is observed in the inner monolayer of small vesicles. The ubiquinol rings are closer to the membrane surface than are the ubiquinone rings. For side chain  $n=9$  or 10, a second resonance from the  $\alpha\text{-CH}_2$  protons of ubiquinones and ubiquinol in vesicles appears in the  $^1\text{H}$  NMR spectrum. This is due to the presence of two types of vesicles with different ubiquinone/phospholipid ratios.

- 56 <sup>31</sup>P NMR Studies of the Phospholipid-Protein Interface in Cell Membranes. Philip L. Yeagle, Dept. of Biochemistry, SUNY/Buffalo, Buffalo, N.Y. 14214.

A fresh approach for studying the phospholipid-protein interface in biological membranes has been developed employing <sup>31</sup>P NMR. This approach offers several unique advantages since the <sup>31</sup>P nucleus is 100% naturally abundant and is present in all phospholipids in a defined location in the phospholipid polar headgroup. The method thus enjoys freedom from perturbations due to chemical modifications or addition of probes. Exploiting these advantages we have studied intact rabbit sarcoplasmic reticulum membranes, human erythrocyte membranes, rod outer segment disk membranes, and vesicular stomatitis virus membranes. Also examined were recombinants with phosphatidylcholine of the purified principle proteins of most of these membranes. The <sup>31</sup>P NMR intensity of the anisotropic resonance exhibited by these membranes was compared with the intensity expected from the known phospholipid content. Data was obtained at 40 MHz and 81 MHz. In most systems such analysis indicated that phospholipids inhabit two environments in these membranes. One is immobilized and represents phospholipid at the lipid-protein interface. Effects of temperature, cholesterol, proteolysis, and phospholipid/protein ratio on this immobilized component were chronicled. The non-immobilized component was characterized in two ways: 1) <sup>31</sup>P T<sub>1</sub> analysis showed that only in the virus system is headgroup rotational rate affected; 2) analysis of the <sup>31</sup>P chemical shift anisotropy indicated that in most of the systems, motional freedom of the headgroups of the non-immobilized phospholipids was similar to pure phospholipid systems. The interpretations of these <sup>31</sup>P NMR data are consistent with <sup>13</sup>C NMR, ESR, differential scanning calorimetry and activity data on these systems and are not necessarily inconsistent with recent <sup>2</sup>D NMR data.

- 57 C-H Bond Order Parameter Distributions for Partially Ordered Systems with Axial Symmetry, James H. Davis, Physics Department, University of Guelph, Guelph, Ontario, Canada N1G 2W1

In the study of liquid crystalline systems, whether of polymers, soaps, biological membranes or digital watches, one must be prepared to deal with the anisotropic molecular dynamics of these partially ordered systems. If rapid molecular motions result in local axial symmetry for the relevant Hamiltonians in a nuclear magnetic resonance (NMR) experiment, the interpretation of the NMR spectrum is considerably simplified. <sup>1</sup>H NMR is frequently used in the investigation of molecular order and dynamics in these systems.

In the presence of rapid axially symmetric molecular motion the quadrupolar splitting of the 90° orientation in the NMR spectrum for <sup>1</sup>H in C-H bonds is reduced from a value  $A_v = (3e^2qQ/4h) - 126 \text{ kHz}$  to a value  $A_v = (3e^2qQ/4h)S$ , where  $S = \langle 3\cos^2\theta - 1 \rangle$  is the C-H bond order parameter with the angular brackets denoting an "average over all motions" which are rapid on the <sup>1</sup>H NMR time scale, and where  $\theta$  is the angle between the C-H bond and the axis of symmetry for the motion.

When powder samples are used the magnitude of this orientational average,  $|S|$ , can be determined by the position of the 90° peaks in the powder pattern spectrum. In systems where the existence of a number of inequivalent sites results in a complex spectrum consisting of a large number of overlapping powder patterns it has often been necessary to resort to spectral simulations to try to extract the distribution of quadrupolar splittings. It has recently been found possible to obtain the distribution of quadrupolar splittings directly from the experimental spectrum.

In the study of model and biological membrane systems the influence of external variables and the effect of variations in the concentrations of solute molecules such as cholesterol or membrane-bound proteins have frequently been discussed in terms of changes in <sup>1</sup>H NMR quadrupolar splittings of membrane lipids, since these are expected to reflect changes in the degree or amount of lipid reorientation. The direct determination of the distribution of quadrupolar splittings permits an accurate comparative study of lipid orientational order. Examples of the use of this technique in the study of lipid/water dispersions, lipid/protein reconstituents, and biological membranes containing cholesterol will be discussed.

- 59 STUDIES OF MOLECULAR DYNAMICS USING  $^{13}\text{C}$  NMR. Robert E. London, Los Alamos National Laboratory, Los Alamos, NM 87545, R. L. Blakley, J. P. Groff, and L. Cocco, Dept. of Biochemistry, College of Medicine, The University of Iowa, Iowa City, Iowa 52240, John M. Stewart, University of Colorado Medical Center, Denver, CO 80220, M. A. Phillippi and G. Kwei, Los Alamos National Laboratory, Los Alamos, NM 87545.

Detailed analysis of molecular dynamics in solution based on nmr relaxation studies constitutes one of the most unique applications of magnetic resonance. A variety of such applications will be reviewed, and the strengths and weakness of dynamic models used in the interpretation of data considered with reference to several specific examples. These will include both simple systems, such as triphenylbenzene, dicarboxylic acids, and benzoic acid, as well as more complex biologically interesting systems such as the nonapeptide, bradykinin and the enzyme, dihydrofolate reductase. The value of frequency dependent measurements as well as temperature dependent measurements in discriminating among dynamic models will be illustrated. Applications involving  $^{13}\text{C}$  enriched systems will also be considered with emphasis on the information content derivable from analysis of the  $^{13}\text{C}$ - $^{13}\text{C}$  dipolar interaction. Enrichment at levels below 100% allows simultaneous measurements for both the  $^{13}\text{C}$ - $^{13}\text{C}$  doublet arising from the doubly labeled molecules, as well as the singlet arising from the singly labeled molecules. This double probe allows the  $^{13}\text{C}$ - $^{13}\text{C}$  dipolar interaction to be specifically evaluated, eliminating the problem of determining the relaxation mechanism. Such measurements are also more free from uncertainties in bond length which have recently been shown to lead to significant discrepancies in the interpretation of natural abundance  $^{13}\text{C}$  relaxation due to  $^{13}\text{C}$ - $^1\text{H}$  dipolar interactions.

- 60 SOLID STATE NMR STUDIES OF PROTEIN AND DNA DYNAMICS. S. J. Opella, Department of Chemistry, University of Pennsylvania, Philadelphia, Pennsylvania 19104

The dynamical properties of high molecular weight DNA and DNA-protein complexes are being studied by solid state NMR. In situations where the overall reorientation of the molecules is negligible, the intramolecular motions influence spectral lineshapes due to chemical shift anisotropy, quadrupolar, and dipolar interactions. Specific labelling with  $^1\text{H}$ ,  $^{13}\text{C}$ , and  $^{15}\text{N}$  in protein and nucleic acid sites as well as the 31p sites of the phosphodiester backbone of DNA mean that a variety of NMR studies are feasible.

- 61 CARBON-13 NMR STUDIES ON PURIFIED, SPECIFICALLY  $^{13}\text{C}$ -LABELED

E. COLI TRANSFER RNAS.

M. P. Schweizer, I. J. Walkiw, J. I. Olsen  
Department of Medicinal Chemistry and  
D. M. Grant, W. J. Horton, W. D. Hamill, Jr.,  
Department of Chemistry  
University of Utah, Salt Lake City, Utah

In this paper we will describe carbon-13 NMR studies on the solution structure and interaction of purified *E. coli* transfer RNAs which have been specifically  $^{13}\text{C}$ -labeled. For example, thermal and magnesium perturbation studies on  $[4\text{-}^{13}\text{C}]\text{uracil}$  labeled tRNA<sup>Val</sup> from *E. coli* S0-187, auxotrophic for uracil, have revealed several interesting tertiary and secondary structure transitions in which differential segmental mobilities are displayed. The tertiary interaction between D- and T<sub>if</sub>C-loops is disrupted around 37°C, whereas a more general break-up of ordered structure occurs between 50-60°C. Removal of Mg(II) results in a more extended conformation in the bend region of the biopolymer. The presence of valine synthetase results in specific alterations in the  $^{13}\text{C}$ -spectra, indicative of certain discrete interaction loci between protein and tRNA. These may represent "recognition" sites. In the native  $[4\text{-}^{13}\text{C}]\text{uracil}$  labeled tRNA<sup>Phe</sup>, the two dihydrouridines separated by three residues are in widely different environments. Initial *in vitro* labeling results with tRNA<sup>Glu</sup> from the *E. coli* K12 mutant, GM23 will also be described. We acknowledge the support of grants GM25512, GM08421, RR07092 and RR00574 from the U. S. Public Health Service.

- 62 Cross Polarization-Magic Angle Spinning  $^{13}\text{C}$  NMR of Carbohydrates Containing Glucose. William L. Earl, National Bureau of Standards, Washington, D.C. 20234 and Los Alamos Scientific Laboratory, Los Alamos, New Mexico 87545 and Phillip E. Pfeffer, D.S. Department of Agriculture, Eastern Regional Research Center, Philadelphia, PA. 19118

Glucose is one of the most common of all sugars, existing as a monosaccharide, many oligosaccharides, and the common polysaccharides cellulose and starch. In the solid state, the glucose residue exists in a variety of different structural forms including  $\alpha$  and  $\beta$  anomers, hydrates, and internally hydrogen bonded structures. All of these variations are potential sources of chemical shift and relaxation time differences.

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The  $^{13}\text{C}$  chemical shifts and some relaxation times of over a dozen glucose containing compounds have been measured by CP-MAS of the solids. In cases where x-ray data on the carbohydrate exists, the NMR parameters will be related to the solid state structure. In cases where the detailed structure is unknown, probable structural information has been deduced from the  $^{13}\text{C}$  NMR spectra.

- 63 LASER PHOTO-CIDNP STUDIES OF ALPHA-LACTALBUMINS. Lawrence J. Berliner, Dept. of Chemistry, Ohio State University, Columbus, Ohio, USA.

The  $\alpha$ -lactalbumins are involved as modifier proteins in lactose biosynthesis. Lactalbumins from different mammalian species are cross-reactive with the galactosyl transferases from others because of their homologous primary and tertiary structure. We have studied the surface exposure of several  $\alpha$ -lactalbumins (bovine, goat, human, guinea pig and rabbit) by the laser photo CIDNP technique, an NMR method which measures the access of a photo excited flavin dye to surface exposed Tyr, Trp and His residues. An exposed histidine 68 residue exists in the bovine and goat species but is missing in other species, replaced with a His 10 in the guinea pig species. The only exposed tryptophan residue was Trp 104 which cross-relaxed to nearby Trp 60. Cross-polarization to the latter residue was proven by taking free induction decays after extremely short light pulses (0.1 sec). Furthermore, this crosspolarized Trp 60 resonance was absent in the guinea pig species which has a substitution at position 60. The chemical shifts of these Trp residues were extremely similar in  $\alpha$ 7 species but rabbit which has substituted His for a Tyr at position 103, situated close to both Trp 104 and 60.

- 64  $^{111}\text{Cd}$  AND  $^{31}\text{P}$  NMR OF METALLO-ALKALINE PHOSPHATASE. Peter Gettins and Joseph E.

Coleman, Dept. of Molecular Biophysics and Biochemistry, Yale University, 333 Cedar St., New Haven, Conn. 06510

Alkaline phosphatase, (AP) of *S. coli* occurs naturally as the dimeric zinc metallo-enzyme, activated by  $\text{Mg}^{2+}$ , and hydrolyses phosphate monoesters via a covalent phosphoserine intermediate. X-ray diffraction studies on the cadmium derivative clearly show two metal binding sites at the active centre of each monomer, spaced  $\sim 5\text{\AA}$  apart, with a third, more poorly occupied, metal site detectable further away. Some or all of these sites can be substituted by several first transition metals in addition to cadmium. The latter, by virtue of the  $I=1/2$  of the  $^{111}\text{Cd}$  isotope and relatively high sensitivity, is a useful NMR probe of the metal binding sites of AP in solution.

Earlier reports have given conflicting evidence concerning cooperativity and stoichiometry of metal and phosphate binding to AP.  $^{111}\text{Cd}$  NMR studies, in conjunction with tandem  $31\text{P}$  NMR experiments observing the resonances arising from both covalent (E-P) and non-covalent (E-P) intermediates, have been used to help answer questions of symmetry between the subunits and of cooperativity. Recent findings are presented here.

#### APPLICATION OF $^{15}\text{N}$ NMR SPECTROSCOPY TO BIOLOGICAL SYSTEMS

Keiko Kanamori, William W. Bachovchin, Timothy L. Legerton, Bert L. Vallee, Richard L. Weiss, and John D. Roberts. California Institute of Technology, Pasadena, CA 91125; Tufts University School of Medicine, Boston, MA 02111; University of California, Los Angeles, CA 90024; Harvard Medical School, Boston, MA 02115, University of California, Los Angeles.

Application of nitrogen-15 nuclear magnetic resonance spectroscopy to the study of the active site conformation of carboxypeptidase A and nitrogen metabolism in Neurospora crassa will be presented.



66 Structurally Specific Proton Relaxation Studies On Solid Polycarbonates. A.A. Jones and J.F. O'Gara, and P.T. Inglefield. Clark University, and College of the Holy Cross, Departments of Chemistry, Worcester, Massachusetts 01610.

Solid state proton relaxation studies were widely employed in the past to examine polymer dynamics but they were subject to interpretational difficulties because resonances from different protons are nearly completely unresolved. Today selective deuteration of polymers can reduce such difficulties allowing a structurally specific investigation. A particularly favorable system is the polycarbonates with phenylene groups bound in the backbone by 1, *U* linkages; and only a few or even no other types of protons. If no other protons are present, the 2,3 phenylene proton dipole-dipole interaction is dominant which is then parallel to the backbone providing an excellent probe of chain dynamics. Two polycarbonates of this type have been studied by traditional proton experiments such as spin-lattice relaxation measurements, spin-lattice relaxation in the rotating frame measurements and line shape study including second moment analysis. At low temperatures, featureless gaussian lines are observed but as temperature is raised the line narrows and the line shape changes to a Pake doublet. The Pake doublet arises from the 2,3 phenylene proton interaction; and the only motion which *can produce* significant narrowing and yet leave the 2,3 phenylene interaction unchanged is phenyl group rotation or rotational oscillation. The spin-lattice relaxation times are observed to decrease monotonically as temperature is raised until a minimum is reached. In the polycarbonate of bisphenol A, the minimum is reached at about 0°C; and then  $T_1$  remains constant over 150°, an unusual phenomenon indicative of an extremely broad distribution of frequencies of motion extending well into the megahertz region.

#### 65 Molecular Motion in Substituted Polystyrenes

Michael D. Sefcik  
Monsanto Co., St. Louis, Missouri

Carbon-13 rotating-frame relaxation times ( $T_{1\rho}$ 's) at 37 kHz have been obtained for several ring- and main-chain substituted glassy polystyrenes at room temperature. While low-frequency main-chain rotational reorientation is responsible for both aromatic and aliphatic-carbon  $T_{1\rho}$ 's, only the former are significantly affected by monosubstitution of the ring. This result is interpreted in terms of the presence in the solid of a main-chain motion in which the rings undergo only limited translations.

#### A CARBON-13 NMR INVESTIGATION OF POLYMERS PREPARED BY GLOW DISCHARGE TECHNIQUES

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The process of plasma polymerization is a way of depositing polymer films onto solid surfaces by injecting an organic vapor into a low pressure glow discharge. Along with the growing technological importance of plasma polymerized coatings is an interest in the fundamental aspects of the chemical and physical structures of the polymer films as well as the routes to their formation, in the plasma.  $^{13}\text{C}$  magic angle spinning NMR spectra have been obtained for solid films synthesized in a glow discharge from a variety of organic monomers. For films formed from ethane, ethylene and acetylene carbon linewidths are broad, reflecting the superposition of peaks from many chemically inequivalent environments. Even so, significant differences in the spectra are observed. Plasma polymerized toluene yields a *more* highly resolved spectrum and, when compared with spectra of polymers prepared from selectively labelled methyl and phenyl C-1 toluene, permits a more detailed analysis of the film structure. The enriched monomers allow determination of where particular carbons in the plasma become incorporated into the polymer. Some of the more important plasma coatings are prepared from fluorinated monomers. We hope to present preliminary  $^{13}\text{C}$  spectra for these systems as well.

"> <sup>31</sup>P SHIFT ANISOTROPIES AND MOLECULAR MOTIONS IN POLYPHOSPHAZENE ELASTOMERS. Ronald Pratt and Jerome Ackerman. Department of Chemistry, University of Cincinnati, Cincinnati, Ohio 45221.

The linear high polymeric phosphazenes ( $-(\text{PR}^i\text{N})_n-$ ) 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 <sup>31</sup>P NMR of several phosphazene elastomers ( $\text{R}=\text{OCH}_3$ ,  $\text{OCH}_2\text{CH}_3$ ,  $\text{OCH}_2\text{CF}_3$ ,  $\text{OC}_2\text{H}_5$ ,  $\text{OC}(\text{CH}_3)_2/\text{p-OC}(\text{CH}_3)_2\text{Et}$ ) at temperatures above and below their glass transitions.

These systems are distinguished in their magnetic resonance properties in that there is strong mutual dipolar interaction among three abundant spin systems, namely <sup>1</sup>H, <sup>31</sup>P and <sup>15</sup>N. With high power proton decoupling and intermediate temperatures it is possible in some cases to resolve an axially symmetric <sup>31</sup>P chemical shift spectrum, whereas at low temperatures where most motions are substantially quenched, a broad, featureless gaussian-like line is observed. However, we may calculate the second moment contribution of P-N coupling to the linewidth (from known P-N distance), measure  $M_2$  from spin echo measurements and thereby obtain  $\Delta\sigma_P$  (<sup>31</sup>P chemical shielding anisotropy) by difference. This quantity, together with the two axial principal values, allows us to unambiguously calculate the low temperature shielding tensor principal values, even though they are never resolved in the spectra.

Specific examples will be presented, along with comparative solid state results from crystalline cyclic trimers.

72 CARBON-13 NMR STUDIES OF POLY(VINYL CHLORIDE): NEW INFORMATION ON STRUCTURAL DEFECTS AND THE MECHANISM OF VINYL CHLORIDE POLYMERIZATION. W. H. Starnes, Jr.,\* F. C. Schilling,\* I. M. Plitz,\* R. E. Cais,\* F. A. Bovey,\* G. S. Park,\*\* and A. H. Saremi.\*\* \*Bell Laboratories, Murray Hill, NJ 07974; \*\*Department of Chemistry, University of Wales Institute of Science and Technology, Cardiff CF1 3NU, Wales, UK.

Our continuing carbon-13 NMR studies on reductively dehalogenated samples of poly(vinyl chloride) (PVC) have provided further insight into the nature of the anomalous structures in this polymer and into the mechanisms by which they are formed. Conclusive evidence has now been obtained for the presence in PVC of 2,4-dichloro-n-butyl branches which are associated with tertiary halogen and are generated via a radical "backbiting" reaction. For a series of ordinary PVC's prepared at temperatures of 43 to 100 °C, the 2,4-dichloro-n-butyl branch concentration has been observed to range from ca. 0.6 to 1.07 (1000 ppm). Initiator end groups derived from azobis(isobutyronitrile) have been detected also, and low concentrations of structures containing primary halogen have been found to remain in Bu<sub>3</sub>SnH-reduced polymers even at high reduction extents. A mechanistic rationalization of the latter observation will be described. For polymers prepared in solution under strictly homogeneous conditions, the chloromethyl branch concentration has been demonstrated to be essentially independent of the concentration of vinyl chloride. This finding relates to the mechanism of chain transfer to monomer in a way that will be discussed.

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QUANTITATIVE ANALYSIS OF THE MICROSTRUCTURE OF DICYCLOPENTADIENE/CYCLOPENTENE COPOLYMERS USING 20MHz <sup>13</sup>C NUCLEAR MAGNETIC RESONANCE SPECTROSCOPY. D. H. Beebe and R. C. Hirst, The Goodyear Tire & Rubber Company, Elastomer & Chemical Research Division, 142 Goodyear Blvd, Akron, Ohio 44316.

There have been relatively few quantitative studies of the copolymerization of cycloalkenes; but in the studies conducted, a wealth of structural data has been accumulated. In the present study we have a detailed interpretation of the <sup>13</sup>C NMR spectra of the ring-opened copolymers of dicyclopentadiene and cyclopentene in terms of the four structural units present: cis- and trans-dicyclopentadiene and cis- and trans-cyclopentene. Also derived was information concerning the dyad distributions and double bond compositions for each dyad.

75 °C,  $^{29}\text{Si}$  and  $^{201}\text{Hg}$  NMR OF POLYMERS AND MODEL SYSTEMS. E. A. Williams, P.E. Donahue and J.D. Cargioli. General Electric Corporate Research and Development, P. O. Box 8, Schenectady, New York 12301.

NMR affords a means of obtaining structural information unavailable by any other analytical technique. In particular, copolymer composition, block lengths and details of the polymer microstructure frequently can be obtained by this method. Since the composition and structure are directly related to the physical properties of these materials, a complete analysis of these parameters is often useful for designing systems with specific properties.

Several examples for which NMR gives unique information will be discussed. These include determinations of block length and microstructure of polydimethylsiloxane block copolymers by  $^{29}\text{Si}$  and  $^{13}\text{C}$  NMR, and  $^{13}\text{C}$  NMR analysis of poly(phenylene oxide) copolymers. In addition,  $^{201}\text{Hg}$  NMR has been used to determine the products of mercuration of several polymers and model systems. The effect of substituents on the mercury chemical shift will be discussed with pertinent examples.

77 TEMPERATURE EFFECTS ON THE  $^{27}\text{Al}$  NMR SPECTRA OF POLYMERIC ALUMINUM HYDROLYSIS SPECIES  
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$^{27}\text{Al}$  NMR spectra have recently been reported for hydrolyzed aluminum solutions at both room temperature and elevated temperatures. A distinct sharpening of the NMR spectral features at 82°C (in comparison with RT data) was noted for basic aluminum complexes in solutions of " $\text{Al}(\text{OH})_3$ " prepared by high temperature hydrolysis of  $\text{Al}(\text{III})$  ion in the presence of aluminum metal. Two unique  $^{27}\text{Al}$  resonance features were attributed to two different polymeric aluminum species of unknown structure containing aluminum in tetrahedral (70 ppm) and octahedral environments (0.3 and 11.0 ppm).

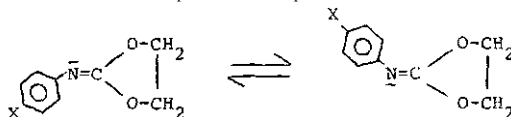
We have recently carried out  $^{27}\text{Al}$  NMR measurements at 82°C and RT for similar " $\text{Al}(\text{OH})_3$ " solutions at various concentrations and supporting electrolytes to more fully explain the chemical origin of these unique  $^{27}\text{Al}$  NMR spectra. We report here  $^{27}\text{Al}$  NMR for fresh and aged solutions of " $\text{Al}(\text{OH})_3$ " complexes over the 5M-1M concentration range at RT, 82°C and at RT following temperature elevation to 82°C. The latter NMR spectra show dramatic irreversible changes in the  $^{27}\text{Al}$  resonances following the high temperature measurements in comparison with RT data obtained for freshly prepared solutions prior to elevation to 82°C. The interpretation of this  $^{27}\text{Al}$  NMR data, together with polymer characterization data obtained using gel filtration chromatography, suggest irreversible depolymerization of polycationic aluminum species upon aging or following elevation of these systems to 82°C for 1 hour. Discussion of the significance of this depolymerization process in understanding important structural features and kinetic processes related to polymeric aluminum hydrolysis species is presented.

73 HYDROGEN NMR SPIN DIFFUSION IN EPOXY POLYMERS." A. C. Lind. McDonnell Douglas Research Laboratories, St. Louis, Missouri 63166.

Pulsed hydrogen NMR was used to study the sizes of rigid and mobile regions in amine-cured epoxy resins as a function of stoichiometry and sorbed  $\text{CHCl}_3$ ,  $\text{C}_2\text{Cl}_4$ ,  $\text{H}_2\text{O}$  or  $\text{D}_2\text{O}$ . The free-induction decay signals from samples containing sorbed solvent or from samples at elevated temperatures contained Gaussian and Lorentzian components. The Gaussian component was assigned to the rigid highly crosslinked regions and the Lorentzian component was assigned to mobile regions containing excess or incompletely reacted amine which became mobile as a result of sorbed solvent or increased temperature. The sizes of the mobile regions were determined from the times required for spin-diffusion to take place between the two regions. Interfering effects of translational diffusion of the hydrogen-containing solvent molecules were investigated. Estimates of the sizes of the rigid regions were deduced from the sizes of the mobile regions and the Gaussian/Lorentzian ratio. The results showed that the sizes of both the mobile regions (0.6 to 1.2 nm) and the rigid regions (19 to 44 nm) decreased with increasing amine content. Conducted under Naval Air Systems Command Contract N00019-79-C-0414 and the McDonnell Douglas Independent Research and Development program.

<sup>79</sup> CARBON-13 NMR INVESTIGATION OF SYN-ANTI ISOMERISM IN 2-PHENYLMINO-1,3-DIOXOLANES. L. E. Over, Mobay Chemical Corporation, Penn-Lincoln Parkway West, Pittsburgh, Pa. 15205

Seven 2(p-substituted-phenylimino)-1,3-dioxolanes were synthesized from the appropriate phenyl isothiocyanates and 2-dibutylstanna-1,3-dioxolane. Ambient temperature Carbon-13 NMR spectra of these seven i"Uno-1,3-dioxolanes showed two resonance lines of equal intensity for the methylene carbons in the dioxolane ring. This results from syn-anti isomerization around the N=C bond. The rate of isomerization was calculated from ambient temperature spectra and correlated well with



Hammett sigma values. Dynamic Carbon-13 NMR experiments allowed the free energy of activation  $\Delta G^\ddagger$  for the isomerization process to be calculated and correlated with Hammett sigma values. A possible mechanism for the syn-anti isomerization is also presented.

<sup>80</sup> CARBON-13 NMR AND OTHER SPECTROSCOPIC STUDIES OF CHEMICALLY MODIFIED SILICA SURFACES. D.S. Kendall, D.E. Leyden, Department of Chemistry, University of Denver, Denver, CO 80208.

Chemically modified surfaces prepared by silylation of oxide surfaces such as those of silica gel or controlled pore glass have found a wide variety of applications. Modified siliceous surfaces have been used extensively in our laboratory as substrates to immobilize chelating functional groups for the purpose of preconcentration of trace metal ions from water. An immobilized acetoacetamide and its copper(II) and iron(III) complexes have been prepared and investigated. Cross polarization/ magic angle spinning solid state carbon-13 NMR spectra will be presented and discussed. Photoacoustic spectroscopy and Fourier transform infrared spectroscopy have also proved valuable in the characterization of these materials. In particular, keto-enol equilibria and hydrogen bonding were investigated. The keto tautomer of the acetoacetamide can bind some metal ions. NMR spectra of several other immobilized silanes will be reported. Differentiation between mono and bis complexes on the surface is possible.

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<sup>81</sup> Determination of the Relative Concentration of Carbohydrate Groups in Fulvic Acid by C NMR. R. L. Wershaw & i. 3. Pinckney, U.S. Geological Survey, Federal Center, Denver, 80^z> and Cornelius Steelink, Kevin Thorn, and M. A. Mikita, Department of Chemistry, University of Arizona, Tucson, AZ 85721.

Fulvic Acid, a natural organic polyelectrolyte, is a ubiquitous constituent of soil and surface waters. Although its chemical structure has not been elucidated, it is known to contain phenolic hydroxy groups, carboxylic groups and possibly carbohydrate groups. The C NMR spectra of fulvic acids however, generally are so broad and ill-defined that it is not possible to unambiguously assign bands to the different hydroxyl and carboxylic acid groups present in the fulvic acid molecule. We have developed a procedure for obtaining definite spectra of these groups by preparing their C-enriched methyl ethers and esters. The C NMR spectra of those methyl fulvates have strong well-defined OCH<sub>3</sub> bands, some of which are in the region where one would expect to find carbohydrate methyl ethers. Integration of areas of these absorption bands allows one to calculate the relative abundances of the various hydroxyl and carboxylic groups present in a fulvic acid sample.

# 82 AQUEOUS RELAXATION REAGENTS FOR CARBON-13 AND NITROGEN-15 NUCLEAR MAGNETIC

RESONANCE SPECTROSCOPY. T. J. Wenzel, M. E. Ashley and R. E. Sievers. Dept. of Chemistry and Cooperative Inst. for Research in Environmental Sciences, Campus Box 215, Univ. of Colorado, Boulder, CO 80309.

Studies have been performed utilizing metal complexes of the ligands ethylenediaminetetraacetic acid (H<sup>+</sup>EDTA), diethylenetriaminepentaacetic acid (H<sup>5</sup>DTPA), and triethylenetetraaminehexaacetic acid (HgTTHA) as aqueous paramagnetic relaxation reagents for <sup>13</sup>C and <sup>15</sup>N nmr. The Fe(III) and Cr(III) complexes of DTPA are quite "inert" towards most compounds and are especially suited for facilitating spin relaxation. The Gd(III) and Mn(II) DTPA complexes are also effective relaxation reagents. These complexes can be used to decrease the relaxation times of non-protonated carbons or nitrogens, resulting in enhanced signal to noise ratios. They also quench the nuclear Overhauser effect (nOe), allowing one to obtain quantitative <sup>13</sup>C nmr spectra, and eliminating the problems associated with the negative nOe observed in <sup>15</sup>N nmr. Through the use of these reagents, pulse angles can be increased and scan times can be decreased, resulting in better signal intensities in shorter times. Examples of compounds studied in the presence of these reagents include arginine, ascorbic acid, nicotinamide, and 5,5-dimethylhydantoin.

# 83 Si-29 NMR CHEMICAL SHIFTS I. ADDITIVE RELATIONS IN ALKYL HALO SILANES. D. Cory,

A. Wong and W.M. Ritchey. Department of Chemistry, Case Western Reserve University, Cleveland, Ohio 44106.

Si-29 NMR chemical shifts of simple alkyl and halosilane have been shown to follow an additive relation with first and second order coefficients via the Grant and Paul Method. 175 pieces of data, from the literature, are fit to 32 dependent variables to the below expression with a correlation of 0.9937 and a standard error of 7.67 ppm,

$$\delta = 60 + \sum \delta_1 + \sum \delta_2$$

where  $\delta$ , is the chemical shift of silane, the  $\delta_1$ 's are first order additive constants and the  $\delta_2$ 's are second order constants responsible for steric effects. The summations are over all atoms in the molecule.

In addition it is observed that all compounds which deviate by more than 1.5 standard deviations from the experimental values are protonated. This suggests that the diamagnetic term in the shielding expression has not been adequately taken into account. Finally the generally held concept that JT-d back bonding contributes to the chemical shift is shown to be consistent with our results from a comparison with C-13 coefficients.

# ^ SOLID-STATE <sup>13</sup>C NUCLEAR MAGNETIC RESONANCE STUDIES OF COALIFIED LOGS AND SAPROPELIC

KEROGENS. Patrick G. Hatcher, Irving A. Breger, U.S. Geological Survey, Reston, VA, 22092, and Gary E. Maciel, Nicofolaus Szeverenyi, and Larry W. Dennis, Colorado State University, Fort Collins, CO, 80523.

Coalified logs and sapropelic algal kerogens of Holocene to Permian and Carboniferous age have been examined by <sup>13</sup>C nuclear magnetic resonance (NMR) using cross polarization and magic-angle spinning. The NMR spectra of the coalified logs clearly demonstrate that lignin is the source of the aromatic structures in coals. Cellulose, abundant in Holocene logs, is hydrolyzed and partly removed during early diagenesis before the wood undergoes coalification to lignite. The lignin that remains as a residue in the lignite is also altered, probably losing most of its methoxyl groups, as well as water and C3 side-chains. Lignitic logs undergo further coalification to the bituminous rank, probably by loss of soluble, oxygen-rich humic acid-like components. NMR spectra of Holocene algal sapropels, analogs of sapropelic coals, and sapropelic kerogens, show as major components carbohydrates, proteins, and complex paraffinic structures containing carboxyl and ether functional groups; they also show the absence of lignin. Differential decomposition of carbohydrates and proteins and preservation of the paraffinic components results in the formation of sapropelic kerogen. During burial, this kerogen undergoes chemical changes involving loss of its oxygenated functional groups so that the resultant materials are predominantly composed of macromolecular paraffinic structures.

- 85 CHARACTERIZATION OF CARBON DEPOSITS IN COAL-CONVERSION CATALYSTS. H. L. Retcofsky, S. S. Pollack, Pittsburgh Energy Technology Center, U. S. DOE, P. O. Box 10940, Pittsburgh, PA 15236, and G. E. Maciel, Department of Chemistry, Colorado State University, Fort Collins, CO 80523

Carbon deposition is considered to be a principal contributor to the deactivation of coal-liquefaction catalysts. The Pittsburgh Energy Technology Center has undertaken time-dependent studies of the deactivation of such catalysts to determine the relative importance of carbon deposition and other possible modes of deactivation. The most useful non-destructive tools to characterize the carbon deposits were found to be cross-polarization carbon-13 magnetic resonance spectrometry (with magic angle spinning) and x-ray diffraction. Preliminary studies of cobalt molybdate catalysts aged in continuous stirred tank reactors at time intervals up to 247 hours revealed (1) that the reaction of carbon atoms in multilayer crystallites increases with time on stream and (2) that the carbon aromaticity of the deposits, although dependent upon the nature of the catalysts investigated, appeared to be essentially independent of time on stream.

- 86 QUANTITATIVE ASPECTS OF CPMAS SPECTROSCOPY IN COALS: RELAXATION EFFECTS AND EXPERIMENTAL REQUIREMENTS. James Lee and K. W. Zilm, University of Utah Research Institute Laboratory for Advanced NMR Applications, MO Chipeta Way, Suite 110, Research Park, Salt Lake City, Utah 84108.

Proton  $T_1$  and  $T_2$ ,  $^1\text{C}$   $T_1$  and  $T_2$ , and TCH data will be reported on six coals ranging from lignite to anthracite. The interaction of these relaxation parameters and their effect on the quantitative nature of the CPMAS spectra of the coals will be discussed. The effects of high speed magic angle spinning and Hartmann-Hahn mismatch will also be explored as well as the experimental requirements needed to insure the best possible data are taken.

- 87 SPIN DYNAMICS IN THE CP/MAS  $^1\text{C}$  STUDY OF FOSSIL FUELS. G. E. Maciel, M. J. Sullivan and N. M. Szeverenyi, Department of Chemistry, Colorado State University, Fort Collins, Colorado 80523.

In order to optimize the efficiency of a  $^1\text{C}$  CP/MAS experiment on a coal or oil shale sample, or to calibrate properly the analytical significance of such experiments, it is necessary to examine the pertinent NMR relaxation phenomena in such samples. Using the  $^1\text{C}$  CP/MAS signal for detection, both  $^1\text{C}$  and  $^1\text{H}$  relaxation studies have been carried out on a series of coals. The results are discussed in terms of the problems and potential of fossil fuel analysis by  $^1\text{C}$  CP/MAS NMR.

- 88 HIGH RESOLUTION NMR AND SELECTIVE DERIVATIZATION OF SOLID FOSSIL FUELS, K. O. Rose and M. T. Melchior, Exxon Research and Engineering Company, 1900 E. Linden Avenue, Linden, NJ 07036

Solid-state NMR experiments which utilize cross-polarization (CP) and high-speed magic-angle sample spinning (MAS) techniques provide new hope for characterizing the distribution of carbon types and reactive heteroatom sites in carbonaceous solids. The NMR spectral resolution typically observed in solid coal and oil shale samples and their solid products is limited by the molecular complexity of the sample and the absence of segmental motion in the solid. Our ability to identify and measure particular classes of carbon types is seriously compromised by these effects. The purpose of this paper is to discuss options for increasing the information content and assessing the quantitative accuracy of CPMAS spectra for fossil fuel samples. As one approach for enhancing spectral detail, mild and selective chemical reactions including trimethylsilylation and alkylation have been combined with solid-state NMR techniques to pinpoint reactive OH and COOH sites in coal which are unresolved in the CPMAS NMR spectrum of the underivatized coal material. Using alkylation techniques previously described and  $^{13}\text{C}$ -enriched alkylating agents, the NMR sensitivity to incorporated groups is significantly improved. Experiments will be presented which demonstrate the advantages of  $^{13}\text{C}$ -enriched alkylation and CPMAS  $^{13}\text{C}$  NMR for investigating a variety of low concentration alkylation sites in solid fossil fuels.

- 8\* AN NMR INVESTIGATION OF EASTERN AND WESTERN SHALE OILS. D. A. Netzel and F. P. Miknis. Laramie Energy Technology Center, P.O. Box 3395, University Station, Laramie, WY 82071

The chemical composition of Eastern and Western Oil Shales differ considerably. These differences, primarily the lower hydrogen content, result in relatively lower oil yield for Eastern shales compared to Western shales. To increase the oil yield for Eastern shales over the conventional retorting process requires retorting with hydrogen such as is done in the IGT process. The composition of oils produced from retorting Colorado, Kentucky New Albany and Kentucky Sunbury oil shales by the IGT Hytort and the Fischer Assay Processes were investigated by Nuclear Magnetic Resonance Spectroscopy. Data will be given which shows differences in the chemical composition of the oils as the result of the retorting process and geographic location of the oil shale. Parameters to be discussed qualitatively and quantitatively are changes in the aromaticity, average alkane carbon chain-length, olefins, branched alkanes and heteroaromatic composition.

- \* TRACE ANALYSIS OF VOLATILE ORGANIC COMPOUNDS IN BIOLOGICAL AND ENVIRONMENTAL PROBLEMS. Albert Zlatkis, Chemistry Department, University of Houston, Houston, Texas, 77004.

Biological samples such as urine, serum, and cerebrospinal fluid yield complex mixtures of low molecular volatile metabolic products. These organic compounds must be concentrated prior to separation and analysis by high resolution gas chromatography and mass spectrometry. The concentration is effected by headspace and transelevator techniques using a hydrophobic porous polymer, Tenax GC or glass beads as the adsorbent. Thermal desorption of the adsorbate prepares the sample for chromatography. Comparison of profiles of normal and pathological fluids (diabetes mellitus) will be presented. Samples as small as 10  $\mu$ l can be used for analysis. These techniques are also applicable to environmental samples at the ppb level. New horizons for trace analysis will also be discussed.

- 91 GAS CHROMATOGRAPHIC STUDY OF MODIFIED PYROLYTICALLY COATED GRAPHITE SUPPORTS. O. A. Ogunkeye, L. ft. Hoi combe Dept. of Chemistry, University of Texas, Austin, TX 787U.

In this study, efforts were directed at designing specific and stable carbon adsorbents by the synthesis of inert and mechanically stable carbon adsorbents followed by chemical modification of their surfaces.

Mechanical stabilization of the graphite particles was achieved by the pyrolysis of benzene vapor on the surface of heated graphite particles. Addition of surface groups to the pyrolytic surface to alter the chemical specificity of the support material will be considered. Gas Chromatographic columns packed with such adsorbents will be characterized on the basis of their efficiency, specificity and stability and will be compared to results obtained from columns packed with untreated graphite particles and modified diatomaceous earth materials.

The feasibility of individual synthesis of specific graphite adsorbents achieved by controlled coating of the particle surfaces with compounds of different functional groups will be discussed.

- 92 SOME FACTORS INFLUENCING REPRODUCIBILITY IN FUSED SILICA COLUMNS. T. J. Stark, P. Larson and R. Dandeneau, Hewlett-Packard Company, Route 41, Avondale, Pa. 19311

An incomplete understanding of the critical physical and chemical properties of stationary phases for WCOT columns has led to an ongoing program of characterization and analysis. Fused silica columns when deactivated with octamethylcyclotetrasiloxane and coated with siloxane gum phases have been found to give highly reproducible Kovats retention indices. Even when *one accounts for* operator to operator, instrument to instrument, and column to column variability, retention indices as reproducible as  $\pm 1$  unit are attainable for polar and aromatic compounds. The effect of column environmental stress parameters such as high column temperature, oxygen content of the carrier gas, and the effect of sample solvent on the retention indices of selected compounds are reported. These effects are compared with thermal, spectroscopic and gel permeation analysis of siloxane phases.

93 DYNAMIC HEADSPACE TECHNIQUES FOR GAS CHROMATOGRAPHIC ANALYSES OF ENZYMIC DECHLORINATION REACTIONS. Bert Ho, Gary Schlickeiser and John A. Thompson. School of Pharmacy, University of Colorado, Boulder, CO 80309.

Dynamic headspace sampling methods are commonly used in analytical chemistry to isolate and concentrate trace organic contaminants from water samples for subsequent GC analyses. We have adapted these techniques to studies of enzymatic reactions involving volatile substrates and/or formation of volatile products. A vessel was designed for incubating organic substrates with subcellular hepatic fraction in a closed system. Following the incubation period, volatile organic materials can be sparged from the incubation mixture and trapped on Tenax. The Tenax traps are then desorbed onto a GC column packed with Carbowax or onto a Carbowax capillary column. Analyses are performed using either a flame ionization detector or a mass spectrometer. Our preliminary work has involved measurements of the oxidative metabolism of several polychloroethanes by rat liver microsomes. At substrate concentrations of  $1 \times 10^{-6} M$ , approximately 30% of 1,1,2-trichloroethane and 17% of 1,1-dichloroethane are metabolized after 1 hr. at 37°. Other polychloroethanes are metabolized at slower rates. The dynamic headspace method has provided a considerably more sensitive assay of enzyme activity than conventional static headspace methods. Other applications of this technique will be discussed.

9>4. QUANTITATIVE DETERMINATION OF 1,2-DIBROMO-3-CHLOROPROPANE(DBCP) IN WHOLE RAT BLOOD AT PART PER TRILLION LEVELS. P. E. Kastl, E. A. Hermann and W. H. Braun Toxicology Research Laboratory, H&ES, U.S.A., Dow Chemical Company, 1803 Building, Midland, MI 48640.

1,2-Dibromo-3-chloropropane (DBCP) has been used as a soil fumigant and nematocide in agricultural cropland since 1955. Reports have associated exposure to DBCP with disruption of spermatogenesis and azoo- or oligo-spermia in male workers. Tests on laboratory animals have shown that exposure leads to testicular atrophy. In support of toxicology studies in animals, an analytical method has been developed to determine DBCP in whole rat blood at part per trillion levels. Spiked DBCP blood standards were extracted with toluene containing an internal standard, hexachloroethane, and analyzed by electron capture-gas chromatography (EC-GC). The mean % recovery of DBCP from whole rat blood was  $96.7 \pm 3.0\%$  for the concentration range  $2.28 \times 10^{-11}$  ng/ml to  $2.28 \times 10^{-9}$  ng/ml DBCP. DBCP blood concentrations above the calibrated detector range of  $2.28 \times 10^{-11}$  ng/ml to  $1.14 \times 10^{-9}$  ng/ml DBCP were diluted into the linear range. In addition, DBCP water standards were extracted with toluene and analyzed by EC-GC. The mean % recovery was  $95.9 \pm 2.6\%$  for the concentration range  $1.14$  ng/ml to  $1.14 \times 10^{-9}$  ng/ml DBCP in water. DBCP water concentrations above the calibrated detector range were also diluted into the linear range.

95 ON-COLUMN INJECTION WITH WCOT COLUMNS: QUANTITATIVE ANALYSIS OF CARBAMATE PESTICIDES, STEROIDS AND VOLATILE ORGANICS. T. J. Stark, S. R. Freeman, K. Augenblick, Hewlett-Packard Company, Route 41, Avondale, Pa. 19311

Sample introduction onto capillary columns has historically involved a flash evaporation of the sample. Such an experience is necessary when using split or splitless sampling; however, when analyzing thermally labile compounds or compounds of low volatility, the flash vaporization step may adversely affect the precision and accuracy of the analysis. Recent work by Grob (J. Chrom., 151 (1978), 311., & J. HRC 4 CC, 1 (1978), 263.), Grob, Jr. (J. HRC & CC, 2 (1979), 15.) and Schomburg (J. Chrom., 142 (1977), 87.) describes a "cool" technique for sample introduction. Such an on-column (Grob) or direct (Schomburg) injection significantly reduces the sample discrimination which commonly occurs in the needle when a flash vaporization injection is used. In addition to reducing sample discrimination, the on-column (cool) injection technique eliminates the contamination and adsorption problems associated with the septum, for the hardware necessary for on-column (cool) injection does not use a septum to isolate the chromatographic system from the external environment. It is interesting to note that with an on-column injection, a recon-



Generation of the sample on the column is still necessary. Quantitative results will be presented for a wide range of compound classes, including polycyclic aromatic hydrocarbons, normal hydrocarbons, steroids and pesticides. Factors which affect the quantitation, such as sample size, rate of injection, column temperature, needle position and carrier gas will be discussed.

96 FLUOROMETRIC POSTCOLUMN REACTION DETECTOR FOR DETERMINATION OF THE ANIONS NO.,  
2031-100> REID, E. IN HPLC > 1977 Y. R. FLEISCHER FOR HPLC 9 >>> Chemistry Department, BG-10  
University of Washington, Seattle, WA 98195.

The sensitive and selective determination of separated anions in eluents from anion exchange columns can be carried out by continuously adding a suitable fluorescence reagent solution to the column eluents and monitoring the fluorescence of the reaction product.

A method is developed for the determination of oxidizable anions in reaction mixtures by the chemical reduction of cerium(IV). Cerium(III) fluoresces whereas cerium(IV) does not. In an on-line reactor, the reaction product cerium(III) is formed by a reaction of the above oxidizable anions with cerium(IV) in sulfuric acid. The fluorescence of this reaction product is monitored at an emission wavelength of 360 nm and an excitation wavelength of 260 nm.

Nanogram quantities of these anions can be determined by means of this fluorescence postcolumn detector.

97 AUTOXIDATION CHEMILUMINESCENCE - J. BLUM (AOCL) FOR LIQUID CHROMATOGRAPHY. >L.S.L.  
Gandelman and J. W. Birks. Department of Chemistry and Cooperative Institute for Research in Environmental Sciences, University of Colorado, Boulder, CO 80309.

A selective liquid chromatography detector sensitive to organic compounds containing oxygen functional groups will be described. The detector is based on the Co(II) catalyzed peroxide-luminol chemiluminescence reaction. The oxygen containing organic compounds, as they elute from the column, are photochemically oxidized at 365 nm in a quinone photosensitized reaction which produces hydroperoxides and/or hydrogen peroxide from the organic solutes. These peroxides are then quantitated within the flow system by the Co(II) catalyzed chemiluminescence reaction with luminol. Oxygen containing organic compounds - acids, alcohols, aldehydes, esters, ethers, ketones, and saccharides - respond with detection limits in the low microgram range.

98 MULTIDIMENSIONAL LIQUID CHROMATOGRAPHY FOR THE ANALYSIS OF COMPLEX SAMPLES. Kenneth Ogan and Elena Katz The Perkin-Elmer Corporation Applied Research Group, Main Ave. Norwalk, CT 06856.

Selectivity chromatographic techniques have been widely used to divide very complex samples into fractions that are more readily analyzed. The utilization of modern chromatographic technology offers the added benefits of speed and efficiency. One analytical method for polycyclic aromatic hydrocarbons and phenols in oil and coal liquid samples utilizes separations on three LC columns in succession. The same type of column is used in the first and third steps, with the fractionation on the first column serving to limit the retention range of the compounds included in the final analytical sample. The second fractionation step utilizes size-exclusion chromatography, and serves to reduce the complexity of the analytical sample by restricting the molecular size range of the compounds included. The coupling between these first two steps has been automated. The final step is a high-resolution analytical separation, which also utilizes the sensitivity and selectivity of fluorescence detection.

" Optimization of Resin Based Column Packing For Rapid HPLC Carbohydrate Analysis, Michael J. Gray, Bio-Rad Laboratories. 32nd & Griffin, Richmond, California 9480\*  
A survey of past chromatographic data pertaining to ion exchange chromatography often contributes to the belief that the separation kinetics are very slow for resin based IMP HPLC columns. Many chromatograms show long retention times in terms of hours and complex solvent systems involving slow flow rates, stepwise

gradients and harsh reagents. Separations research conducted at Bio-Rad laboratories is proving that when all important variables effecting resolution and retention time are optimized: when selectivity is focused on a specific compound or class of compounds rapid chromatographic analysis is possible in many cases unsurpassed by any other method.

The chromatographic variables which were examined are as follows: 1. Resin Cross Linkage, 2. Resin Ionic Form, 3. Resin Particle Size, 4. Column Configuration, 5. Column Temperature, 6. Column Flow Rate, 7, Eluant Composition. Optimization of these variables produced significant improvements in resolution and speed of analysis for oligosaccharides, disaccharides, pentose sugars and carbohydrates in fermenting solutions.

100 SELECTIVITY OF PACKINGS AND SOLVENTS. T. Hanai and J. Hubert. Univ. de Montreal, Dep. de Chimie, C.P. 6210, Succ. A, Montreal, Quebec H3C 3V1.

Chromatographic behaviour of different types of compounds depends upon their molecular interactions with the surface of packings. The interaction can be hydrophobic, <sup>11-11</sup>, charge transfer, ion-ion, hydrogen bonding etc. When we discuss about the chromatographic behaviour of phthalates, hydrophobic, <sup>11-11</sup> or contact charge transfer interactions should be recognized. The difference of interactions between some packings like ion-exchangers, silica gel and hydrophobic packings are demonstrated in aqueous and non-aqueous eluents. Polystyrene divinylbenzene co-polymers is a specific packing for the study of <sup>11-11</sup> interactions and on ion-exchanger is one for the study of Lewis acid-base interaction. In reversed phase mode liquid chromatography acetonitrile was a non selective solvent and tetrahydrofuran was a selective one. Therefore we can mathematically controll the retention of non-ionic compounds in the system of an octadecyl bonded packing and acetonitrile-water mixtures. Method of prediction of retention time from the structure of solutes is demonstrated. The controll of the retention in tetrahydrofuran remains to explain.

101

IMPORTANCE OF SOLVENT CHOICE AND SOLVENT HANDLING IN CHROMATOGRAPHY. J. W. Huber and J.T.Przybytek, Burdick & Jackson Laboratories, Inc. 1953 S. Harvey Street, Muskegon, Michigan 19442

In designing a chromatographic separation, the choice of solvent and its handling may have significant effects. The wrong procedure can result in lost time, poor data, extraneous peaks, unstable baselines, lost peaks, irreproducible results, safety hazards and unnecessarily high chromatography costs.

Significant differences between solvents of similar physical properties will be discussed, along with techniques developed in our laboratory for setting up a separation and generating the required background data. Advantages of "new" alternative solvents will also be described.

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THE THREE MICRON COLUMN - A SYSTEM CONSIDERATION, Marlin Bensinger, Terry Meyers, Laboratory Data Control, P.O. Box 10235, Riviera Beach, FL 33404.

System considerations for the practical use of the 3 micron ODS column are discussed. Plate count and resolution comparisons using various types of detectors are shown. Consideration of techniques, solvent characteristics, and column characteristics are presented.

103 HIGH-SPEED SEPARATION OF ULTRAVIOLET ABSORBING CONSTITUENTS IN URINE BY LIQUID CHROMATOGRAPHIES. T. Kauai and J. Hubert. Univ. de Montreal, Dep. de Chimie, CP. 6210, Succ. A, Montreal, Quebec H3C 3V1

Urine from babies, children and adults were analyzed in different liquid chromatographic systems. The first used a weak anion exchanger (TSK-IEX 540 DEAE, 5µm bonded silica gel) as the packing and mixtures of acetonitrile and ammonium acetate buffer pH 4.5 as the eluents. The separation was done with gradient and took about 40 minutes. The second system used a macro porous strong anion exchange resin (Hitachi 3013N, 5µm, the matrix is polystyrene-divinyl benzene co-polymer) as the packing and an acetonitrile, ammonium acetate buffer and octyl sodium sulfate mixture as the eluent. The separation was done in about 20 minutes. The theoretical plate number of the ion-exchange resin column was about 3000/15cm for acids and 5000/15cm for monosaccharides. The third system used was a reversed-phase mode. The packing was an octadecyl bonded packing (TSK LS10P5) and the eluents were mixtures of phosphoric acid and acetonitrile. The separation was completed in 30 minutes with a gradient. Some metabolites were identified by their retention times in different systems. New born baby's urine had small amount of organics, therefore the sample was injected without pre-treatment like deproteinization. Urines from children were similar to that from adults and on the chromatogram metabolites of foods were found. Even so, urines from normal subjects were different from those from patients. The detail of the finger-prints of urines will be discussed.

104 VERY HIGH-SPEED LIQUID CHROMATOGRAPHY FOR ENERGY AND ENVIRONMENTAL RESEARCH. M. IV. Dong, K. Ogan and J. L. DiCesare. Perkin-Elmer Corp., Main Ave., Norwalk, CT 06856

Very high-speed liquid chromatography (VHSLC) means doing high efficiency LC in a short time span. This is accomplished by using small particle packings to obtain high efficiencies and short column lengths to decrease analysis times. Miniaturization of the hardware for reduction of extra-column band-broadening effects is necessary to obtain the full benefits of VHSLC. Typical performance levels of VHSLC are 200-300 plates per second; thus allowing many useful analyses to be performed in less than one minute with more than 10,000 theoretical plates. Benefits of VHSLC are short analysis time, high sensitivity and low solvent consumption. In addition, rapid gradient analyses are feasible with this system. Typical gradient cycle times are 5-7 minutes. The design of the high-speed LC columns and hardware will be described. Results from the application of this technique to the analysis of polycyclic aromatics, aza-arenes, alkyl- and chloro-phenols in environmental and fossil fuel samples will be presented. The use of coupled column techniques for rapid sample cleanup and high-resolution analysis will also be discussed.

105 Chloramphenicol Analysis By HPLC. D. L. Swafford, Laboratory Data Control, Interstate Ind. Park, P.O. Box 10235, Riviera Bch., FL 33404; J. Trueting, Ph.D., University of Texas Medical School, Houston, TX.

Laboratory Data Control in conjunction with Dr. John Trueting from the University of Texas Medical School, currently with Bio Science, have developed an isocratic HPLC method for the separation and quantitation of chloramphenicol in serum. The reverse phase analysis requires less than 15 minutes, uses a fixed wavelength detector at 280nm and a simplified sample preparation. Data was collected using both spiked pool serum and actual patient samples. This paper includes discussion of interference, and linearity studies as well as internal standard selection.

Use of this technique can yield relatively rapid quantitative results for therapeutic drug monitoring of this compound.

THE DETERMINATION OF CALCIUM PANTOTHENATE IN NUTRITIONAL SUPPLEMENTS BY HIGH PERFORMANCE LIQUID CHROMATOGRAPHY USING A VARIABLE WAVELENGTH DETECTOR

T.J. Hudson, Forrest C. Shaklee Research Center, 1992 Alpine Way, Hayward, CA 94545

A rapid and accurate procedure for the determination of calcium pantothenate in nutritional supplements by high performance liquid chromatography is described. Advantages of the method over the traditional microbiological assay technique for this nutrient are presented. The sample is dissolved in distilled water with the aid of sonication, filtered to remove particulate matter and injected directly into the HPLC. The analytical column eluent is monitored using a variable wavelength spectrophotometer operated at 210 nm. The method is applicable to multivitamin tablets, premix powders and raw material. The method has yielded an average recovery of 97.5% and a relative standard deviation of 2.1%. Results are compared with those obtained using the microbiological assay technique. The method has been successfully used for automated routine determinations.

107 -AN HPLC METHOD FOR THE DETERMINATION OF QUINIDINE IN SERUM. C. P. Patel, Analytical Services Laboratory, Ames Division, Miles Laboratories, Inc., P.O. Box 70, Elkhart, IN 46515

An HPLC method for the determination of serum quinidine has been developed. This method is isocratic, uses ambient temperature and conventional fixed wavelength (254 nm) detector, and is free of potential interferences from quinidine metabolites. The method involves initial addition of both quinine as an internal standard and a sodium carbonate solution to a serum sample, followed by extraction with methylene chloride. The top layer of serum is discarded. The quinine and quinidine contained in the organic layer are re-extracted with an aqueous hydrochloric acid solution. An aliquot of this acidic solution is injected onto a reverse phase ODS column. The chromatographic resolution of quinidine and its metabolites is accomplished by using a mobile phase composed of distilled water + 1 M sodium dihydrogen phosphate + conc. phosphoric acid + 1 M sodium perchlorate in the proportions of 850 + 20 + 10 + 10 + 110 mL respectively. The method is capable of measuring down to 0.5 ppm and is linear to 10 ppm quinidine in serum. Experiments have shown that the method is precise (2.3-4.4% CV for both within a day and between days) and accurate (recovery of 96-100.5% from spiked serum samples). The method is simple, quick and reliable for routine use in clinical laboratories.

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~~'''Dor'''trtaent~~ of Chemistry, XUniversity of Colorado, Colorado Springs, 50 COW.

An analytical method has been developed for the separation of nucleoside and nucleotide derivatives having a purine base. The method employs an isocratic elution of derivatives having a purine base. Adenine derivatives tested and separated in order of elution are: 2',3'-cyclic, 3',5'-cyclic and adenosine, 5'-phosphate. Interactions are not the only forces that influence retention behavior because 1'-phosphate derivatives show better retention than adenosine derivatives. The retention behavior in the presence of an organic modifier (methanol, acetonitrile, or DMSO) in the mobile phase is also a factor. The method was utilized for the separation of the products obtained by the phosphorylation of adenosine. A comparison with results obtained previously shows that the method is satisfactory and more accurate, order of elution of the adenine derivatives will also be discussed.

109 Use of HPLC in the Detection of Phenols in Industrial Aqueous Effluents. G. Rehagen, K. Thomas, and J. Goings. Midwest Research Institute, 425 Volker Boulevard, Kansas City, Missouri 64110.

An HPLC method for the analysis of five phenols in wastewater from a petrochemical facility is described. Samples were first prepared for analysis by gas chromatography by adjusting the pH to < 1 and extracting three times with dichloromethane (distilled in glass). Analysis by GC/EID was inadequate due to high background noise and poor chromatography. Therefore, an analytical method using HPLC/UV was developed which gave improved sensitivity. The extracts were re-extracted into 0.1 N sodium hydroxide and injected onto a reversed phase system. An acidic acetonitrile eluant was used and UV detection was at 280 nm. The discussion includes minimum detection limits, extraction efficiencies, and some comparisons of detection limits by GC/FID and HPLC/UV.

110 LIQUID CHROMATOGRAPHIC SEPARATION OF SHALE OILS AND SYNCRUDES BY HYDROCARBON TYPE. R. L. Miller, K. Ogan and L. Hellinger. The Perkin-Elmer Corporation, Main Avenue, Norwalk, CT 06856.

The complexity of crude oils and crude oil replacements derived from coal liquids, shale oils, and tar sands demands very complex analytical schemes for characterization. The ability of normal phase liquid chromatography to separate these complex mixtures into paraffin, olefin, aromatic, and resin fractions makes the technique quite useful as a first step in the characterization process. Fractions are retained on the basis of polarity, with the least polar paraffin fraction eluting first. Subsequent analyses by gas chromatography, liquid chromatography, and spectroscopy are greatly simplified by the availability of fractions containing only one chemical class.

Very low solvent strengths are required to separate paraffins and olefins. On the other hand, polar constituents of oils are tightly bound and require high solvent strengths. Column backflush and other multidimensional techniques may be exploited to isolate specific fractions. These techniques are presented in the context of separations adaptable to automation and preparative scale-up using turnkey hardware systems.

111 DIFFERENTIAL PULSE POLAROGRAPHIC DETERMINATION OF BROMIDE IN BRINE SOLUTIONS.

L. Jackson and S. Wilson. U.S. Geological Survey, Box 25046, MS 928, Denver Federal Center, Denver, CO 80225-

The determination of trace levels of bromide in the presence of high levels of chloride has presented a continuing problem to the analytical chemist. The chloride interference has been eliminated by oxidizing the bromide to bromate with hypochlorite solution and then quantifying the bromate with differential pulse polarography.

The oxidation is performed using calcium hypochlorite as the oxidizing agent in a pH 5.5 acetate buffer. After the oxidation is complete, the pH is adjusted to 1-1.5 with concentrated nitric acid and the bromate is determined polarographically at -0.5 V versus Ag/AgCl (pulse modulation 50 mV).

This technique has been successfully applied to the determination of ppm levels of bromide in naturally occurring brines with 10 percent chloride. The simultaneous determination of iodide is possible with this technique.

The pulse polarographic determination of bromide as bromate gives approximately a six-fold increase in sensitivity over the direct polarographic determination of bromide. The use of ion chromatography was compared to the polarographic technique.

112 HIGH PRECISION COMPLEXOMETRIC TITRATION OF CADMIUM IN THE PRESENCE OF URANIUM.

J. R. Qelmaestro, Exxon Nuclear Idaho Company, Inc., P. O. Box 2800, Idaho Falls, Idaho 83401.

A method is described for the determination of cadmium to an accuracy of better than 0.65% in acid solutions containing 2-24 mg Cd/mL in the presence of approximately 500 mg U/mL. Cadmium is determined by complexometric titration with EDTA at pH 5.5, after masking the uranium with sodium tartrate. Under these conditions, uranium does not interfere by consuming titrant, but it appears to slightly block the Cu-PAN

(PAN - 1-[2-Pyridylazo]-2-naphthol) indicator used. Iron and aluminum, present as impurities in the uranium, are masked by addition of fluoride. A reliable procedure is described for the automated titration of Cd in these solutions, using a spectrophotometric probe to detect the equivalence point. The precision attainable with this procedure is better than **0.20%**. Results are presented for the analysis in duplicate of a series of Cd-U solutions generated for nuclear criticality measurements.

113 VACUUM ULTRAVIOLET CIRCULAR DICHROISM: APPLICATIONS TO POLYSACCHARIDES. E.S. Stevens, Department of Chemistry, State University of New York at Binghamton, Binghamton, New York 13901.

Vacuum ultraviolet circular dichroism (VUCD) spectroscopy is now being used to characterize carbohydrates and polysaccharides. The technique is of special relevance for those molecules with no electronic transitions above 190 nm such as glucans. We have measured and compared the VUCD of (1->6)-**B**-D-glucan (pustulan) and (1->6)-**ci**-D-glucan (dextran). The random coil chains of both polysaccharides show only high energy bands at  $\lambda < 180$  nm. Upon gelation, however, pustulan displays a negative 184 nm band. A band at this position is usually not seen in unsubstituted polysaccharides. However, since we also observe it in gels and in solutions of (1->4)-**a**-D-glucan (amylose), we take it to reflect a high degree of local inflexibility. The significance of this result lies in being the first case of a saccharide CD band of known sign (negative) being attributable to a specific transition ( $\pi^*$ -H<sub>i</sub>) in a fixed and known geometry (amylose). We have now reproduced this observed CD by theoretical calculation using random phase theory. This is the first step in placing polysaccharide conformational analysis by VUCD on firm theoretical grounds.

11\* ENCAPSULATED XAD-2 EXTRACTION TECHNIQUE FOR A RAPID QUANTITATION OF BASIC DRUGS IN SERUM. Nasik Elahi, Department of Toxicology, 520 First Avenue, New York, NY 10016.

I describe a novel, simple and economical method for a rapid and efficient quantitation of basic drugs in serum, using a combination of encapsulated XAD-2 and 'microphase' extraction technique followed by gas chromatographic analysis using a nitrogen detector. The drugs are adsorbed from serum onto 400 mg- of XAD-2 resin encapsulated within a rigid, porous, polypropylene sphere, 2 cm. in diameter. Adsorption is carried out by agitating the contents for 20 minutes under positive pressure in a syringe apparatus equipped with a two-way stopcock and a clip for locking the plunger in place. The drugs are desorbed using 2 mL of methanol containing 1% tartaric acid. The methanol is collected in a centrifuge tube and made basic with at least an equal volume of pH 9.8 carbonate buffer. The contents are thoroughly mixed and 100  $\mu$ L of chloroform is added. The mixture is vortexed for 30 seconds and the layers allowed to separate. One  $\mu$ L is injected into gas chromatograph. A temperature program run of 130-260°C at 80°C/min. using a 4 ft. column packed with 3% DB2250 and a nitrogen detector, allows quantitative resolution of 17 basic drugs, from amphetamine to haloperidol, in both therapeutic and toxic ranges for all drugs. Extraction efficiencies are comparable to those reported in the literature for XAD-2 column extractions. The extracts exhibit minimal background interference. Total time for both extraction and analysis is less than 60 minutes. The procedure uses 2 mL of solvent, requires only one set of glassware and no centrifugation.

115 REACTIVITY OF SUBSTITUTED PHENYLNADIMIDES, Richard W. Lauver and William B. Alston, NASA Lewis Research Center, 21000 Brookpark Road, Cleveland, OH 44135

Addition-type polyimides end-capped with 5-norbornene-2,3-dicarboxylic acid (i.e. nadimides) are a class of thermally crosslinked resins of current interest for aerospace applications. These polyimides, particularly the version known as PMR-15 are employed as high temperature resistant matrix resins for use in advanced composites. There is a need to improve the processability of these resins which currently require temperatures near 300°C for initiation of the addition reaction. The reactivity of the norbornenyl moiety (presumably the retro-Diels-Alder reaction) must reflect the electron density and corresponding bond strengths of the nadimide group. This electron density can be altered by varying the chemical substituents adjacent to the nadimide group, and this variation can potentially decrease the initiation temperature of the addition reaction. For this study, a series of substituted phenylnadimide compounds were synthesized and characterized. Substituents were chosen to provide a broad range of electronic effects. It was observed that, in general, electron withdrawing substituents caused a significant decrease in the reaction temperature of the model nadimides while electron releasing substituents caused a perceptible increase in the reaction tempera-

ture. Changes in electron density and bond strengths were confirmed by monitoring C-13 chemical shifts and the infrared vibrational spectra of the model compounds. The potential applicability of this chemical approach in the synthesis of matrix resins having lower curing temperatures will be discussed.

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SEPARATION OF INORGANIC AND ORGANIC ANIONS ON A HPLC REVERSED-PHASE COLUMN - A NEW APPROACH. Norman E. Skelly, Analytical Laboratories, The Dow Chemical Company, Midland, HI 48640

A novel method for the separation, inorganic and organic anions on reversed-phase high performance liquid chromatographic columns is presented. By use of an eluent containing the octylamine salt of a mineral acid, inorganic anions such as bromide, iodide, nitrite, nitrate, iodate, cyanate, etc. can be separated. In the area of weak acids, the anions\* acetate, glycolate, oxalate, propionate, formate, monochloroacetate, dichloroacetate, trichloroacetate, acrylate are also separated. These separations have been applied to the determination of nitrate and nitrite in sulfuric acid, bromide and iodide in brine, glycolate, oxalate, nitrite, nitrate in nitration waste water, formic acid in 2,4-D waste water, nitrite and nitrate in silage. Separations are made on conventional liquid chromatographic apparatus and monitored by an ultraviolet detector at 205 nm. Mechanism for separation is attributed to ion exchange rather than ion pair formation.

118 DETERMINATION OF PYROLIZIDINE ALKALOIDS IN PLANT EXTRACTS BY GC (CI) MS.

J. H. McCoy, R. K. Skogerboe, and F. R. Stermitz. Department of Chemistry, Colorado State University, Fort Collins, CO 80523

Pyrolizidine alkaloids are known to occur naturally in plants in grazing areas. Some of these alkaloids are quite toxic. Due to the basicity of these compounds, they are amenable to determination by methane and ammonia chemical ionization mass spectrometry. Due to extensive fragmentation, electron impact M.S. often offers inconclusive information. By implementing G.C. as the sample introduction method, plant extract residues may be screened for potentially toxic alkaloids. The use of such techniques for this purpose will be discussed.

119 THE GENERATION AND DETERMINATION OF VOLATILE METAL CHELATES BY ANALYTICAL REACTION GC/CHROMATOGRAPHY. Steven R. Hill and R. K. Skogerboe, Department of Chemistry, Colorado State University, Fort Collins, Colorado 80523

Several attempts have been made to determine the trace metals present in various matrices by gas chromatographic techniques. The efficacy of this approach has been limited by the difficulties involved in the formation of volatile metal species. An on-column reactor for the generation of volatile metal chelates (tfa and hfa) has been developed. The effluents of the reactor and the chromatographic process is fed into an atomic absorption spectrometer for unambiguous identification of the chelated species. Various parameters relating to the analytical utility of this technique will be discussed.

120 ELECTROCHEMICAL DETERMINATION OF Cu SPECIES TOXIC TO RAINBOW TROUT. C. R. Gumina Jr., R. K. Skogerboe, Patrick H. Davies\*, Department of Chemistry, Colorado State University, Fort Collins, CO 80523, \*Colorado Division of Fish and Wildlife, Prospect Street, Fort Collins, CO 80523.

In the past decade a large emphasis has been placed on ascertaining the effects of man's waste management practices on aquatic life. It is important that these effects be accurately characterized in order for responsible legislation to be drafted. Since the chemistry that a specific pollutant undergoes determines its availability and, hence, its toxicology, it is mandatory that this chemistry be defined. Differential Pulse Polarography (DPP), Anodic Stripping Voltametry (ASV), and Differential Pulse Anodic Stripping Voltametry (DPASV) have been used to determine the chemical form(s) and kinetic parameters of Cu in three types of waters. The observed toxicological effects seen in rainbow trout fingerlings may be correlated to these Cu species.

- 128 AN AUTOMATIC SOLID STATE GAS ANALYZER- John Salsgiver, United Technical Corporation, P.O. Box 1065, Concord, MA 017\*2.

A general purpose automatic solid state gas analyzer would be a welcome addition to the arsenal of analytical tools available to the chemist and others who are involved in the determination of gaseous mixtures. This is particularly true, if the total analytical system is low cost, self-contained, provides reasonable accuracy, has sufficient sensitivity, and gives a rapid sample thruput. A new instrument system, the model GA-800, has been developed to meet these criteria.

A "stereo" approach has been taken to sample/column gas flows which permits rapid sample thruput. Here, a specifically designed gas sampling valve allows a single sample stream to supply a sample mixture to two different chromatographic columns simultaneously. Separate thermal conductivity detectors are used for each column. Thermoelectrically cooled, these detectors offer enhanced sensitivity over existing designs.

Electronically, each chromatographic channel contains signal amplification, baseline compensation and peak integration. Retention times and percent concentrations are outputted to a digital printer. A "quick look" strip chart recorder is also provided.

Utilities, including both power and gas supplies, are also self contained. A solid state gas sampling pump is included. Provision is made for automatic sample line flush prior to each analysis, if desired. The instrument is, therefore, suitable for both laboratory and field investigations. Typical chromatograms and potential areas of application for the new instrument will be presented.

- 129 OPTICAL ABSORPTION OF SEMICONDUCTING KTN (KTA Nb O<sub>3</sub>) SINGLE CRYSTALS. Masayuki Tsukioaka, Junzo Tanaka and Bin Okai. National Institute of Researches in Inorganic Materials, 1-1 Namiki, Sakura-Mura, Niihari-Gun, Ibaraki, 305 Japan.

The optical absorption was observed in semiconducting KTN (KTA Nb O<sub>3</sub>) single crystals in the wavelength more than 700 mμ. In order to clarify the relation between the optical absorption and electrical conduction in this system, the optical absorption measurement was performed in the temperature region from 60 K to 287 K. Both the Hall coefficient measurement and the Seebeck coefficient measurement were also done for these materials below room temperature. The experimental results show that the carrier concentration of these semiconducting KTN vary exponentially with temperature, whereas the intensity of the absorption does not change with temperature. Generally, the absorption coefficient of conduction electrons,  $\alpha$ , is written as follows:  $\alpha = N \exp[-E_A/kT]$ ,

where N is the concentration of conduction electron, X wavelength, AE activation energy. If the optical absorption was due to conduction electron, the absorption coefficient should vary exceedingly in accordance with the above relationship. It is therefore concluded that the temperature-independent absorption, more than 700 mμ, is not due to conduction electrons.

- IMPACT OF MICRO RAMAN ANALYSIS ON MOLECULAR IDENTIFICATION AND MICRO STRUCTURE CHARACTERIZATION. Fran Adar, Ph.D., Instruments SA, Inc. Metuchen, N. J. 08840.

Examples of micro Raman analysis from MOLE applications studies document the usefulness of the technique in industrial analytical laboratories and in academic laboratories. Origins of failure analysis can be clarified by identifying contaminants in situ, non-uniform distribution of polymers, defects in the crystallinity of materials. In addition, we have demonstrated that Raman spectra in some instances monitor the coherence length of crystallization in a range where no other probes offer useful information (20 - 150Å). Thus, while the resolution of the Raman microprobe is limited (by diffraction limited optics), the information content of the spectra provides a monitor of much smaller regions.

In the area of microanalysis, a fisheye in high impact polystyrene film (containing 5-10% polybutadiene) was attributed to the formation of a defect around an inclusion of pure polystyrene. The transformation zone around a stress-induced crack in a tetragonal zirconia ceramic was measured and found to extend no further than a single particle of the pre-sintered material, in some cases.

The outstanding example of Raman spectra monitoring long-range order is that of laser annealed silicon. As annealing proceeds, the band sharpens and moves towards that of crystalline silicon. The influence of the probe itself was detectable, but not significant. Thus, the Raman microprobe could be used for quality control and failure analysis in the manufacture of integrated circuits.



131 DETERMINATION OF WEAK ACIDS BY ION CHROMATOGRAPHY WITH CONDUCTOMETRIC DETECTION. T. Sunden and M. Lindgren. Dept. of Analytical Chemistry, S-901 87 Umea, Sweden.

Ion chromatography (IC) has been shown to be a very useful technique for the analysis of anions. Owing to the suppressor reaction (where X<sup>-</sup> is the anion)



there is a limit when conductometric detection is used; the acid corresponding to the anion must have a pK<sub>a</sub>-value below 7. Acids with pK<sub>a</sub>-values above 7 are not sufficiently dissociated to be detected conductometrically. Using post-column technique the degree of dissociation of the "weak" acids is increased adequately for conductometric detection. A comparison with other analytical techniques shows acceptable agreement.

132 USE OF A DIONEX ANION SEPARATOR COLUMN FOR CATION SEPARATIONS. 3. W. Wimberley, CONOCO, Inc., Research and Development Department, P.O. Box 1267, Ponca City, Oklahoma 74603.

It has been determined that cations can be separated very well on Dionex anion separator columns using standard cation eluents. Also it was shown that pumping cation (acidic) eluents through the anion separator column has no deleterious effects on the column when used to separate anions. In fact, evidence is shown that indicates that separating ability is improved for anions after use of the column for cation separations.

133 NEW ELUENT FOR THE ION CHROMATOGRAPHIC SEPARATION OF ALKALINE EARTH METALS. 3. W. Wimberley, CONOCO, Inc., Research and Development Department, P.O. Box 1267, Ponca City, Oklahoma 74603.

It has been determined that dilute nitric acid solutions containing 2 to 4 grams per gallon of Zn(NO<sub>3</sub>)<sub>2</sub>·2H<sub>2</sub>O are good eluents for the separation of the alkaline earth metal ions. The Zn<sup>2+</sup> ions are removed in the strong base suppressor column as Zn(OH)<sub>2</sub><sup>-</sup>. Upon regeneration of the suppressor column with strong base, the Zn(OH)<sub>2</sub> is dissolved and removed from the column. Advantages of this eluent, when compared to others commonly employed, are given.

TECHNIQUES FOR THE ROUTINE ANALYSIS OF AMBIENT SULFUR DIOXIDE BY ION CHROMATOGRAPHY. Margaret J. Zimmerman, J. Maxine Jenks, and George Dean. Texas Air Control Board, Laboratory Division, 6330 Highway 290 East, Austin, Texas 78723.

In April 1978, the Laboratory Division of the Texas Air Control Board began using a new ion chromatographic method for the analysis of ambient sulfur dioxide. Samples are collected in 50 milliliters of sodium carbonate-sodium bicarbonate buffer solution. In order to insure complete oxidation of sulfite to sulfate, one milliliter of 30% hydrogen peroxide solution is added to each sample. Samples are then heated to 40°C for two hours to destroy excess hydrogen peroxide. Background levels of sulfur dioxide are usually six to ten yg/M<sup>3</sup> (0.05 to 0.10 ug/ml in solution). To analyze at this level routinely required the modification of the ion chromatograph and development of techniques to handle these samples. All containers are presoaked in buffer to remove possible sulfate contamination. The size of the sample introduced to the ion chromatograph was increased to improve sensitivity. An electronic filter used to remove the effects of the pump pulse also increases sensitivity. To increase time between suppressor column regenerations, a longer suppressor column was installed. To increase analytical column life an in-line filter was installed before the eluent pump. Sample absorber and eluent are filtered before use, and in addition samples are filtered as they are injected into the ion chromatograph. These procedures have allowed the Laboratory Division to handle on a routine basis almost 4000 samples per year from the Texas Non-Continuous Monitoring Network.

- 135 DETERMINATION OF BROMIDE IN GEOLOGIC MATERIALS OF HIGH CHLORIDE CONTENT BY ION CHROMATOGRAPHY. S. Wilson and L. Jackson. U.S. Geological Survey, Box 25046, MS 928, Denver, CO 80225.

The determination of ppm levels of bromide in the presence of percent levels of chloride or nitrate is not possible with conventional anion chromatographic separation columns. The development of a new anion separator column by Dionex Corporation has now made this determination possible. The elution order is changed from  $\text{Cl}^-$ ,  $\text{Br}^-$ ,  $\text{NO}_3^-$ , and  $\text{SO}_4^{2-}$  as found using a conventional separator to  $\text{F}^-$ ,  $\text{Cl}^-$ ,  $\text{SO}_4^{2-}$ ,  $\text{Br}^-$ , and  $\text{NO}_3^-$ . In this case not only is the  $\text{Cl}^-$  and  $\text{Br}^-$  separation greatly enhanced, but the  $\text{Br}^-$  and  $\text{NO}_3^-$  separation is as well. This permits the use of 1 percent nitric acid for dissolution of geologic materials, either directly or as a fusion cakes.

The direct determination of bromide at ppm levels in naturally occurring brine solutions and evaporites has been studied.

(Use of brand or manufacturer's names is for descriptive purposes only and does not constitute endorsement by the U.S. Geological Survey.)

- 136 DETERMINATION OF DISSOLVED BORON IN NATURAL WATERS BY D. C ARGON PLASMA EMISSION SPECTROMETRY. Ann M. Nefcy, U.S. Geological Survey, 5293 Ward Road, Arvada, Colorado 80002.

The application of D. C. Plasma Emission Spectroscopy to the determination of boron in natural waters was evaluated. Cesium chloride was added to both samples and standards to provide a common background matrix. Emission intensity measurements were made on the basis of the average of three replicates, 10 second integrated intensity exposures. Samples containing between 0 and 1000  $\mu\text{g/L}$  Boron as B can be analyzed without dilution. This analytical range is consistent with B concentrations commonly found in surface and groundwaters. Potential interference typically found in natural waters were negligible. Analysis of USGS Standard Reference Water Samples with B concentrations ranging from 5 to 315  $\mu\text{g/h}$  gave standard deviations of 1.3 to 5.6%. Samples containing known added amounts of boron yielded 100  $\pm$  10% recoveries. Comparison with results from the colorimetric dianthrime method indicates good agreement between the two techniques. The plasma emission method appears superior in terms of precision, accuracy, simplicity, and speed.

- EFFECTS OF STREET SALTING ON AMBIENT AIR MONITORING OF PARTICULATE  
137 POLLUTANTS IN DETROIT. Peter O. Warner, John O. Kermoshchuk and  
\*James O. Jackson. Wayne County Health Department, Air Pollution Control Division, 1311 E. Jefferson, Detroit, Michigan, 48207. \*Los Alamos Scientific Lab., P.O. Box 1662-MS 486, Los Alamos, New Mexico, 87545.

Analysis by x-ray diffractometry has confirmed the presence of crystalline salt as sodium chloride in Detroit urban suspended particulate. This finding has given rise to a concern for the relationship between the occurrence of suspended salt and incidence of winter salting of streets in Detroit and greater metropolitan Detroit area. Furthermore, since air in most major cities is routinely continuously monitored for suspended particulate by soil-haze densitometry as a part of the air pollution alert program for emergency episode avoidance, it is important to assess the weight contribution of translucent crystalline salt to the measurement of these otherwise opaque particulates. Analyses have been made to determine salt as chloride in the measurement of both coefficient of haze (COH) and of actual total suspended particulate (TSP) using side by side sample collection. Correlation of these data has been made with days of actual street salting and a weight relationship has been established to show the influence of salt particulate on COH and suspended particulate. Coincident with this study are data which express the relationship between COH and high-volume sampled suspended particulate collected at the same site.

138 STANDARD REFERENCE MATERIALS. R. K. Kirby. Office of Standard Reference Materials, National Bureau of Standards, Washington, D.C

SRM's have been produced and distributed by the National Bureau of Standards (NBS) since 1906. SRM's are well-characterized homogeneous materials which have one or more chemical or physical property accurately measured and certified by NBS. SRM's are used to calibrate analytical instruments, to evaluate the precision and accuracy of analytical methods, and to help assure long-term quality control of measurement system. Last year NBS distributed approximately 40,000 units to over 10,000 customers throughout the world. Examples of SRM's for use in environmental, clinical, and forensic areas will be shown as well as those that can be used to calibrate spectroscopic, EPR, and NMR equipment.

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CHARACTERIZATION OF POLYMERIC PLASTICIZERS BY SIZE EXCLUSION CHROMATOGRAPHY AND HIGH PERFORMANCE LIQUID CHROMATOGRAPHY. Clyde E. Kurachi, K. him Wong and Donald EL Solomon. American McGaw, 2525 McGaw Avenue, Irvine, California, 92715.

There has been an increasing interest in higher molecular weight plasticizers. This is primarily due to the rising concern with the migration of low molecular weight plasticizers such as DEHP from the containers, components wrappings used to package food and pharmaceutical products.

Polyester glutarates and adipates are among the more common polymeric plasticizers, having estimated molecular weights ranging from 1800-6500. This study characterizes a number of polymeric plasticizers by size exclusion chromatography and intrinsic viscosity. Accelerated aging studies have been conducted to examine the thermal degradation properties of the polymeric plasticizers via change in molecular weight. Organic extraction procedures and an HPLC method for determining a number of common polymeric plasticizers in PVC is also presented.

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EPR STUDIES OF MULTI-PROTEIN COMPLEXES. B. J. Gaffney. Department of Chemistry, The Johns Hopkins University, Baltimore, MD 21218.

The phosphocarrier proteins of the bacterial sugar phosphotransferase system (PTS) act to transfer phosphate from phosphoenolpyruvate to several sugars as the latter are transported through *membranes*. The association of pairs of proteins in this system can be measured by physical techniques which are sensitive to the rotational motions of the proteins. We have spin labeled the smallest component of the system, HPr, a protein of molecular weight 8900. The labeled derivative retains full activity and the EPR signals respond to the rotational correlation time of the protein in media of varied viscosity, although spectral simulations indicate that the details of the motion are more complicated than simple Brownian diffusion. Binding of spin labeled HPr to a 60,000 dalton component of the system has been detected by EPR under conditions of varied divalent ion concentration and phosphorylation of the proteins.

Experiments are also in progress using selectively spin labeled membrane proteins to study motion of these membrane components.

4m ADVANTAGES OF <sup>15</sup>N AND DEUTERIUM SUBSTITUTED SPIN LABELS FOR QUANTITATIVE SIMULATION OF EPR AND ST-EPR SPECTRA IN BIOLOGICAL STUDIES. A.H. Beth, K. Balasubramanian, R.T. Wilder, S.D. Venkataramu, B.H. Robinson, L.R. Dalton, D.E. Pearson, C.R. Park, and O.H. Park. Vanderbilt University, Nashville, TN 37232

Binding of the enzyme, glyceraldehyde-3-phosphate dehydrogenase (GAPDH), to the cytoplasmic segment of band 3 protein in the red blood cell (RBC) membrane has been examined by EPR and saturation transfer EPR (ST-EPR) spectroscopies with the resolution enhancing spin label N-(15N-i-oxyl-2,2,6,6-tetramethyl-4-piperidinyldi7) maleimide (<sup>15</sup>N-DMSL). The spin label was covalently bound to the enzyme at the catalytic site cysteine-149 residue. Experimental EPR lineshapes from soluble and membrane bound enzymes were analyzed by direct simulation of spectra and indicated a structural alteration in the catalytic center of the bound GAPDH. A rigorous theoretical analysis of the ST-EPR spectra of soluble and membrane bound enzyme was carried out and utilized in conjunction with model system analysis to demonstrate that the motion of

membrane bound GAPDH could be characterized by an effective isotropic rotational correlation time of 20 usec. This indicated that the GAPDH-band 3 complex exhibits motional freedom relative to the membrane spanning segment of the band 3 protein or the RBC. The doubly substituted, <sup>15</sup>N-deuterium spin label affords gains in sensitivity and resolution which permit studies of membrane bound enzymes at physiological levels and quantitative simulations of the EPR and ST-EPR lineshapes with reasonable computation times.

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ANISOTROPIC MOTIONAL MODELS IN SATURATION TRANSFER EPR AT 9 AND 35 GHZ. L. Lee and L. W.-M. Fung, Chemistry Department, Wayne State University, Detroit, Michigan 48202, and M.E. Johnson, Medicinal Chemistry Department, University of Illinois Medical Center, Chicago, Illinois 60680.

As an empirical approach to the problem of anisotropic motional behavior in the saturation transfer (ST-EPR) time domain, we have developed two well-defined phospholipid bilayer model systems for y- and z-axial motion, and have compared spectral behaviors at X-band (9 GHz) and Q-band (35 GHz) observational frequencies. The two model systems are: (1) dipalmitoylphosphatidylcholine (DPPC) and cholesterol with a fatty acid analog spin probe whose nitroxide z-axis is approximately parallel to the diffusional symmetry axis, and (2) DPPC and cholesterol with a cholesterol analog spin probe whose nitroxide y-axis is approximately parallel to the diffusional symmetry axis. At X-band the behavior of the two systems is qualitatively similar, provided that motion is slow enough for stationary "turning points" to be observed. At Q-band the two types of motion are distinguishable even on a simple qualitative basis. Quantitative comparison of the behavior of spectral parameters demonstrates significant differences at both X- and Q-band, with more differences being observed at Q-band. In general, Q-band appears to yield more information about slow anisotropic motion than does X-band (provided that Q-band sample requirements can be met).

(Supported in part by the NIH, the Chicago Heart Association and the Michigan Heart Association; MEJ is an Established Investigator of the American Heart Association.)

143 Ca(II) AND Mn(II) BINDING TO  $\alpha$ -LACTALBUMIN. *Kentaro Murakami, Hiroyasu Hiehkawa, Piet Jan Andree and Laurence J. Berliner*. Department of Chemistry, The Ohio State University, Columbus, Ohio 43210 USA.

Metal binding equilibria to bovine  $\alpha$ -lactalbumin were measured for Ca(II), Mn(II) and some lanthanides by fluorescence and ESR spectroscopy. At  $\alpha$ -lactalbumin concentrations in the 2 to 8pM range dissociation constants were obtained from protein intrinsic fluorescence quenching for Ca(II) and Mn(II) of  $0.01 \pm 0.05$  and  $0.81 \pm 0.05$   $\mu$ M, respectively. ESR measurements of Mn(II) binding to  $\alpha$ -lactalbumin at protein concentrations above 50  $\mu$ M gave dissociation constants of  $34.4 \pm 2.0$   $\mu$ M and  $2.4$  mM respectively, corresponding to a single strong site and a very weak secondary site, exclusively. ESR measurements of Ca(II) displacement of Mn(II) gave a Ca(II) dissociation which was too low to measure. Evidence of similar binding affinities for  $Tb(III)$  and  $Eu(III)$  was found. Proton FT-NMR at 200 or 300 MHz of Ca(II)- $\alpha$ -lactalbumin clearly showed evidence for direct Ca(II) coordination to His 68 as proven by a downfield shifted pH independent C-2 resonance. Laser photo CIDNP NMR experiments of Mn(II) binding clearly showed the specific paramagnetic broadening of the C-2 and C-4 protons of His 68, localizing the strong cation binding site in the proximity of this residue.

14\* A PROBE OF DIFFERENTIAL COVALENCY OF METAL-LIGAND BONDS IN METALLO ENZYMES. M. Y. Makinen, L. C. Kuo, and M. B. Yim. Department of Biophysics and Theoretical Biology, The University of Chicago, Chicago, Illinois 60637-

In paramagnetic metalloproteins and enzymes, we have observed that selective coordination of <sup>17</sup>O-enriched ligands induces a perceptible change in the (electronic) spin-lattice relaxation time (T<sub>1</sub>) measured by the c.v. power saturation technique in the U-15 K range. The change can correspond to either an increase or decrease in T<sub>1</sub> in comparison to the <sup>16</sup>O system. To assign the origins of these observations, we have characterized the power saturation properties of structurally defined small molecule complexes and, in particular, high- and low-spin ferrihemoproteins in which the axial Fe-O bond distance can be varied. The decrease in T<sub>1</sub> is ascribed to the introduction of cross-relaxation from <sup>17</sup>O hyperfine levels, as expected for an essentially ionic metal-O bond. The increase in T<sub>1</sub> is ascribed to the influence of covalency on the orbit-lattice interaction [Ovchinnikov, Fiz. Tverdogo Tela 5, 188T (1963)]. The presence of the (1=5/2) nucleus alters the probability of a and B spins differentially at the <sup>17</sup>O atom through scalar and

dipolar coupling. With respect to the  $^0$  case, this results in an effective enhancement of ligand  $\gamma$  triplet charge-transfer. When  $^0$  is selectively enriched into solvent or substrate in cryoenzymologically stabilized (penta-coordinate) reaction intermediates of  $\text{Co}^{II}$ -substituted *enzymes*, power saturation data indicate that the two types of  $\text{Co}^{II}$  bonds do not exhibit equivalent covalency. This spectroscopic method for differentiating the extent of metal-ligand covalency provides an insightful means towards understanding the catalytic function of metal ions in metalloenzymes. (Supported by NIH GM 21900).

- H5 USE OF METHYLMERCURY(II) AS A SPIN-ORBIT PROBE IN OPTICALLY DETECTED MAGNETIC RESONANCE TO DISTINGUISH BETWEEN SINGLE-STRANDED AND DUPLEX DNA.\* C. K. Ott and A. H. Maki. Department of Chemistry, University of California, Davis, CA 95616.

The binding of  $\text{CH}_3\text{Hg(II)}$  to duplex and to single-stranded DNA leads to an external heavy atom effect due to the formation of complexes directly with purine and pyrimidine bases. Enhanced phosphorescence quantum yields and reduced lifetimes of the complexed bases allow them to be studied selectively using phosphorescence detected ODMR spectroscopy. Comparison of the ODMR spectra of DNA with those of specific mononucleotide- $\text{CH}_3\text{Hg(II)}$  complexes allows the identification of complexed bases, as well as the binding sites. The site affinities for  $\text{CH}_3\text{Hg(II)}$  binding near pH 7 decrease in the order  $\text{T(N)} > \text{G(N)} > \text{Gfl(?)}$ , with negligible affinity at other base sites. Each of these complexes produces a characteristic ODMR spectrum. The  $\text{T(N)}$  and  $\text{G(Nj)}$  sites engage in Watson-Crick base pairing in duplex DNA and do not bind  $\text{CH}_3\text{Hg(II)}$  without disruption of the duplex. The  $\text{G(N)}$  site, however, is accessible in duplex DNA. In single-stranded DNA, all sites are accessible. Complexes of  $\text{CH}_3\text{Hg(II)}$  with duplex DNA produce ODMR spectra dominated by  $\text{G(N)}$ , whereas  $\text{T(N)}$  signals dominate the complexes with single-stranded DNA. Extension of this method to detection and quantitation of single stranded regions in predominantly duplex DNA will be discussed.

\*Supported by NIH grant ES-02662.

- 1\*6 THE SYNTHESIS AND EPR SPECTRA OF THREE NOVEL SPIN-LABELED CROWN ETHERS. M. Eastman 6 D. Patterson, Dept. of Chemistry, U. of Texas at El Paso, El Paso, Tx. 79968, D. Bartsch 5 Y. Liu, Dept. of Chemistry, Texas Tech Univ., Lubbock, Tx. 79409, & P. Eller, Los Alamos Scientific Lab., Los Alamos, N.M. 87545.

The following nitroxide spin-labeled crown ethers have been synthesized: 2,2-(sym-dibenzo-16-crown-5)-4,4-dimethyloxazolidine-N-oxyl (I), 2,2-(sym-dibenzo-16-crown-5)-4,4, S.S-tetramethylimidazoline-N-oxyl (II), and 2,2,5,5-Tetramethyl-3-pyrrolin-I-oxyl-3-carboxylic Acid Hydroxy-sym-dibenzo-16-crown-5 Ester (III). I and II are characterized by having the nitroxide near the crown and rigidly bound to a carbon atom in the ring of the crown. I, II and III have been studied by EPR and the proton hyperfine splittings have been determined by second harmonic out of phase detection. The values obtained for the proton hyperfine splittings of (I) were checked by ENDOR and found to agree within experimental error. X-ray structure studies of I have been completed and the data is presently being analyzed. The effects on proton hyperfine splitting constants and Heisenberg spin exchange rates of the complexation of alkali metal cations by the spin labeled crowns have been determined and found to be relatively small. This work was supported by the Robert A. Welch Foundation.

- 147 PARAMAGNETIC DEFECT SPECIES IN SILICON DIOXIDE. 3. A. Weil, R. H. D. Nuttall and J. Isoya. Department of Chemistry and Chemical Engineering, University of Saskatchewan, Saskatoon, Saskatchewan, S7N 0W0, Canada.

A review will be presented of information obtained by electron paramagnetic resonance and electron spin echo spectroscopy about various radiation-induced paramagnetic defects in crystalline silicon dioxide. Emphasis will be placed on exact analysis of high-resolution spectra, and on temperature dependences and dynamic effects encountered. Among the  $\alpha$ -quar\*? caters discusse^ will h» various oxygen electron-hole species, as well as excess electron cations (ex.,  $\text{Ge}^{II}$ ,  $\text{Ti}^{II}$ ,  $\text{P}^{III}$ , ...) substituted at silicon tetroxide quasi-tetrahedral sites.

## 1\*8 PHOTOCHEMICAL STUDIES OF DEFECT STATES IN INORGANIC SOLIDS. R. S. Ekeh.

Eastman Kodak Company, Research Laboratories, 1669 Lake Avenue, Rochester, New York 14650.

Many inorganic materials have potential application in information-recording devices. For light-registering systems, they are generally band-gap solids which have complex photochemistries. They respond to excitation by the generation of electrons and holes. Charge transport must be efficient, and a useful image is generally formed by carrier annihilation processes. The photochemical reactions are affected by defects in the crystalline solids such as impurities and lattice imperfections. We have used EPR to study the role of such defects in the most familiar image-recording medium – the silver halide-based photographic system. Magnetic resonance data have been obtained from stable photoproducts and from transient species which were isolated by cryogenic methods. Kinetic data referring to electron/hole trapping rates, relative trap cross-sections, and trap depths have been obtained for many second- and third-row transition metal impurities in AgBr and AgCl. Evidence has been found for synergistic interactions between lattice defects and impurities. Synergistic processes involving combinations of foreign anions and/or cations also occur. These interactions add a further degree of complexity to the interpretation of the static and dynamic EPR data.

A review of our results and comments on their relevance to the photochemistry of inorganic solids will be presented.

## 19. OPTICALLY DETECTED MAGNETIC RESONANCE OF THE TRIPLET STATES OF THIOURACILS.\* M. R. Taherian and A. H. Maki. Department of Chemistry, University of California, Davis, CA 95616-.

Optically detected magnetic resonance (ODMR) in zero magnetic field has been observed in the phosphorescent states of 1-methyl-2-thiouracil ( $m's^*U$ ), 1-methyl-4-thiouracil ( $m's''U$ ), and 1-methyl-2,4-dithiouracil ( $m's's^*U$ ). The vibronic structure of the phosphorescence indicates that the triplet state is  $(^1r,7r^*)$  in each case. The zero field splittings (ZFS) are considerably larger than those of uracil, and increase in the order  $m's^*U < m's's^*U < m's's''U$ . The triplet lifetimes decrease in the same order. Both the increased magnitude of the ZFS and the reduced triplet lifetimes are attributed to an internal heavy atom effect of exocyclic S, particularly at position 4. ODMR transient methods were used to obtain the sublevel decay constants, as well as the relative radiative rate constants and quantum yields. The low phosphorescence quantum yields of  $m's^*U$  and  $m's's^*U$  were shown to result from efficient radiationless deactivation of the triplet state. Extended Hückel calculations on  $s^*U$  indicate the presence of relatively low-lying  $^1n,ir^*$  states, and a weak absorption band was assigned to  $^1n,ir^* \leftarrow S_0$ . The ZFS was shown to result largely from spin-orbit coupling interaction between the  $^1T,TT^*$  state and the  $^1n,ir^*$  states. Possible causes for the anomalous in plane polarization of thiouracil phosphorescence are considered.

\*Supported by NSF grant CHE79-10391.

## j., EPR INVESTIGATION OF U.V.-IRRADIATED RDX SINGLE CRYSTALS AT 77K. M. P. Pace and W. E. Moniz. Naval Research Laboratory, Code 6120, Washington, D. C. 20375

Cyclotrimethylene-trinitramine [ $C^*H^*N^*O^*$ , RDX, cyclonite] is a widely used primary explosive. RDX is a white solid which melts near 202 C. It can be crystallized as single crystals from a variety of solvents including acetone and acetic acid. We have completed an analysis of the EPR spectra obtained from a u.v.-irradiated single crystal of RDX at 77 K. Our results show that the  $-NO_2$  free radical is formed as the stable radiation product at 11 K and that there are two inequivalent conformations of the  $-NO_2$  radical in the crystal lattice. These two different radicals have slightly different g-tensors and N-14 hyperfine coupling tensors. For radical I the principal N-14 hyperfine couplings are  $A = 47.0$  G;  $A = 48.6$  G;  $A = 62.0$  G. For radical II the principal N-14 hyperfine couplings are  $A = 48.1$  G;  $A = 51.4$  G;  $A = 66.4$  G. The origin of the different radicals is attributed to loss of  $^1NO_2$  from inequivalent positions of the RDX parent molecule. (There are 3  $N-NO_2$  groups in an RDX molecule. When a mirror plane is taken perpendicular to the plane of the carbons and coincident with the C(2) - N(1) direction, two of these groups are symmetrical to each other, but not to the third group.) The experimental hyperfine couplings and g-tensors were used to calculate the EPR powder spectrum and this spectrum is compared to the experimental u.v.-generated powder spectrum of RDX.

- 151 THE VARIED GUISES OF ALKOXY RADICALS. Harold C. Box, Biophysics  
Department, Roswell Park Memorial Institute, Buffalo, New York 14263.

The alkoxy radical is a primary oxidation product observed in many carbohydrates, nucleosides, nucleotides and other compounds containing hydroxy groups following exposure to ionizing radiation at low temperature. Several of these alkoxy radicals have been characterized by ESR and ENDOR spectroscopy. These species appear in different guises depending upon the conformation of the radical. In serine, thymidine and bromodeoxyuridine the hyperfine patterns of the alkoxy radicals are generated by strong couplings between the unpaired electron and two  $\beta$  protons. In xylitol, dulcitol, deoxycytidine 5'-monophosphate, cytidine 3'-monophosphate and uridine 5'-monophosphate (barium salt) the alkoxy radical hyperfine patterns are generated by a multiplicity of weak proton couplings arising from one  $\beta$  proton and two or more  $\gamma$  protons. The  $g$  tensors associated with alkoxy radicals also exhibit considerable variability. Thus, two conformations of the alkoxy radical observed at slightly different temperatures in uridine 5'-monophosphate have markedly different  $g$  tensors. For one conformation maximum  $g$  value is 2.0710, which is a typical maximum value; however, for the other conformation the maximum value is only 2.0211. The recognition that a diversity of ESR and ENDOR spectra can arise from chemically similar species affords a more unified picture of radiation-induced oxidation processes in these compounds.

- 152 SPIN DIFFUSION IN SINGLE CRYSTALS OF ALKALI BIPHENYL. E. de Boer and O. Takizawa,  
Department of Physical Chemistry, University of Nijmegen, Toernooiveld, 6525 ED  
Nijmegen, The Netherlands.

It has been shown that single crystals can be grown from solutions of alkali aromatic ion pairs. These crystals always contain solvent molecules which are surrounding the positive alkali ions. The crystal structures of the single crystals prepared from alkali biphenyl (Bp) solutions consist of layers of negative ions of biphenyl molecules separated from each other by alkali solvent clusters. So magnetically speaking these crystals belong to the category of quasi-two-dimensional magnetic systems and should therefore exhibit effects of spin diffusion in their electron spin resonance spectra.

We have thoroughly investigated the ESR linewidth of NaBp.2Tg (Tg = triglyme = CH<sub>3</sub>O(CH<sub>2</sub>CH<sub>2</sub>O)<sub>3</sub>CH<sub>3</sub>). Experiments were performed at 9.4 GHz (X-band) and at 0.0332 GHz (resonance field 11 Gauss). At X-band, the linewidth has a  $(3 \cos^2 \theta - 1)$  angular dependence ( $\theta$  is the angle between the magnetic field and the normal to the two-dimensional magnetic plane). Especially at the magic angle ( $\theta = 54^\circ 44'$ ) the linewidth is frequency dependent. Perpendicular to the magnetic plane ( $\theta = 0^\circ$ ) the linewidth is independent of the frequency. These results are typically for two-dimensional magnetic systems and are caused by spin diffusion. A good quantitative explanation of the results can be given by the linewidth theory of Richards and Salamon (Phys. Rev. B9, 32, 1974) developed for two-dimensional magnetic systems.

- 153 AN EPR STUDY OF THE FREE RADICAL PROCESSES OCCURRING IN THE REACTION  
OF ASF<sub>5</sub> WITH A p-TERPHENYL SINGLE CRYSTAL, L. D. Kispert and K. Ezell,  
Chemistry Department, The University of Alabama, Tuscaloosa, AL 35401.

Recently highly conducting polymers have been prepared by the reaction ... of ASF<sub>5</sub> with single crystals of biphenyl, p-terphenyl, p-quarterphenyl, p-quinquephenyl and p-sexiphenyl, [Shacklette, et. al., J. Chem. Phys., 73, 4098 (1980)]. The highest conductivity has been obtained with p-terphenyl as the starting material. In an effort to identify the mechanism responsible, we have carried out EPR studies of the reaction between p-terphenyl crystals and ASF<sub>5</sub> (gas) from -120°C to 300°C. It has been observed that the reaction of ASF<sub>5</sub> with a thin crystal plate proceeds at -90°C via a free radical process to form a emerald green complex. The resulting EPR spectrum increases by a factor of 21 in 38 minutes at -84°C when the ASF<sub>5</sub> pressure equals 300 torr. Upon crystal rotation, the resulting EPR spectrum exhibits an anisotropic  $g$  value for each of the 2 monoclinic crystal sites. The spectrum for each radical site at the onset of the reaction is approximately 2 Gauss wide with no resolved hyperfine structure being detected, indicative of rapid spin exchange being present for each site but apparently

not between sites. Upon warming to near room temperature the spectrum narrows, the crystals turn black and the conductivity increases rapidly as evident by the loss of cavity Q. The results of an ELDOR study of the spin exchange process over a wide temperature range will be given as well as the EPR study of the reaction of SbFs with p-terphenyl in SO<sub>2</sub> solution.

154 STRUCTURE AND REACTIVITY OF SIMPLE ALKANE CATIONS AND CHARACTERIZATION OF HYDROGEN ATOM REACTIONS WITH ALKANES IN LOW TEMPERATURE SOLIDS. M. Iwasaki, Government Industrial Research Institute, Nagoya, Hirate, Kita, Nagoya 462, Japan.

Recent ESR studies on hydrogen atom reactions with alkanes at cryogenic temperatures (10 - 50K) will be surveyed together with the first ESR observation of simple alkane cations and the results will be discussed in relation to the radiation chemistry of alkanes. Contrary to the ordinary assumption that thermalized hydrogen atoms are unreactive at low temperatures, it has been found that they easily abstract hydrogen from alkanes except methane forming alkyl radicals at 10-50K. The hydrogen atom reactions in such low temperature solids are characterized as diffusion-controlled tunneling reactions, that is, the reactions take place by the tunnel process during first encounter. With increasing diffusion velocity of hydrogen atoms at higher temperature the reactions with lower activation energies become more and more favorable leading to ordinary processes. ESR spectra of n-alkane<sup>+</sup> from C<sub>1</sub> to C<sub>10</sub> and some branched alkane<sup>+</sup> have been observed at 4.2 or 77K in irradiated frozen matrices. Clear evidence has been obtained for Jahn-Teller distortion of C<sub>1</sub>H<sub>4</sub><sup>+</sup>, iso-C<sub>2</sub>H<sub>7</sub><sup>+</sup>, and neo-C<sub>4</sub>H<sub>9</sub><sup>+</sup>. The unpaired electron orbital of n-alkane<sup>+</sup> with the extended structure is delocalized in the in-plane  $\sigma$  molecular orbital over the entire chain, whereas that of the branched alkane<sup>+</sup> is rather confined to the C - C  $\sigma$  bond. Formation of alkyl radicals from these alkane<sup>+</sup> has been also observed. From some branched alkane<sup>+</sup> olefinic cations are formed by loss of H<sub>2</sub> or CH<sub>3</sub><sup>•</sup>. Based on these results probable mechanisms of solid phase radiolysis of alkanes will be proposed.

155 ENDOR STUDIES OF COAL AND ITS PROTIATED AND DEUTERATED PRODUCTS.

Ira B. Goldberg, Rockwell International Science Center, P.O. Box 1085, Thousand Oaks, CA 91360, and Hans Thomann and Larry R. Dalton, Chemistry Department, State University of New York, Stony Brook, NY 11794.

Pittsburgh seam coal (80.2 % C, moisture and ash free basis) was reacted with either <sup>2</sup>H<sub>2</sub> or <sup>3</sup>H<sub>2</sub> and either tetralin or tetralin-d<sub>8</sub> at 400°C and 13.8 MPa for times up to one hour.

The reacted mixture was separated by fractionation with benzene and tetrahydrofuran. The initial coal and the insoluble coal products were then studied by electron paramagnetic resonance and electron-nuclear double resonance spectroscopies. Results indicated that the radicals initially present in the coal remained unreacted throughout the hydrogenation reaction. A new, unidentified radical was formed when tetralin solvent was used, was indicated by a small hyperfine splitting not present in the original coal or coals treated with hydrogen. While the radicals initially present do not seem to react, they appear to be significant in the hydrogen transfer mechanism as evidenced by the decrease in signal intensity when deuterated reactants are used in the hydrogenation process.

156 ELECTRON PARAMAGNETIC RESONANCE OF WHOLE P.R. SPRING TAR SAND AND ITS VARIOUS FRACTIONS. V.M. Malhotra and W.R.M. Graham. Department of Physics, Texas Christian University, Fort Worth, TX 76129.

The 9.2 GHz electron paramagnetic resonance (EPR) spectra of whole P.R. spring tar sand, bitumen, asphaltene, the heptane soluble fraction, clay, and mineral matter have been studied at 10-530 K. EPR spectra of whole tar sand are very complicated due to the presence of a number of paramagnetic species such as organic free radicals, Mn<sup>2+</sup> and Fe<sup>3+</sup> at various sites, defects in mineral structure, and forbidden transitions. The bitumen, asphaltene, and heptane soluble fraction in the solid as well as dissolved in various solvents exhibit a single structureless EPR transition due to organic free radicals at a g-value of -2.0033. The temperature dependence of this EPR transition in asphaltene indicates a decrease in linewidth with increasing temperature while the g-value is unaffected. It is concluded that the magnetic interactions lead to exchange narrowing of the transition at higher temperatures. The spin-spin relaxation time T<sub>2</sub>, has been determined from the linewidth. The g-value, the number of unpaired spins gram (Ng), and the linewidth for bitumen, asphaltene, and the heptane soluble fraction have been determined and compared to tar sands from other locations. The vanadium EPR



spectra could only be observed at very low temperatures ( $\sim 15$  K). The clay spectrum reveals the presence of  $\text{Mn}^{2+}$  and  $\text{Fe}^{3+}$ . Spectra of  $\text{Mn}^{2+}$  indicate two magnetically inequivalent sites with very small zero field splitting. The spectra of  $\text{Fe}^{3+}$  are characteristic of its presence in kaolinite and illite clays. At 77 K the  $\text{Fe}^{3+}$  transition at  $g = 4.3$  completely changes its phase. The spin Hamiltonian parameters have been computed at various temperatures and compared with known spectra in clays. EPR spectra of the sand residue show that  $\text{Fe}^{3+}$  is present at several sites. Cooling or heating the sand component causes various reversible and irreversible phase changes to occur. On heating the sand sample in air the spectra of some of the  $\text{Fe}^{3+}$  sites gain intensity indicating the oxidation of  $\text{Fe}^{2+}$  into  $\text{Fe}^{3+}$ . On cooling the samples down to 77 K the  $\text{Fe}^{3+}$  transitions at  $g \sim 2.5-3$  are completely smeared out which is interpreted as resulting from ferromagnetic ordering.

[57] AN EPR STUDY OF A BITUMINOUS AND A SUB-BITUMINOUS COAL AND THEIR IN SITU OXIDATION, V.H. Malhotra and W.R.M. Graham, Department of Physics, Texas Christian University, Fort Worth, TX 76129.

The 9.2 GHz electron paramagnetic resonance (EPR) spectra of a high-volatile bituminous coal from the Pittsburgh, No. 8 seam and a sub-bituminous Montana coal from the Rosebud seam have been studied at 77-530 K. The  $g$ -factor, peak-to-peak linewidth  $\Delta B_p$ , the number of unpaired electrons per gram  $N_g$ , and susceptibility  $\chi$  have been computed from the organic free radical spectrum at various temperatures. The linewidth of the free radical absorption has been studied as a function of temperature as well as pressure. It is concluded that the major contributions to the linewidth are from unresolved hyperfine structure and unresolved  $g$ -factors. When a sample of the high-volatile bituminous coal is evacuated to low pressures a sharp resonance ( $\Delta B_p = 0.06$  mT) appears superimposed on a broad transition ( $\Delta B_{pp} = 0.61$  mT). The sharp resonance is tentatively assigned to the fusinite or tar component in the coal. Hyperfine effects due to the presence of the transition metal ion Mn are observed in both coal samples. The hyperfine splitting is independent of temperature and has a magnitude  $\sim 0.27$  GHz. Both samples exhibit spectra at  $g = 4.3$  attributable to the presence of  $\text{Fe}^{3+}$  in kaolinite and illite clays. This resonance, which is very temperature sensitive, indicates the presence of  $\text{Fe}^{3+}$  at two different sites at 77 K. A very broad transition ( $\Delta B_{pp} = 120$  mT) at  $g \sim 2.5$  which shifts to higher field on lowering the temperature, has been assigned to magnetic  $\text{Fe}^{2+}$ . On  $\text{CM. b/JJbi}$  oxidation of the coal samples at various temperatures the intensity of the spectrum at  $g = 4.3$  is enhanced, which is indicative of the conversion of  $\text{Fe}^{2+}$  into  $\text{Fe}^{3+}$ . An attempt has been made to estimate the presence of  $\text{Fe}^{3+}$ .  $\text{Fe}^{3+}$  transition at  $g = 4.3$  is studied as a function of acid removal of the mineral matter as well as magnetic removal and results are presented.

"~ EPR SPECTRA OF STABLE FREE RADICALS ADSORBED ON METAL SURFACES.  
R. D. Allendoerfer and J. B. Carroll, Jr. Department of  
Chemistry, State University of New York at Buffalo, Buffalo,  
New York 14214.

Using a recently developed coaxial microwave cavity, EPR spectra can be obtained for a variety of stable free radicals adsorbed on metal surfaces. Satisfactory spectra have been obtained for submonolayer coverage of a series of 4- substituted 2,2,6,6-tetramethyl piperidinoxy radicals; tanane( $\text{R}=\text{H}$ ), tanol( $\text{R}=\text{OH}$ ), and tanamine( $\text{R}=\text{NH}_2$ ) adsorbed on a polished gold surface. The EPR spectra of these materials have been studied as a function of surface coverage and temperature. Markedly different spectra are obtained as a function of substituent, revealing detailed information about the nature of the motion of the radicals while attached to the metal surface. Spectral simulations following L. R. Dalton et. al. have been done to confirm our interpretation. The tetra-*t*-butyl carbazyl radical was also studied in an attempt to measure its orientation with respect to the metal surface from its measured orientation with respect to the magnetic field.

SPIN-TRAPPING OF PHOSPHORUS CENTERED RADICALS. Rajagopalan Sridhar, Oklahoma Medical Research Foundation, Oklahoma City, Oklahoma 73104.

Phosphoranyl free radicals were generated from triethylphosphite, tri-methylphosphite and hexamethylphosphorotriamide by thermal and photochemical reactions. The phosphoranyl radicals were detected by spin-trapping with phenyl-t-butyl nitroxide (PTN) and 5,5-dimethylpyrroline-N-oxide (DMPO). In some cases, the trapped free radical was isolated by column chromatography. Details of ESR spectra and experimental methods will be discussed.

... NMR AND ESR EVIDENCE OF MOLECULAR AGGREGATES IN SODIUM DIBUTYLPHOSPHATE AQUEOUS SOLUTIONS. S. Belaid and C. Chachaty. Departement de Physique-Chimie, C.E.T. de Saclay, 91191 Gif-sur-Yvette Cedex (France).

A magnetic resonance study in progress on the conformation and dynamical properties of metal complexes of the dibutylphosphate anion (DBP<sup>-</sup>) in aqueous solution has shown by the increase with concentration of the correlation time governing the nuclear relaxation that this compound gives rise to molecular aggregates. A rough estimate of the aggregation number  $n$  has been performed by ESR measurement of the reorientation correlation time of the [DBP]<sub>n</sub> complex. In a concentration range  $1M < [DBP] < 3M$  it appears that the molecular volume increases by a factor  $< 10$  with respect to the monomer, at room temperature. Rayleigh light scattering measurements give under similar experimental conditions  $9 < n < 12$ . The longitudinal relaxation rate vs.  $1/[DBP]$  is constant below  $[DBP] = 0.8 M$  and increases linearly for  $1.5 M < [DBP] < 3M$ , indicating an exchange of [DBP] between the solution and aggregates of  $\sim 10$  molecules. A sharp transition in the  $1/T_1$  relaxation rate occurs for  $[DBP] = 3M$ , which corresponds to the appearance of a liquid crystalline phase clearly observed under the polarizing microscope. The conformation of butoxy chains has been investigated by the Ni<sup>2+</sup> induced paramagnetic relaxation of and by <sup>1</sup>H relaxation showing a trans-gauche-trans preferential conformation of the POCCCC fragment in both DBP<sup>-</sup> monomeric and aggregated states. This conformation seems incompatible with a micellar aggregate; more likely this association occurs by water links between phosphodiester groups.

161 ELECTRON TRANSFER BETWEEN DISTANT WEAKLY INTERACTING FUNCTIONAL GROUPS - EVIDENCE FOR A NON-ADIABATIC PROCESS, S. Mazur, V.M. Dixit, and F. Gerson. Dept. of Chemistry, the University of Chicago and the Physical Chemical Institute of the University of Basel.

The majority of electron transfer reactions in solution are adiabatic processes with rates governed by reorganization of molecular structure and solvation within a single electronic state. In the framework of the Absolute Rate Theory, the transmission coefficient,  $k$ , is close to unity. Exceptions to this behavior may be anticipated for situations where interactions between donor and acceptor are extremely weak such that the rate limiting event is actually an electronic transition between reactant and product states. Experimental evidence for this behavior (a low value of  $k$  for example) has been rare for reactions in condensed phases.

We have investigated the magnitude of interaction and the rate of electron transfer between a pair of aromatic rings bridged by a macrocyclic ether. For certain conditions the rate of the transfer process can be determined by ESR. The activation parameters were found to be exceptional for the very low values of both the activation energy and the pre-exponential frequency factor. The latter is regarded as strong evidence for a non-adiabatic mechanism.

162 CONTEMPORARY ISSUES IN FIELD-SWEPT EPR OF SOME HIGH AND LOW SYMMETRY SYSTEMS J.R. Pilbrow, Department of Physics, Monash University, Clayton, Victoria 3168, Australia.

EPR of low symmetry systems, compared with high symmetry ones, involves greater complexity with regard to turning directions in crystals and a different spectral distribution for non-crystalline samples. Thus for low symmetry spin  $\frac{1}{2}$  systems with hyperfine structure (h.f.s.) principal hyperfine couplings cannot, in general, be measured directly from line positions on experimental spectra due to powders or frozen

solutions. The EPR of cobalt (II)O<sub>2</sub> adducts will be reviewed and, in some cases, re-interpreted in the light of more correct low symmetry models of oxygen bound to planar complexes in solution as well as in the protein matrix of myoglobin. Possible indirect spin polarisation contributions to h.f.s. in these systems will be discussed. Recent work by the author and R.P. Bonomo on some low symmetry copper salts with approximately C<sub>4v</sub> point symmetry at the copper sites will be reported. When  $S > h$ , looping of fine-structure transitions occurs at magnetic fields where energy levels vary non-linearly. Asymmetric lines were predicted near the ends of loops, as a direct consequence of the frequency-to-field transformation of the symmetric electronic density of states  $g(\mathbf{u})$ . The EPR of Cr<sup>3+</sup> in ruby single crystals shows evidence for such asymmetries.

#### 163 EPR and Chemistry in Single Crystals of Nitrosylhemoglobin'

David C. Poetschman      Department of Chemistry  
and S. G. Utterback      S.U.N.Y. Binghamton  
Binghamton, NY 13901

The electron paramagnetic resonance (EPR) of nitrosylhemoglobin (HbNO) is measured in single crystals of converted human oxyhemoglobin (HbO<sub>2</sub>). Several chemical and physical processes in the crystals are observable by means of the EPR. At 9°C HbO<sub>2</sub> a-subunits exchange O<sub>2</sub> for NO faster than b-subunits. The subunit spectra display both <sup>15</sup>N and histidine-<sup>1</sup>H hyperfine structure. Power saturation between 1.6 and 4.2°K and temperature dependence above 80°K point to efficient spin-spin and spin-lattice relaxation processes that involve heme-heme magnetic dipolar interactions between both kinds of subunits. With a Hg-Xe lamp, HbNO photolysis quickly occurs < 4.2°K resulting in the disappearance of the EPR spectrum. The HbNO spectrum returns upon warming the sample from 4.2 to 85°K.

16\* E.P.R. STUDY OF Fe<sup>2+</sup> AND Cr<sup>3+</sup> IN DIFFERENT FORSTERITE CRYSTALS. J.M. Gaite, Laboratoire de Cristallographie (ERA 841) - UER Sciences - Université d'Orléans - 45046 Orléans Cedex ; S.S. Hafner and H. Rager, Geowissenschaften Kristallographie - Universität Marburg, 3550 Marburg, Lahnberge ; L.V. Bershov, IGEM, Staromonetny 35 - Moscow 109017.

A study of the E.P.R. spectra of Fe<sup>2+</sup> and Cr<sup>3+</sup> in forsterite (MgSiO<sub>3</sub>) has been made. For the crystal doped with Fe<sup>2+</sup>, this ion is mainly located at the Si position. All the spin Hamiltonian constants were determined for the two different spectra. From the fourth order constants, we determined the distortions of the environment of Fe<sup>2+</sup>. The results are compared to the one previously obtained with Mn<sup>2+</sup> and Gd<sup>3+</sup> and to the distortions of the non substituted sites. For the Cr<sup>3+</sup>, spectra responsible for this ion in both M<sub>1</sub> and M<sub>2</sub> sites have been observed. An additional spectrum which exhibits lines characteristics of a superhyperfine interaction with an ion having a 5/2 nuclear spin has been observed. This spectrum arises from Cr<sup>3+</sup> in interaction with Al<sup>3+</sup> substituted for Si<sup>4+</sup> in the neighbourhood of Cr<sup>3+</sup>. Although only a very small amount of aluminium may be present in the crystal, the intensity of the spectrum is very important. Such a situation is explained and factors that may influence the repartition of these paramagnetic ions in the structure are discussed.

\*\*\* SUPERPOSITION-MODEL ANALYSIS OF Gd<sup>3+</sup> SPIN-HAMILTONIAN PARAMETERS DOPING RARE-EARTH TRIFLUORIDE SINGLE CRYSTALS. S. K. Misra, P. Mikołajczak and N. R. Lewis. Physics Department, Concordia University, 1455 de Maisonneuve Boulevard West, Montreal, Quebec, Canada H3G 1M8.

3+

The spin Hamiltonian parameters for Gd<sup>3+</sup> doped single crystals of RF<sub>3</sub> (R = La, Ce, Pr, and Nd) are analysed using the linear superposition model of Newman. It is found that the parameters can be adequately described within the framework of the superposition model for values of  $\alpha$  and  $t^{\lambda}$  being 9 and 14 respectively, provided that one considers small distortions (within  $\pm 3^\circ$ ) of the azimuthal angles of eight nearest F<sup>-</sup> ions to Gd<sup>3+</sup> in the various hosts due to the presence of Gd<sup>3+</sup> ion. The significance of the success in the application of the superposition model to the analysis of

Gd<sup>3+</sup> spin Hamiltonian parameters in isostructural hosts is discussed. It is found that the zero-field splitting is a linear function of the intrinsic parameter  $\alpha$  for the Gd<sup>3+</sup> ion doping the various hosts.

166 A 9.3 GHz EPR STUDY OF DYNAMICAL INTERACTIONS IN  $\text{Gd}^{3+} : \text{Eu}(\text{OH})_3$ , SINGLE CRYSTALS AT 10-300 K. V.M. Malhotra, H.A. Buckmaster\*, and W.R.M. Graham, Department of Physics, Texas Christian University, Fort Worth, Texas, 76129, \*Department of Physics, The University of Calgary, Calgary, Alberta, Canada, T2N 1N4.

9.3 GHz electron paramagnetic resonance experiments on  $\text{Gd}^{3+}$  impurity ions in singlet, ground-state  $\text{Eu}(\text{OH})_3$  have been used to study the various possible dynamical interactions in this system at 10-300 K. The spin-Hamiltonian parameters of the  $^8\text{S}$  ground state of the  $\text{Gd}^{3+}$  ion, which substitutes for  $\text{Eu}^{3+}$  in the lattice at  $\text{C}_{3h}$  site symmetry, have been measured in the temperature range. The temperature dependent part of the zero field splitting is discussed in terms of implicit and explicit contributions. The experimental results indicate that the magnitude of the zero field splitting of  $\text{Gd}^{3+}$  increases with temperature, which is opposite to its behavior reported in  $\text{La}(\text{C}_2\text{H}_5\text{SO}_4)_3 \cdot 9\text{H}_2\text{O}$  ( $\text{C}_3$  site symmetry). The low temperature value of the zero field splitting which reflects the contribution from the static lattice is discussed in terms of models involving exchange correlated electric fields. The low lying, degenerate, excited states of  $\text{Eu}^{3+}$  in this compound can produce dynamical electric, magnetic and exchange fields in the lattice which are manifested in g-value shifts and unusual variations in linewidths for  $\text{M} = +1$  transitions at  $\sim 200$ -300 K. The linewidths decrease progressively as the magnitude of M increases;  $-1/2 \leq M \leq 1/2$  has the maximum linewidth. The exchange interaction parameter  $J^*$  for the nearest neighbor  $\text{Gd}^{3+}$ - $\text{Eu}^{3+}$  pair has been computed. From the ratios of the linewidths in the fine structure spectra of  $\text{Eu}(\text{OH})_3$ , it has been found that the dynamical dipolar and/or exchange fields are dominant over the dynamical electric fields caused by the Jahn-Teller effect. From the relative magnitude comparison with other Eu host lattices it is concluded that exchange interactions are more important than magnetic dipolar effects.

167 AN EPR INVESTIGATION OF  $\text{Gd}^{3+}$  IN SINGLE CRYSTAL AND POWDER SPECIMENS OF  $\text{Y}(\text{OH})_3$ , AT 10-300 K. J.M. Boteler, V.M. Malhotra, H.A. Buckmaster\*, and W.R.M. Graham, Department of Physics, Texas Christian University, Fort Worth, Texas 76129, \*Department of Physics, The University of Calgary, Calgary, Alberta, Canada, T2N 1N4.

The 9.2 GHz electron paramagnetic resonance spectrum of the  $[4f^7, ^8\text{S}] \text{Gd}^{3+}$  ion dilutely substituted ( $\sim 5:103$ ) into  $\text{Y}(\text{OH})_3$  has been measured and analyzed. The angular variation of the allowed transitions has been carried out in the ZX and XY plane and the site symmetry at  $\text{Gd}^{3+}$  has been determined. Spin-Hamiltonian parameters have been computed by exact diagonalization using a least-squares procedure in which all the resonant transition positions obtained from the Z- and X-axis are fitted simultaneously. The zero field splitting has been computed over a range of temperatures and the spectrum at 10 K is used to deduce the absolute sign of the splitting. Various zero field splitting mechanisms are discussed in the light of the observed zero field splittings. The analysis of the power pattern spectrum for  $\text{Gd}^{3+}$  in  $\text{Y}(\text{OH})_3$  is also presented.

169 EPR SPECTROSCOPY AT ZERO MAGNETIC FIELD. Steven J. Strach and Richard Bramley. Research School of Chemistry, Australian National University, P.O. Box 4, Canberra, A.C.T. 2600, Australia.

Zero field resonance (ZFR) spectroscopy is a method for observing electron spin transitions at zero external magnetic field by using frequency swept EPR techniques. We have used ZFR to study several systems and have found significant differences between the EPR derived spin Hamiltonian parameters in the literature and those necessary to fit the ZFR spectra. For example, in the system  $\text{Mn}^{2+}/\text{MgSO}_4 \cdot 7\text{H}_2\text{O}$  the latest EPR literature values for the spin Hamiltonian parameters include  $E = 266 \pm 28$  MHz whereas a value  $E = 183 \pm 2$  MHz is required to fit the ZFR spectrum. Other systems where we have found significant errors in EPR analyses will also be discussed. Systematic errors of a typical EPR experiment, insufficiently accurate analytical procedures and the use of inappropriate spin Hamiltonians are all believed to contribute to errors in EPR derived parameters. It will be shown that ZFR spectroscopy has great value in indicating errors in EPR analyses and also provides a technique for accurately determining the non-Zeeman terms in the spin Hamiltonian. The technique is applicable to transition and rare earth paramagnetic compounds and also to simpler species such as doublet states with large hyperfine or quadrupolar interactions.

170 EPR STUDY OF THE BINDING OF CuL' TO CAT AND NORMAL HUMAN HEMOGLOBINS. W. E. Antholine and F. Taketa. Departments of Radiology and Biochemistry, The Medical College of Wisconsin, P. O. Box 26509, Milwaukee, WI 53226.

The nature of the interaction of CuL', 2 formylpyridine monothiosemicarbazone copper II, with proteins is of interest because of its known cytotoxic effect and its potential use as an antitumor agent. The possibility that human and cat hemoglobin might demonstrate differences in their response to CuL' was examined by analyzing its effect on their oxygen equilibria and epr spectra. CuL' increases the oxygen affinity of both hemoglobins. A decrease in the P<sub>50</sub> value of 14 mm for cat hemoglobin at a molar ratio of CuL'/Hb of 4/1 and a decrease of 6 mm for human hemoglobin at a molar ratio of CuL'/Hb of 5/1 was observed. The X-band epr spectrum for CuL' and human hemoglobin is consistent with adduct formation between CuL' and a nitrogen donor atom. The S-band (3 GHz) has more clearly resolved hyperfine structure on the m<sub>s</sub> = -1/2 and +1/2 lines. The splitting pattern of 1,4,9,13,13,9,4,1 accounts for three nitrogen and one proton with approximately equivalent hyperfine coupling constants. The epr spectra for CuL' and cat hemoglobin suggest a CuL'-nitrogen like complex superimposed on a CuL'\*thiol complex. Differences such as that between cat and human hemoglobin with respect to adduct formation with CuL' might help explain why 2-formylpyridine monothiosemicarbazone drugs appear to be more effective as an antitumor agent in some animals than in man.

Supported by NIH Grants AM-15770 and 5-P41-RR01008

171 EPR AND QUANTUM CHEMISTRY STUDIES OF ADENOSYLCOBALAMIN. R.E. Coffman and Vinay D. Ghemkar, Chemistry Department, University of Iowa, Iowa City, Iowa 52242

What features of the electronic and spin quantum mechanics of adenosylcobalamin (coenzyme B<sub>12</sub>) are responsible for the homolytic cleavage of the Co-C bond either in the dark (enzymatically) or during photolysis with visible light? In order to obtain some direct experimental information on this question, we have undertaken a study of laser-induced photolysis of polycrystalline adenosylcobalamin, for which a crystal structure is known. We report on the results of this study, which have led to identification of the degree of crystalline hydration (in the vicinity of the 5'-methylene carbon of the nucleoside) as an important variable affecting the chemistry which follows incipient homolysis of the Co-C bond, as well as the detection and stabilization of a Co(II)... free radical pair state which we believe to be the Cob(II)alamin...5'-deoxyadenosyl free radical pair. In addition, we are undertaking a first-principles study of the potential energy curves of the important singlet and triplet states of this molecule. This information will eventually help us to understand the mechanisms of activation of the Co-C bond, and the quasistabilization of the Cob(II)alamin...5'-deoxyadenosyl free radical pair state, and be of use in interpreting the meaning of ESR lineshapes and spin-Hamiltonian parameters in the moderately strong exchange coupling domain, which we now recognize as being of primary importance for this problem.

172 A comparative study of the active sites of atropinesterase and other esterases by using spin labeling techniques.

B.A.C. Rousseeuw, E. van der Drift, Technical University of Delft, The Netherlands.

A.C.M. van der Drift, T.N.O. Rijswijk, The Netherlands.

Atropinesterase (AE) from bacteria *Pseudomonas Putida* is a serine esterase like Chymotrypsin (Chymo) and Subtilisin (Sub), Specific spin labeling of AE, Chymo and Sub on the active serine position allows a comparison of the geometry of their binding sites. The experimental spectra are found to reflect very anisotropic motions in all three enzymes and support the description

of the active site region in terms of a pocket model. Using spin labels of different length and applying the rigorous relaxation theory of slow tumbling, a quantitative and comparative description of the active site geometry in the three enzymes is attempted.

- 173 HIGH RESOLUTION ENDOR STUDIES OF FLAVIN AND FLAVIN ANALOG FREE RADICALS, H. Kurreck, M. Bock, and W. Lubitz, Freie Universitat Berlin, Institut fur Organische Chemie, Takustr. 3, D-1000 Berlin 33, West Germany.

Flavoenzymes are known to be important redox catalysts in the respiratory chain and thereby in oxidative phosphorylation. Since paramagnetic species are involved in flavoenzyme catalysis, ESR and ENDOR techniques should, in principle, give detailed information regarding structure and properties of these radicals. However, studies performed so far were limited by the low resolution of standard ESR and even solid state ENDOR experiments.

This paper describes the first successful high resolution proton and nitrogen-14 ENDOR (electron nuclear double resonance) on several flavin and flavin analog radicals in liquid solution. The complete sets of isotropic proton and nitrogen hyperfine coupling constants have been measured, e.g. for riboflavin cation radical (vitamin B<sub>2</sub>). The signs of the couplings could be determined by performing the electron nuclear TRIPLE resonance technique. Assignments of the couplings to specific molecular positions could be established by using partially deuterated derivatives of the flavin radicals.

We wish to thank Professor H. Fenner and Dr. R. Grauert, Institut fur Pharmazie der Freien Universitat Berlin, for supplying us with some of the diamagnetic precursors.

17U

- ENDOR INVESTIGATIONS OF AN ORGANIC QUINTET STATE TETRARADICAL. B. Kirste, H. Kurreck and W. Harrer. Freie Universitat Berlin, FB 21, WE 2, 1000 Berlin 33, West Germany.

A novel tetrakis galvinol with approximately tetrahedral symmetry has been prepared. Stepwise oxidation yields the respective paramagnetic species, viz. the galvinoxyl mono-, bi-, tri- and the tettraradicals exhibiting doublet, triplet, quartet and quintet spin states, respectively. Whereas the EPR spectrum of the monoradical shows a well-resolved quintet hyperfine pattern, resolution decreases drastically on passing to the higher oxidation steps. However, well-resolved ENDOR spectra could be obtained for the different species, definitely proving the presence of a quintet spin state in the case of the tettraradical. The ENDOR line positions in the different spin states are discussed and compared with those of other galvinoxyl oligo radicals.

Tetrahedral symmetry of the tettraradical is considered important for the success of the ENDOR experiment for two reasons. Firstly, the electron exchange interaction is the same for all pairs of galvinoxyl moieties thus giving rise to the formation of a thermally populated quintet state. Secondly, the zero field splitting parameters (D and E) should be zero for symmetry reasons which is desirable in view of the EPR/ENDOR line broadening caused by the electron electron dipolar interaction.

- 175 EPR STUDIES OF THE EFFECTS OF ETHANOL ON PHOSPHOLIPID BILAYER MEMBRANES.

John D. Zimbrick and James A. McFaul. Radiation Biophysics, University of Kansas, 140 NRC, W. 15th Street, Lawrence, KS 66045.

The purpose of this research project is to determine the effects of membrane composition and environment on the response of the membrane to ethanol, and to examine the effects of membrane changes as the membrane becomes tolerant to ethanol. Various nitroxide spin labeled lipids were used to monitor the fluidity of the bilayer. Experiments were performed on both model and biological membranes (rat synaptic membranes). Previous research has indicated that ethanol and other alcohols increased the fluidity of the bilayer. Our research has indicated that ethanol, in the ranges of .4 to 4 mM can cause a slight decrease in membrane fluidity. This effect is only seen in model

membrane vesicle suspensions, under certain aqueous buffer conditions. **Low** concentrations of ethanol also affect the phase transition temperature of the bilayer. Experiments performed with certain local anesthetics have indicated that the aqueous ion concentration affects the response of the membranes to the local anesthetic. The effect of cations on the membranes response to ethanol, the effects of ethanol on phase transition temperatures, and the effects of various other alcohols and various local anesthetics on the bilayer will be presented. (Work supported by Grant //1-R01-AA04732 from the National Institute of Alcohol Abuse and Alcoholism.)

**176 LIGHT-INDUCED TRANSIENTS OF SPIN LABEL SIGNAL AMPLITUDE IN SPINACH THYLAKOIDS.**

**S. P. Berg.** Department of Biological Sciences, University of Denver, Denver, CO 80208.

In the presence of a broadening agent (chromium oxalate) and using the non-ionic spin label 4-oxo-2,2,6,6-tetramethylpiperidine-1-oxyl (Tempone) we have measured a light-induced decrease in signal amplitude. Upon the termination of illumination, the signal relaxes back to near its original levels. This decrease in signal amplitude can be prevented by agents (gramicidin, methylamine) which dissipates the light-driven accumulation of protons into the thylakoid lumen.

The corresponding amine spin label 4-oxo-2,2,6,6-tetramethylpiperidine-1-oxyl (Tempamine) displays much different light-induced behavior when present with thylakoids. Upon illumination the signal strength of Tempamine arising from the lumen increases sharply before beginning a much slower reduction in signal amplitude. Since the rapid Tempamine transient is also completely sensitive to gramicidin and methylamine one can speculate that both the decrease in Tempone signal and the increase in Tempamine signal are related to the light-driven proton accumulation in the thylakoid lumen. These and other results are discussed in terms of a light-driven decrease in lumen volume which accompanies the light-driven proton accumulation-

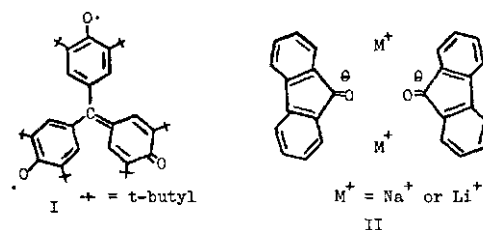
... EXAMINATION OF EPOXY MORPHOLOGY USING NITROXIDE FREE RADICALS.\* **T. C. Sandreczki** and **I. M. Brown.** McDonnell Douglas Research Laboratories, St. Louis, MO 63166.

It is thought that amine-cured epoxy resin networks are composed of regions of high-crosslink density dispersed in and bound to a surrounding matrix of lower-crosslink density. In this study, nitroxide spin labels and spin probes were used to investigate the microstructure of these networks. EPR lineshapes of nitroxides in cured epoxies were examined as a function of temperature in samples containing no solvent and as a function of solvent content at room temperature. Spectra recorded at different temperatures contained only one component and were interpreted at each temperature in terms of nitroxide motions described by a single correlation time. Spectra recorded at different solvent contents were often a superposition of two components and were thus described by two correlation times that differed by over one and a half orders of magnitude. The correlation times obtained from the temperature-dependence studies and those obtained from the mobile spectral component of the solvent-dependence studies exhibited a simple functional dependence on epoxy fractional free volume. Also, the presence of two spectral components in the solvent-dependence studies implies selective plasticization of low-crosslink density regions of the epoxy network.

\*This research was conducted under the McDonnell Douglas Independent Research and Development program.

... ENDOR ON BIRADICALS RANDOMLY ORIENTED IN FROZEN SOLUTION. **Hans van Willigen** and **Charles F. Mulks,** Department of Chemistry, University of Massachusetts at Boston, Boston, MA 02125

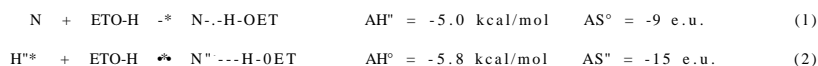
An EPR study has been made of a series of biradicals in frozen solution (100 K). Systems investigated include Yang's M radical (I) and the biradicals formed upon dimerization of the (alkali metal generated) fluorenone anion (II). By recording the ENDOR



signals for selected magnetic field positions in the rigid matrix ESR spectra, information is obtained on the signs and magnitudes of hyperfine tensor components of some of the magnetic nuclei ( $^1\text{H}$ ,  $^{13}\text{C}$ ,  $\text{Li}$ ). In addition, the study of the  $^{19}\text{F}$ -fluorenone system has given information on the  $^1\text{H}$  quadrupole tensor components. The hyperfine and quadrupole data give an insight in the structure of the biradicals.

179 EFFECT OF AN ADDED ELECTRON UPON THE VIABILITY OF A HYDROGEN BOND ACCEPTOR: AN  
EPR AND NMR STUDY, Gerald R. Stevenson and Mohamad Pourian, Department of  
Chemistry, Illinois State University, Normal, Illinois 61761

EPR techniques were utilized to measure the thermodynamic parameters controlling the hydrogen bond exchange reaction between the ninhydrin anion radical (N<sup>-</sup>) and hexamethylphosphoramide hydrogen bonded to ethanol (HMPA--H-OET). NMR was used to determine these parameters controlling the hydrogen bond exchange reaction between neutral ninhydrin (N) and HMPA hydrogen bonded to ethanol. NMR was also used to study the hydrogen bonding to HMPA. All of the ESR and NMR results were placed into a thermochemical cycle to yield the thermodynamic parameters controlling the hydrogen bond formation between ethanol and both the ninhydrin neutral molecule and the anion radical eqs 1 and 2.



The enthalpy of hydrogen bonding to the anion radical is more exothermic due to the fact that the added electron increases the affinity of the ninhydrin for the hydrogen bond. However, the free energy of hydrogen bond formation is less negative for the anion radical than it is for the neutral species. This is due to the very large negative entropy change upon hydrogen bond formation to the anionic species.



**180 EPR STUDIES OF THE PHOTOPHYSICS OF SILVER CHLORIDE AND SILVER BROMIDE**  
**R. S. Eachus** and M. T. Olm. Eastman Kodak Company, Research  
 Laboratories, 1669 Lake Avenue, Rochester, New York 14650.

The primary products of photolysis in pure samples of AgCl are free and trapped electrons, self-trapped holes ( $\text{AgClg}^{\bullet}$ ), and self-trapped excitons. We report the first direct detection of these species by steady-state epr spectroscopy at 1.8°K and 35 GHz. A comparison to the results of optically detected magnetic resonance experiments on silver chloride will be presented.

By contrast, the only species observed in exposed samples of silver bromide were free electrons [g...r ~ 1.495 ± 0.005 (10°K)]. The g-value was temperature dependent and the signal amplitude was affected by the history of the sample. Kinetic epr spectroscopy at 9.5 GHz has been used to study generation and loss processes for conduction band electrons in this material.



181 CICEP AND HEISENBERG SPIN EXCHANGE IN TWO MIXED RADICAL SYSTEMS. Joseph P. Horrak and Richard V. Fessenden. Radiation Laboratory and Department of Chemistry, University of Notre Dame, Notre Dame, IN U6556.

Time-resolved ESR signals have been recorded for various concentrations of  $\text{SO}_3^{2-}$  and  $\text{PO}_4^{3-}$  produced by pulse radiolysis of basic aqueous solutions of sulfite and phosphate, respectively. A comparison of the signals observed with and without  $\text{K}^+$  shows several effects arising from encounters between  $\text{e}^-$  and  $\text{SO}_3^{2-}$  or  $\text{PO}_4^{3-}$ . Analysis of signal amplitudes at longer times yields the rate constant for cross reaction with  $\text{e}^-$ . Curves for  $\text{SO}_3^{2-}$  show a growth for  $V > 10^6 \text{ sec}^{-1}$  which is attributed to a weak negative polarization and Heisenberg exchange with  $\text{e}^-$ . The high- and low-field lines for  $\text{PO}_4^{3-}$  show strong positive and negative contributions for  $V > 10^6 \text{ sec}^{-1}$  which must be caused by polarization by cross reaction with  $\text{e}^-$ . Parameters determined by fitting of solutions to modified Bloch equations are for  $\text{SO}_3^{2-}$  and  $\text{PO}_4^{3-}$ , respectively,  $k(\text{e}^- + \text{B})$  [ $2 \times 10^9$  and  $1 \times 10^9 \text{ M}^{-1} \text{ sec}^{-1}$ ],  $k(\text{Heisenberg spin exchange})$  [ $1.6 \times 10^{10}$  and  $9 \times 10^9 \text{ M}^{-1} \text{ sec}^{-1}$ ], and polarization,  $P/P_0$  [1.0 and 0.525 (high-field), 0.755 (low-field)]. The large polarization for  $\text{PO}_4^{3-}$  is also evident in values of  $J \sim 1000$  for self reaction.

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

EPR spectra of  $\text{PtO}_2$  and  $\text{MnO}_2$  interacting with isopropanol and DPPH were used to characterize the radical species involved. The surface species active in the dehydrogenation reaction of isopropanol on  $\text{MnO}_2$  may be  $\text{O}^\cdot$  or  $\text{HO}^\cdot$ . The radical formed by the

(83) EPR STUDIES OF SURFACE MOBILITY, J. Lopata, W. Timmer, S. Abdo and R. F. Howe, Laboratory for Surface Studies and Department of chemistry. University of Wisconsin-Milwaukee, Milwaukee, Wisconsin 53201.

The superoxide ion  $\text{O}_2^\cdot$  can be formed on many different metal oxide surfaces. This paper will describe the use of EPR and STEPR spectroscopy to study the mobility of  $\text{O}_2^\cdot$  on various surfaces. On silica gel,  $\text{O}_2^\cdot$  is sufficiently mobile to modify the line shape of the normal EPR spectrum. On zinc oxide, line shape changes occur only in the Saturation Transfer signals, whereas on molybdenum oxide  $\text{O}_2^\cdot$  is immobile on the longest time scale accessible through STEPR. The experimental spectra will be presented, along with computer simulations of the EPR and STEPR line shapes, and the difficulties associated with extracting correlation times for surface motion from the experimental spectra discussed.

184 LOCATION AND MOVEMENT ON DEHYDRATION OF CATIONS IN ZEOLITES FROM ELECTRON SPIN ECHO MODULATION ANALYSIS. M. Narayana and Larry Kevan. Department of Chemistry, University of Houston, Houston, Texas 77004.

It is shown that paramagnetic ions like  $\text{Cu}^{2+}$  can be located and that their motion upon dehydration in zeolites can be monitored by electron spin echo modulation analysis. In  $\text{Cs7NaA}$  zeolite,  $\text{Cu}^{2+}$  is located inside the B and a-cages. The  $\text{Cu}^{2+}$  is coordinated to three lattice oxygens and one water molecule. On dehydration  $\text{Cu}^{2+}$  moves out of the S-cages along the threefold axis of the hexagonal window to about 0.1 nm above the hexagonal window into the a-cage. Other systems will also be discussed.

"" SPIN-SPIN INTERACTION THROUGH SATURATED AND UNSATURATED LINKAGES. K. M. More and G. R. Eaton. Department of Chemistry, University of Denver, Denver, CO 80208. S. S. Eaton. Department of Chemistry, University of Colorado at Denver, Denver, CO 80202.

A series of spin-labeled copper porphyrins have been prepared in which the spin label is attached to the porphyrin pyrrole ring by saturated and unsaturated linkages of varying lengths. The effects of the linkage, solvent, and temperature on the spin-spin interaction between the copper and nitroxyl electrons has been examined.

^' SPIN-LABELED PYRIDINE ADDUCTS OF COPPER AND VANADYL S-DIKETONATES. B. M. Sawant, A. L. W. Shroyer, and G. R. Eaton. Department of Chemistry, University of Denver, Denver, CO 80208. S. S. Eaton, Department of Chemistry, University of Colorado at Denver, Denver, CO 80202.

Nitroxyl radicals have been attached to the 3- or 4-position of a pyridine ring by ester, amide, and Schiff base linkages, when these pyridine derivatives form adducts with vanadyl bis(trifluoroacetylacetonate), VO(tfac>2» or vanadyl bis(hexafluoroacetylacetonate), VOJhfac^\* electron spin-electron spin splitting is observed in the solution EPR spectra at room temperature. These spectra provide the first examples of fully resolved AB splitting patterns due to vanadyl-nitroxyl interaction. For the vanadyl complexes the magnitude of the spin-spin coupling constant, J, is about four times larger for a 4-substituted pyridine than for a 3-substituted pyridine. When the same ligands form adducts with copper(II) bis(hexafluoroacetylacetonate), Cufhfac^f J is about the same magnitude for the 3- and 4-substituted pyridines. Mechanisms of spin delocalization which could account for these differences will be discussed.

COLLISION BROADENING OF NITROXYL RADICAL EPR SPECTRA BY TRANSITION METALS. D. Reddy, D. Dalai, and G. R. Eaton. Department of Chemistry, University of Denver, Denver, CO 80208. S. S. Eaton. Department of Chemistry, University of Colorado at Denver, Denver, CO 80202.

The effects of paramagnetic first row transition metals on the linewidths of the EPR spectra of nitroxyl radicals have been examined. The effect of electrostatic interactions has been explored by using 4-oxo-2,2,6,6-tetramethylpiperidyl-1-oxyl, 4-amino-2,2,6,6-tetramethylpiperidyl-1-oxyl, and 3-carboxy-2,2,5,5-tetramethylpyrrolin-1-oxyl in aqueous solution at pH 7. The importance of metal electron derealization has been examined by varying the ligands in Cr(III) complexes. The effect of solution viscosity on the broadening of the nitroxyl EPR signal by various metal complexes will also be discussed.

189 EXCHANGE INTERACTIONS IN *tropylium* bis[1,2-dicyanoethylene dithiolato]nickelate(I)I}{(CH.)'[Ni{mnt).]}". E. de Boer, P. T. Manoharan, J. H. Noordik, and C. P. Keijzers. Department of Physical Chemistry, University of Nijmegen, Toernooiveld, 6525 ED Nijmegen, The Netherlands.

The compound (CyH^)\*[Ni(mnt)y]- has been prepared and its crystal structure determined, the space group is P2w » 2 = 2, the unit cell axes are a = 6.364, b = 7.458, c = 17.991 Å and g = 91.22°. The Ni(mnt)~ and C.H. ions form segregated stacks in the direction of the b-axis.

The susceptibility appears to be dominated by a strong 1-dimensional, isotropic, antiferromagnetic exchange coupling (J<sub>s</sub> = -4.4 cm<sup>3</sup>). However, the angular dependence of the EPR linewidth at ambient temperature has to be explained with an additional anisotropic exchange interaction of 0.26 cuT\*. Furthermore, Q-band EPR measurements in the ab plane reveal a very small interstack exchange interaction (0.015 cur\* at room temperature) which increases by a factor of 4 upon lowering the temperature to 8 K and which might be responsible for a possible long range order at low temperature.

THE ELECTRIC QUADRUPOLE MOMENT OF NIOBIUM-93. D. Attanasio, C. Bellitto, and A. Flamini. C.N.R. Lab., Area delta Ricerca di Roma, Po.B. 10, Monterotondo Staz., Roma, Italy.

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Numerical values for the electric quadrupole moment of the Nb isotope have been obtained from optical studies. X-ray emission of muonic niobium, and atomic beam magnetic resonance. However, the experimental results covered a wide range of values, from -0.20 to -0.37 barn. We measured the 35GHz EPR spectra of the two eight-coordinated complexes tetrakis(dithiobenzoato)V(IV) and tetrakis(diethyldithiocarbamato)Nb(IV), diluted in single-crystals of suitable diamagnetic analogues. The complete quadrupole coupling tensors of the two compounds could be obtained from the analysis of the  $AM_J = \pm 1$  lines. The experimental results gave -0.35 barn for the Nb quadrupole moment and +220 MHz/barn for the electric field gradient. The accuracy of the method, with respect to previously reported results, will be discussed.

191 SUPERPOSITION ANALYSIS OF ZERO FIELD SPLITTINGS (ZFS) FOR  $Mn^{2+}$ .

RESULTS AND APPLICATIONS. H. Heming, and G. Lehmann, Institut für Physikalische Chemie, WWU, Schlossplatz 4, D-4400 Münster, F.R.G.

Correlation of second order ZFS parameters and directions of their magnetic axes for  $Mn^{2+}$  in diamagnetic hosts with site distortions of the  $MX_6$  polyhedra known from crystal structure data yielded consistent intrinsic ZFS parameters for a number of ligands and proved the second order ZFS to be - at least for the by far largest part - determined by the distortion of the first coordination sphere. A strong increase with covalency and a marked influence of coordination number indicate contributions of opposing mechanisms. A method is presented which allows a very detailed comparison of the measured anisotropy with that calculated from the site distortions. The results were used for structure refinements of  $HX_6$  layer compounds from b for  $Mn^{2+}$ . Possible applications for solution of other structural problems are discussed.

... EPR OF BINUCLEAR VANADYL(IV) COMPLEXES. Robert E. Tapscott, Eileen Duesler, and Richard B. Ortega, Department of Chemistry, University of New Mexico, Albuquerque NM 87131

X-ray crystallographic studies confirm the shortened V-V distance in the binuclear complex  $[(VO)_2(IV)-dmt)((-)-dmt)]^{2+}$  ("dmt" = dimethyltartrate) predicted from earlier EPR studies in glasses at 77K; however, the structure of the sodium salt of  $[(VO)_2((+)-mmt)((-)-mmt)]^{2+}$  ("mmt" = monomethyltartrate) shows a V-V distance which is considerably longer than that found in the studies using glasses. On the other hand, EPR studies on the solid crystalline materials give zero-field splitting values which can be predicted almost exactly using a dipolar model from the structural parameters ( $D_{eff} = 0.0468$  cm<sup>-1</sup>,  $D_{eff} = -0.063$  to  $-0.033$  cm<sup>-1</sup> (depending on assumed direction of quantization) for the dmt complex;  $|D_{eff}| = 0.028$  cm<sup>-1</sup>,  $D_{eff} = -0.0279$  cm<sup>-1</sup> for the mmt complex). That this is true indicates that the structure of the dmt complex varies between the glass at 77K and the crystal. Additional ESR studies have been carried out on second crystal forms of both the dmt and mmt complexes (as sodium salts) and on the tetraethylammonium salt of the unsubstituted tartrate complex. The latter compound, whose structure has been recently reported, has been found to be magnetically dilute with well-resolved hyperfine structure indicative of a triplet state.

- 193 COMPUTER SIMULATIONS OF QUANTUM MIXED-SPIN AND HIGH-SPIN EPR SIGNALS OF FERRIC HEME. T. Lutton and M. M. Maltempo. Departments of Chemistry and Physics, University of Colorado at Denver, 1100 14th Street, Denver, Colorado 80202.

A quantum mixed-spin state has been monitored in several ferric heme proteins, hemes, and related iron complexes. This unusual magnetic species corresponds to a quantum mechanical mixture of mid-spin  $S = 3/2$  and high-spin  $S = 5/2$  configurations. The charge density of the iron 3d electrons is a hybridization of high-spin and mid-spin wave functions, and the spin expectation value is intermediate between  $3/2$  and  $5/2$ . Measurements of electron paramagnetic resonance over a wide temperature range are probably the most reliable way to make an unambiguous identification of the quantum mixed-spin state ( $4 < g \leq 6$ ,  $g_{\parallel} = 2$ ). Often some amount of the common high-spin ( $g \approx 6$ ) EPR signal is present when a  $g \approx 5$  mixed-spin species is observed. Accurate computer simulations are then required to quantitate a broad  $g \approx 5$  signal (150 - 400 G width, 77 K) superimposed on a sharp  $g \approx 6$  signal (75 G width, 77 K). We present computer simulations of mixed-spin and high-spin EPR signals for various  $g$ -values, line widths, and weight factors.

- 194 GENERALIZED EPR PARAMETER REFINEMENT FOR  $S = 5/2$  IONS IN LOW SYMMETRY SITES.

W.C. Tennant, Chemistry Division, Department of Scientific and Industrial Research Private Bag, Petone, New Zealand.

In this paper we combine and extend the generalized matrix refinement technique of McGavin, et al. (1) and the use of symmetry-related matrices, Weil, et al. (2), to analyse spectra and to refine parameters of the spin-Hamiltonian for ions with  $2 \leq S \leq 3$  in low-symmetry sites. It is shown: (i) fourth-degree crystal field parameters  $B_k^q$  (integers  $|m| \leq 4$ ) can be refined generally, along with possibly non-coaxial parameter matrices  $g$ ,  $D$ ,  $A$ ,  $P$ , expressed in an arbitrary coordinate frame.

(ii) the conclusions of Weil, et al. (2) regarding the use of symmetry-related matrices remain valid when fourth-degree crystal field terms are present; in particular the use of data from measurements (B) in fewer than three distinct planes is always sufficient except in the triclinic case.

The procedures are illustrated for  $\text{Fe}^{3+}$  in sites of  $C_2$  symmetry in  $\alpha$ -quartz, and for  $\text{Fe}^{3+}$  in low symmetry (possibly 1) sites in tetragonal  $\text{CaWO}_4$ .

References (1) D.G. McGavin, R.A. Palmer, W.A. Singers and W.C. Tennant, J. Magn. Reson. 40, 69 (1980).

(2) J.A. Weil, T. Buch and J.E. Clapp, Advances in Magn. Reson. 6, 183 (1973).

19. HIGH SPIN  $\text{Fe}^{3+}$  IN LOW SYMMETRY SITES: ANALYSIS OF POLYCRYSTALLINE EPR SPECTRA.

W.C. Tennant, Chemistry Division, Department of Scientific and Industrial Research, Private Bag, Petone, New Zealand.

Many minerals, complexes and proteins containing high-spin  $\text{Fe}^{3+}$  are obtainable only in polycrystalline form. Analysis of their EPR spectra is in terms of the spin-Hamiltonian

$$H = \beta H_z \sum_i S_i^z + \sum_j D_j S_j^2 + \sum_k A_k S_k^2 + \sum_l P_l S_l^2 + \dots$$

and for powdered samples is relatively simple if

(i)  $g \approx 6$ ,  $B \gg |D| \gg E$ , the weak field case, or (ii)  $|D| \gg gB, E = 0$ , the strong tetragonal field case, eg. heme proteins, or (iii)  $D = \pm 3E$  and  $|D| \gg gB, E$ , the complete rhombic distortion. In the intermediate situation when  $D = \pm 3E$  but  $|D| \approx gB$ , significant magnetic field mixing of Kramers' doublets may occur and powder spectra are more complex. A simple method of simulating and analysing such spectra involving a combined matrix diagonalisation-effective "g-tensor" curve fitting procedure is described. The application to  $\text{Fe}^{3+}$  in low symmetry sites, is illustrated by reference to  $\text{Fe}^{3+}$  in the mineral scheelite, to the model complex  $(\text{NH}_4)_2\text{Co}(\text{EDTA})$  and to the human proteins lactoferrin and transferrin.

TRIPLET-STATE SPIN COHERENCE IN PHOTOEXCITED BENZYL CRYSTALS AT 77 K: OPTICALLY DETECTED TRANSIENT NUTATION AND ADIABATIC RAPID PASSAGE.\* R. Gillies and A. M. Ponte Goncalves, Department of Chemistry, Temple University, Philadelphia, PA 19122.

Spin coherence in triplet-state traps in neat benzil single crystals at zero magnetic field was observed at 77 K by optical detection of magnetic resonance (ODMR). Pulsed nitrogen laser excitation and time-resolved detection of the phosphorescence were made with 10 nanosecond resolution. Microwaves were generated by a frequency-agile oscillator capable of sweep rates in excess of 25 MHz/ns and were amplified to over 1 kU by a pulsed broadband amplifier. Application of long microwave pulses at 4349 MHz produced a rapidly damped oscillation in the phosphorescence intensity. No oscillation was observed when the microwave power was attenuated by 6b dB or more, or when the duration of microwave pulses at full power was shortened to 60 ns or less. The phosphorescence oscillation corresponds to the coherent population transfer between the  $T_1$  and  $T_2$  spin states, with a coherence time  $T_2 \approx 100$  ns. Adiabatic rapid passage (ARP) experiments were performed by sweeping through the whole resonance line shortly after each laser pulse. Sweeps 2  $\mu$ s long with 0.1 MHz/ns sweep rate achieved roughly complete population inversion. Much faster sweeps did not meet the adiabatic condition and left the spin populations incompletely inverted. A lower bound for the coherence time was obtained from ARP experiments:  $T_2 \gg 400$  ns.

\* Research supported by National Science Foundation Grant #CHE-8009219.

197 MEASUREMENT OF ELECTRON AND NUCLEAR SPIN LATTICE RELAXATION TIMES BY MAGIC ANGLE SPIN LOCKING. J. M. McNally and R. W. Kreilick. Department of Chemistry, University of Rochester, Rochester, New York 14627.

We have measured the nuclear spin lattice relaxation times of matrix nuclei surrounding a series of different types of transition metal complexes. The dominant mechanism for nuclear relaxation in these complexes is dipolar coupling to the unpaired electron spins of the transition metal and the experimental data can be analyzed to obtain information about the correlation time for electron spin relaxation. The experiments were conducted with the nuclear spins locked at the magic angle to eliminate the first order contribution of nuclear spin diffusion to the nuclear spin-lattice relaxation time. With this technique one is able to measure electron spin-lattice relaxation time in the range from about  $10^{-7}$  seconds to  $10^{-12}$  seconds. Electron spin lattice relaxation times were measured over a wide concentration range to determine the effect of electron spin-spin interactions on the correlation time for relaxation. Both the inherent electron spin-lattice relaxation time and the correlation time for spin exchange are found to contribute to the observed correlation time. The exchange interaction is found to vary exponentially with the average metal-metal separation and to contribute to the observed correlation time out to relatively large metal-metal separations ( $\sim 40$  Å). The technique has the promise of allowing one to directly measure metal-metal separations in metalloproteins containing more than one metal atom.

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DIGITALLY CONTROLLED ENDOR SPECTROMETER. R. B. Clarkson. Varian Associates, 611 Hansen Way, Palo Alto, CA 94303

The control of ENDOR experiments by means of a small computer has many advantages over other controller options. In particular, the ENDOR experiment may gain substantially in sensitivity and in resolution as a result of one or more of the following procedures:

- Rapid acquisition and signal averaging of the ENDOR spectrum
- Non-linear rf sweep rates to maximize resolution and spectrometer/signal contact time.
- Digital processing of acquired ENDOR data.

We have developed a new control system, which, in conjunction with a Varian E-935 EPR Data Acquisition System and E-1700 BB ENDOR Accessory, allows experiments (a) - (c) above to be performed. Sensitivity enhancements as a function of experimental format will be discussed for a variety of ENDOR spectra of solids and radicals in solution. Resolution in the digital mode will be compared to earlier, analogue results.

- 199 ENDOR Detected NMR (EDNMR) Studies in Single Crystals. Amikam Reuvenj and Alvin L. Kwiram. University of Washington, Seattle, Washington 98195.

The EDNMR method is a sensitive way to obtain enhanced wide-line NMR spectra in the solid state. A paramagnetic center is introduced into the crystal (by irradiation or by doping) and its polarization is transmitted through cross-relaxation pathways to distant nuclei, not interacting directly with the electrons. The effective coupling of the spin temperature of the nuclear pool to that of the paramagnetic electron pool can be observed as changes in the intensity of the partially saturated EPR line upon irradiating at the nuclear frequency. The detection of changes in EPR offers higher sensitivity and makes the spectra easy to obtain at 4.2K where vibrations and librations are reduced. As a demonstration of the power of the EDNMR method in elucidating molecular structure information we present studies of enhanced EDNMR spectra of single crystals of N-D compounds. The analysis of the spectra and the correlation of the deuterium quadrupole tensors with N-D and O...D bond-lengths and D-N-D angles is shown. Extensions of the EDNMR method to other nuclei, such as  $^{31}\text{P}$  and  $^{13}\text{C}$  are explored as is a possible application of the method at temperatures higher than 4.2K.

- 200 Pulsed Microwave Characterization of Electron Spin Relaxation in Organic Solids. H. Thomann and L. R. Dalton. Department of chemistry. State University of New York, Stony Brook, NY 11794; M. Bowman and J. R. Norris, Chemistry Division, Argonne National Laboratory, Argonne, IL 60439; B. H. Robinson and A. L. Kwiram, Department of Chemistry, University of Washington, Seattle, WA 98195.

Electron relaxation (spin-spin, spin-lattice, and spectral diffusion) times have been measured by pulsed microwave techniques for a variety of organic materials including three classes of organic conductors. A new hybrid spin-echo, saturation-recovery pulse spectrometer employing an ECL logic pulse programmer, fast microwave phase modulation, and a bimodal TE $^{10}$  induction cavity to realize nanosecond response and high dynamic range sensitivity is utilized to discriminate between static and dynamic interactions and to resolve the effects of multiple relaxation processes and mechanisms. Numerical theoretical techniques have been developed to analyze the results of sophisticated pulse sequences applied to these systems; such analysis is required not only by the spectroscopic complexity of the systems studied but also by the fact that multiple dynamic processes are studied over a wide dynamic range, e.g., from the rigid lattice to the fast motion limits. Major new insights into the relaxation of organic radicals have been realized. Considering as an example the organic conductor polyacetylene, four distinct dynamic processes contributing to spin-spin relaxation and two processes contributing to spin-lattice relaxation have been characterized. The magnetic interactions modulated by the dynamic processes and the activation energies associated with the *dynamic* processes have been measured. This information in turn permits complete characterization of electron mobility in this conductor. Similar results are realized for phenylthiazoles.

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- APPLICATION OF COMBINED FOURIER TRANSFORM AND TIME DOMAIN SIMULATION OF ELECTRON SPIN ECHO MODULATION DATA TO ION SOLVATION GEOMETRY. P. A. Narayana and Larry Keyan. Department of Chemistry, University of Houston, Houston, Texas 77004.

The solvation structure of  $\text{O}_2^{2-}$  in deuterated dimethylsulfoxide (DMSO) has been investigated by analysing the electron spin echo modulation at 4.2K. The analysis has been carried out by Fourier transforming the three pulse echo modulation and by simulating the two pulse echo modulation. The analysis indicates that each  $\text{O}_3^{2-}$  interacts with two different groups of deuterium nuclei, each group containing six nuclei. It is found by simulating the modulation that one group is located at a distance of 0.25nm from  $\text{O}_3^{2-}$  with an isotropic coupling of 0.5 mHz while the second group is located at a distance of 0.35nm with a negligible isotropic coupling. These results suggest a structure with each  $\text{O}_3^{2-}$  solvated by two DMSO molecules arranged asymmetrically about the  $\text{O}_2^{2-}$ . The two different distances appear to reflect the solvating molecule orientation with respect to the  $\text{O}_2^{2-}$  bond.

202 CURRENT TRENDS AND NEW DIRECTIONS IN ATOMIC SPECTROSCOPY. S. M. Hieftje, Indiana University, Department of Chemistry, Bloomington, Indiana.

Use of linear response theory has heralded a whole new class of spectroscopic observations. From linear response theory, it is possible to probe time-dependent chemical reactions and excited states using simple, fluctuating light sources. In turn, temporal information can be extracted following these perturbations through use of correlation methods. Applied to atomic spectroscopy, this linear response approach enables the determination of atomic excited-state lifetimes using either simple light sources or complex laser devices. In turn, atomic lifetimes can be used in either a fundamental way to determine such things as quenching cross sections of species in flames and plasmas or in practical studies to eliminate the effects of quantum efficiency variations in atomic fluorescence or to overcome the effects of scattering in practical AFS determinations. In this presentation, the basic concepts behind linear response theory will be discussed in simple terms and instrumentation necessary for implementation of the methods will be examined. Finally, a range of applications of linear response theory to both atomic and molecular spectroscopy will be reviewed.

203 USING AN INTEGRATED, MICROCOMPUTER-CONTROLLED, ADJUSTABLE-WAVEFORM SPARK SOURCE FOR SPECTROCHEMICAL ANALYSIS WITH SYNCHRONOUSLY-GATED DETECTION. Steven G. Barnhart and John P. Walters, Department of Chemistry, University of Wisconsin-Madison, Madison, WI 53706.

Electrical schematics, construction details, and performance examples for an electronic, adjustable-waveform spark source will be presented. The source operates at high voltage, under microcomputer control, is series switched with a hydrogen thyatron, produces long-duration, pulsating unidirectional *current waveforms*, yet does not require high-voltage diodes in parallel with the spark gap or thyatron for current waveshaping. Preliminary work on synchronous time-gated detection methods as a new form of signal averaging will be reported. Circuitry and mechanical construction of the source as well as the generation of a time-gate signal which is synchronized to the current waveform will be illustrated.

204 OBSERVATIONS ON THE INTERFACING OF THE ICP TO CHROMATOGRAPHS FOR ELEMENT SPECIFIC DETECTION. Dennis A. Yates, Dave Fraley, Stanley Manahan, Dennis Duebelbise, Shubender Kapila, and C. R. Vogt, Environmental Trace and Substances Research Center and Department of Chemistry, University of Missouri, Columbia, Missouri 65201.

In our laboratory we have been utilizing the ICP as an element specific detector for gas and liquid chromatography. The initial goals of our work were to develop appropriate interfacing hardware, evaluate instrument performance and determine instrumental limitations for several types of chromatography.

It is apparent through our work (1) as well as the *work of others* (2,3), that the ICP is a suitable element specific detector. It is also apparent that the conventional approach to sample nebulization and data acquisition is not necessarily appropriate to chromatography. In this paper, the ICP as a detector (both single and multielement) for chromatographic effluents will be discussed. The interface hardware and data acquisition approach will be described for HPLC (aqueous and organic solvents) and capillary *column gas* chromatographic effluents.

1. D.M. Fraley, D.A. Yates, S.E. Manahan, *Analy. Chem.*, 51 (13), (1979) 2225.
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205 ACCURATE ANALYSIS OF HIGH SOLIDS CONTAINING SOLUTIONS BY ICAP-OES. A. F. Ward, R. K. Brown, L. Carrara, S. Solosimo, V. Luciano, L. Marciello, Jarrell-Ash Division Fisher Scientific Company, 590 Lincoln Street, Waltham, Massachusetts, 02254.

One sample type that has often presented difficulties in atomic spectroscopy is the solution that contains a high solid content. The major problems incurred are clogging of the nebulizer and the variation of sample uptake as the solids content and viscosity of the solution changes.

Several commercially available nebulizers were investigated with regards to stability, detection limit and tolerance to high solid containing solutions. This study showed that nebulizers utilizing the pneumatic principles were unsuitable for long term analysis when solids contents rose above 1% w/v but that a nebulizer based upon the Babington or Vee-groove concepts successfully aspirated solid contents approaching the solubility limit of the matrix.

The application of the high solids nebulizer to the trace elemental determination of lines, plating solutions, photographic solutions and other difficult samples will be discussed.

206 CHARACTERIZATION OF EFFECTS FROM LARGE DISSOLVED-SOLID CONCENTRATIONS ON TRACE-ELEMENT DETERMINATIONS BY INDUCTIVELY COUPLED PLASMA SPECTROMETRY. 3. R. Garbarino, G. Kimber, and H. E. Taylor, U. S. Geological Survey, 5293 Ward Road, Arvada, CO 80002

Determination of trace elements in saline solutions, digested natural whole-water samples, or digested bottom materials requires a method that is unaffected by relatively large concentrations of dissolved solids. To use inductively coupled plasma spectrometry for analysis of these types of samples, a study characterizing the effects of varying concentrations of dissolved solids has been conducted, in which the effects resulting from major cationic and anionic species commonly occurring in these samples have been identified and characterized.

Line-profile scans of analytical wavelength regions indicate two major spectral effects resulting from the dissolved species: (1) Most elemental wavelengths are affected only by spectral background shifts that are shown to be a linear function of dissolved solids concentration, and (2) some analytical wavelengths incur spectral overlap from nearby line broadening. Data presented show that accurate quantitative analytical results are obtained for samples containing relatively large concentrations of dissolved solids when a simple background correction procedure is used. Evaluation of the accuracy and precision of this procedure is based on results obtained for samples with a wide range of dissolved-solid concentrations.

207 A MODULAR APPROACH TO INDUCTIVELY COUPLED PLASMA ANALYSIS. J. Katzenberger, R. Randazzo, S. Berman, Instruments SA, Inc., 173 Essex Avenue, Metuchen, NJ 08840.

In ICP Spectroscopy, each potential user may fit into the two general categories of ICP analysis; that is, simultaneous and sequential analysis. Many analysts may, in fact, not have analysis requirements which place them completely in either of these categories.

This type of user needs more flexibility in building his system so that his system can grow with his needs. Such a system would consist of several modules, some of which are common to both a simultaneous and sequential system and others which may be unique to one or the other.

A system will be described which offers several configuration possibilities utilizing independent modules. By choosing only the modules which are most appropriate for his needs, the analyst can start with the minimum system required, without sacrificing future expandability of his system.



- 208 OPTIMIZATION STUDIES OF A SPUTTERING ATOMIZATION — METASTABLE TRANSFER EMISSION SOURCE. Steven D. Hornung and Thomas M. Niemczyk, Department of Chemistry, University of New Mexico, Albuquerque, NM 87131

Metastable transfer emission spectroscopy (MTES) has been shown to be very sensitive for the determination of trace levels of several elements. In this technique an atomic vapor is mixed with active nitrogen and is excited by energy transfer from the NZ(A 1) electronic state providing relatively efficient, nonthermal excitation. The active nitrogen is produced in a low pressure microwave discharge away from the observation zone of the cell. Because of the low pressure at which the active nitrogen is produced a sputtering atomizer can be employed to produce the analyte vapor. Sputtering atomizers of various types and modes of operation will be discussed. This provides the ability to atomize trace amounts of metals in conductive solids as well as solutions dried onto a conducting support. Knowledge of the concentration of the various states of molecular and atomic nitrogen produced in the microwave discharge as a function of pressure and other experimental conditions can aid in improving the technique. For this study the relative concentrations of some species of interest was determined by spectroscopic techniques. Optimization of a sputtering atomization — MTES emission source based on these studies will be discussed.

- 209 RAPID DISSOLUTION TECHNIQUE FOR MULTIELEMENT ANALYSIS OF CROP SAMPLES BY ICP-A-S. Roy VL Kuennen and J. A. Caruso, University of Cincinnati, Cincinnati, Ohio 45221  
Karen A. Wolnik and Fred L. Fricke, Food and Drug Administration, Cincinnati, Ohio 45202

A method is described which utilizes a *pressure* dissolution technique that allows multielement analysis of raw agricultural crops by Inductively Coupled Argon Plasma - Atomic Emission Spectrometry while minimizing sample pretreatment. The procedure employs a 30 min. pressure dissolution of sample composite with 6M HCl at 80°C in 60 mL Nalgene bottles. A non-adjustable cross-flow pneumatic nebulizer utilizing high pressure argon flow through a sapphire orifice enables direct atomization of complex organic matrices. The procedure compares favorably to more time-consuming conventional dry or wet ashing methods for the determination of major, minor and trace elements occurring in lettuce, potatoes, soybeans, spinach, sweet corn and wheat. Recoveries for spiked samples, precision studies and analyses of NBS reference materials demonstrate the reliability and accuracy of the procedure. Advantages and limitations of this technique relative to conventional dry or wet ashing methods are discussed.

- 210 ANALYSIS BY INDUCTION COUPLED PLASMA SPECTROMETRY USING PHOSPHORIC ACID AS SOLVENT BY Dr. Larry Morgenthaler. Applied Research Laboratories, 9545 Wentworth Street, Sunland, California 91060.

For analysis by Induction Coupled Plasma (ICP), samples must be in solution. In most dissolution procedures prior to analysis, phosphoric acid is avoided as an analytical reagent because it forms strong complexes with many elements and acts as an interferent in the analysis. The extreme temperatures reached in the ICP cause complete dissociation of the phosphate and thus prevent it from interfering with the emission of the other elements in the sample. Phosphoric acid and phosphoric-nitric acid mixtures are excellent solvents for many sample types. They have been used to solubilize samples ranging from plant tissue to iron ores to tungsten carbide. While the dissolution procedures work easily and well, the chemistry involved is somewhat obscure. This is especially true for those reactions involving nitric acid dissolved in phosphoric acid as a solvent. The theory and operation of the ICP spectrometer will be discussed as well as the properties of phosphoric acid as a solvent for complex samples. This long neglected reagent can now be used to prepare difficult samples for analysis by ICP.

- 211 AUTOMATED SIMULTANEOUS MULTIELEMENT DETERMINATION OF THE HYDRIDE FORMING ELEMENTS AND MERCURY BY CONTINUOUS HYDRIDE EVALUATION / ICP - OES BY J. E. Goulter and D. M. Painchaud. Applied Research Laboratories, 95<sup>th</sup> Wentworth Street, Sunland, California 9101<sup>st</sup>0.

The technique of inductively coupled plasma - optical emission spectroscopy (ICP-OES), using pneumatic nebulisation as a means of sample presentation, generally yields adequate sensitivity for the analysis of most elements of the trace level. In common with flame atomic absorption (FAA) however, the detection limits obtainable for the group IVA - VIA elements (arsenic, antimony, bismuth, germanium, lead, selenium, tellurium, tin) and mercury are not sufficiently low for the direct determination of these elements at the ultratrace level, particularly in environmental samples. In AAS either graphite furnace or hydride generation techniques are employed in order to enhance sensitivity for these elements. This paper describes the development and characterisation of an automatable continuous hydride generation system compatible with both simultaneous and sequential scanning ICP systems. Overall sub part per billion detection limits could be established for the hydride forming group of elements under compromise conditions and calibration curves exhibited linear ranges of  $>10^4$ . Relative standard deviation of 1 - 2% were generally obtainable for analyte concentrations greater than the background equivalent concentrations and preflush and integration times similar to those employed for direct solution nebulisation could be used (20 s and 10 s respectively).

- 212 METHODS DEVELOPMENT FOR ICP SPECTROSCOPY, H. L. Kahn, J. J. Sotera, and A. L. Ratttonetti. Instrumentation Laboratory Inc., Jonspin Road, Wilmington, Massachusetts 01887.

It has proved possible to devise an orderly and reasonably routine procedure to develop analytical methods for a rapid-scanning sequential ICP spectrometer. For each element, the wavelength and plume observation height can be chosen independently. The plasma power level, in seven steps, is selected on the basis of the sample to be analyzed often lower power produces better detection limits, while higher power gives a greater freedom from interferences. Background correction can also be selected independently for each element. The use of an instrument with a double monochromator, which essentially eliminates the effects of stray light, often times eliminates the need for background correction. Computer-controlled graphics are used to simplify selection of the emission line for each element, measure optimal plume observation height, and determine the conditions for background correction. The result is a program for the determination of several elements in rapid sequence, where background correction and observation height are optimized automatically for each element. The program is then stored on a cassette and can be rapidly re-entered every time the analysis is required.

- 213 SAMARIUM METAL ANALYSIS BY DC PLASMA SPECTROMETRY. G. W. Johnson and T. E. Sisneros, Molycorp, Inc., Box 607, Louviers, Colorado 80131.

A principal use of samarium metal is as an alloy with cobalt in the production of permanent magnets. Compared with other permanent magnets of equal magnetic field and stored magnetic energy, the samarium-cobalt magnets are far lighter and smaller. The metal is produced by high temperature reduction of  $\text{Sm}_2\text{O}_3$  in an inert atmosphere under reduced pressure. Likely impurities in the samarium metal in this process were identified as La, Ce, Pr, Nd, Eu, and Gd (probably present at levels  $>0.01\%$  in the  $\text{Sm}_2\text{Cl}_3$ ) and Yb (sublimation temperature less than that of Sm). As a means of product quality assurance, an analysis method based on use of a direct current plasma-echelle spectrometer atomic emission technique was developed for the determination of these elements in Sm metal. Procedures used to select analysis lines, to compensate analytical measurements for background emission due to elevated Sm content of the samples, and to ascertain and insure accuracy of the analysis will be discussed. As an example of analysis results the (determined concentration, detection limit) pair are listed following each impurity for one Sm metal sample (all concentrations in % w/w): La(0.057, 0.0038); Ce(0.12, 0.006); Pr(0.44, 0.0077); Nd(0.32, 0.0041); Eu(0.036, 0.00061); Gd( $<0.005$ , 0.0042); and Yb(0.0036, 0.00016).

- 214 THE DETERMINATION OF THE RARE EARTH ELEMENTS IN GEOLOGICAL MATERIAL BY ICP-OES.  
J. G. Crock and F. E. Lichte, U.S. Geological Survey, Box 25046, MS 928, Denver  
Federal Center, Denver, Colorado 30225

There is an increasing demand for the analysis of geological materials for the rare earth elements (REE), both individually and together as a select, unified group.

Inductively coupled argon plasma optical emission spectroscopy (ICAP-OES) is a proven, simultaneous, multielement analytical technique for the determination of trace elements in geological materials. A new method for the determination of trace level REE in geological materials using a 63-channel ICAP polychrometer is described. The method involves the dissolution of the sample by a multiacid digestion or a LiBO<sub>2</sub> fusion and then subsequent separation and preconcentration of the REE as a group using ion exchange procedures. Background correction is accomplished using blank subtraction, off-peak measurement and interelement corrections. The other ICAP parameters such as power and viewing height, are optimized for the REE. Precision, sensitivities, and detection are compared to literature values. Accuracy is demonstrated by the analysis of standard geological materials of a diverse nature.

- 215 APPLICATION OF A SEQUENTIAL SCANNING ICP TO THE ANALYSIS OF GEOLOGICAL MATERIALS. G. E. Wallace. The Perkin-Elmer Corporation, Main Avenue, Mail Station 906, Norwalk, Connecticut 06X56

Inherent in the design of the sequential scanning type of ICP emission spectrometer is the capability to freely select the most important parameter in the development of an analytical method — the analyte wavelength(s). Background interferences, the only type of interference which is of real importance in ICP emission spectroscopy, can be minimized and, in many cases, avoided by the judicious selection of this parameter. Careful wavelength selection is especially important for sample types such as geological materials which contain high concentrations of metallic constituents.

A recent publication<sup>1</sup> contains information which will aid the analyst in selecting analyte wavelengths. A section of this publication is entitled "Wavelength Characterization Tables" and is organized by element. The use of these tables together with the ICP/5000 System GRAPHICS utility for selecting optimum wavelengths and background correction intervals for the determination of low levels of chromium and vanadium in some USGS reference rock samples, will be discussed.

1. Analytical Methods Development for Inductively Coupled Plasma Emission Spectroscopy, The Perkin-Elmer Corporation, 1981.

- 216 SIMULTANEOUS MULTIELEMENT ANALYSIS OF DIFFICULT SAMPLES WITH AN ICP ATOMIC FLUORESCENCE SPECTROMETER. D. R. Demers and D. A. Busch, Baird Corporation, 125 Middlesex Turnpike, Bedford, Massachusetts 01730.

This paper will describe a commercial atomic fluorescence instrument for simultaneous multielement analysis. The instrument uses an ICP as the atomization cell, pulsed hollow cathode lamps for excitation and optical interference filters at the detection end of the instrument. The instrument's spectrometer comprises up to twelve independent element (channel) modules encircling the ICP. The element modules are rapidly interchangeable by the operator, thereby permitting whatever element mix he may desire.

Compared to flame atomic absorption systems, this instrument offers the advantages of simultaneous multielement analysis, 4 to 5-1/2 orders of linearity, fewer matrix interferences and baseline stability. Compared to ICP atomic emission systems, it offers optical stability, lower cost, and most important, virtual freedom from spectral interferences. Moreover, by virtue of the use of the ICP as the atomization source, molecular fluorescence interferences are absent and particulate light scattering interferences are rare.

Because spectral interferences are rare with this instrument, corrections for background shifts and for unresolved spectral lines are seldom required. As a result, accurate analysis of even complex (spectral line rich) samples is straightforward. The application of this instrument to the analysis of steels, soil extracts, and a variety of other complex materials will be presented.

217 ABSOLUTE ATOMIZATION EFFICIENCY OF THE GRAPHITE FURNACE. R.E. Sturgeon. Division of Chemistry, national Research Council Canada, Ottawa, Ontario, Canada KIA 0R9.

The atomization efficiency of flame systems used in analytical atomic spectroscopy has been frequently evaluated. This parameter remains essentially uncharacterized for electrothermal atomization systems. The absolute atomization efficiencies of several elements in an HGA-2200 furnace have been determined from measurements of microwave attenuation by electrons generated during analyte atomization. Included among the several assumptions made in applying the technique are those of thermal equilibrium and the validity of the Saha equation. The efficiency of the furnace varies with the element in question (as expected) but averages about 10% with a range from 1% (Ho, Sr) to 25% (Na). Theoretical and experimental consideration of the above calculations and assumptions will be discussed.

... GRAPHITE FURNACE TECHNIQUES USING THE ZEEHAN/5000 ATOMIC ABSORPTION SPECTROPHOTOMETER. Kenneth U. Olson, Perkin-Elmer Corporation 15042-A Parkway Loop, Tustin, CA 92680.

Two limitations of Graphite Furnace Atomic Absorption Spectrophotometry are (1) matrix interferences in the determination of the analyte, and (2) nonspecific absorbances from the sample matrix at the analyte wavelength. The first limitation has been compensated for by the method of additions, while continuum source background correction has been used to compensate for the second limitation. Because the method of additions is quite tedious, it is desirable to reduce or eliminate its frequency of use. Because continuum sources cannot accurately correct for background absorbances greater than one absorbance unit, and because this limitation often sets the method detection limit, alternate means of background correction must be considered.

The Perkin-Elmer Zeeman/5000 System and its unique ability to provide extended background correction without sacrifice of analyte sensitivity will be described. The L'vov platform and its advantages in the control of matrix interferences without the use of the method of additions will also be discussed. Applications involving the use of the L'vov platform with the Zeeman/5000 will also be presented.

219 SECOND SURFACE ATOMIZATION: A NEW APPROACH TO ELECTROTHERMAL ATOMIZERS. Michael Sheehan and James A. Holcombe, Department of Chemistry, University of Texas at Austin, Austin, Texas 78712.

A new atomizer design which is readily adaptable to any commercially available atomizer has been developed to provide atomization conditions which are more conducive to interference-free analysis from a wide variety of sample types. A graphite "plug" is located within the furnace and is capable of dissipating a sufficient amount of heat to keep it several hundred degrees below the wall temperature. The sample is initially micropipetted onto and atomized from the furnace wall. During a very high temperature ash, the analyte is vaporized from the wall and condensed on this secondary surface while many of the pyrolysis products from the matrix (e.e., O<sub>2</sub>, NO<sub>2</sub>, etc.) diffuse out of the furnace. Thus, when the atomizer is pulse heated to a final, high temperature, the analyte is released from this second surface into a nearly isothermal environment with minimal gas phase concomitants. Data demonstrating the effectiveness of this approach in minimizing common interference effects for several metals will be presented. The utility of using this atomizer configuration for direct solids analysis and for sample preconcentration also will be discussed.

- 220 IMPLICATIONS OF RADIALLY NON-UNIFORM ABSORBANCE PROFILES WITHIN GRAPHITE FURNACE ATOMIZERS. Gary D. Rayson, James A. Holcombe. The University of Texas at Austin, Department of Chemistry, Austin, Texas 78712

Studies involving matrix effects and vaporization processes within graphite furnace atomizers have previously neglected the possible effects of mass transport of various species within such atomizers. The kinetic and equilibrium explanations traditionally used to account for 1) the role of graphite as a reducing agent, 2) dimer formation, and 3) other molecular species containing the analyte hinge on the assumption of uniform concentrations within the furnace. When the finite rate of diffusion and the interactions at the graphite surface are taken into account, the non-uniform, atomic distributions observed can be more fully explained. Methods for gathering radial distributions of the vaporized analyte have been developed and, contrary to the commonly made assumption, demonstrate that the free atom distribution is typically non-uniform during the early portion of the absorbance profile. The degree of non-uniformity in proceeding from the bottom of the furnace (where the sample is deposited) to the top of the furnace is element dependent. Increased vaporization rates and strong chemical interactions between the analyte and the graphite tend to produce sharper concentration gradients along the graphite diameter. Results for the CRA-90 atomizer show that the atomic distribution within the atomizer is negligibly affected by the flowing sheath gas. Thus, suggesting that diffusion and convection by thermal expansion are the main mechanisms of atom removal.

- 221 PROGRESS TOWARDS MAKING THE GRAPHITE FURNACE FREE OF INTERFERENCES. Walter Slavin and Gordon Wallace. The Perkin-Elmer Corp., Main Avenue, Norwalk, CT. 06856.

The graphite furnace was originally designed by L'vov to provide a very fast signal for the metal analyte after completely vaporizing the total sample. Integration of the total absorbance signal under the appropriate experimental conditions then provided an accurate analysis. However, L'vov's system was simplified by Massmann and was adapted to spectrophotometers which were designed for steady-state signals. By now some of the commercial instruments are very close to the theoretical requirements. When such instruments are used correctly, the L'vov Platform converts the furnace to steady-state temperature and the use of newly improved graphite tubes make it possible to get analytical results that are remarkably free of matrix interference for most metals up to limits set by the background corrector. With the recent introduction of the Zeeman background corrector these limits are still further improved. For example, we have determined Mn in seawater by direct analysis against standards made up in seawater without interference from the matrix. We could detect about as little Mn in a 75- $\mu$ l seawater sample as we could detect in a pure water solution.

- 222 REDUCTION OF ANALYTICAL INTERFERENCES BY FURNACE ATOMIC ABSORPTION. R. N. Savage, J. J. Sotera, H. L. Kahn and A. L. Battonetti, Instrumentation Laboratory Inc, Jonspin Road, Wilmington, Massachusetts 01887.

Analytical interferences with AA determinations, when furnace atomizers are used, can be rather severe even for elements and matrices that give relatively little trouble with flame atomization. To cope with the interferences, the method of standard additions is frequently employed. This technique, however, is time-consuming, cumbersome, likely to add contamination, and by no means foolproof. Recently, two systems have shown signs of success in reducing interferences in commercially available atomizers: the XL micro-boat system, which is inserted into the graphite cuvette and is said to bring the samples closer to temperature equilibrium; and the FASTAC aerosol deposition system, which inserts the sample into the cuvette in the form of microscopic droplets. It seemed reasonable to make an effort to combine the two techniques using the FASTAC deposition of samples into an insert, made of graphite or other material, placed in a graphite cuvette. The two interference-reduction mechanisms then combine to produce very useful results. Details of the performance improvements will be presented. Analytical examples will include the determination of Pb in Nickel Alloys and Pb in National Bureau Standards (NBS) Orchard Leaves (SRM 1571).

- 223 THE RAPID DETERMINATION OF SELENIUM IN NUTRITIONAL SUPPLEMENTS BY A FLAMELESS ATOMIC ABSORPTION TECHNIQUE USING A NOVEL SAMPLE PREPARATION. D. D. Thompson and R. J. Allen. Forrest C. Shaklee Research Center, 1992 Alpine Way, Hayward, Ca. 94545

An accurate, precise and rapid procedure for the determination of selenium in selenized yeasts and selenium nutritional supplement products is described. The sample is suspended in an acidified emulsion of mixed nonionic surfactants prior to analysis by flameless atomic absorption spectroscopy. Nickel is used as a matrix modification reagent to prevent pre-atomization volatilization of the selenium. The advantage of using pyrolytically coated graphite tubes is shown. The procedure was found to yield an average recovery of 101.6% and an overall relative standard deviation of 4.34%. It is shown to be applicable to the analysis of selenium nutritional supplements ranging from 10mcg/unit to 50 mcg/unit selenium. The procedure as described is well suited for the analysis of high lipid containing samples (>30% lipid). Ten commercial selenium supplements and seven selenized yeast raw materials were analyzed.

- 224 THE DETERMINATION OF PRIORITY POLLUTANTS IN WATERS AND WASTES BY FURNACE ATOMIC ABSORPTION, Margaret A. Cunliffe and Douglas E. Shrader, Varian Instrument Group, 375 Distel Circle, Los Altos, CA 94022.

Because of an increasing concern over the potential detrimental effects of trace metals in our environment, regulation of maximum levels for many elements has been assigned to government agencies such as the EPA. In the case of the EPA, the first thrust was drinking water where eight primary metals are controlled (As, Ba, Cd, Cr, Pb, Hg, Se, and Ag). The second thrust was effluents where up to 35 metals may be of concern for NPDES permits. Most recently, thirteen metals (Sb, As, Be, Cd, Cr, Cu, Pb, Hg, Ni, Se, Ag, Tl, and Zn) have been designated priority pollutants to be monitored and controlled in solid and liquid wastes.

The potentially low concentrations of metals encountered in drinking waters, effluents, and wastes may many times be extremely difficult or impossible to determine by flame atomic absorption. Because of this, graphite furnace methods (typically 100 times more sensitive than flame methods) are part of approved EPA methodology.

The priority pollutant metals have been determined in waters and effluents/wastes utilizing the Varian CRA-90 Carbon Rod Atomizer. Results of this study including optimum parameters, performance, and results for samples will be presented along with interference and accuracy data.

- 225 DETERMINATION OF CADMIUM IN WHOLE BLOOD AND PLACENTAL TISSUES BY GRAPHITE FURNACE ATOMIC ABSORPTION SPECTROSCOPY. P. M. Kuhnert, B. R. Kuhnert, and P. Erhard. Perinatal Clinical Research Center, Case Western Reserve University, 3395 Scranton Road, Cleveland, Ohio, 44109.

A graphite furnace A.A. method is described for measuring cadmium (Cd) at "natural" levels in whole blood and placental tissues. The samples were collected in polypropylene syringes and stored in polystyrene containers. Prior to digestion, 1.5, 3.0, and 6 ng of Cd were added to the blood samples and 2.5, 5, and 10 ng of Cd to the placental samples (Method of Standard Additions). The samples were digested using concentrated ultrex nitric acid and hydrogen pyroxide in teflon containers. Following digestion, the samples were diluted 1:3 and twenty microliter aliquots were injected into a graphite furnace which was temperature programmed in the following manner: drying - 100°C for 40 s; ashing - 325°C for 60 s; and atomizing - 1950°C for 7 s. The drying and ashing stages were both ramped for 30 s. Within-run precision studies for whole blood Cd and placental Cd determinations gave coefficients of variation of 15.1% and 15.2% for 2.5 and 11.8 ng/ml of tissue Cd, respectively. Day-to-day variation of the blood Cd determinations gave a coefficient of variation of 17.4%. The detection limit in the diluted specimen was 0.2 ng/ml. This method was successfully used to quantitate the "natural" levels of Cd in maternal blood, fetal cord blood, and placental tissues.

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- 226 THE INTERFERENCE OF ALUMINUM ON TITANIUM AND URANIUM IN FLAME ATOMIC SPECTROMETRY, Charles B. Boss, North Carolina State University, Department of Chemistry, Raleigh, North Carolina 27650.

When Al is present in solutions that contain Ti and U salts, the flame atomic spectrometric signals observed for Ti and U are enhanced. When the fuel to oxidant ratio and the observation height are critically optimized, Ti signals in  $N_2O/C_2H_2$  flames are enhanced by more than a factor of two. Similarly, U shows a four fold enhancement with Al added.

The mechanism of these enhancements are of particular interest in my laboratory. The accepted mechanism for the enhancement of Ti by Al is that the Al reduces the oxides of Ti aiding in vaporization and atom formation. We have observed that TiO emission bands, as well as Ti atom lines, are enhanced by Al. Using a uniform droplet generator, we have observed that droplets containing Ti or U salts explode as they vaporize if Al is present. These experiments indicate that the mechanism of the enhancement involves the violent vaporization of Ti or U oxides followed by a normal reduction to atomic species. This enhancement is plainly evident even when  $TiO_2$  particles are slurry injected into an  $N_2O/C_2H_2$  flame with an Al salt solution.

- 227 CHEMISTRY ON A GRAPHITE SURFACE. I-Hsuing Yin and Thomas M. Niemczyk, Department of Chemistry, The University of New Mexico, Albuquerque, New Mexico 87131.

Flameless atomic absorption spectroscopy has been shown to be very sensitive for trace metal analysis. However, as the sample matrix becomes complex the utility of the technique may be diminished due to various matrix interferences. These matrix effects include both chemical and physical interactions among the analyte, the matrix, and the surface. Physical interactions such as occlusion can change the shape of the absorbance vs. time profile. Chemical interferences, on the other hand, may or may not affect the peak height but generally will reduce the integrated absorbance due to a depletion in the atomic population. This paper will focus on the latter type interference and will show that some of the interferences seen are due to chemical reactions occurring on the atomizer surface prior to the atomization step.

- 228 TRACE SELENIUM ANALYSIS IN NEW MEXICO WATERS. Maria W. Tjckanen and Lynn Branvold. HED, SLD, 700 Camino de Salud, NE, Albuquerque, New Mexico. New Mexico Bureau of Mines and Minerals Resources, Socorro, New Mexico.

Analytical methods are generally developed with ideal conditions in mind. Dealing with matrix problems comes as an afterthought. Both of the Environmental Protection Agency's approved methods for selenium use atomic absorption spectrophotometry. Both are subject to matrix interference.

New Mexico surface and ground waters, particularly those from the Grants Mineral Belt area have relatively high TDS (500-1500 ppm), carbonate (as  $CaCO_3$ , 1000-1500 ppm) and sulfate (with levels as high as 2000 ppm). An interlaboratory study of Se analysis of a particular set of these water samples will be presented. The graphite atomic absorption spectrophotometric analysis for Se has been found to be the most sensitive and accurate for these type samples. This method is also highly sensitive to inorganic matrix interference. Matrix modifications studies in the graphite furnace AA method for Se performed at the Scientific Laboratory Division will be presented.

229 AUTOMATED HYDRIDE DETERMINATION BY ATOMIC ABSORPTION. J. J. Sotera, H. L. Kahn and A. L. Rattonetti. Instrumentation Laboratory, Inc., Jonspin Road, Wilmington, Massachusetts 01887.

Volatile hydride generation combined with atomic absorption serves as a simple and sensitive analytical method for the determination of many metalloids. This paper describes an electronically controlled atomic vapor accessory (AVA) which automatically performs the various steps involved in the hydride generation process. In normal operation a Fleaker™ containing the acidified sample (up to 200 mL) is placed into the reaction vessel of AVA. The operator then simply presses the START button to initiate the reaction cycle. From this point on the cycle is automatic, AVA adds the correct amount of sodium borohydride solution, stirs the solution for a pre-selected time, and carries the evolved hydride gas into a flame-heated quartz absorption cell with a stream of inert gas (N<sub>2</sub> or Ar). This paper will discuss the parameters used in the optimization of the hydride generation technique, and the effect of pH, sample size, and purge gas flows on the sensitivity of As. Accuracy of the technique will be evaluated by the analysis of National Bureau of Standards (NBS) standard reference materials (SRM). Analytical examples will include the determination of As in HBS Orchard Leaves (SRM 1571) and in Bovine Liver (SRM 1577).

230 ENVIRONMENTAL CHEMICAL CHARACTERIZATION OF WATER CONTAMINATED BY *IN SITU* SYNTHETIC FUELS TECHNOLOGIES. Parry J. Bornhop and Stanley E. Manahan, Department of Chemistry, 123 Chemistry Building, University of Missouri, Columbia, Missouri 65211; David C. Sheesley, U.S.D.O.E. Laramie Energy Technology Center, P.O. Box 3395, University Station, Laramie, Wyoming 82071.

One of the more important environmental considerations involved with underground (*in situ*) conversion of coal, oil shale, or tar sands to gaseous or liquid synthetic fuels is the contamination of water on site. The effects of contamination may be minimized by factors such as proper site selection. Even contaminated water can be viewed as a resource that may be put to beneficial use. It is essential to have effective means for the environmental chemical characterization of water affected by *in situ* energy conversion technologies. In particular, a general scheme of characterization is needed that ranges in sophistication from very simple routine monitoring to gas chromatographic/mass spectrometric identification of specific organic compounds present at very low levels. A solvent-based separation and analysis scheme is described which divides contaminants into classes reflecting their general chemical nature and biogeochemical behavior, followed by *analysis* of the total organics in each class or analysis of specific organic compounds in each class by gas chromatography. Applications of this scheme to water from *in situ* coal gasification, oil shale retorting, and tar sand oil extraction are discussed.

231 THE EFFECT OF STEAM STRIPPING TREATMENT ON THE QUALITY OF OIL SHALE WASTEWATER. R. E. Sievers, M. K. Conditt, and R. S. Hutte. Dept. of Chemistry, CIRES, and ETSRP, Campus Box 215, Univ. of Colorado, Boulder, CO 80309.

Steam stripping is a method of wastewater treatment that is intended to remove ammonia, hydrogen sulfide, and other volatile compounds from oil shale wastewaters. During the exposure of wastewater to steam, *some* of the more *volatile organic compounds* may be removed as well. The effectiveness of steam stripping treatment for removing specific organic compounds was evaluated by a critical comparison of the wastewater before and after steam stripping. The organic compounds in the wastewater were identified by high-resolution fused-silica capillary chromatography combined with mass spectrometry and were verified by matching retention times and mass spectra. It was found that only 7% of the dissolved organic carbon content is removed from oil shale retort water by this treatment. The steam stripping removed primarily hydrophilic compounds as well as some quinolines. Anilines and long chain carboxylic acids remained in the wastewater after treatment.



- 32 THE UTILIZATION OF GAS CHROMATOGRAPHY/FOURIER TRANSFORM INFRARED SPECTROSCOPY (GC/FTIR) TO IDENTIFY TOXIC ENVIRONMENTAL CONTAMINANTS. D. E. Gurka, P. R. Laska and R. Titus. U. S. Environmental Protection Agency, Quality Assurance Division, 944 East Harmon, Las Vegas, NV 89102. Kenneth Shafer, Battelle-Columbus Laboratories, 505 King Ave., Columbus, OH 43201.

The minimum identifiable quantities of 55 toxic substances have been determined by on-the-fly gas chromatography/Fourier transform infrared spectroscopy (GC/FTIR). Identification of each CC effluent component was accomplished with an IR reconstructed chromatogram, subsequent interferogram transformation and on-line library search. GC/FTIR exhibited its greatest sensitivity to aliphatic and aromatic organic compounds containing carbonyl or other oxygenated functional groups and its poorest sensitivity to alkyl halides and aromatic hydrocarbons. GC/FTIR sensitivity was inversely proportional to the light pipe temperature. Extracts from hazardous waste samples were analyzed and their volatile components were identified by an on-line library search. The relative merits of packed and capillary column GC/FTIR for hazardous waste analysis is discussed.

- 233 THE ANALYSIS OF HAZARDOUS WASTE EXTRACTS BY COMBINED GC/FTIR AND GC/MS. D. E. Gurka, A. D. Sauter, L. D. Betowski and H. Webb. U.S. Environmental Protection Agency, Quality Assurance Division, 944 E. Harmon, Las Vegas, NV 89102.

The unequivocal identification of trace environmental contaminants is a primary task of the Environmental Protection Agency. The burden of these identifications thus far, has been borne by gas chromatography/mass spectrometry (GC/MS) analytical techniques. However, the diversity of environmental contaminants necessitates supplemental analytical techniques to substantiate GC/MS results or to utilize for those situations when GC/MS is not applicable. The versatility, sensitivity, speed and information content of the gas chromatographic/Fourier transform infrared (GC/FTIR) method, make it a likely candidate to supplement or complement GC/MS. To assess the relative merits of GC/FTIR and GC/MS for "real world" sample analysis, hazardous waste extracts were analyzed by each method. On-line mass spectral and infrared library searches were compared.

- 234 ENVIRONMENTAL APPLICATIONS OF SERIES PID/FID DETECTION IN GAS CHROMATOGRAPHY. G. F. Hewitt, J. N. Driscoli, HNU Systems Inc., 30 Ossipee Road, Newton, Massachusetts 02166.

The PID has been shown to be a structure sensitive detector, its response being a function of the degree of pi bonding of a molecule. Since it is non destructive, it can be coupled in series with an FID, the resulting chromatograms can be used to "identify" eluted components on the basis of retention time and relative detector response. Applications in the field of air pollution and hazardous waste will be discussed. PID-ECD series detection will also be discussed.

1. Driscoli, J. N., Ford, J., and Jaramillo, L., 3. Chrom., 158, 171 (1977).
2. "A Rapid Screening Method for On site Identification of Hazardous Waste", Driscoli, J. N., Hewitt, G. F., Presented at the Second Oil and Hazardous Materials Spill Conference, Philadelphia, Dec. 1980.

- 235 DETERMINATION OF PCBs, PAHs AND AZA-ARENES IN LAKE SEDIMENT SAMPLES. T. M. Engel and J. S. Warner. Battelle Columbus Laboratories, 505 King Avenue, Columbus Ohio 43201.

The adverse environmental impact of petroleum components has long been recognized in the scientific community. Large amounts of effort have been invested in the study of certain classes of petroleum compounds, such as the polycyclic aromatic hydrocarbons (PAHs) which are of interest because of their carcinogenicity. Methods have been devised for detecting PAHs in a variety of environmental samples such as soil, sediment, biota, and water. There are other groups of petroleum compounds, however, that may be similar to PAHs in environmental importance. For instance, nitrogen-containing heterocyclic aromatics have been demonstrated to be potentially dangerous carcinogens. This

paper describes our approach to the analysis of the nitrogen-containing heterocyclics in sediment samples, as well as the analysis of two other classes of compounds, namely PAHs and polychlorinated biphenyls (PCBs). A cleanup procedure has been devised by which these three classes of compounds are isolated using adsorption chromatography with alumina. A novel approach involving the addition of a small amount of trimethylamine to the elution solvent to facilitate the desorption of the more strongly bound nitrogen-containing heterocyclics is described. Capillary column gas chromatography using an electron capture detector for PCBs, a flame ionization detector for PAHs and an alkali flame detector for nitrogen-containing heterocyclics is demonstrated. Capillary column gas chromatography coupled with, mass spectrometry is used for compound identification.

226 ISOMER-SPECIFIC DETERMINATION OF 2,3,7,8-TETRACHLORODIBENZO-P-DIOXIN VIA FUSED SILICA GC COMBINED WITH ATMOSPHERIC PRESSURE IONIZATION MASS SPECTROMETRY. W. A. Korfmacher, R. K. Mitch<sup>TM</sup> and G. F. Moler, National Center for Toxicological Research, Jefferson, Arkansas 72079.

Due to the high toxicity of 2,3,7,8-tetrachlorodibenzo-p-dioxin (2,3,7,8-TCDD), there is much interest in the detection of very low levels of this in the environmental samples. Because of the lower toxicity of the other TCDD isomers, it is important to have an isomer-specific methodology for 2,3,7,8-TCDD. A moving needle injector was connected to a 50 m fused silica capillary GC column which was inserted directly into the source of the mass spectrometer. In an oxygen-rich plasma, 2,3,7,8-TCDD forms the 4,5-dichloro-1,2-benzoquinone anion which is used for detection of 2,3,7,8-TCDD by our method. The ability to detect the 2,3,7,8-TCDD isomer in the presence of the other 21 TCDD isomers will be shown. Results from the analysis of TCDD-contaminated fish samples will be discussed.

227 REMOVAL OF METAL IONS FROM AQUEOUS SOLUTION BY ION EXCHANGE ON SULFURIC ACID-TREATED PEAT. John P. Ansted and Patrick MacCarthy, Department of Chemistry and Geochemistry, Colorado School of Mines, Golden, Colorado 80401.

Removal of metal ions from aqueous solution by simple and inexpensive techniques is of considerable importance in the control of water pollution. The large-scale application of synthetic ion-exchange resins for this application is frequently considered impractical due to the high cost of resin. Peat, which is widely available, has a native cation exchange capacity. However, as a result of its impermeability toward water and its propensity for leaching, peat is not suitable for use as an ion-exchanger in the column mode. It has previously been shown that the product resulting from the treatment of peat with hot concentrated sulfuric acid has the following properties: (i) granular form suitable for column use, (ii) enhanced cation exchange capacity compared to the untreated peat, and (iii) resistant to leaching at pH  $\geq$  9.0. We have now evaluated the use of this treated peat for simultaneously removing a wide variety of heavy metal ions from aqueous solution. The variables investigated were total concentration of heavy metal ions, ionic strength, pH and flow-rate. The species studied were:  $Mn^{2+}$ ,  $Co^{2+}$ ,  $Ni^{2+}$ ,  $Cu^{2+}$ ,  $Zn^{2+}$ ,  $Cd^{2+}$ ,  $Pb^{2+}$  and  $UO_2^{2+}$ . Treated peat was found to be very effective in removing all of the above species over a wide range of the parameters investigated.

23. MONITORING MINE TAILINGS IN NEW MEXICO FOR TRACE METALS Maria W. Tikkanen, New Mexico Scientific Laboratory Division, Health & Environment Dept., 700 Camino de Salud, NE, Albuquerque, New Mexico 87106.

As the analytical arm of New Mexico's Environmental Improvement Division, the Scientific Laboratory Division routinely analyzes monitoring well samples for heavy metal contamination of groundwater in the Grants Mineral Belt of New Mexico. The July 1979 United Nuclear Tailings pond break provided SLD with a multitude of tailings samples for refinement of trace metal methodology with heavily matrixed samples. Presently, special interest has been shown in the tailings seepage problems experienced in the Churchrock, New Mexico area. Analyzing these raw mine tailings samples and the adjacent monitoring well water samples for trace metals involves atomic absorption spectrophotometry (both flame and furnace) as well as inductively coupled plasma spectrometry. Dealing with the attending matrix problems is of particular importance with these analyses. Comparative trace metal studies, of these monitoring samples, involving both atomic absorption spectrophotometry and inductively coupled plasma spectroscopy will be presented.

239 EVALUATION OF SAMPLE PREPARATION PROCEDURES FOR THE ANALYSIS OF POTW SLUDGES FOR BE, CD, CR, CU, PB, NI, AG AND ZN. M. Williams, L. Petrie, J. Frank, J. Hurt, B. Jones, S. Swanson, E. Hansen, Midwest Research Inst., 425 Volker Blvd., Kansas City, MO 64110.

An EPA-sponsored project to determine metals in POTW sludges by atomic absorption spectroscopy (AAS) was conducted at Midwest Research Institute (MRI). As part of this study, MRI evaluated several sample preparation procedures for the flame AAS analysis of Be, Cd, Cr, Cu, Pb, Ni, Ag, and Zn. Samples from four representative POTW plants in different stages of treatment (primary, secondary and combined) were digested using three procedures: (a)  $\text{HNO}_3/\text{H}_2\text{O}_2/\text{HCl}$ , (b)  $\text{HNO}_3/\text{H}_2\text{O}_2/\text{HNO}_3$ , and (c)  $\text{HNO}_3/\text{HClO}_4/\text{H}_2\text{SO}_4$ . To provide quality assurance, fortified and duplicate samples were prepared. Results obtained at MRI were verified through interlaboratory comparisons with two EPA laboratories (Region VII and EMSL, Cincinnati). Region VII analyzed six samples from each of MRI's three digestions by an alternative method, inductively coupled plasma (ICP) emission spectroscopy. Also, these same six samples were digested by Region VII using procedure (b) and a  $\text{HNO}_3/\text{HCl}$  digestion followed by ICP analysis. EMSL digested and analyzed by ICP an additional five samples that had been analyzed at MRI. EMSL used procedure (b) and a E2S04/dry ash method. The calculated recoveries and relative concentrations obtained for the three MRI sample preparation procedures will be discussed, as will the results of the interlaboratory comparisons. The digestion procedure yielding the most reliable results for each element will be recommended.

240 EFFECTS OF STREET SALTING ON AMBIENT AIR MONITORING OF PARTICULATE POLLUTANTS IN DETROIT. Peter O. Warner, John O. Kermoshchuk and \*James O. Jackson. Wayne County Health Department, Air Pollution Control Division, 1311 E. Jefferson, Detroit, Michigan, 48207. \*Los Alamos Scientific Lab., P.O. Box 1662-MS 486, Los Alamos, New Mexico, 87545.

Analysis by x-ray diffractometry has confirmed the presence of crystalline salt as sodium chloride in Detroit urban suspended particulate. This finding has given rise to a concern for the relationship between the occurrence of suspended salt and incidence of winter salting of streets in Detroit and greater metropolitan Detroit area. Furthermore, since air in most major cities is routinely continuously monitored for suspended particulate by soil-haze densitometry as a part of the air pollution alert program for emergency episode avoidance, it is important to assess the weight contribution of translucent crystalline salt to the measurement of these otherwise opaque particulates. Analyses have been made to determine salt as chloride in the measurement of both coefficient of haze (COH) and of actual total suspended particulate (TSP) using side by side sample collection. Correlation of these data has been made with days of actual street salting and a weight relationship has been established to show the influence of salt particulate on COH and suspended particulate. Coincident with this study are data which express the relationship between COH and high-volume sampled suspended particulate collected at the same site.

241 ACCEPTANCE TESTING CRITERIA AND PROCEDURES FOR HI-VOLUME FILTERS USED IN MONITORING NETWORKS. C. F. Turlington. Northrop Services, Inc., P.O. Box 12313, Research Triangle Park, NC 27709.

Several hundred thousand glass fiber filters for hi-volume sampling are procured annually by E.P.A. for all agencies reporting particulate monitoring data. Before these filters are accepted and approved for use, a random sampling of the entire annual supply of filters must be selected and subjected to various tests and analyses to determine their acceptability based upon preset criteria for each of the tests performed. Initially, the selected filters are subjected to a visual inspection by light table screening, whereby each is judged as acceptable, defective, or reject. The filters are then evaluated for both physical and chemical characteristics by the appropriate tests or analyses. The physical characteristics evaluated include size, thickness, brittleness, integrity, tensile strength, flow rate, and retention. The chemical characteristics of interest are pH, weight loss on ignition, selected non-metals, benzo-a-pyrene, and

SELECTED METALS. THE TESTS OR ANALYSES USED FOR BOTH PHYSICAL AND CHEMICAL CHARACTERISTICS EVALUATED ARE EITHER ASTM METHODS OR ACCEPTED E.P.A. METHODS OF ANALYSIS. THE PRE-SET ACCEPTANCE CRITERIA WILL BE PRESENTED IN ADDITION TO THE PROCEDURES FOR EACH OF THE QUALITY CHARACTERISTICS OUTLINED. DATA FOR SIZE, BHTTLENESS, INTEGRITY, AND FLOW RATE SUBMITTED BY NSI-QAD PERSONNEL; DATA FOR PH, BENZO-A-PYRENE, AND SELECTED METALS CONTRIBUTED BY USEPA-EMSL-EMD, POLLUTANT ANALYSIS BRANCH, TRACE ELEMENT ANALYSIS SECTION.

2\*2

**ANALYSIS OF TOXIC ORGANIC COMPOUNDS  
IN AMBIENT AIR BY GAS CHROMATOGRAPHY/MASS SPECTROMETRY**

**DAVID E. SMITH, WILLIAM C. SCHNITZLER**, Finnigan Corroration, 845 West Maude Avenue, Sunnyvale, CA 94086

In response to continuing concern by federal agencies about the possible deleterious effects of air pollution on human health and the environment, various techniques for the analysis of toxic chemicals in the atmosphere are being explored for their relevance and effectiveness. Combined gas chromatography/mass spectrometry (GC/MS), with its proven effectiveness for analysis of toxic organics in water, is being utilized by various laboratories. This paper explains the configuration of a GC/MS instrument adapted specifically for organics-in-air analysis, and describes the software employed for rapid identification of compounds.

Standard mixtures of 15 volatile compounds were analyzed over a 6 day period to determine precision of the analyses. Multiple internal standards were employed, mean relative response factor deviations varied from 65% to 279% with an average of 163%. Sampling times up to 30 minutes with sampling rates of 30 ml/minute are possible without breakthrough of any compound using a Tenax/silica gel trap.

243 **OPTICAL DESIGN OF U.V. SECOND DERIVATIVE ENVIRONMENTAL GAS ANALYZERS** **D. E. Osten**, Lear Siegler, Inc., 74 Inverness Drive East, Englewood, CO 80111.

State-of-the-art instrumentation for monitoring such environmental pollutants as SO<sub>2</sub> and NO include Ultraviolet second derivative monitors. Key to performance of these monitors is their optical throughput, resolution, and stability. Optimization of design of these monitors for the above parameters will be discussed. Measurement techniques used to evaluate performance will also be described.

24\* **VAPOR PRESSURE MEASUREMENTS OF TOXIC AND CARCINOGENIC MATERIALS OF INTEREST IN INDUSTRIAL HYGIENE.** Dorothy C. Sterling and George M. Breuer, National Institute for Occupational Safety and Health, 4676 Columbia Parkway, Cincinnati, OH 45226.

The Knudsen effusion technique with mass spectrometric extrapolation to low temperature was used to measure the vapor pressures and their temperature dependences for zinc, cadmium, benzoic acid, naphthalene, anthracene, pyrene, and several isomeric dimethylphenols. The importance of the vapor pressure in establishing an accurate sampling method for industrial hygiene is shown: trapping the vapor may be necessary for all the measured compounds except zinc and cadmium.

2\*5 **DOSIMETRY IN THE WORKPLACE.** **3. K. Samuels**, Republic Steel Corporation, Research Center, 6801 Brecksville Road, P.O. Box 7806, Independence, Ohio 44131.

Evaluation of employee exposure to toxic gases and vapors has been significantly simplified through the development and use of passive dosimeters. Field sampling has become much safer. The use of badges for the collection of organic vapors has become common in the workplace. Several different badges will be described. The charcoal badges rival the charcoal tubes in many instances. Other badges for the collection of mercury and inorganic gases have recently been developed. Several side-by-side field tests have taken place in the working environment. The results of these studies, as well as the analytical methodology of the badges, will be described.

2\*6 IMPROVED MEASUREMENT TECHNIQUES FOR ASBESTOS FIBRES IN WORKPLACE ATMOSPHERES.

J.C. Meranger<sup>1</sup>, and E.J. Chatfield<sup>2</sup>. National Health and Welfare, Ottawa, Ontario, KIA 0L2\ Ontario" Research Foundation, Mississauga, Ontario, L5K 1B3<sup>3</sup>, Canada.

The use of phase contrast optical microscopy for monitoring of asbestos fibres in the workplace atmospheres has been shown to be unreliable. Recent work indicates that this technique does not measure fibres in the range of diameters which are strongly correlated with carcinogenic activity and that these outnumber those actually counted by a factor of at least 50:1. Therefore a detailed study of alternative measurement techniques was undertaken. During the course of this study several avenues will be explored. These include detailed investigation of the relative performance and limitations of the current methods used for fibre measurements in workplace atmospheres such as phase contrast optical microscopy, scanning electron microscopy SEM, transmission electron microscopy TEM, the development of an improved image analyzing microanalyzer system coupled to the SEM and the development of a measurement technique which is not based on the counting of fibres and can be applied as a rapid routine screening method. For this purpose the magnetic alignment effect of asbestos fibres reported by Timbrel was investigated as a means of measurement of asbestos fibre concentrations.

247 MEASUREMENT OF AIRBORNE GLASS FIBRES IN RESIDENCES DUE TO INSULATING MATERIALS.

J.C. Meranger<sup>1</sup>, and E.J. Chatfield<sup>2</sup>. National Health and Welfare, Ottawa, Ontario, KIA 0L2<sup>3</sup>, Ontario Research Foundation, Mississauga, Ontario, L5K 1B3<sup>3</sup>, Canada.

Residual airborne glass fibre concentrations were measured in one new home and also in four older homes in which glass fibre insulation had been recently installed. Air samples were collected on Nuclepore filters and these were examined using the scanning electron microscope with energy dispersive X-ray analysis for fibre identification. It was found that during installation of insulation on basement walls, respirable fibre concentrations of 0.2 fibres/mL were observed in the basement; these values were confirmed by measurements on breathing zone air samples. Other locations in the home experienced fibre concentrations of 0.02 fibres/mL. After 24 - 48 hours, respirable fibre concentrations returned to the detection levels of about 0.0001 fibres/mL. Immediately after blowing of glass fibre into a roof cavity, respirable fibre concentrations in the home rose to about 0.0013 fibres/mL. Respirable fibre concentrations returned to the detection levels of about 0.0001 fibres/mL after 24 - 48 hours.

248 THREE-DIMENSIONAL FLUORESCENT SPECTRA OF HUMIC ACIDS. M. C. Goldberg, E. R. Weiner, and R. L. Wershaw. U. S. Geological Survey, P.O. Box 25046, Mail Stop 424, Denver Federal Center, Lakewood, Colorado 80225.

Three-dimensional fluorescence spectroscopy allows one to examine the emission and excitation spectra over the response range 200-800 nanometers and present this data to the viewer on a single figure. By combining the excitation wavelength, emission wavelength and emission intensity in this manner, a spectral pattern of a compound can be obtained which is unique even though the conventional emission scan done at a single wavelength for a given material might be indistinguishable from the spectra of a number of other materials.

The technique of three-dimensional spectroscopy is presented and illustrated for humic acid fractions. Florida muck samples were fractionated on a Sephadex column into four fractions. These fractions vary in molecular weight, molecular number and composition of reactive groups. The fractions were examined by collecting a three-dimensional fluorescence spectrum in the form of a contour map. The axes were: excitation wavelength, emission wavelength and fluorescence emission intensity. The latter is presented as contour lines at 10 percent intensity intervals. The unfractionated sample had excitation peaks at 210 and 300 nanometers with a single emission peak at 465 nanometers. As the fractions were examined, in order of elution from the Sephadex column, the spectral pattern no longer showed the single emission line at 465 nanometers, but different patterns emerged. The final pattern had excitation peaks at 320 and 510 nanometers and emission peaks at 450 and 580 nanometers. In addition to the fluorescence pattern, these spectra made possible the selection of 465 nanometers as the proper wavelength to obtain an excitation spectrum on the unfractionated sample which should best match the absorption spectrum. Several absorption spectra were determined with the absorption maxima confirmed by U.V. analysis.

2\*9 An Automated Procedure for Simultaneously Determining Total Cyanide and Thiocyanate in Industrial Wastewaters. J. H. Lowry, T. J. Meszaros and R. C. Ross. Environmental Protection Agency, National Enforcement Investigations Center, Box 25227, Bldg. 53, Denver Federal Center, Denver, CO 80225.

A continuous segmented flow system has been developed to determine thiocyanate in the presence of cyanide in industrial wastewaters. Several improvements in the existing UV digestion total cyanide methodology are also presented. Automated total cyanide methodology for waters is based on the breakdown of complex cyanides by UV digestion and separation of hydrocyanic gas by either flash distillation or thin film evaporation. The gas is absorbed and measured colorimetrically. A major disadvantage of the UV digestion is that thiocyanate can not be distinguished from cyanide. This has been an inhibiting factor in the acceptance of this technique in the NPDES monitoring program. The developed thiocyanate procedure circumvents this problem by providing a means to subtract the thiocyanate concentration from the total cyanide value. In the developed procedure, thiocyanate is converted to cyanogen chloride gas by reaction with chloramine-T. This gas is sparged from possible colorimetric interference, absorbed and reacted in a mixed pyridine-barbituric acid solution and the complex measured colorimetrically. Cyanide is masked prior to the chloramine-T reaction by the addition of formaldehyde which reacts with only cyanide to form cyanohydrin. In this system 0.005 mg/L CN<sup>-</sup> as potassium thiocyanate can be detected in the presence of 10 mg/L CN<sup>-</sup> as potassium cyanide. A number of solutions of metallic thiocyanate complexes were analyzed and recovery data for both systems is presented. Several SIC wastewaters were also analyzed.

250 DETERMINATION OF TOTAL NITROGEN IN WATER BY PYROLYSIS AND CHEMILUMINESCENCE DETECTION. C. E. Arozarena and V. C. Marti, U.S. Geological Survey, 5293 Ward Road, Arvada, Colorado 80002.

A method was developed for the rapid determination of total nitrogen in natural and waste waters using pyrolysis with chemiluminescence detection. This method is useful in the evaluation of water contaminated by organic substances containing nitrogen functional groups, such as nitrile, nitro, nitroso, azo, azide, azine, oxime, and semi carbazone. These organic contaminants are not converted to ammonia-nitrogen during Kjeldahl oxidation. Microliter quantities of the water sample were injected into a heated quartz combustion tube, where inorganic and organic nitrogen form nitric oxide (NO). Nitric oxide reacts with ozone to form nitrogen dioxide (NO<sub>2</sub>) in the excited state. Relaxation of the excited nitrogen dioxide NO<sub>2</sub> to the nonexcited state produces the chemiluminescence that is measured by a photo multiplier detector system. Variables affecting the response of the detector were optimized, including the sample volume injected, injection rate, argon and oxygen flow rate, ozone generation rate, and combustion tube temperature. The detector response was linear from 0.10 to 5.00 milligrams per liter of total nitrogen. The determination of total nitrogen in natural water samples by this method had a correlation coefficient of 0.998 with results obtained by both the Kjeldahl and Nitrate plus Nitrite methods. Overall precision of this new method is 5.0 percent for the range tested. Total nitrogen recoveries of 99 percent were obtained from samples of water spiked with picric acid, trinitrotoluene, and cyclotrimethylenetrinitramine. Total nitrogen on the same samples by the classical Kjeldahl method produced only 15 percent recovery.

251 CONFORMATIONAL AND DYNAMICAL PROPERTIES OF BIOLOGICAL MEMBRANES BY RAMAN SPECTROSCOPY. Ira W. Levin, Laboratory of Clinical Physics, National Institute of Arthritis, Metabolism and Digestive Diseases, National Institutes of Health, Bethesda, Maryland 20205.

Since the conformational and dynamical behavior of membrane assemblies reflect the concerted interactions of both intrinsic and extrinsic bilayer components, the nature and origins of structural rearrangements within the lipid matrix are often difficult to resolve in even the simplest reconstituted liposomal systems. Of the variety of physical techniques available for examining membrane reorganizations, Raman spectroscopy provides exquisitely sensitive molecular probes both for monitoring bilayer disturbances on the vibrational time scale (the order of 10<sup>-13</sup> sec) and for identifying the specific region of the lipid molecule responding to the perturbation. In particular, changes in spectral intensities and frequencies for selected lipid head group and acyl chain vibrational modes reflect intra- and inter-molecular adjustments arising within the bilayer matrix from either temperature effects or the insertion of bilayer components. In the present discussion we will examine several types of membrane behavior based upon, first, the packing characteristics exhibited by lipid-sterol complexes and, second, the bilayer effects resulting from lipid-protein interactions. Our treatment of lipid-protein associations will deal specifically with both the bulk membrane lipids and either (a) the boundary lipids immediately surrounding an incorporated protein (as, for example, in myoglobin containing myoglobin) or (b) the immobilized lipids influenced by an extrinsic bilayer protein (as demonstrated in bilayer recombinants of Apo-A1, a protein isolated from high density lipoprotein complexes).

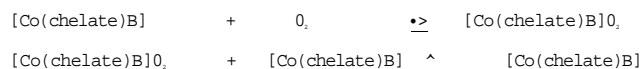
In general, we will emphasize several distinct uses of vibrational spectroscopy as a probe of membrane structure; namely, the measurement of gel to liquid crystalline phase transitions, the effect of inserted bilayer components upon lipid organization, the flexibility of the phospholipid matrix in terms of intrachain and interchain disordering processes and the detection of two classes of immobilized, boundary lipids associated with membrane constituents.

252 DETERMINATION OF  $\beta$ -TURN CONFORMATION BY LASER RAMAN SPECTROSCOPY. Hiroyuki, Ishizaki} P. Balaram, R. Nagaraj, Y. V. Venkatachalapathi and Anthony T. Tu. Department of Biochemistry, Colorado State University, Fort Collins CO 80523 and Molecular Biophysics Unit, Indian Institute of Science, Bangalore, 560 012 India.

In order to use Raman spectroscopy as an analytical tool to identify and characterize the 8-Turn conformation, three peptides known to contain 6-turn structure were examined. The compounds examined were BOC-Cy<sup>+</sup>-Pro-Val-Cy<sup>+</sup>-CONHCH<sup>+</sup> Z-Aib-Pro-Aib-Ala-COOCH<sub>3</sub> and Z-Aib-Pro-CONHCH<sup>+</sup> S -S. The amide I band of these compounds is seen at 1668, 1665, and 1677 cm<sup>-1</sup> and the amide III band appears at 1267, 1265 and 1286 cm<sup>-1</sup>, respectively. Combined with the published Raman data of other compounds which contain 6-turn conformation, it is concluded that the amide I band appears in the range between 1663-1677 and the amide III band between 1255-1300 cm<sup>-1</sup>. By combining amide I and III bands, it is possible to identify  $\alpha$ -helix,  $\beta$ -sheet and  $\gamma$ -turn conformation of proteins.

253 RESONANCE RAMAN STUDIES OF MOLECULAR OXYGEN ADDUCTS OF Co(II) CHELATES IN SOLUTION EQUILIBRIA. R. Nakamoto, M. W. Urban, Y. Nonaka and T. Ishiguro. Department of Chemistry, Marquette University, Milwaukee, Wis. 53233

When a Co(II) chelate in a nonaqueous solvent absorbs oxygen in the presence of a base(B), the following equilibria are established:



The resonance Raman spectrum of this solution at low temperatures exhibits the  $\text{O}_2$  stretching bands of both 1:1 and 1:2( $\text{O}_2$ /metal) adducts. Effects of the base ligand, chelating ligand, temperature,  $\text{O}_2$  pressure and solvent polarity on the  $\text{O}_2$  stretching frequencies and the equilibria have been studied.

254 RESONANCE RAMAN SPECTRA, EXCITATION PROFILES AND NORMAL COORDINATE ANALYSIS OF POTASSIUM BIS(DITHIOOXALATO)NICKEL(II). R.CzernUSzewicz, P.P. Strommen and K.Nakamoto. Department of Chemistry, Marquette University, Milwaukee, Wisconsin 53233

Resonance Raman spectra of  $\text{K}_2[\text{Ni}(\text{dto})_2]$  (dto: dithiooxalato anion) have been measured in solution as well as in the crystalline state. A complete normal coordinate analysis has been made using a modified Urey-Bradley force field. The average deviation between observed and calculated frequencies was less than 1%. Two series of overtones were observed in the resonance Raman spectra; the  $\text{nv}_i$  ( $\nu_i = 1085 \text{ cm}^{-1}$ ) progression up to  $n = 6$  and the  $\text{nv}_j + \nu_j$  ( $\nu_j = 1602 \text{ cm}^{-1}$ ) up to  $n = 4$ . Using these progressions, the anharmonicity constant was calculated for  $\nu_j$ . Excitation profiles for  $\nu_j$  and  $\nu_j(316.4 \text{ cm}^{-1}, \text{Ni-S stretch})$  indicate that the  $\nu_j$  mode gains intensity from interaction with two electronic transitions, while the  $\nu_j$  is enhanced by only one of them. Two forms (red and black) of  $\text{K}_2[\text{Ni}(\text{dto})_2]$  which give significantly different spectra can be obtained. These differences are explained in terms of small variations in their crystal structures.

255 EXTENDED-RANGE RESONANCE RAMAN INCLUDING UV-LASER EXCITATION. P. J. Trotter. Eastman Kodak Research Laboratories, Kodak Park, Rochester, N.Y. 14650.

We have been exploring the selective enhancement of structural group spectra in complex molecules and mixtures via resonance Raman with the following capabilities:  
1) Analytical Sensitivity through specific group enhancements (with intensity increases of  $10^3$  to  $5 \times 10^4$ ).  
2) Selectivity in enhancements of vibrational bands in groups, bonds, and species in mixtures (e.g., azo and quinone, metal-azo, metal-metal, aqueous ions, and donor acceptor systems).

- 3) Structural Assignments via simplification of spectra through molecular group selectivity in metal complexed molecules.
- 4) Band Shape Analyses in terms of structural group contributions via detailed resonance excitation intensity maps.

The utility of the large resonance enhancements was tested with indicator dye system analyses in aqueous mixtures. The specificity of structural group and bond spectral enhancements is achieved through laser tuning into electronic transitions, and our samples showed UV-resonance selection. Continuous and pulsed (Nd:YAG) laser systems are being utilized in these studies.

- 256 OBJECTIVE CONSIDERATIONS IN THE MEASUREMENT OF POLARIZED RAMAN SPECTRA WITH THE MOLE, Mark E. Andersen, Walter C. McCrone Associates, Inc., 2820 South Michigan Avenue, Chicago, IL 60616.

The polarization properties of Raman scattered light are useful in characterizing the symmetry or orientation of molecules in gases, liquids, glasses, crystals and polymers. These properties have not been studied in detail using Raman microprobes largely because of errors introduced by the use of high magnification, high numerical aperture of collection optics. These optics collect light from a large solid angle and single crystals or particles thus yield Raman spectra which are very similar to the powder patterns obtained with macro-instruments. It is just this property which has made Raman microprobes a useful analytical tool for small particle identification. The micro-capabilities of these instruments should not be limited to this application if useful polarization data can also be obtained. The reduction in solid collection angle necessary to perform these measurements is readily carried out in the MOLE using lower numerical aperture objectives. Carbon tetrachloride was studied to demonstrate the capability and individual oriented polymer fibers as small as 16  $\mu\text{m}$  in diameter were chosen as applications of the technique. Polarization scrambling effects from surface irregularities were reduced by immersing the samples in liquid media. The relationships between the objective magnification, numerical aperture, and tubelengths must be kept in mind when choosing the best objective for use with the MOLE.

- 257 MECHANISMS OF AQUEOUS SORPTION ON GIBBSITE MEASURED BY RAMAN SPECTROSCOPY. K.M. Cunningham and Marvin C. Goldberg. U.S.Geological Survey, P.O.Box 250<sup>th</sup> 6, MS U2U, Denver Federal Center, Lakewood, CO 80225.

A substantial change in the Raman intensities of the OH<sup>-</sup> stretching bands of solid powdered gibbsite [ $\alpha\text{-Al}(\text{OH})_3$ , surface area 10  $\text{m}^2/\text{g}$ ] has been attributed to surface interactions with the sorbates  $\text{Ca}^{2+}$ ,  $\text{H}_2\text{PO}_4^-$ , silicic acid, and mixtures thereof. The four OH<sup>-</sup> stretching bands of gibbsite occur at 3360, 3520 and 3618  $\text{cm}^{-1}$ ; the intensity relative to untreated gibbsite of the 3360  $\text{cm}^{-1}$  band was observed to diminish 60 percent upon  $\text{CaCl}_2$  treatment at one extreme, and to increase 180 percent after  $\text{I}^+\text{PO}_4^-$  treatment at the other extreme. Small changes in the relative peak heights of the four bands were observed, depending on the treatment utilized. The results were interpreted in terms of different surface OH<sup>-</sup>-adsorbate interactions.

Such interactions, however, should have little effect on what is essentially a Raman spectrum of bulk OH<sup>-</sup>. We have re-examined this system using an internal intensity standard [ $\text{Na}_2\text{Oxalate}$  crystals] and gibbsite with surface area of one  $\text{m}^2/\text{g}$ . Adsorbate solutions, treatment regimes, and spectroscopic techniques were similar to previous studies. Our results show no effects, within probable error, of the different adsorbates on OH<sup>-</sup> band parameters.

- 258 REMOTE RAMAN SPECTROSCOPY - ITS SUCCESSES AND FAILURES. Stanley M. Klainer, Lawrence Berkeley Laboratory, University of California, Berkeley, CA. 94720

Remote Raman Spectroscopy has been a subject of much discussion and limited research. In the early 1970's many researchers attempted to use this technique for atmospheric studies, pollution monitoring, flame diagnostics, oceanographic measurements and a variety of other technical problems which were amenable to remote analysis. Now, in the 1980's, much of the enthusiasm for this technique has vanished. In this paper the potential of remote Raman Spectroscopy is reviewed, the reasons for its successes and failures are analyzed, and its future as an analytical tool is postulated.



SOLAR BLIND RAMAN LIDAR. John A. Cooney, Drexel University, 3101 Chestnut Street, Philadelphia, PA 19104

performance characteristics are presented for a solar blind Raman lidar having a variable output wavelength. A figure of merit is defined which maximizes signal to noise ratio (S/N). This (S/N) arises for a particular output wavelength which depends upon the instantaneous total ozone overburden as well as the ozone content from the surface to the target altitude. Figures of merit for water vapor and temperature profiles are presented. Specific optimal output wavelengths are given and total output energies required to yield certain prespecified levels of measurement accuracy are computed. Recent preliminary measurements are assessed.

260 HIGH RESOLUTION RAMAN LIDAR FOR WATER VAPOR STUDIES. S. H. Melfj, M. Z. Hansen, J. D. Spinhirne, D. Clem. NASA/Goddard Space Flight Center, Greenbelt, MD. 20771

This paper will present a description of a Raman lidar system designed to provide fundamental data on the evolution of water vapor in the atmospheric boundary layer (the first several kilometers of the atmosphere).

The evaporation of water is a major mechanism for transferring heat from the earth's surface to the lower atmosphere. The movement, flux, and motion of the resultant water vapor through the boundary layer and into the free troposphere needs to be clearly understood. It is only after reaching these heights that water vapor and its condensation can begin to effect global meteorology and circulation. High spatial (50 meters) and temporal (60 seconds) resolution measurements of water vapor profiles from the earth's surface through the boundary layer and into the lower free troposphere will contribute to this understanding.

An evaluation of the two most promising lidar methods for remote water vapor measurements (Raman and differential absorption) was performed and will be presented. The analysis shows that when short range, high spatial resolution measurements of reasonably high concentration molecular species is desired (the case for water vapor measurements in the boundary layer) the Raman lidar is preferred over differential absorption lidar.

The paper will be concluded with a description of the design and construction of the Lidar system and a discussion of our plans for using the system in future meteorological studies of the atmospheric boundary layer.

261 LASER MEASUREMENTS IN FLAMES AND THE ATMOSPHERE. Carl M. Penney, G. E. Research & Development, Schenectady, New York 12301.

There are a surprising number of similarities between laser measurements in flames and in the atmosphere. These similarities will be emphasized in a description of simultaneous laser velocimetry in Raman scattering experiments on turbulent hydrogen/air flames. The resulting information has motivated consideration, in combustion models, of effects not previously anticipated to be important within these flames. In particular, significant deviation between data and simple models seem to be explained by inclusion of differential diffusion and finite rate chemistry effects.

262 REMOTE RAMAN SPECTROSCOPY IN THE OCEAN. D. A. Leonard, Computer Genetics Corporation, 18 Lakeside Office Park, Wakefield, MA 01880

This paper describes the application of Raman scattering from liquid water molecules to the remote sensing of subsurface ocean temperature, salinity and attenuation profiles. The theoretical basis of the method is discussed, including an estimation of the potential of the measurement technique in terms of accuracy and depth penetration as a function of laser power and other system parameters. Both laboratory and field experiments conducted over the previous years are discussed. Since the Raman scattering cross section for water is known, the performance of a Raman lidar remote subsurface measurement system, if not limited by interferences, can be exactly calculated as a function of water turbidity, laser power and other system parameters. Environmental interferences are expected to be dominated by volume depolarization producing a temperature

**uncertainty of 0.1°C per diffuse attenuation length of depth. Field experiments have obtained laser Raman temperature data in a variety of natural waters and open ocean waters. The results of these experiments have demonstrated 1 C temperature accuracy and data retrieval down to 4 diffuse attenuation lengths of depth. Recent experiments in a 10 meter high stratified tank are reported in which a temperature gradient is measured under controlled conditions. Additional data is reported which shows measurements of salinity and attenuation under field conditions.**

263 HIGH RESOLUTION EFFECTS IN REMOTE SENSING WITH LASER BACKSCATTER.

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High spectral and spatial resolution enhances remote measurement of atmospheric temperature profiles, humidity profiles, and ocean temperature profiles from back-scattered laser light. Brillouin effects modify the central peak in atmospheric Rayleigh scattering, which is Gaussian if the molecules act as independent scatterers. If the width of the central line is accurately measured and Brillouin effects are properly included in the lineshape model, it is possible to determine temperature profiles in the atmosphere with a lidar system. The Landau-Placzek ratio in scattering from a fluid (ratio of central component to Brillouin wings) depends on temperature. Although the ratio is small, a change of 10% per °C near 15-25°C is a temperature-dependent effect that should allow remote measurement of ocean temperature using an airborne lidar. The vibrational Raman spectrum of water vapor has been used for remote humidity profiling. High spatial resolution, which is a natural outgrowth of the high spectral resolution being studied for remote temperature measurement, promises to improve humidity lidar performance by reducing the noise from daylight sky background compared to the Raman return from water vapor.

264 THE EFFECTS OF RAMAN AND RAYLEIGH-BRILLOUIN SCATTERING ON FRAUNHOFER LINES AS SEEN IN SCATTERED LIGHT. George W. Kattawar, Department of Physics, Texas A&M University College Station, Texas 77840

In 1961, Grainger and Ring (1962)\* found that Fraunhofer lines are a few percent less deep in the light of the blue sky than in direct sunlight. Several subsequent investigations have explored this so-called "Ring effect" but with divergent results. The only general agreement is that this excess light appears to be unpolarized, so most observers have measured the component of the radiance with the electric vector in the plane determined by the Sun and the Zenith to suppress the diluting effect of singly-scattered light. We will show that a combination of Rayleigh-Brillouin scattering (RBS) and rotational Raman scattering (RRS) in an aerosol-free atmosphere are more than sufficient to explain the filling-in of solar Fraunhofer lines, and that one does not have to invoke aerosol fluorescence. We will also show that RBS will only be significant for narrow lines whose FWHM is of the order of a few tenths of an angstrom. The effect of the ground albedo also plays a dominant role in the filling-in for small solar Zenith angles.

Results will also be presented showing the effect of RRS on the degree of polarization across a Fraunhofer line. Finally, we will show the effect of aerosols on both the radiance and degree of polarization across a Fraunhofer line and implications of this effect in terms of a new technique for probing atmospheric aerosols.

\*Grainger, J. F., and Ring, J., 1962, *Nature*, 193, 762.

265 HIGH PRESSURE  $^1\text{H}$  NMR INVESTIGATIONS OF PHASE TRANSITIONS IN DOUBLE PROPIONATES BY  
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The results of  $^1\text{H}$  NMR studies in polycrystalline samples of  $\text{Ca}_2\text{M}(\text{CH}_3\text{CH}_2\text{COO})_4$  where  $\text{M}=\text{Ba}$ ,  $\text{Sr}$  or  $\text{Pb}$  (the salts being called DBP, DSP and DLP respectively) subjected to hydrostatic pressures up to 12 Kbar and in the temperature range 77 K - 300 K will be presented in relation to the phase transitions in these compounds. The dependence of  $^1\text{H}$  second moments on temperature and pressure clearly brings out the importance of re-orientational motion of the  $\text{CH}_2$  groups in the transitions and enable us to propose models for these motions which explain the differences in the behaviours of DBP on one hand and of DSP and DLP on the other. The tetragonal, paraelectric ( $\text{P4}^{2,2}$ ) to tetragonal ferroelectric ( $\text{P4}^1$ ) transition at 281.5 K in DSP and at 333 K in DLP are inferred to be accompanied by a change-over from free rotations to flipping type motion of the  $\text{CH}_2$  groups around the  $c$  axis whereas the cubic to orthorhombic structural transition at 267 K in DBP is found to be caused by a freezing of free rotations of 2 of the 6  $\text{CH}_2$  groups. In addition DBP shows a second moment transition around 3-5 Kbar at room temperature itself which is not explained by the known phase diagram of the substance. The differences in the pressure dependences of the compounds also will be discussed.

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## DOWNTOWN DENVER



1. CONVENTION COMPLEX
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