Rocky Mountain Conference on Magnetic Resonance

Volume 30 30th Rocky Mountain Conference Article 1

July 1988

30th Rocky Mountain Conference

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30th Rocky Mountain Conference

Abstract

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PROGRAM
AND
ABSTRACTS

JULY 31 - AUGUST 5, 1988

RADISSON HOTEL DENVER
1550 COURT PLACE
DENVER, COLORADO

SPONSORED BY

ROCKY MOUNTAIN SECTION
SOCIETY FOR
APPLIED SPECTROGRAPHY

ROCKY MOUNTAIN
CHROMATOGRAPHY
DISCUSSION GROUP

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## Symposia Schedule

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WELCOME

On behalf of the conference committee I am pleased to welcome you to the 30th Rocky Mountain Conference. Our meeting has grown into one of the most prominent summer analytical meetings in the United States. Thanks to all the exhibitors whose displays are as important to the scientific content of the conference as their booth fees are to our financial viability. I encourage all attendees to pay careful attention to the exhibits. You'll find exciting new products and ideas this year.

For our out-of-state visitors we welcome you to Denver and Colorado. We hope you have time to enjoy our many recreational and scenic opportunities and to plan more activities around your visit to the 31st Rocky Mountain Conference in 1989!

Sincerely,

Michael M. Reddy
Conference Chair

Future Conferences

31st Conference, July 30-August 4, 1989
32nd Conference, July 29-August 3, 1990
33rd Conference, July 28-August 2, 1991
CONFERENCE LOCATION

Technical sessions and the exhibition for the 30th Rocky Mountain Conference will be held in the Radisson Hotel Denver, 1550 Court Place, Denver, Colorado.

REGISTRATION

Admission to all technical sessions and the exhibition is by a name badge for the 30th Rocky Mountain Conference. Conference fees are payable by check (denominated in $US, only) made payable to the Rocky Mountain Conference.

Registration Fees – 1988

| Registration - on site          | $50.00 |
| Registration - one specified day | 30.00  |
| Student registration            | 10.00  |
| Additional Vendor registration  | 35.00  |
| Unemployed or retired registration | No charge |
| Film Festival only              | No charge |
| Exhibition only (non-vendor)    | No charge |

Times

On-site registration for the 30th Rocky Mountain Conference will be held in the Convention Lobby of the Radisson Hotel Denver during these times:

- Sunday, July 31: 5:00 pm - 9:00 pm
- Monday, August 1: 7:30 am - 3:30 pm
- Tuesday, August 2: 7:30 am - 3:30 pm
- Wednesday, August 3: 7:30 am - 3:30 pm
- Thursday, August 4: 8:00 am - 10:00 am

Smoking is not permitted in the meeting rooms at the Rocky Mountain Conference.
EXHIBITION

The Rocky Mountain Conference exhibition provides an opportunity to see and discuss the latest in analytical instrumentation, apparatus, supplies, and services. The exhibitors support the Rocky Mountain Conference - please support them! Beverages will be served in the Exhibit area during the breaks between papers.

Hours

Monday, August 1.......................... 9:30 a.m. - 5:00 p.m.
Tuesday, August 2........................ 9:30 a.m. - 5:30 p.m.
Wednesday, August 3..................... 9:30 a.m. - 2:00 p.m.

For space or information about the exhibition, contact:

Glenda Brown
127 South Washington Ave.
Louisville, CO 80227
(303) 966-7817 (7:30 a.m. - 4:00 p.m.)

The following exhibitors have reserved space as of June 1, 1988:

Affiliated Scientific, Inc.
Applied Research Laboratories
Applied Technical Products
Bio-Rad, DigiLab Div.
Bomem Inc.
Bruker Instruments
CEM Corp.
Dionex
Doty Scientific, Inc.
Finnigan MAT
Instruments SA, Inc.
JEOL USA, Inc.
Jones Chromatography
Kontron Instruments

Lee Scientific
Nicolet Instruments
Orion Research Inc.
Oxford Instruments
Perkin-Elmer Co.
Sadler Research Labs
Scott Specialty Gases
Telegation Associates
Thermo Jarrell Ash Corp.
Tracer Instruments
Varian Instruments Group
VG Instruments, Inc.
Waters Division of Millipore
Wilms Glass Co., Inc.
Zymark Corporation

SESSION TAPE RECORDING AVAILABLE

For your convenience, audiotape cassettes will be available for selected sessions immediately following the presentation. Tapes may be ordered and picked up prior to departure from the Sound Images distribution center at the Radisson Hotel. For those unable to attend this year's conference, tapes may be ordered by mail from Sound Images, Inc., P.O. Box 460519, Aurora, Colorado 80015. Phone orders may be placed by calling (303) 693-5511.
SOCIAL PROGRAM

Registration Night Mixer

A cash bar will be open in the conference registration area of the Radisson Hotel Denver on Sunday evening from 7:00 to 9:00 p.m. Plan to meet other conference attendees and beat the Monday rush to pick up your conference badge and abstract book.

Conference Mixer

All conferees and spouses are invited to attend this lively affair on Monday, August 1. This year's mixer will be held in the Exhibition area from 5:00 to 7:00 p.m.

Conference Banquet

The conference Banquet will be Tuesday, August 2 at 7:00 p.m. in the Majestic Ballroom of the Radisson. Tickets are $19 each. There will be a cash bar in the Majestic Lounge at 6:00 p.m.

Dr. John T. Rieves, our banquet speaker, is a Professor of Medicine at the University of Colorado Medical Center. Dr. Rieves' interests are in the area of cardiovascular pulmonary research. His talk for the evening will be "Tibet, Medical Research in a Troubled Land". The University of Colorado research team was in Lhasa, Tibet, prior to, during and following the political uprising October 1, 1987. The team investigated high altitude effects in both Tibetan and Chinese subjects. The research was productive in gaining insight both into adaptations of the Tibetan population at high altitude and into the political problems of Tibet.

IMAX Theater Night

On Wednesday, August 3, the Denver Natural History Museum will put on a program for us. The evening will begin with a mixer in the Bailey Lounge and South American and Australia Halls. Cold and hot hor d'oeuvres will be served. Two drink tickets are also included in the ticket price. We will have preferred seating at the giant screen IMAX theater for a showing of "On the Wing" and "Freedom to Move". British Double Decker bus transportation will be provided from the Radisson Hotel. We will leave the hotel at 5:30 p.m. and return around 10 p.m. Cost per person is $24 including bus transportation. Tickets are limited for this event, so register early.
ADDITIONAL ACTIVITIES

Visitor Information

Although no specific program is planned for the guests and families of conferees, Denver and the surrounding area boast a large number of activities that are enjoyable for both young and old. For additional information contact the Denver Metro Convention and Visitors Bureau, 225 W. Colfax Ave., Denver CO 80202. (303) 892-1112. For information about statewide attractions contact the Colorado Tourism Board, 1625 Broadway, Suite 1700, Denver CO 80202. (303) 592-3410.

Film Festival

Several films of scientific interest will be shown throughout the Rocky Mountain Conference. Admission to the film festival is by a paid or complimentary conference badge. Titles and a schedule will be posted in the registration area. These films will be shown in the Capitol Room.

Employment Clearing House

Space will be provided for employees to post job announcements and for conferees to file resumes. The Rocky Mountain Conference assumes no obligation for the confidentiality of information filed with the employment clearing house, the qualifications of job candidates, or the descriptions of jobs offered.

Message Center

Incoming telephone messages for conferees will be posted at the message center in the registration area. The telephone number is (303) 893-3333, ext. 337. Ask for the Rocky Mountain Conference message center. This service will be available from 8:00 a.m. to 3:30 p.m. Monday-Wednesday and from 8:00-10:00 a.m. on Thursday.

Speaker Preparation Room

The Birch Room will be open Monday through Wednesday for speakers to organize and preview slides. A 35 mm projector will be available.

Restaurant Service

The Communications Department of the Denver Metro Convention and Visitors Bureau's will provide a FREE restaurant reservation service designed to let out-of-town delegates know about Denver's world-class dining opportunities, from casual to elegant. The Dining Desk will have a header that reads "Free Restaurant Reservations", and will also have an experienced reservation person, a phone and a cart featuring poster-size menus that delegates can browse through. This service has been in operation for four years and has been extremely successful in providing delegates with convenient, courteous, and efficient service.
SPECTRASPN USERS' GROUP MEETING

Tuesday, August 2, from 5:00 p.m. to 6:30 p.m.

at the Radisson Hotel
Spruce Room

Applied Research Laboratories is sponsoring a users group meeting for users of the DCP SpectraSpan instrumentation.

The purpose of this meeting is the exchange of ideas among DCP SpectraSpan users and technical experts in a relaxed informal atmosphere. Improvements and new developments for the DCP will be discussed.

For registration and further information, please call 1-800-551-8741 or 1-800-631-6841 (California only).

UTILIZATION OF A PC NETWORK FOR AUTOMATIC DATA COLLECTION AND LABORATORY INFORMATION MANAGEMENT

Wednesday, August 3, from 10:00 a.m. to 12:00 noon

at the Radisson Hotel
Spruce Room

Telecetion Associates will sponsor a laboratory computer users' seminar featuring discussion and demonstration of a PC-based system for automatic data collection and laboratory information management (LIMS). Topics to be discussed include: (1) Techniques for interfacing PCs to current laboratory instrumentation. (2) Connectivity options for data transmission throughout the laboratory. (3) Avoiding the pitfalls in PC-based LIMS. (4) Designing a networked LIMS system with an off-the-shelf integrated software package. (5) Review of a modular approach to a networked LIMS system.

For preregistration or further information, please call Telecetion Associates at (303) 838-2088. At the Conference obtain information at exhibit booth #45.

PURGEABLE ORGANIC ANALYSIS USING PID AND HALL DETECTORS IN SERIES: THEORY, PRACTICE AND TROUBLESHOOTING TECHNIQUES

Thursday, August 4, from 8:30 a.m. to 4:30 p.m.

at the Radisson Hotel
Denver Room

Tracor Instruments will sponsor a workshop on Purgeable Organic Analysis Using PID and HALL Detectors in Series: Theory, Practice and Troubleshooting Techniques. This is a one day class designed to increase the working knowledge and skills required for EPA analysis of volatile organic compounds using the PID and HALL detectors in series. This class will be presented in conjunction with the Rocky Mountain Conference. We are pleased to offer the class at a special conference rate of $45.00. This fee includes all classroom materials and a catered lunch. Enrollment is limited to 30. For more information, please contact Carol Thilen at 303-696-0238 or 800-421-0036.
ENVIRONMENTAL ANALYSIS WORKSHOP AND SEMINAR

Thursday, August 4, from 8:30 a.m. to 4:30 p.m.
at the Radisson Hotel
Colorado Room

Waters Chromatography Division of Millipore will sponsor a workshop and seminar at the 30th Rocky Mountain Conference. This workshop will include presentations by four speakers with extensive experience in environmental analysis using liquid chromatography, ion chromatography, and other "state of the art" techniques.

Extraction, preparation, and analysis of environmental samples containing herbicides, pesticides, and other hazardous materials will be discussed in detail by representatives from Millipore, Waters, and a contract laboratory.

Tuition is $75 if registration is made before July 5, 1988, and $175 after July 5, 1988. Tuition includes attendance, manual and handouts, lunch, and morning and afternoon refreshments. For further information, please phone Waters/Millipore, 448 Grandview Drive, South San Francisco, CA 94080, 415/932-9200, ext. 160.

APPLICATIONS OF ION TRAP MASS SPECTROMETRY

Thursday, August 4, from 9:00 a.m. to 12:00 noon
at the Radisson Hotel Denver
Gold Room

Finnigan MAT will sponsor a workshop on Applications of Ion Trap Mass Spectrometry. Presentations will be made by experts on the analysis of pesticides, priority pollutants, environmental contaminants and forensic applications. New developments in ion trap mass spectrometry will also be discussed. There will be an operating ion trap mass spectrometer for sample analysis.

Ion trap users are encouraged to attend for a questions and answers session. Enrollment is limited to 30. For preregistration or more information, please contact Adrian W. Pike at 303-988-5557.
ORGANIZERS OF THE 30th ROCKY MOUNTAIN CONFERENCE


Registration - Sandy Grande - Manville Services Corp., R & D Center, P.O. Box 5108, Denver, CO 80217, (303) 978-5386.

Treasurer - Rik Getty, 1085 Tantra Park Circle, Boulder, CO 80303, (303) 966-4791 (work), 494-4394 (home).


Staff - George Aiken, U.S. Geological Survey, 5293 Ward Road, Arvada, CO 80002, (303) 236-1927.

Publicity - Jan Gurnsey, 5531 Bitterbush Way, Loveland, CO 80537, (303) 669-9216.

Short Courses/Film Festival - Carlos Arzorarena, U.S. Geological Survey, 5293 Ward Road, Arvada, CO 80002, (303) 236-5345.


SYMPOSIA CHAIRPERSONS

Atmospheric Sciences - D. Stedman, Dept. of Chemistry, Univ. of Denver, Denver, CO 80208, (303) 871-3530.

Atomic Spectroscopy - Thomas Niemczyk, Dept. of Chemistry, University New Mexico, Albuquerque, NM 87131, (505) 277-5319.

Chromatography - Vanessa Bush, Adolph Coors, Mail #BC600, Golden, CO 80401, (303) 277-5886.

Computer Applications - John Lanning, Dept. of Chemistry, Box 171, Univ. of Colo. at Denver, Denver, CO 80204, (303) 396-2597.

EPR - Gareth Eaton, Dept. of Chemistry, University of Denver, Denver, CO 80208, (303) 871-2980 and Sandra Eaton, Dept. of Chemistry, Box 171, Univ. of Colo. at Denver, 1200 Larimer Street, Denver, CO 80204, (303) 396-3204.


IR - Marvin Goldberg, U.S. Geological Survey, P.O. Box 25046, MS 424, Lakewood, CO 80225, (303) 236-4728.

Ion Chromatography - Bill Williams, Manville Service Corp., Manville Tech Center, P.O. Box 5108, Denver, CO 80217, (303) 978-5995.


NIR - Donald Burns, 54 Canopus Hollow Road, Putnam Valley, NY 10579, (914) 526-3223.

NMR - James Haw, Dept. of Chemistry, Texas A&M University, College Station, TX 77843, (909) 845-1966.

Supercritical Fluid Chromatography - Bernd Wenclawiak, Dept. of Chemistry, University of Toledo, 2801 W. Bancroft St., Toledo, OH 43606, (419) 337-2664.

SYMPOSIUM ON ATMOSPHERIC SCIENCE
Organized by Donald H. Stedman

Monday Morning, August 1

9:00  PLENARY LECTURE

1. AIR-WATER EXCHANGE OF PCBs AND PAHs IN LARGE LAKES. Steven J. Eisenreich and Joel E. Baker, University of Minnesota.

10:00  2. THE EFFECTS OF THE HIGH OXYGEN FUELS PROGRAM ON THE CONCENTRATIONS OF FORMALDEHYDE AND ACetaldehyde IN DENVER'S AIR. Charles M. Machovec and Larry G. Anderson, University of Colorado at Denver.

10:20  BREAK


11:05  4. ON VARIATIONS IN SULFATE CONCENTRATIONS IN PRECIPITATION AT YAMPA, COLORADO. Theresa Barnard and Perry J. Samson, University of Michigan.

11:25  5. REGIONAL ANOMALIES IN CHRONIC OBSTRUCTIVE PULMONARY DISEASE, ASSOCIATION WITH ACID AIR POLLUTION PARTICULATE CHARACTERISTICS. John W. Winchester, Florida State University.

12:00  LUNCH

Monday Afternoon, August 1


2:10  8. ACTINOMETRIC MEASUREMENT OF J(O3), THE PHOTOLYSIS FREQUENCY OF OZONE TO O(1D) USING A LUMINOL DETECTOR. Solomon T. Bairaj, Donald H. Stedman, University of Denver.

2:30  BREAK

3:00  9. CO/CO2 RATIO MONITORING AS A MOBILE SOURCE EVALUATION TOOL. Kamal A. Mohammed and Donald H. Stedman, University of Denver.

3:40  PLENARY LECTURE

11. A COMPARATIVE STUDY OF THE ASSOCIATION OF AEROSOL SULFUR WITH SOIL DUST, POTENTIAL FOR ATMOSPHERIC DEPOSITION OF SOLUBLE ALUMINUM TO AQUATIC SYSTEMS. John W. Winchester, Florida State University and Dale A. Gillette, NOAA GMCC.

SYMPOSIUM ON ATOMIC SPECTROSCOPY

Organized by Thomas M. Niemczyk

Monday Morning, August 1

8:30  INVITED SPEAKER

12. FUNDAMENTAL STUDIES IN ATOMIC SPECTROSCOPY: NEW APPROACHES TO OLD QUESTIONS. Gary D. Rayson, Yang Shen, and Mark Fresquez, New Mexico State University.


9:30  14. USING A PC WITH A GRAPHICS INTERFACE AND MOUSE POINTING DEVICE FOR AA INSTRUMENT CONTROL. Glen R. Carnrick and Randy Hergenreder, Perkin-Elmer Corporation.


10:10  BREAK

10:40  16. AUTOMATED MICROWAVE DIGESTION. Angelo C. Grillo, Questron Corp. and Daniel Mathe, Prolabo, Paris, France.

11:00  17. AUTOMATED ULTRASONIC MIXING OF SLURRY SAMPLES FOR ANALYSIS BY GRAPHITE FURNACE ATOMIC ABSORPTION. Glen R. Carnrick, Perkin-Elmer Corporation.


12:00  LUNCH

Monday Afternoon, August 1

1:30  KEYNOTE SPEAKER

20. DETECTING ATTOGRAM OF ATOMS AND MOLECULES. Jim Winefordner, University of Florida.
2:10  21. APPLICATION OF THE FOURIER TRANSFORM SPECTROMETER TO PROBLEMS IN PLASMA ATOMIC EMISSION. Larry Layman, Jill Angus, Byron Palmer, Tom Niemczyk, Los Alamos National Laboratory.

2:30  22. "MASTER BLASTER" HIGH PRESSURE - HIGH TEMPERATURE DIGESTION. Angelo C. Grillo, Questron Corp., Prof. Gunter Knapp, Technical University, Graz, Austria, and Peter Kettisch, Anton Paar KG, Graz, Austria.


3:10  BREAK


4:00  25. FUNDAMENTAL INVESTIGATIONS OF AN ATMOSPHERIC PRESSURE Ar/N₂ MICROWAVE PLASMA. T. M. Niemczyk and J. T. Clay, University of New Mexico.


4:40  27. COLLISIONAL-RADIATIVE PROCESSES FOR UNDERSTANDING EXCITATION MECHANISMS IN PLASMAS. Hiroki Haraguchi, University of Tokyo, Tokyo, Japan.

Tuesday Morning, August 2

8:30  28. SLURRY ATOMIZATION GRAPHITE FURNACE ATOMIC ABSORPTION DETERMINATION OF Pb, Cd, Ni, Cr, and Se IN FRESH BEEF LIVER. Andy Weber, Prakash Venkatesan, Ron Fietkau, and Bob Fry, Kansas State University.

8:50  29. THE CORRELATION OF VARIOUS SPECTROSCOPIC OIL ANALYSIS METHODS WITH EACH OTHER. Eric Fox, William Edwards, Marc Rippen, Pratt & Whitney.

9:10  30. A KINETIC STUDY OF ANALYTE TRANSFORMATION IN AN ICAP. Kuang-pang Li, University of Lowell and J. D. Winefordner, University of Florida.


10:10  BREAK
10:40  33. AN EVALUATION OF SPARK ABLATION (SA) ICP-AES AND GLOW DISCHARGE (GD)-AES FOR THE ANALYSIS OF NON CONDUCTING MATERIALS. Joe Brenner and Alain Lemarchand, Jobin Yvon, Longjumeau, France.

11:00  34. NEW TECHNIQUES FOR ELEMENTAL ANALYSIS OF THE ENVIRONMENT. Angelo C. Grillo, Questron Corp., Dr. Peter B. Stockwell, P. S. Analytical Ltd., Orpington Kent England, Dr. Arthur D'Silva, Cetac Technologies.


**SYMPOSIUM ON CHROMATOGRAPHY** 
Organized by V. Bush

**Wednesday Morning, August 3**

V. Bush, Presiding

8:20  Introductory Remarks - V. Bush

8:30  37. ANALYSIS OF OLEFINs AND ADDITIVES IN GASOLINES AND FUELS. R. S. Hutte, R. E. Sievers and J. W. Birks, Sievers Research, Inc. and University of Colorado, Boulder.

8:55  38. GC DETERMINATION OF WATER USING 2,2-DIMETHOXYPROPAINE AND A SOLID ACID CATALYST. K. D. Dix and J. S. Fritz, Iowa State University.


9:45  BREAK


11:10  41. CATALYSIS IN A CHEMILUMINESCENCE CHROMATOGRAPHIC DETECTOR BY A SUPERCONDUCTOR PEROVSKITE. E. A. McNamara, R. M. Barkley and R. E. Sievers, University of Colorado, Boulder.

11:35  42. UNDERSTANDING THE REDOX CHEMILUMINESCENCE DETECTOR. S. A. Montzka, R. M. Barkley and R. E. Sievers, University of Colorado, Boulder.
Wednesday Afternoon, August 3

V. Bush, Presiding

2:00  43. SELECTIVE REACTION PROCESSES APPLIED TO REDOX CHEMILUMINESCENCE DETECTION FOR LIQUID CHROMATOGRAPHY. J. J. DeAngelis, R. M. Barkley and R. E. Sievers, University of Colorado, Boulder.

2:25  44. CROSS CONFIRMATION WITH CONDUCTIVITY AND UV DETECTION IN HPLC WITH REVERSED-PHASE AND ION EXCHANGE COLUMNS. T. J. Ward and R. C. Dubin, Dionex Corp.

2:50  BREAK

3:20  45. SYNTHESIS OF AN N-METHYL-N-NITROSOUREA LINKED TO A METHIDIUUM CHLORIDE ANALOGUE. REACTIONS WITH [32P]-END LABELED DNA. B. Gold, K. M. Church and R. Wurdeman, University of Nebraska Medical Center.


4:35  WINE AND CHEESE RECEPTION.

SYMPOSIUM ON COMPUTER APPLICATIONS

Organized by John A. Lanning

Wednesday Afternoon, August 3

John A. Lanning, Presiding

1:00  Opening Remarks - John A. Lanning

1:05  PLENARY LECTURE

48. EXPLORING SCIENTIFIC DATA WITH CHEMOMETRICS. Robert Meglen, University of Colorado at Denver.

2:10  49. LABORATORY INFORMATION MANAGEMENT SYSTEMS: A MODULAR APPROACH. Richard D. Beaty and Leigh A. Richardson, Telecations Associates.

2:35  50. APPLICATION OF SPREADSHEET PROGRAMS TO INSTRUMENT REPORT GENERATION. Marc L. Salit and Cindy Anderau, Perkin-Elmer Corporation.

3:00  BREAK

SYMPOSIUM ON ENVIRONMENTAL CHEMISTRY

Organized by Marvin Fishman, Peter Rogerson, and Mark Peden

Monday Morning, August 1

Marvin Fishman, Presiding

8:25   Introductory Remarks


9:45   BREAK


11:30  61. GROUNDWATER SAMPLING: A KEY TO IT ALL. Judy A. Blair, Rockwell International.

-15-
Monday Afternoon, August 1

Gerald Hoffman, Presiding


2:20 64. IMPROVED DETECTION LEVELS FOR NITROGEN AND SULFUR IN PESTICIDES AND HERBICIDES USING CAPILLARY CHROMATOGRAPHY AND THE HALL 1000 DETECTOR. Don Clay, Dave Williams, Robert Wenske, Tracor Institute.

2:45 BREAK


4:05 67. ANALYSIS OF AIRCRAFT TURBINE ENGINE FUELS FROM WASTEWATER CONTAINING HIGH CONCENTRATIONS OF SURFACTANTS. William D. Schulz, Eastern Kentucky University and Howard T. Mayfield, Tyndall AFB.


Tuesday Morning, August 2

Peter Rogerson, Presiding

8:25 Introductory Remarks


8:55 70. GEOCHEMICAL PATTERNS OF SEDIMENTS IN THREE DEPOSITIONAL BASINS OF LAKE ONTARIO. Alena Mudroch, National Water Research Institute, Canada.

9:20 71. PARTICLE-MEDIATED FRACTIONATION AND TRANSPORT OF PCBS IN LAKE MICHIGAN. David E. Armstrong and Lisa F. Lefkovitz, University of Wisconsin.
9:45  BREAK

10:15  72. CYCLING OF NON-POLAR ORGANIC CONTAMINANTS IN LARGE LAKES. Steven J. Eisenreich and Joel E. Baker, University of Minnesota.

10:40  KEYNOTE SPEAKER - Introduction, Edward Furlong

73. IS MASS SPECTROMETRY ESSENTIAL FOR FURTHER DEVELOPMENTS IN ENVIRONMENTAL SCIENCE? Ronald A. Hites, Indiana University.

Tuesday Afternoon, August 2

Peter Rogerson, Presiding

2:00  74. MODELLING THE PHYSICAL CHEMISTRY OF HUMIC SUBSTANCES IN ACID WATERS AND SOILS. Edward Tipping, Freshwater Biological Association, United Kingdom.

2:25  75. DISSOLVED ORGANIC CARBON IN ANTARCTIC LAKES. George Aiken, Diane McKnight, and Carol Bowles, U.S. Geological Survey.

2:50  76. LOW LEVEL XRF SCREENING ANALYSIS OF HAZARDOUS WASTE SITES. Randy Perlis, Annette Sackman, Mark Chapin, Ecology & Environment Inc.

3:15  BREAK

3:45  77. CHLORINE DETERMINATION BELOW 0.1 MG/L. C. O. Huber, University of Wisconsin-Milwaukee.


4:35  79. DETERMINATION OF TOTAL AND WEAKLY BOUND CYANIDE. Michael J. Doyle, Robert J. Joyce, Dionex Corporation.

Atmospheric Deposition

Wednesday Morning, August 3

Mark E. Peden, Presiding

8:25  Introductory Remarks


9:45 BREAK


11:05 KEYNOTE SPEAKER

85. SAMPLING AND ANALYSIS OF HIGHER MOLECULAR WEIGHT TOXIC ORGANIC COMPOUNDS IN THE ATMOSPHERE AND IN DEPOSITION. Thomas J. Murphy, DePaul University.

Wednesday Afternoon, August 3

LeRoy J. Schroder, Presiding

1:30 86. REAL-TIME MONITORING OF THE ATMOSPHERE USING FLOW INJECTION ANALYSIS. Steven H. Hoke and Victor R. Rivera, U.S. Army Biomedical Research and Development Laboratory.


2:45 89. PRELIMINARY RESULTS OF THE ROCKY MOUNTAIN DEPOSITION MONITORING PROJECT. Denise Link, United States Environmental Protection Agency.

3:10 BREAK

3:30 90. ACCUMULATION OF Al, Cd, Cu, Pb AND Se IN THE TISSUES OF TWO SPECIES OF FISH FROM LAKES WITH DIFFERENT pH VALUES. R. A. Stripp, M. Heit, D. C. Bogen, U.S. Department of Energy, and J. Bidanset, St. John's University.


4:45 93. WITHIN-EVENT VARIATION IN RAINFALL COMPOSITION. Frederic C. Laquer, University of Nebraska at Omaha.
11TH INTERNATIONAL EPR SYMPOSIUM

Organized by Gareth R. Eaton and Sandra S. Eaton

Monday Morning, August 1, 1988

Session I - ENDOR

G. R. Eaton, Presiding

8:30
Opening Remarks, G. R. Eaton

8:40
PLENARY LECTURE


9:40

10:00
BREAK

10:30
96. ENDOR DETERMINED STRUCTURES OF SUBSTRATES AND ENZYME REACTION INTERMEDIATES. M. W. Makinen, University of Chicago.

11:05

11:40
98. $^1$H, $^{14}$N, $^{15}$N, and $^{59}$Co POWDER ENDOR OF OCTAETHYLPORPHRYRINATO COBALT(II) AND ITS SUPEROXO ADDUCT. M. Baumgarten, C. J. Winscom, and W. Lubitz, Free University, Berlin.

12:00
LUNCH

Monday Afternoon, August 1, 1988

Session II - B. Bales, Presiding

1:30

2:00
100. SENSITIVITY ENHANCEMENT IN SLOW MOTION STUDIES BY MONITORING LONGITUDINAL SPIN RELAXATION. M. Giordano, D. Leporini, M. Martinelli, L. Pardi, and S. Santucci, University of Pisa.

2:20
101. 2D-FT-ELDOR APPLIED TO MOTIONAL DYNAMICS, J. Gorcester, S. Ranavare, and J. H. Freed, Cornell University.

2:45
BREAK

3:15
102. EPR CHARACTERIZATION OF METALLOPROTEINS RESPONSIBLE FOR THE OXIDATION OF ARSENITE TO ARSENATE. R. Hille and G. Anderson, Ohio State University.
<table>
<thead>
<tr>
<th>Time</th>
<th>Session Title and Details</th>
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<tbody>
<tr>
<td>4:15</td>
<td>110. PROGRESS IN IN VIVO OXYMERTY AND IMAGING WITH A LOW FREQUENCY ELECTRON SPIN RESONANCE SPECTROMETER. H. J. Halpern, M. Peric, J. Van Polen, D. P. Spencer, B. A. Teicher, and M. K. Bowman, University of Chicago, Harvard Medical School, and Argonne National Laboratory.</td>
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<tr>
<td>4:35</td>
<td>110. STRUCTURE OF PHOTOSYNTHETIC AND MICROSOMAL SYSTEMS STUDIED BY ESR SPIN-RELAXATION TECHNIQUE. G. I. Likhitenstein, Academy of Sciences of USSR.</td>
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**Tuesday Morning, August 2, 1988**

Session III - High Temperature Superconductors, L. Belford, Presiding

<table>
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<tr>
<th>Time</th>
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<tr>
<td>8:30</td>
<td>PLENARY LECTURE</td>
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<tr>
<td>9:15</td>
<td>111. MICROWAVE ABSORPTION OF THE YBa_{2}Cu_{3}O_{7−δ} SUPERCONDUCTOR. L. Kevan, J. Bear, M. Puri, Z. Pan, and C. L. Yao, University of Houston.</td>
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<td>10:05</td>
<td>BREAK</td>
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<tr>
<td>10:35</td>
<td>112. MICROWAVE ABSORPTION IN HIGH-Tc SUPERCONDUCTORS. R. N. Schwartz, D. Rytz, and K. W. Kirby, Hughes Research Laboratory, Malibu, CA.</td>
</tr>
<tr>
<td>11:00</td>
<td>112. AN EPR STUDY OF SINGLE CRYSTALS OF THE SUPERCONDUCTOR YBa_{2}Cu_{3}O_{7−δ}. S. A. Marshall, D. J. Keeble, D. R. Yoder-Short, J. P. Rice, and D. M. Ginsberg, Michigan Technological University and University of Illinois-Urbana.</td>
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<tr>
<td>11:50</td>
<td>General discussion of EPR of high-Tc superconductors</td>
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<td>12:00</td>
<td>LUNCH</td>
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**Tuesday Afternoon, August 2, 1988**

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<tr>
<th>Time</th>
<th>Session Title and Details</th>
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<tr>
<td>1:30</td>
<td>Follow-up discussion of 1987 Workshop on the Future of EPR Instrumentation</td>
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</tbody>
</table>
Session IV - posters, S. S. Eaton, Presiding

3:00 - 4:00 authors present for posters labeled A
4:00 - 5:00 authors present for posters labeled B


B 114. EPR AND ENDOR STUDIES OF AROMATIC SULFUR HETEROCYCLES ON CATALYST SURFACES. R. B. Clarkson, R. L. Belford, D. J. Youn, and H. C. Crookham, University of Illinois.


A 119. SIMULATION OF ESR SPECTRA FOR A CUPRIC BISTHIOSEMICARBAZONE COMPLEX IN ORIENTED ARTIFICIAL MEMBRANES. M. Pasenkiewicz-Gierula, W. E. Antholine, and J. S. Hyde, Medical College of Wisconsin.

B 120. NUMERICAL STUDIES OF STIMULATED ESEEM WAVEFORMS. H. Jin and H. Thomann, Exxon Research Laboratory.

A 121. CLOSED-FORM EXPRESSIONS FOR ANISOTROPIC MAGNETIC RESONANCE INTENSITIES. D. B. Fulton and J. A. Weil, University of Saskatchewan.


A 123. EPR SPIN-HAMILTONIAN PARAMETERS FOR CRYSTALLOGRAPHIC SITE SYMMETRIES. D. G. McGavin, Dept. of Scientific and Industrial Research, New Zealand.

B 124. GENERATING FUNCTIONS FOR ANGULAR MOMENTUM TENSOR OPERATORS. H. A. Buckmaster and S. A. Marshall, University of Calgary and Michigan Technological University.


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127. 27Al FOURIER TRANSFORM ELECTRON SPIN ECHO MODULATION OF Cu$^{2+}$ DOPED ZEOLITES A AND X. D. Goldfarb and L. Kean, Weizmann Institute of Science and University of Houston.


133. RARE GAS MATRIX ISOLATION ESR AND ENDOR SPECTROSCOPY, Allan J. McKinley, Juliusz G. Radziszewski, and Josef Michl, University of Texas at Austin.

134. EPR STUDY OF THE SO$_4^-$ RADICALS IN K$_4$LiH$_3$(SO$_4$)$_4$. Jozef Minge and T. Krajewski, Institute of Molecular Physics, Poznan, Poland.

Wednesday Morning, August 3, 1988

Session V - D. Gatteschi, Presiding

8:30 135. MAGNETIC RESONANCE EXPERIMENTS ON SODIUM CLUSTERS IN SODALITES. E. de Boer and G. Geismar, University of Nijmegen and University of Duisburg.

8:55 136. EPR OF Gd(III)-DOPED SINGLE CRYSTALS OF Li$_y$Y$_{1-x}$Yb$_x$F$_4$. L. E. Misiak, S. K. Misra, and P. Mikolajczak, Concordia University and Maria Curie-Skłodowska University, Poland.


9:35 138. PARAMAGNETIC STATES AND LUMINESCENCE STATES IN SILICAS. P. Wang, R. Haglund, Jr., D. Kinser, N. Tolk, and R. Weeks, Vanderbilt University.

10:00 BREAK
10:30 139. MULTIFREQUENCY ESR AND ENDOR OF Cu(II) AND Ti(III) IN PERFLUORINATED IONOMERS. S. Schlick, M. G. Alonso-Amigo, L. Sjöqvist, and A. Lund, University of Detroit and University of Linkoping, Sweden.

10:50 140. EPR OF OXOVANADIAM TETRAKIS (CUMYLPHENOXY)-PHTHALOCYANINE LANGMUIR-BLODGETT FILMS. M. D. Pace, W. R. Barger, and A. W. Snow, U.S. Naval Research Laboratory.


11:30 142. THE DESCRIPTION OF S-STATE ION EPR SPECTRA USING SYMMETRY-ADAPTED GENERALIZED HAMILTONIANS. H. A. Buckmaster and R. Chatterjee, University of Calgary.

12:00 LUNCH

Wednesday Afternoon, August 3, 1988

Session VI - Pulsed EPR, I. M. Brown, Presiding

1:30 143. MULTIPULSE FT-EPR OF ELECTRON SELF-EXCHANGE IN CHLOROPHYLL. M. K. Bowman, A. Angerhofer, and T. J. Michalski, Argonne National Laboratory.

2:00 144. EPR PULSE SEQUENCES FOR THE SOLID STATE: EXPERIMENTS IN CRYSTALLINE SILICON DIOXIDE. J. A. Weil, J. Isoya, R. J. Massoth, and M. K. Bowman, University of Saskatchewan and Argonne National Laboratory.

2:30 BREAK

Session VII - posters, S. S. Eaton, Presiding

3:00 - 4:00 authors present for posters labeled C
4:00 - 5:00 authors present for posters labeled D

C 145. DEVELOPMENT OF PHOTOCOUSTICALLY DETECTED MAGNETIC RESONANCE (PADMR) SYSTEM. K. Oikawa, T. Ogata, M. Ono, and H. Kamada, Yamagata University, Japan.

D 146. LOOP-GAP RESONATOR FOR TIME-RESOLVED ODMR INVESTIGATIONS AT LOW TEMPERATURES IN CHEMICALLY MIXED MOLECULAR CRYSTALS. B. Stein, T. Kirskj, and C. v. Borczyskowski, Free University, Berlin.

C 147. THE LLR (LOOP-LINE) AND THE CLR (CROSS-LINE) RESONATORS FOR S-BAND ESR SPECTROSCOPY. C. Franconi, J. Holowacz, and C. A. Tiberio, University of Rome.


D 150. EPR LINIESHAPE AND RELAXATION FUNCTIONS FOR MOBILE SPINS ON FINITE 1-D CHAINS OF CHLOROPHYLL. M. K. Bowman, Argonne National Laboratory.

C 151. SPIN-LABEL-SPIN-PROBE STUDIES OF SODIUM DODECYL SULFATE MICELLES. C. Stenland and B. L. Bales, California State University, Northridge.


C 153. STUDY OF PHASE SEPARATION IN SEGMENTED POLYURETHANES AND OF MISIBILITY IN POLYMER BLENDS USING NITROXIDE SPIN LABELS. S. Schlick, R. D. Harvey, and W.-P. Chen, University of Detroit.

D 154. IN VIVO ANALYSIS OF NITROXIDE RADICALS INJECTED INTO SMALL ANIMALS BY L-BAND ESR TECHNIQUE. S. Ishida, H. Kunashiro, N. Tsuchihashi, T. Ogata, M. Ono, and H. Kamada, Fukushima Medical College and Yamagata University.


D 156. EPR SPECTRA OF LOW DIMENSIONAL METAL-NITROXIDE COMPOUNDS. A. Caneschi, D.Gatteschi, R. Sessoli and P. Rey, University of Florence and CNRS, France.


D 160. GAMMA-IRRADIATED FOODS: IDENTIFICATION AND DOSIMETRY BY ELECTRON PARAMAGNETIC RESONANCE SPECTROSCOPY. M. F. Desrosiers, National Bureau of Standards, Gaithersburg.

C 161. FREE RADICAL COMPLEX OF ORGANOTIN WITH AMINOPHENOLS. AN ESR SPECTROSCOPIC STUDY OF A NOVEL ORGANOTIN RADICAL COMPLEX OF 2-AMINO-4-TERTIARY BUTYL PHENOL. S. K. Sur and J. P. Colpa, University of Oregon and Queen's University, Kingston.


C 165. RESOLUTION ENHANCEMENT OF ESE-DETECTED ESR SPECTRA DUE TO ALKYL RADICALS IN IRRADIATED SOLID ALKANES. Tsuneaki Ichikawa, Hokkaido University, Sapporo, Japan.

D 166. RAPID SINGULAR VALUE DECOMPOSITION FOR THE TIME-DOMAIN ANALYSIS OF MAGNETIC RESONANCE SIGNALS BY USE OF THE LANCZOS ALGORITHM. G. L. Millhauser, A. A. Carter, D. J. Schneider, J. H. Freed and R. E. Oswald, N.Y.S. College of Veterinary Medicine, Cornell University, and IBM Corporation.


Wednesday Evening, August 3, 1988

7:30 pm OPEN HOUSE at the University of Denver, EPR Laboratory

Thursday Morning, August 4, 1988

Session VIII – Pulsed EPR, I. M. Brown, Presiding

8:30 168. PLENARY LECTURE

NOVEL EXPERIMENTAL SCHEMES OF ELECTRON SPIN ECHO SPECTROSCOPY. A. E. Schweiger, ETH-Zentrum, Switzerland.


10:25 BREAK


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12:00  LUNCH

Thursday Afternoon - Bruker User's Meeting. Please contact Dr. Art Heiss to make your reservations, 617-663-7883 or 203-775-6252.

NOTE TO AUTHORS OF POSTERS: To permit browsing we request that authors put up their posters Monday morning and leave them up until the coffee break on Thursday.

SYMPOSIUM ON INDUCTIVELY COUPLED PLASMA
MASS SPECTROMETRY

Organized by Howard E. Taylor

Wednesday Morning, August 3

J. W. McLaren, Presiding

9:00  Opening Remarks - H. E. Taylor

9:10  KEYNOTE LECTURE


10:35  BREAK

10:50  KEYNOTE LECTURE

177. SAMPLE INTRODUCTION STRATEGIES FOR ICP-MS. R. F. Browner, and G. Zhu, Georgia Institute of Technology.

11:25  178. ANALYTICAL APPLICATIONS OF ETX-ICP-MS TECHNIQUES. E. Pruczkowski and R. D. Ediger, Perkin-Elmer Corp.


12:15  LUNCH

Wednesday Afternoon, August 3

R. S. Houk, Presiding

1:30  KEYNOTE LECTURE


2:55  BREAK

3:25  183. LOW LEVEL RARE EARTH ELEMENT ANALYSIS by ICP-MS: WITH OR WITHOUT DOUBLY CHARGED IONS?. K. E. Jarvis, Univ. of Surrey, Guildford, England.

3:50  KEYNOTE LECTURE


4:25  185. TRACE METAL DETERMINATION IN NBS BOVINE SERUM USING ICP-MS ISOTOPE DILUTION. E. S. Beary and P. J. Paulson, National Bureau of Standards.

4:50  186. HIGH PRECISION MEASUREMENT OF STABLE ISOTOPE RATIOS FOR IRON IN HUMAN BLOOD. J. Erve, B. T. G. Ting and M. Janghobnani, Univ. of Chicago.


SYMPOSIUM ON INFRARED SPECTROSCOPY

Organized by Marvin C. Goldberg

Tuesday Morning, August 2

Marvin C. Goldberg, Presiding

8:25  Introductory Remarks - M. C. Goldberg

8:30  188. REACTION OF NITROGEN OXIDES WITH BLACK CARBON: AN FT-IR STUDY. Dwight M. Smith, William F. Welch and Abdul R. Chughtai, University of Denver; Brian G. Wicke and Karin A. Grady, General Motors Research.

9:00  189. COAL-WATER INTERACTIONS AND DESORPTION KINETICS OF WATER FROM COAL: A FTIR STUDY. R. Mu and V. M. Malhotra, Southern Illinois University.


10:00  BREAK
10:30  191. DIFFUSE REFLECTANCE INFRARED SURFACE ANALYSIS OF MODIFIED INORGANIC OXIDE CATALYSTS. Aurobindo Nair and Robert L. White, University of Oklahoma.

11:00  192. GC/FTIR APPLICATIONS IN DIOXIN ANALYSIS. Charles J. Wurrey, University of Missouri; Billy J. Fairless and Harry E. Kimball, US EPA.


Tuesday Afternoon, August 2

2:00  194. ESTIMATION OF THE COMPOSITION OF COMPLEX MIXTURES VIA INFRARED SPECTROSCOPY. Howard B. Powell, Eastern Kentucky University.

2:30  195. PROBE OF PHASE TRANSITIONS IN $\text{NH}_4\text{La(}SO_4\text{)}_{2.4}\text{H}_2\text{O MONOCRUSTALS BY FTIR AND DSC TECHNIQUES. S. G. Jasty and V. M. Malhotra, Southern Illinois University.}$

3:00  196. HIGH RESOLUTION INFRARED STUDIES OF THE CORIOLIS COUPLE $v_6$ AND $v_9$ BANDS OF FORMIC ACID. R. E. Bungarner, Jong-In Choe and S. G. Kukolich, University of Arizona.


4:00  Concluding Remarks.

SYMPOSIUM ON NIR
Organized by Donald A. Burns

Wednesday Morning, August 3

Donald A. Burns, Presiding

1. Overview and Data Treatments

9:00  Opening Remarks

9:05  198. NIR ANALYSIS: WHY ALL THE FUSS ABOUT THIS SPECTRAL REGION? Donald A. Burns, Putnam Valley, NY.


10:05  KEYNOTE SPEAKER


10:35  BREAK

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II. Enhancements and Theories


Wednesday Afternoon, August 3

III. Applications

1:30   203. MONITORING COATING LEVELS ON PHARMACEUTICALS USING NEAR-INFRARED SPECTROPHOTOMETRY. Paul J. Brimmer, Pacific Scientific.

1:50   204. NIRA STRUCTURAL INVESTIGATIONS OF NYLON YARNS. James F. Rodgers, III and Shirley Lee, Monsanto Chemical Company.

2:10   205. QUALITY ASSURANCE FOR TEXTILES USING THE NIR METHOD. Subhas Ghosh, Donna Di Ianni, Tammy Ebersole, and James Hassick, Institute of Textile Technology.

2:40   BREAK

3:00   206. NEAR INFRARED ANALYSIS OF PAPER AND PAPER COATINGS. Frank A. DeThomas, Pacific Scientific.

3:20   207. NIRA CALIBRATION PROCEDURES APPLIED TO IR TRANSMISSION SPECTRA OF PORTLAND CEMENTS PREDICTS POTENTIAL COMPOUNDS. David B. Stokes and H. Preston Hayward, Delaware State College.

SYMPOSIUM ON ION CHROMATOGRAPHY
Organized by F. W. Williams

Monday Morning, August 1

F. W. Williams, Presiding

8:20   Introductory Remarks - F. W. Williams


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9:55  BREAK


Monday Afternoon, August 1

R. M. Merrill, Presiding


2:20  BREAK


4:10  218. ION CHROMATOGRAPHIC DETERMINATION OF LOW LEVEL ANIONS FOLLOWING HYDROFLUORIC ACID DIGESTION. R. M. Merrill, Sandia National Laboratories.

Tuesday Morning, August 2

S. J. Van Hook III, Presiding

8:25  Introductory Remarks

8:30  219. DETERMINATION OF FLUORIDE IN SEMICONDUCTOR PROCESS CHEMICALS BY ION CHROMATOGRAPHY WITH ION SELECTIVE ELECTRODE DETECTION. R. T. Talasek, Texas Instruments.

8:55  220. HIGH PERFORMANCE ION CHROMATOGRAPHY OF ANIONS. G. Vautour, M. C. Mehra, and V. Mallet, Universite de Moncton, Canada.

9:20  221. SINGLE COLUMN ION CHROMATOGRAPHIC DETERMINATION OF CHROMATE IN SLUDES AND SOILS. H. C. Mehra, and W. T. Frankenerberger, University of California at Riverside.
9:45  BREAK


**SYMPOSIUM ON MASS SPECTROMETRY**

Organized by P. V. Fennessey

**Wednesday Morning, August 3**

Paul Fennessey, Presiding

8:50  Introductory Remarks


10:00  BREAK


11:00  228. THE HUMAN EYE, A UNIQUE SPECTROMETER. John Quenzer, Robert L. Spraggins, Manville Corp.

**Wednesday Afternoon, August 3**

2:00  229. MASS SPECTROMETRY OF VOLATILE METAL CHELATE PRECURSORS OF SUPERCONDUCTING THIN FILMS. S. S. Banning, R. M. Barkley, and R. E. Sievers, University of Colorado.

2:30  230. PHARMACOKINETIC STUDY OF LIDOCAINE IN BURN VICTIMS USING GC/MS. Lynette Lobmeyer, Duane Bloedow, and Keith Clay, University of Colorado Health Sciences Center.

3:00  BREAK
3:30 231. EVALUATION OF TECHNIQUES FOR THE QUANTITATIVE ANALYSIS OF DISACCHARIDES IN URINE. S. S. Tjøa, and P. V. Fennessey, University of Colorado Health Sciences Center.


4:30 233. APPLICATIONS OF A NEW HELIUM DISCHARGE IONIZATION DETECTOR. Don Clay, David Williams, Tracer Instruments.

SYMPOSIUM ON NUCLEAR MAGNETIC RESONANCE

Organized by James F. Haw

Monday Morning, August 1

8:25 Welcoming Remarks - James F. Haw

NMR OF Catalysts - B. C. Gerstein, Chair

8:30 234. NMR STUDIES OF MODIFIED METAL-EXCHANGED ZEOLITES. R. Johnson, B. Marshik and T. Apple, University of Nebraska-Lincoln.

8:50 235. ALUMINUM-27 MAS NMR SPECTROSCOPY OF LAYER ALUMINOSILICATES. Donald E. Woessner, Mobil Research and Development Corporation.


10:00 BREAK

10:30 237. CHANNEL DYNAMICS IN UREA/n-ALKANE CLATHRATES. Nicholas J. Heaton, Regitze R. Vold and Robert L. Vold, University of California-San Diego.

11:00 PLENARY LECTURE

238. PROTON MAGNETIC RESONANCE STUDIES ON ZEOLITES AND RELATED CATALYSTS. Harry Pfeifer, Karl-Marx-University, Leipzig, German Democratic Republic.

Monday Afternoon, August 1

NMR of Polymers - Chair to be Announced

2:00 239. SOLID-STATE $^{13}$C NMR STUDY OF THE STRUCTURE AND DYNAMICS OF PLANT POLYESTERS. Joel R. Garbow, Monsanto Company, Tatyana Zlotnik-Mazori, Lisa M. Ferrantello, and Ruth E. Stark, College of Staten Island, City University of New York.


https://digitalcommons.du.edu/rockychem/vol30/iss1/1
3:00 BREAK


4:00 242. STRUCTURE AND CURING IN UREA-FORMALDEHYDE RESINS STUDIED BY C-13 CP/MAS NMR. L.-S. Chuang and Gary E. Maciel, Colorado State University.

Tuesday Morning, August 2

New Techniques - Organized by Robert A. Wind and Bruce Hawkins


9:30 244. ROTATIONAL ECHO DOUBLE RESONANCE. Terry Gullion, Vincent Bork, and Jacob Schaefer, Washington University.

10:00 BREAK


11:00 246. NMR OF SOLIDS WITH HIGH FIELDS AND HIGH SPINNING SPEEDS. Steven F. Dec, Bruce L. Hawkins, Ming Zhang, Robert C. Ziegler, James S. Frye, Robert A. Wind, David W. Duff, and Gary E. Maciel, Colorado State University.

11:30 247. NEW ANGLES IN SAMPLE SPINNING. Alex Pines, University of California-Berkeley.

Tuesday Afternoon, August 2

2:00 248. EXPERIENCES WITH LOW TEMPERATURE NMR. Costantino S. Yamoni, IBM Research Laboratory.

2:30 249. DEUTERIUM RELAXATION AND MOLECULAR DYNAMICS IN CLATHRATES. Robert L. Vold, Regitze R. Vold, Jong H. Ok and Alan D. Ronemus, University of California-San Diego.

3:00 BREAK

3:30 250. NMR OF "TETHERED" BIOLOGICAL SYSTEMS. Lynn W. Jelinski, Ronald W. Behling, and Tetsuo Yamane, AT&T Bell Laboratories.


4:30 252. Title to be announced. David VanderHart, National Bureau of Standards.
Wednesday Morning, August 3

MRI: Materials Require Imaging - James F. Haw, Chair

8:30 253. NMR IMAGING OF MECHANICALLY AND CHEMICALLY INDUCED DEFECTS IN INORGANIC SOLIDS. B. H. Suits and J. L. Lutz, Michigan Technological University.

8:50 254. NMR "MICROSCOPY" OF MATERIALS USING A 2.0 T SYSTEM. Christopher H. Sotak, GE NMR Instruments.


9:45 BREAK

NMR and the Single Electron - James F. Haw, Chair

10:15 256. NMR AND EPR DETERMINATION OF SPIN DENSITY IN [Ru(3-X-acac)(acac)]_2 (X = -H, -CHO) AS A PROBE OF LIGAND MEDIATED ELECTRON TRANSFER. Robert A. Binstead, Margaret H. Rakowsky and John C. Cooper, Naval Research Laboratory.

10:30 257. AN NMR VIEW OF MAGNETIC SUPEREXCHANGE IN TRANSITION METAL COMPLEXES. G. C. Campbell, P. Shepard, and James F. Haw, Texas A&M University.

11:00 258. ROTATING-FRAME DYNAMIC NUCLEAR POLARIZATION. Robert A. Wind, Liyun Li, Herman Lock and Gary E. Maciel, Colorado State University.

11:30 259. SOLITON LOCALIZATION IN POLYACETYLENE REVEALED BY ELECTRON-NUCLEAR SPIN COHERENCE STUDIES. Hans Thomann and Haiyong Jin, EXXON Research and Engineering Company.

Wednesday Afternoon, August 3

Instrumentation and Applications - Herb Retcofsky, Chair

1:30 260. Poster Presentation. MULTINUCLEAR NMR STUDY OF POLY(PARAPHENYLENE) AND DERIVATIVES. Krzysztof Erdmann, Marek Pruski, Wojciech Czerwinski, and B. C. Gerstein, Iowa State University.

2:00 261. A HIGH Q TUNEABLE PROBE FOR NMR STUDIES AT LOW TEMPERATURE. Luisita DeLaRosa and B. C. Gerstein, Iowa State University.

2:15 262. TEMPERATURE DEPENDENCE OF CHEMICAL SHIFT TENSORS OF MOLECULES IN SOLUTION. Thomas C. Farrar, John Decatur, and Michael Jablonski, University of Wisconsin.

2:35 263. MULTINUCLEAR NMR STUDIES OF C-18 DERIVATIZED SILICAS. Robert Ziegler and Gary E. Maciel, Colorado State University.

3:00 BREAK

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3:30  264.  A STUDY OF CARBON AND HYDROGEN AROMATICITY IN COALS BY HIGH RESOLUTION SOLID STATE NMR AND FT-IR SPECTROSCOPY. B. C. Gerstein, P. D. Murphy*, M. Pruski, and P. R. Solomon**, Iowa State University, *IBM Instruments, **Advanced Fuel Research Inc.


SYMPOSIUM ON SUPERCRITICAL FLUID CHROMATOGRAPHY
Organized by Bernd Wenclawiak

Tuesday Morning, August 2

9:00  PLENARY LECTURE

268.  INTEGRATION OF SUPERCRITICAL FLUID EXTRACTION INTO ANALYTICAL METHODOLOGY. Jerry W. King, U.S. Department of Agriculture.


10:10  BREAK


11:00  PLENARY LECTURE


Tuesday Afternoon, August 2

2:00  272.  THE ANALYSIS OF ENVIRONMENTAL RESIDUEUS USING SUPERCRITICAL FLUID EXTRACTION AS INJECTION METHOD IN SUPERCRITICAL FLUID CHROMATOGRAPHY. Marion R. Andersen, Nathan L. Porter, Erin R. Campbell, and Bruce E. Richter, Lee Scientific.

2:40  274. WATER AS A STATIONARY PHASE MODIFIER IN SUPERCritical FLUID CHROMATOGRAPHY. Fiona Geiser, Steven Yocklovich, Marc Sims, and Eugene J. Levy, Computer Chemical Systems, Inc.

3:00  POSTER BREAK

275. OPTIMIZATION OF THE SEPARATION OF POLYETHYLENES AND POLYSTYRENEs BY SUPERCritical FLUID CHROMATOGRAPHY. Amrit S. Boparai and Daniel V. Applegate, Argonne National Laboratory.

276. SPLIT CONTROL FOR FUSED SILICA CAPILLARY COLUMN SFC. M. Bohm, F. Umland, B. Wenclawiak, Westfalische Wilhelms Universitat Munster, West Germany.


4:00  278. A COMPARISON OF REDOX CHEMILUMINESCENCE DETECTION AND FLAME IONIZATION DETECTION IN SUPERCritical FLUID CHROMATOGRAPHY. B. Wenclawiak, University of Toledo.

4:30  Discussion

SYMPOSIUM ON QUALITY ASSURANCE

Organized by Victor J. Janzer

Tuesday Morning, August 2
V. J. Janzer, Presiding

8:30  Opening Remarks

8:35  KEYNOTE SPEAKER


10:00 BREAK


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Tuesday Afternoon, August 2


2:00  284. THE SAN JOAQUIN VALLEY DRAINAGE PROGRAM: A COMPARISON OF MULTILABORATORY DETERMINATION OF SELENIUM IN REFERENCE MATERIALS AND OTHER ENVIRONMENTAL SAMPLES. W. J. Walker and R. G. Burau, University of California, Davis.


Wednesday Morning, August 3

V. J. Janzer, Presiding

8:30  Opening Remarks

8:35  KEYNOTE SPEAKER

286. ORDER OUT OF CHAOS - OR CHAOS OUT OF ORDER? Sydney Abbey, Geological Survey of Canada (retired).

9:30  287. VARIATIONS IN THE CONCENTRATION OF TRACE CONSTITUENTS EXTRACTED FROM SEDIMENT STANDARDS USING SEVERAL ACID DIGESTION PROCEDURES. Ralph Poulsen and Frank E. Polniak, ACZ Laboratories.

10:00  BREAK


11:00  289. QUALITY ASSURANCE PROGRAM FOR GROUNDWATER MONITORING AT AN UNDERGROUND COAL GASIFICATION SITE. Lora S. Johnson, Western Research Institute.

Wednesday Afternoon, August 3


2:00  291. CHEMICAL ANALYSIS OF FIELD-MOIST VERSUS AIR-DRY FOREST SOIL SAMPLES. Wayne P. Robarge and John D. Bailey, North Carolina State University.

2:30  292. AN ALTERNATIVE STANDARDIZATION METHOD FOR THE ANALYSIS OF GASEOUS ORGANIC COMPOUNDS. Thomas Bernstiel, BCM Eastern Inc.
GENERAL POSTERS
Organized by Carlos E. Arozarena

Monday Afternoon, August 1 - Convention Lobby

Authors will be present from 2:00 p.m. until 4:00 p.m. for discussion

C. Arozarena, Presiding

293. A HAZARDOUS WASTE RESEARCH PROGRAM FOR ILLINOIS. Jacqueline M. Peden, Hazardous Waste Research and Information Center.

294. CHARACTERIZATION OF NATURAL WATER SAMPLES BY EXCITATION, EMISSION MATRIX(EEM) SPECTROSCOPY. Marvin C. Goldberg and Patricia M. Negomir, U.S. Geological Survey.


298. LIQUID CHROMATOGRAPHIC DETERMINATION OF THE AMOUNT OF EPIMERIZATION OF CHLOROTETRACYCLINE RESIDUE TO 4-EPI-CHLOROTETRACYCLINE RESIDUE IN ANIMAL FEED. Elizabeth E. Martinez, and Wilbert Shimoda, U.S. Food and Drug Administration.


302. DETERMINATION OF CHLORAMPHENICOL IN VARIOUS MATRICES BY GAS CHROMATOGRAPHY ANALYSIS. Susan B. Torda, U.S. Food and Drug Administration.


305. DETERMINATION OF SODIUM NITROFERRICYANIDE BY HPLC. C. P. Patel, M. V. Rebec, QAD-Analytical Services, Miles Inc.

306. THE REACTION OF 6-MERCAPTOPURINE WITH SUPEROXIDE IN APROTIC SOLVENTS. Carolos E. Barrios, May E. Cruz, Juan M. Guerrero, I-Ling Lu, Oscar A. Paez, and Conrad M. Valdez, East Los Angeles College.


309. ANISOTROPIC ROTATIONAL REORIENTATION OF 2,2,6,6-TETRAMETHYL PIPERIDINE-1-OXIDE IN ANION EXCHANGE RESINS: AN EPR LINE SHAPE STUDY. Jimmy S. Hwang, Wahid A. Al-Rashid, and Mohammed M. Saleem, King Fahd University of Petroleum & Minerals, Saudi Arabia.

310. CONDENSATION, GELATION, AND DRYING OF SILICA SOL-GELS CHARACTERIZED BY $^{29}$Si AND $^1$H NMR. Alexander J. Vega and George W. Scherer, E. I. du Pont de Nemours and Company.

311. ZERO FIELD NMR ENTIRELY IN HIGH FIELD. Robert Tycko, AT&T Bell Laboratories.

312. EVALUATION OF DOUBLE TUNED CIRCUITS USED IN NMR. Toby Zens, Varian Associates.

313. SOLID STATE ADVENTURES WITH ODD QUADRUPOLES. Evan Williams, Varian Associates.

316. CHARACTERIZATION OF NADPH-INDUCED NITROXIDE REDUCTION IN LIVER MICROSONES. H. Utsumi, M. Kashiwagi, A. Shimakura, and A. Hamada, Showa University, Tokyo, Japan.
1

AIR-WATER EXCHANGE OF PCBs AND PAHs IN LARGE LAKES
Steven J. Eisenreich and Joel E. Baker, Environmental Engineering Sciences, Department of Civil and Mineral Eng., University of Minnesota, Minneapolis 55455

During early August, 1986, air and surface water concentrations of PCBs and PAHs were determined over Lake Superior onboard the RV Seward Johnson. Air concentrations were separated operationally into vapor and particle phases, and water concentrations separated into dissolved and particle phases. The concentrations of all compounds were typical of remote environments. The atmospheric vapor and water dissolved components were closely linked (i.e., co-varied). The ratios of the atmospheric vapor concentrations and the surface water dissolved concentrations for specific chemical components (air-water partition coefficients) were compared to Henry's Law constants. Congener-specific PCB data suggest water to air transport whereas PAHs were in apparent equilibrium. Volatilization fluxes are estimated, compared to model results and placed in perspective of whole-lake chemical cycling.

2


The concentration of aldehydes in vehicle exhaust gases is increased when ethanol or methyl tert-butyl ether (MTBE) additives are used. The effect of high-oxygen fuels on aldehyde concentrations in Denver's ambient air was studied by observing formaldehyde to acetaldehyde ratios and carbon monoxide to aldehyde ratios before, during, and after the mandated oxygenated fuels program. Carbonyls were collected in 2,4-dinitrophenyl-hydrazine-coated silica cartridges and the resulting hydrazone derivatives were extracted with acetonitrile and quantified by high-performance liquid chromatography. Samples, lab blanks, and field blanks were continuously collected from early December to mid-April at the Tivoli air monitoring site adjacent to downtown Denver where the Environmental Protection Agency and the Colorado Department of Health were also collecting data for the EPA air toxics program. This location was also one of the main sites used during the 1987-88 Denver Brown Cloud Study. The diurnal variations of formaldehyde and acetaldehyde concentrations were studied by collecting four-hour averaged 720-liter samples six times each day, seven days per week.

3


Elementary reactions involved in the homogeneous gas phase oxidation of SO₂ by hydroxyl radicals have been studied using a discharge flow resonance-fluororescence system. The initial step in the formation of H₂SO₄ is generally believed to be

\[ \text{OH} + \text{SO}_2 \rightarrow HOSO_2 \]

There is evidence to support the reaction of the bisulfite radical \((HOSO_2)\) with \(O_3\), \(HOSO_2 + O_3 \rightarrow H_2O + SO_3\), followed by the \(SO_3\) reaction with water to form \(H_2SO_4\). There is some uncertainty regarding the other reactions of the bisulfite radical in the atmosphere that may prevent the formation of \(H_2SO_4\). Kinetic and mechanistic studies concerning the fate of the bisulfite radical \(H_2SO_2\) (which is experimentally made by the reaction of hydroxyl radicals with \(SO_2\)) in two different reactions will be discussed. The reaction of \(NO + HOSO_2 \rightarrow \)

products has been studied experimentally and the results analyzed using chemical kinetic modeling to yield a rate constant for this reaction. Speculation about the possible formation of a bisulfite water complex and a discussion of experiments designed to determine whether such a complex has any atmospheric kinetic significance on \(HOSO_2\)'s mechanistic route to \(H_2SO_4\) are presented.

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ON VARIATIONS IN SULFATE CONCENTRATIONS IN PRECIPITATION AT YAMPA, COLORADO. Tsuchi, J. et al.: 30th RMC Program and Abstracts. Atmospheric, Oceanic & Space Sciences, Space Physics Research Laboratory, University of Michigan, Ann Arbor, Michigan 48109-2143.

Oppenheimer et al. (1985) reported that a linear relationship existed between annual nonferrous metal smelter emissions of SO\textsubscript{2} in the western United States and annual precipitation-weighted concentrations of sulfate at National Acid Deposition Program monitoring locations in the Rocky Mountain states from 1980 through 1983. This paper examines this hypothesis using independent data from an individual monitoring location operated by the Utility Acid Precipitation Sampling Program (UAPSP) at Yampa, Colorado over the period 1983 to 1985. Precipitation samples at UAPSP sites are collected on a daily basis which permitted us to make a gross estimation of air flow preceding each precipitation event. This allowed us to identify samples with an above-average probability of air flow from 13 regions of the western United States. The goal was to ascertain whether similar trends existed between nonferrous metal smelter emissions of SO\textsubscript{2} and sulfate concentrations only when there was a high probability of transport from the nonferrous metal smelter emission regions or whether the proportionality existed for all air flows. Results showed that annual precipitation-weighted sulfate concentrations at Yampa decreased over the three-year period for those precipitation events with a high probability of transport from the smelter regions. During the same period, we found that the precipitation-weighted mean sulfate concentrations at Yampa increased with a high probability of transport from non-smelter regions. A comparison with emission trends will be presented.


REGIONAL ANOMALIES IN CHRONIC OBSTRUCTIVE PULMONARY DISEASE, ASSOCIATION WITH ACID AIR POLLUTION PARTICULATE CHARACTERISTICS. John W. Winchester, Dept. of Oceanography, Florida State University, Tallahassee, FL 32306.

Mortality rates due to chronic obstructive pulmonary disease (COPD) in standard metropolitan statistical areas are highest in two broad regions of the U.S. One is the western plains, with rates high in Colorado and north Texas but decreasing toward south Texas. The other is the southeast, with rates high in Georgia and north Florida but decreasing toward south Florida. Rates are low in the northeast, upper midwest, and far west, as well as in the largest cities of these regions. Evidence is presented that the ambient atmosphere in the two high COPD regions may be especially irritating to the respiratory tract because of aerosol particles that contain acid air pollutants. In the western plains, alkaline dust concentrations are high and can scavenge acid air pollutants to particle surfaces. In the southeast, sulfuric acid aerosol concentrations are high because of the climate as well as transport of primary pollutants from the north. The acid air pollutants carried by aerosols in both regions may lead to unusually high human exposure to the respiratory tract and account for the high COPD mortality rates.

DETERMINATION OF FLUXES OF OXIDES OF NITROGEN BY EDDY CORRELATION, B.A. Watkins, D.W. Stocker and D.H. Stedman University of Denver, University Park, Denver, Co. 8001

The emission densities of biogenic sources of NO\textsubscript{x} are likely to be small and highly variable and as yet are poorly quantified. The eddy correlation technique was employed to determine fluxes of the oxides of nitrogen at an agricultural site in eastern Colorado. The study investigated dry deposition to a field of growing winter wheat from mid January through May 1986. The average NO\textsubscript{x} concentration remains constant during the data acquisition period while the net flux changes. The 5 day average contribution to the overall flux by the negative or downward flux remains at -1.0 ± 1.0 cm s\textsuperscript{-1} during the season while the average contribution by the upward flux increases significantly from 0.5 to greater than 6.0 cm s\textsuperscript{-1}. It is impossible to isolate the effect of the ambient NO\textsubscript{x} concentration on the NO\textsubscript{x} flux because the flux is overwhelmingly correlated with temperature. Microbial activity is dependant on the temperature of the soil, thus this correlation is not surprising. The results of this study aid in quantitating the emission densities of NO\textsubscript{x} from biogenic sources.
The \( \text{NO}_3^{-} \)-\( \text{N}_2\text{O}_5 \) equilibrium is highly temperature dependent when compared with the reactions of \( \text{NO}_3^{-} \)-\( \text{N}_2\text{O}_5 \) with organics. This temperature dependence provides a method to determine which species is the primary participant in the reaction with an organic. To achieve the necessary temperature control, the experiments were performed in a teflon film reaction chamber inside a temperature controlled enclosure. Temperature control was maintained to within better than 0.5 K. Known concentrations of \( \text{NO}_3^{-} \) and organics were introduced into the reaction chamber by measuring the pressures of the gases in a known volume. Ozone concentration and its wall loss rate were determined using an ozone analyzer. A gas chromatograph with a flame ionization detector was used to analyze the reaction mixture and to monitor the rate of decay of the organic reactant. Sampling of the reaction mixture was done at fixed time intervals using a gas sampling valve on the gas chromatograph. By taking advantage of the large temperature dependence of the \( \text{NO}_3^{-} \)-\( \text{N}_2\text{O}_5 \) equilibrium, we have been able to determine the \( \text{NO}_3^{-} \)-\( \text{N}_2\text{O}_5 \) wall loss rate constant. This wall loss is the decrease in the concentration of \( \text{NO}_3^{-} \)-\( \text{N}_2\text{O}_5 \) by processes other than reaction with the organic being studied. To determine the wall loss rate constant for \( \text{NO}_3^{-} \)-\( \text{N}_2\text{O}_5 \), reactions with \( t-2 \)-butene were run at 303 K, 308 K and 313 K. Using the known reaction rate constant for the reaction with \( \text{NO}_3^{-} \) and the assumed negligible reaction with \( \text{N}_2\text{O}_5 \), the important wall loss process was determined to be the temperature independent \( 168 \text{ s}^{-1} \) of \( \text{N}_2\text{O}_5 \). This wall loss constant was then included in the computer modeling for the determination of the rate constants for reactions of other organics with \( \text{NO}_3^{-} \) and/or \( \text{N}_2\text{O}_5 \).

ACTINOMETRIC MEASUREMENT OF \( j(\text{O}_3) \), THE PHOTOLYSIS FREQUENCY OF OZONE TO \( \text{O}_3^{-}(\text{D}) \)

USING A LUMINOL DETECTOR. Solomon T. Bairaie, Donald H. Stedman. University of Denver, Chemistry Department, Denver, CO 80208.

A low concentration of ozone (10 ppm) mixed with \( \text{N}_2\text{O} \) is photolyzed by sunlight and a series of reactions take place. The reaction conditions favor the production of \( \text{NO}_3 \) which is detected by its chemiluminescence reaction with luminol. The system uses only aqueous solvents, so no special purification procedures are necessary and commercially available apparatus is used for all the system components. These characteristics make our system simpler and safer than the previous ones used by Dickerson (1980) which is based on the detection of \( \text{NO} \) by high temperature reduction and by Blackburn (1984) based on methanol conductivity detection. The actinometer was optimized for sensitivity and gas flow rates in the lab and was set on the roof of the chemistry lab of the University of Denver. Data collected in the spring of 1988 and the dependence of \( j(\text{O}_3) \) on solar zenith angle, ozone column density, altitude and temperature and its comparison versus global and ultraviolet radiation under various ozone column densities will be discussed.

CO/CO\(_2\) RATIO MONITORING AS A MOBILE SOURCE EVALUATION TOOL

Kamal A. Mohammed and Donald H. Stedman, Chemistry Department, University of Denver, University Park, Denver, CO 80208-8179.

Oxygenated fuels were mandated for the Colorado Front Range during the months of January and February 1988. The program is predicted to reduce the CO automobile emission by approximately 18%. It would be wonderful if the results of the oxy-fuel program are detectable in the ambient air monitoring data; however, the effect of meteorology on ambient air monitoring data makes such a goal unlikely. Therefore, we propose a new method which directly monitors CO and \( \text{CO}_2 \) simultaneously at the Colorado Department of Health monitoring site (CAMP). During rush-hours, peaks of CO and \( \text{CO}_2 \) are observed; thus, we avoid using mathematical models. Looking at the rush-hour peaks which are acquired directly on a computer, plots of CO/\( \text{CO}_2 \) are made and their average slope determined. If a 18% CO emission improvement has occurred, then approximately a 18% decrease in the average rush-hour CO/\( \text{CO}_2 \) slope will result. Data monitoring of CO and \( \text{CO}_2 \) was carried out from November 1987 through April 1988. The advantages and disadvantages of monitoring ratios to \( \text{CO}_2 \) as a mobile source apportionment method are discussed.
INTERACTIONS BETWEEN OZONE AND ATMOSPHERIC CARBON AEROSOLS: TODAY AND FOLLOWING NUCLEAR WAR. Sherry L. Stephens, Jack G. Calvert* and, John W. Birks Department of Chemistry and Biochemistry, and Cooperative Institute for Research in Environmental Sciences, University of Colorado, Boulder, Colorado 80309, (303)492-6535, and *National Center for Atmospheric Research, Boulder, Colorado 80307-3000, (303)497-1000

In recent years the expected environmental consequences of nuclear war have been expanded to include the global impact of the injection of huge quantities of smoke into the atmosphere. Solar heating could cause this smoke cloud to rise to stratospheric heights, increasing local temperatures as much as 100 K. The lofting of carbonaceous soot particles into the stratosphere could cause the total ozone column to be reduced due to: (1) increases in catalytic destruction of ozone; (2) transport of ozone rich, stratospheric air to regions where it is more quickly photolyzed as the ozone poor, tropospheric air associated with the smoke cloud pushes into the stratosphere; and (3) direct reaction of ozone with the carbon aerosols. It has been shown that ozone reacts with soot and carbon surfaces producing an oxygen molecule for every ozone lost. The odd oxygen of the reacted ozone molecule left on the surface can remain there as a surface oxide or can be released as CO or CO₂. The rate limiting step for further ozone oxidation, after the equivalent of a monolayer of ozone has reacted, is the removal of the surface oxides. The liberation of these surface oxides is accelerated with increases in temperature; thus the overall reaction between carbonaceous particles and ozone is temperature dependent. The reaction of ozone with several types of soot is found to have an activation energy of 10.9 ± 1.0 kcal/mole and an order of 0.89 ± 0.14 with respect to ozone.

A COMPARATIVE STUDY OF THE ASSOCIATION OF AEROSOL SULFUR WITH SOIL DUST, POTENTIAL FOR ATMOSPHERIC DEPOSITION OF SOLUBLE ALUMINUM TO AQUATIC SYSTEMS, John W. Winchester, Dept. of Oceanography, Florida State University, Tallahassee, FL 32306, & Dale A. Gillette, NOAA GMCC, 325 Broadway, Boulder, CO 80303.

In both dusty areas, such as Colorado or the Pacific region downwind of Asian deserts, and in rather dust-free areas, such as eastern North America, fine particulate sulfur can be internally mixed with soil mineral constituents. The strong acidity that is expected at ambient humidities for sulfuric acid coatings of mineral particles is sufficient to solubilize both carbonate and clay minerals. We have examined sets of time sequence elemental composition measurements in the Asia-Pacific region and in northeastern U.S. by multivariate statistical analysis to resolve sulfur-rich components from the external mixture with other aerosol components. Mostly remote Asia-Pacific components approach but do not exceed carbonate or clay mineral stoichiometric limits of an atmospheric titration of alkaline mineral with sulfuric acid. In northeastern U.S., however, this limit is exceeded. Aluminum is associated with aerosol sulfur at each of 9 sites, Indiana to Massachusetts. Highest Al concentrations and Al/S ratios in the sulfur component are in Midwest agricultural major land resource areas (MLRA) with highest predicted dust fluxes by soil erosion, in Massachusetts and eastern Pennsylvania, average equivalent Al/S = 0.04 in the sulfur component. In approximate agreement with 1982-84 average compositions of 20 Adirondack lakes, geometric mean equivalent Al/S=0.072 (50x3.1).

FUNDAMENTAL STUDIES IN ATOMIC SPECTROSCOPY: NEW APPROACHES TO OLD QUESTIONS. Gary D. Rayson, Yang Shen and Mark Fresquez, Department of Chemistry, New Mexico State University, Las Cruces, NM 88003

The use of high temperature sources in atomic spectroscopy has experienced widespread acceptance in the analytical laboratory. Among this arsenal of sources, the inductively coupled plasma and the graphite furnace have emerged as important sources in atomic emission and atomic absorption spectrochemical measurements, respectively. Although great strides have been recently made toward the understanding of the complex chemical and physical environments of these sources, several fundamental questions yet remain fully unanswered. Such questions include: How are the analyte atoms (or ions) formed within the sources? How is the sample matrix involved in that process and how might its interference on the analytical measurement be minimized? New approaches to answering these questions with regard to argon plasmas and electrothermally heated graphite furnaces have been developed and will be presented. The approaches which will be discussed will include the power amplitude modulation of plasma discharges and a kinetics probe of analyte loss and sample decomposition mechanisms occurring within the graphite furnace during the thermal pretreatment stage of the analysis.

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Solutions containing high levels of dissolved solids present several problems to the analyst:
- blockage of the nebulizer
- memory effects
- blockage of the burner slot
- reduction of the absorbance signal
- high noise levels

The design of an atomization system should minimize and preferably eliminate such problems. The system to be described has the following features:
- aspiration of high dissolved solids solutions
- reduction of interferences
- fast rinsing and rapid clearing of the spray chamber
- minimal carry over ensuring better accuracy
- improved signal/noise ratio ensuring better precision

The method of measurement (PRoMPT—PRecision Optimized Measurement Time) also contributes to accuracy, precision and speed.

Results from a range of high dissolved solids solutions will be presented to show the applicability of the system to general flame AAS.

THE IN-LINE REMOVAL OF INTERFERENCES IN ATOMIC-ABSORPTION SPECTROPHOTOMETRY USING HYDRIDE GENERATION.

Atomic-absorption spectrophotometry using hydride generation is a sensitive technique for the determination of certain group IV, V, and VI elements. However, this analytical technique is subject to numerous interferences that are normally overcome by time-consuming batch methods of sample manipulation. Flow-injection techniques have been used in a variety of analytical procedures for reproducible sample manipulation. This paper describes rapid procedures based on flow-injection principles whereby some of these interferences can be overcome on an in-line basis in a miniature flow-injection hydride generator. Particular attention is given to the elimination of transition metal and certain interelement interferences for some of the hydride-forming elements by the use of an in-line cation-exchange column in a flow-injection manifold. It is shown that, by the use of such a flow-injection manifold, far higher interferent-to-analyte ratios are tolerable. Analysis is performed at a rate of 30 samples per hour, and no further sample manipulation is necessary after the sample has been dissolved. The precision of measurement, as indicated by the relative standard deviation, $s_r$, is of the order of 0.03, and the sensitivity is only slightly less than that obtained without the in-line column. Other in-line methods by which interferences can be overcome are also discussed.
In this paper we will present the results of work done on solutions of different samples ranging from organic to inorganic compounds. Solutions represent examples from highly varied origins including plant products, blood and organ specimens, food stuffs, metals, polymers and pharmaceutical raw materials. All of the digestions are done by IR heating and a totally automated microwave digestion system. The digested solutions, which include the solutions prepared by IR heating, are then analyzed by Atomic Absorption or ICP Spectroscopy. The results of this work are twofold. First, we wish to establish a comparison in the results of digestion, (IR heating vs. microwave digestion), for many varied solutions. Second, we wish to compare the benefits to performance ratio of manual to automated digestion.

Over the past decade, graphite furnace atomic absorption has proven to be a valuable technique for the determination of trace metals in a variety of samples including many solid materials such as soils and plants. Until recently, solid materials such as these were analyzed either after acid dissolution or by the direct insertion of a portion of the solid material into the graphite furnace. For some solid materials, an alternative approach to acid dissolution or solid sampling is the use of a slurry or suspension of the powdered sample. However, a limitation of this approach is that the suspended particles quickly settle upon standing. To overcome these problems, Miller-Ihli (1) used a vortex mixer or a hand-held ultrasonic probe to agitate the samples just prior to sampling by the autosampler. Both of these techniques, though, were not automated and therefore, required constant interaction. In this paper, I will describe a system that uses an ultrasonic probe attached to an air actuated piston to automatically mix sample slurries just prior to sampling by the autosampler. In this system, all operations are firmware controlled, eliminating the need for user interaction. Results obtained with this system will be discussed.


Few spectroscopic techniques match the ability of Atomic Absorption spectrometry to produce fast, sensitive, precise and analyte-specific results from liquid samples. However, for solid samples, labor intensive dissolution procedures using strong mineral acids add significant time and cost. A new, unique atomizer (Atomsource) now allows the determination of trace to major metal constituents by AAS directly from solid samples.

The Atomsource atomization device was used to determine a wide range of metals and metalloids in solid metal samples. Appropriate sputtering conditions and spectrometric parameters were established and calibration curves generated using certified standards to demonstrate the analytical utility of the technique. General characterization studies will also be presented which outline the relationship between sputtering conditions (voltage, current, pressure) and the atomic absorption signal. Three dimensional plots were useful in defining the relationship between these factors and could be used to establish optimal operating conditions.

Determination of major and trace metals was made using microwave dissolution techniques followed by spectrometric measurements for separate size fractions of suspended sediment collected from the Mississippi River. The suspended sediment was separated into two general size fractions, silt and clay. The silt includes particle sizes ranging from generally 2-63 micrometers. The clay particle size was generally less than 2 micrometers. A commercial microwave oven was modified to allow full or partial dissolution of samples using mineral acids. Teflon perfluoroalkoxy (PFA) sealed vessels were used for the sediment digestion. Analytical methods included Inductively Coupled Plasma-Atomic Emission Spectrometry, Inductively Coupled Plasma-Mass Spectrometry and other spectrometric techniques. Data will be presented demonstrating the utility of this approach for trace metal analysis.

DETECTING ATTOGRAM OF ATOMS AND MOLECULES. Jim Winefordner, Department of Chemistry, University of Florida, Gainesville, Florida 32611

Detecting atoms and molecules at low levels is limited by selectivity or interferences, sensitivity and noise. As long as the number of analyte species exceeds about 100, the detection is determined by the extrinsic noise, namely the detection, the source fluctuations, and shot noise. If the number of analyte species drops below 100 within the observation region, then the intrinsic detection limit becomes important and totally significant if the number is below a few (1-10) species. Detection limit estimates in atomic and molecular spectrometry will be given for typical current experimental conditions. The difficulties in achieving such detection limits under practical conditions will be discussed as well as the effect of spectral selectivity upon such limits. Current experimental approaches by our laboratory to achieve low detection limits in atomic and molecular spectrometry will be given. For example, by means of dye laser excited atomic fluorescence in graphite furnaces, we are approaching an attogram. We will discuss the experimental problems in achieving such detection limits for atomic species as well as molecules. The ultimate analytical methods will be envisioned.

APPLICATION OF THE FOURIER TRANSFORM SPECTROMETER TO PROBLEMS IN PLASMA ATOMIC EMISSION. Larry Layman, Jill Angus, Byron Palmer, Tom Niemczyk, Los Alamos National Lab, Los Alamos, NM 87545.

The modern Fourier Transform Spectrometer generates a great deal of spectral information. The simultaneous properties of high resolution and broad wavelength coverage allow many measurements to be made more easily and with greater precision than previously possible. Extracting useful information out of this flood of data is the problem currently being addressed. For direct atomic emission elemental analysis, multivariate analysis techniques allow the extraction of much more information from the spectra generated. The high resolution of the spectrometer, allows detailed measurement of line shapes. This data allows several questions about the fundamental properties of the source to be answered. Doppler broadening measurements allow the calculation of the "thermal" temperature of the plasma. Stark broadening of atomic emission lines is used to calculate the electron density in the plasma.
"MASTER BLASTER" HIGH PRESSURE - HIGH TEMPERATURE DIGESTION.

Angelo C. Grilli, Instrument Co., PO Box 2387, Princeton NJ 08540. Prof. Gunter Knapp, Technical University, Graz, Austria. Peter Kettisch, Anton Paar KG, A-8054 Graz, Postfach 58, Karterstrasse 322 Austria.

"Master Blaster" is the term which chemists are using with affection to describe a high pressure digestion technique which was developed by Prof. Gunter Knapp and his group at the University of Graz, Austria. In this paper we will present the results of several difficult digestions we have encountered to date. Our work includes ceramic oxides, noble metals, biologicals, coal samples, pharmaceuticals, wood products and geologicals. Our concern is not only with digestion of these and other difficult samples, but also with the complete recovery under ideally safe conditions.

The methodology to set up operating procedures for unknown samples will be described. Safety considerations will be illustrated and computer print-outs showing control of the operating parameters are presented with our results.

ANALYSIS OF TISSUE ELECTROLYTES BY INDUCTIVELY COUPLED PLASMA SPECTROPHOTOMETRY

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It has been shown that damage to heart tissue is related to changes in calcium, magnesium and other electrolyte levels of the damaged tissue. Monitoring these electrolytes may therefore be useful in the assessment of drug induced tissue damage and repair. Previously, analysis of tissue electrolytes has been carried out either by wet chemical methods or by atomic absorption spectrophotometry. We report here an inductively coupled plasma (ICP) spectrophotometric method which offers several advantages over the atomic absorption (AA) method. For example, (a) the linear dynamic range of the ICP method is much wider than that of the AA method; (b) in contrast to AA, several electrolytes can be measured simultaneously by ICP; (c) the use of an internal standard with the ICP method provides superior precision and accuracy. A study was undertaken to evaluate the usefulness of measuring tissue electrolytes by the ICP method. Isopropylene dichloride was used to effect tissue injury in rats and the organ electrolytes were determined by ICP and AA. Further details of the methodology, method validation and a statistical comparison of results will be presented.


ICP-AES OF THE ACTINIDE ELEMENTS. Edmund A. Huff and Delbert L. Bowers, Analytical Chemistry Laboratory, Chemical Technology Division, Argonne National Laboratory, 9700 South Cass Avenue, Argonne, Illinois 60439.

A sequential Inductively Coupled Plasma/Atomic Emission Spectrometry system of moderate resolution, interfaced to a glove box, was used for the characterization of radioactive samples, primarily α-emitters. The objective of this study was to determine sensitivities, spectral interferences, and wavelength selections for the actinide elements. Detection limits for the most-sensitive atomic emission lines of americium, curium, neptunium, plutonium, and uranium will be presented. However, the line-rich actinide spectra precluded the measurement of trace metal impurities in these samples directly at the required levels of detection. As a consequence, a chemical separation technique with subsequent ICP excitation was used to determine metal contaminants, including americium, in plutonium metals. Data will be presented that document excellent analytical figures of merit--detectability, specificity, accuracy--for the developed method.

* Work supported by the U.S. Department of Energy under Contract W-31-109-Eng-38.
Microwave plasmas show considerable promise as analytical atomic/molecular emission sources. Operation of a microwave plasma at atmospheric pressure and with molecular gases, such as nitrogen, calls for special consideration when designing a cavity and torch. We will discuss the design of a cavity/torch combination that allows us to operate using atmospheric pressure mixtures of Ar and N₂. We have characterized the operation of the plasma as a function of percent N₂ in the support gas. Observations regarding energy transfer in the plasma will be presented. Particular attention has been paid to the consequences of energy resonance between the N₂(3P₃₃) state and the Ar metastable states. The import of these energy transfer processes on the analytical utility of such a mixed gas plasma will be discussed.

Obtaining accurate analysis near the limit of detection in the presence of major components such as Al and Fe requires tight controls on ICP operating parameters. Attention has been given to the control of ICP gas flows and observation zone to maintain consistent excitation conditions. This paper focuses on maintaining wavelength position during the analytical cycle. Examples of errors in positional accuracy expressed as units of instrument bandpass or analytical accuracy for Pb 220.3 and Se 196.0 nm will be given. Positional accuracy is also significant for measurement of background, especially in the case of structured background. Selection criteria for background measurement points will be given along with examples of wavelength shifts on correction accuracy. It appears that the selection of the position is not as important as getting back to the same location.

Excitation mechanisms including ionization in various plasmas have been extensively studied, but such mechanisms are still difficult to be understood comprehensively. Recently we have applied the collisional-radiative process (CRP) theory to the study on the excitation mechanisms in the argon ICP. According to the previous works for argon and magnesium, electron collisions with both plasma gas and analyte atom are dominant processes for excitation and ionization, and non-LTEs of the Boltzmann distributions are caused by radiative processes of atom and ion in the excited states. In the present paper, the collisional population and kinetic processes of cadmium are calculated by using the CRP theory. The results are also useful for the discussion of cadmium excitation mechanisms in the argon ICP. Compared to magnesium, cadmium has the larger first excitation energies from the ground states for both atom and ion. As the result, Penning ionization and charge transfer processes contribute more to the excitation and ionization in the case of cadmium, although electron collision is still predominant in cadmium excitation. It is noted that the lower excited levels of both atom and ion are in the non-LTE, while the higher levels are close to the LTE conditions of the Boltzmann distributions. More detailed results for cadmium will be shown in comparison with those for argon and magnesium.

For greater sensitivity than flame or plasma systems, a slurry approach to graphite furnace AA will be described that involves only a two minute sample preparation based on rapid particle size reduction with a Polytron homogenizer. 11% animal tissue slurries are robotically pipetted directly into the graphite furnace. An "in furnace" oxygen ashing step or reduced palladium modification are employed to stabilize the analyte to much higher ashing temperatures than normal. This leads to better oxidation of the protein bulk of the sample and serves to reduce spectral background (smoke signal) during the atomization step to values below even the normal level encountered with wet ashing. The slurry method is calibrated with aqueous standard additions and finally gives the same metal values directly in homogenized beef liver as conventional, lengthy wet ashing schemes.

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A KINETIC STUDY OF ANALYTE TRANSFORMATION IN AN ICAP

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An analyte introduced into an inductively coupled argon plasma (ICAP) as tiny droplets undergoes many physical/chemical processes, e.g., desolvation, vaporization, atomization, excitation, ionization, recombination, etc., as a function of height. Some of these processes may occur simultaneously and some sequentially; some may proceed very rapidly and some relatively slowly. As a result, vertical and radial spatial distribution of atomic, ionic, and molecular species of the analyte is established in the plasma. If the sample droplets are mobile and if the plasma conditions are constant, the distribution of each species will be time independent and can be conveniently measured with space-resolved spectrometry. The resultant signal-height profile is the overall result of the kinetics of processes which generate of remove the species. Hence, the features characteristics of the signal-height profile, e.g., peak area, maximum, width, etc., are fundamentally related to the kinetics and to the rate constants. The present study is to correlate these profile features to the kinetics of analyte transformation and to provide workable means for estimation of reaction rate constants. Signal profiles of Ca, Mg, and Fe will be employed for demonstration.

MICROWAVE DISSOLUTION OF BIOLOGICAL MATERIAL: APPLICATION TO MICROWAVE-INDUCED PLASMA ANALYSIS.

Henryk Matulionisz and Ralph E. Sturgeon, National Research Council of Canada, Division of Chemistry, Analytical Chemistry, Ottawa, Ontario K1A OR6, Canada.

The use of a closed vessel and microwave oven for acid and hydroden peroxide dissolution of biological samples is investigated. Compared with conventional procedures, microwave assisted dissolution offers the advantage of substantially shorter sample preparation times, and increased output and efficiency. Trace elements from dissolved samples are determined by microwave-induced plasma atomic emission spectrometry (MIP). A study is presented utilizing a new designed and constructed ceramic frit based on ZrO2 nebulizer and plasma torch for use in MIP. The method has been tested on a variety of standard reference materials, with reproducible and accurate results.

On leave as a Distinguished Visiting Scientist, from Technical University of Poznan, Department of Analytical Chemistry, 60-965 Poznan, Poland.

CHARACTERIZATION OF A NEW ULTRASONIC NEBULIZATION SYSTEM FOR PLASMA EMISSION SPECTROMETRY.


A new Ultrasonic Nebulization and Desolvation system has been designed and evaluated for introduction of samples in Plasma Emission Spectrometry. Sample is pumped via peristaltic pump onto the face of a piezoelectric transducer which is energized at 1.4 MHz by a radio frequency generator. Physical vibration of the transducer produces standing waves in the liquid sample which lead to production of a large population of uniformly small droplets. The resultant vapor cloud is swept with argon into a heated chamber which separates the solvent from the sample via evaporation and condensation. Dry aerosol is subsequently swept into the plasma for analysis. In addition to the basic design description, we will present results of an evaluation study, including optimum operating conditions, detection limits, stability, memory effects, calibration linearity, and reliability.
AN EVALUATION OF SPARK ABLATION (SA) ICP-AES AND GLOW DISCHARGE OES AND AES FOR THE ANALYSIS OF NON-CONDUCTING MATERIALS. JOE BRENNER AND ALAIN LEMARCHAND JOBIN YVON (ISA), 16-18 RUE DU CANAL, LONGJUMEAU, CEDEX 91163, FRANCE, AND OLESEN AV. EDISON, NEW JERSEY, 08820.

The analysis of refractory nonconducting materials by conventional dissolution protocols and atomic spectrometry is difficult and time-consuming due to chemical resistance of these materials. Hence an accurate rapid direct solid technique would improve sample throughput. In this presentation, the performance of SA ICP-AES and GD-AES will be compared for the analysis of a of nonconducting materials. A wide range of standard reference materials, briquetted in copper were analysed by both techniques. The surface morphology of the GD sputtered materials indicates that sample transport is mainly physical, and as a result the technique is free from the influence of the physical and chemical compositions of the sample. Whereas in SA-ICP the transport includes volatilization and results in significant bias of the analytical data. The precision, accuracy, dynamic range of calibration and interferences will be evaluated.

NEW TECHNIQUES FOR ELEMENTAL ANALYSIS OF THE ENVIRONMENT.
Angelo C. Grillo, Questron Corp, PO Box 2387, Princeton NJ 08540. Dr. Peter B. Stockwell, P.S. Analytical Ltd, Arthur House, Far North Bldg, Cray Ave, Orpington Kent England. Dr. Arthur D'Silva, Cetac Technologies, PO Box 104, Omaha NB 68010.

ICP is available for high production automated elemental analysis of environmental samples. However, in order to meet EPA and CLP criteria for As, Se, Pb and Hg, the analyst must resort to alternate and less automated techniques. In this paper we will present the results of analysis by ICP with an Ultrasonic Nebulizer for all elements of concern except Hg. For Hg we will present the results of analysis by an Automated Fluorescence technique. The conclusion which we present will demonstrate that the use of ICP-Ultrasonic Nebulization and Automated Fluorescence for Hg offer at least comparable results to existing techniques but with drastic reductions in time, labor and errors.

DCP: USE OF EPA METHODOLOGY FOR ENVIRONMENTAL WASTEWATERS.

Specific multielement procedures for the determination of the concentration of 23 designated metals (Al, Ba, Be, B, Cd, Ca, Cr, Co, Cu, Au, Fe, Pb, Mg, Mn, Mo, Ni, Pd, Pt, Ag, Na, Ti, V and Zn) in effluent discharge are approved by the US E.P.A. Method AES0029 describes the approved technique for the simultaneous or sequential determination of these 23 trace elements by Direct Current Plasma spectroscopy. Operation, calibration and background correction techniques are detailed. And, of particular importance to analysis of wastewater samples, procedures for interference corrections are enumerated. Use of these procedures to compensate, when necessary, for spectral, physical and chemical interferences will be demonstrated with specific examples. In particular, the determination of refractory elements in a variety of complex matrices will be discussed.

Slurry atomization is a means of eliminating or minimizing sample preparation of solid materials for atomic spectral analysis via the direct nebulization of suspensions. The critical factors in developing a high recovery slurry method will be shown to be small particle size, favorable spray chamber geometry, and extended residence time in the plasma (for refractory particles). Numerous slurry reports have appeared that fail in one or more of these three areas, with the result being low elemental recovery and the use of correction factors to compensate for this error.

This paper will show simple approaches to rapid particle size reduction and will include the use of unusually efficient spray chambers and long plasma residence time to eliminate the need for correction factors. High recovery slurry methods will be described for the rapid plasma emission analysis of plant and animal tissue, coal, and refractory oxide materials using nothing more than aqueous standard calibration.

ANALYSIS OF OLEFINS AND ADDITIVES IN GASOLINES AND FUELS


The analysis of trace components in complex hydrocarbon matrices, such as gasolines and other fuels requires the use of selective detectors. The Redox Chemiluminescence Detector (RCDTM) for gas chromatography is based reactions of analytes with nitrogen dioxide to form nitric oxide, which is detected by a chemiluminescent reaction with ozone. The detector is insensitive to saturated hydrocarbons, but can sensitively detect alcohols, olefins and many other oxygen-, nitrogen-, and sulfur-containing compounds.

Olefins and particularly cyclic di-olefins are suspected in causing problems with fuel injection systems, but the separation and detection of these compounds in gasoline is extremely difficult. Another important class of compounds in gasolines are the alcohol- and ether-based additives. Recent research has been aimed at developing techniques for the selective detection of MTBE, alcohols and olefins in gasoline using the RCD.

GC DETERMINATION OF WATER USING 2,2-DIMETHOXYPROPRANE AND A SOLID ACID CATALYST. Kevin D. Dix and James S. Fritz. Ames Laboratory and Department of Chemistry, Iowa State University, Ames, Iowa 50011.

The determination of water in various organic and inorganic compounds is important to many fields of science as well as chemistry. The most common method, a Karl Fischer titration, has several interferences and lacks easy endpoint indication. Here we present a fast, simple, quantitative determination of water in various inorganic salts and organic solids and solvents. 2,2-Dimethoxypropane, a ketol, reacts with water in the presence of an acid catalyst. The reaction yields acetone which is easily determined using capillary gas chromatography with flame ionization detection (GC-FID). Nafion, a solid acid catalyst, is effective in catalyzing the reaction in less than 5 minutes and is easily removed prior to injection into the GC. Several experiments were conducted to optimize the amount of catalyst, reaction time, and other parameters. A linear calibration curve was obtained for the amount of water in various organic and inorganic compounds. The range of water that has been determined is between 0.001-4.0%. An even larger percentage can be determined by simply reducing the sample size or increasing the amount of reactant. Ascorbic acid, an interferent in the Karl Fischer titration, presents no problems with this method.
Chemiluminescence detectors for gas and liquid chromatography have proven to be valuable instruments for difficult analyses where a high degree of selectivity and sensitivity is required. An extremely sensitive and selective chemiluminescence detector has been developed for reduced organosulfur compounds. The selectivity of this detector for organosulfur compounds over many hydrocarbons, halogenated hydrocarbons, alcohols, aldehydes and ketones is about 10^6, with a linear response range for the sulfur compounds of three to four orders of magnitude. The detector signal results from a chemiluminescent reaction between the organosulfur compound and molecular fluorine which takes place in a small, low pressure reaction chamber. One application for which the Sulfur Chemiluminescence Detector has proven useful is the food and beverage industry. Organosulfur compounds are responsible for the distinctive odors and flavors of beer and other food products. Some of these applications will be presented, as will the theory of operation, and performance characteristics of the SCD including selectivity, sensitivity and linearity.

SUPERCRITICAL FLUIDS IN THE ANALYTICAL LABORATORY: SUPERCRITICAL FLUID CHROMATOGRAPHY (SFC) AND SUPERCRITICAL FLUID EXTRACTION (SFE). Steven B. Hawthorne, David J. Miller, and Mark S. Krieger, Univ. of N.D., Energy and Mineral Research Center, Grand Forks, ND 58202)

The unique properties of supercritical fluids have lead to their recent popularity as chromatographic mobile phases (supercritical fluid chromatography, SFC) and as solvents for the extraction of organic analytes from complex matrices (supercritical fluid extraction, SFE). Supercritical fluids have lower viscosities and higher solute diffusivities than liquids, which leads to increased efficiencies for both chromatography and extraction. The solvent power of a supercritical fluid can be controlled by simply changing its density, which allows SFC separations based on pressure programming, and allows class-selective extractions to be performed using a single supercritical fluid.

SFC yields high-efficiency separations of larger and more polar organics than GC, and is more easily interfaced with GC-type detectors (e.g., MS and FID) than LC. We have developed a simple interface for SFC/MS which allows a single instrument to be used for both GC/MS and SFC/MS, and yields good sensitivities (ng for full scan spectra). SFC/MS and SFC/FID analyses of a variety of samples including waxes, polymers, and high molecular weight PAHs will be presented.

SFE of complex sample matrices can yield quantitative recovery of trace organic analytes in 10 to 30 minutes. Since many supercritical fluids are gases at room temperature, analyte concentration steps are simplified and the direct coupling of the supercritical fluid extraction step with gas chromatography (SFE-GC) is possible. The use of SFE and coupled SFE-GC for the extraction and quantitation of PAHs from NBS standard reference materials, PCBs from sediment, and flavor compounds from a variety of spices and food products will also be discussed.

CATALYSIS IN A CHEMILUMINESCENCE CHROMATOGRAPHIC DETECTOR BY A SUPERCONDUCTOR PEROVSKITE. Elizabeth A. McNamara, Robert M. Barkley, and Robert E. Stevers, Department of Chemistry and Biochemistry and Cooperative Institute for Research in Environmental Sciences, University of Colorado, Boulder, Colorado, 80309-0215

The catalytic properties of YBa$_2$Cu$_3$O$_y$, the recently discovered high temperature superconductor, were studied in a gas chromatography detection system. The powdered superconducting perovskite material was substituted for gold in a redox chemiluminescence detector, in which the oxidation of organic analytes by NO$_3$ produces a pulse of NO which is measured downstream. Differences in sensitivity of response of components in an analyte mixture were measured at varying catalyst bed temperatures and flow rates through the reaction zone. Selectivity ratios for various organic compounds were determined at temperatures ranging from 200°C to 375°C, and flow rates from 3.5 mL/min to 36.5 mL/min. Of the compounds studied, alcohols and alkenes were the most sensitively detected under all conditions, while benzene and saturated hydrocarbons gave the weakest responses. The detection limit for ethanol was found to be 0.5 ng. Under optimal catalyst temperature and flow rate conditions, the response for ethanol was 681 compared to that of benzene. Higher catalyst temperatures and lower flow rates yielded the most sensitive detection of all analytes studied, but better selectivity was attained using low catalyst temperatures and relatively high flow rates. Classes of compounds tested for response include nitrogen and sulfur-containing groups, alcohols, amines, ethers, aromatics, aldehydes, ketones, and saturated hydrocarbons. Application of the system to the analysis of methyl t-butyl ether in commercial gasoline samples and of gasoline itself will be discussed.
The redox chemiluminescence detector (RCD) involves the reaction of NO₂, or another nitrogen-containing reagent, with easily oxidizable compounds over a heated catalyst surface to produce a surrogate pulse of NO. The nitric oxide is then sensitively detected downstream by measuring the chemiluminescence produced in the reaction with ozone. In chromatography applications, the detector has been shown to be highly selective in detecting readily oxidizable compounds in a matrix of unreactive species such as hydrocarbons. Temperature programmed reaction and desorption studies using the RCD and a quadrupole mass spectrometer have allowed further identification of products and intermediates in the redox reactions. The selectivity of the detector is primarily determined by the composition and the operating conditions of the catalyst. Gold, palladium, or the superconducting perovskite, YBa₂Cu₃O₇, is used as the catalyst in the redox detector. The catalytic surfaces contain labile oxygen atoms that can rapidly oxidize various species at 300-400°C. NO₂ is able to fill the oxygen vacancies created on the catalyst surface, thereby producing NO. The NO produced quickly exits the catalyst chamber and is detected downstream. Evidence also indicates that the direct reaction between NO₂ adsorbed on the surface and reducing species can occur. Discussion will center around the differences between these materials with an emphasis on understanding how the redox catalysts function in this detector.

The post-column oxidation of many chemical species with dilute nitric acid, nitrous acid or nitrite ion produces nitric oxide which is subsequently detected by its chemiluminescence reaction with ozone. Compounds that react with dilute HNO₃(aq) and produce a surrogate pulse of NO on a chromatographically useful time scale may be sensitively detected. For liquid chromatography, a capillary reactor system has been developed to provide reaction temperatures as high as 300°C and pressures of several kbar. Under such conditions, 0.1N HNO₃(aq) reagent oxidizes many organic and inorganic species to produce NO. For example, saccharides, which are difficult to measure by conventional means, have been quantitated at ppm levels using this post-column system. Ultraviolet irradiation can initiate the redox reactions of easily oxidized inorganic species with dilute HNO₃(aq) at 25°C, and it also enhances the reactivity of analytes at elevated temperatures. Aqueous sodium nitrate is not effective as a redox reagent while nitrous and nitrite ion are less potent oxidizing agents than nitric acid. Other oxidizing reagents can be used to generate nitric oxide from reduced nitrogen-containing compounds.

Conductivity has traditionally been viewed as a means of detection associated with ion exchange separations. While conductivity does provide a rapid, efficient means by which ionic solutes can be detected, it is also a valuable alternative to general UV detection in reversed-phase separations. This is especially true for low - wavelength or non-chromatophoric species which may be ionic. In this paper, the separation and detection of several phenoxycetic acids will be presented and discussed. Separations were performed by ion exchange and reversed-phase columns, with the solutes showing different selectivities in each scheme. This gives the analyst a means to confirm peak identities, especially when another species may co-elute with the solute of interest in one of the separation modes. Likewise UV and conductivity detection were employed to confirm peak identities. This also provides a means to discriminate between species of interest and other components in the matrix.
The synthesis of an N-methyl-N-nitrosourea (MNU) that is covalently linked to a methidium analogue is reported. The final step in the synthesis involves the condensation of p-(2-aminoethylcarbamoyl)methidium with N-nitroso-N-methylcarbamic acid N'-hydroxysuccinimide ester in 79% yield. The resulting compound, MNU-methidium, hydrolyzes with a calculated t1/2 = 7.2 min. To determine the methylation activity of this compound, it was incubated with a [32P]-end-labeled DNA restriction fragment. The yield of N7-methylguanine (N7-MeG) from MNU-methidium and MNU was determined using polyacrylamide gels. The results show that at low ionic strength MNU-methidium is far less efficient than MNU in forming N7-MeG. However, the addition of NaCl (< 200 mM) enhances the production of N7-MeG for MNU-methidium. This is in contrast to the inhibitory effect of salt on N7-MeG observed for MNU. MNU-methidium methylated all G-sites equally, while MNU shows a clear preference for oligo d(G) runs and a non-symmetrical methylation pattern within these dG-rich regions. Supported by CA36727 and CA29088.

Organic compounds containing reduced sulfur react with molecular fluorine resulting in the emission of light (chemiluminescence). The Sulfur Chemiluminescent Detector (SCD) exploits this chemistry to selectively and sensitively detect a wide variety of organosulfur compounds, including thiophosphate pesticides. The SCD is linear over at least three orders of magnitude and can be easily interfaced to a high pressure liquid chromatography system to provide broad analysis capabilities. Interfacing a Waters HPLC system with the SCD has allowed the detection of thiophosphate pesticides (e.g., malathion and parathion) at concentrations on the order of 100 ppb without interference from either solvents or other contaminants. Molecular fluorine is produced in situ by the electrical discharge of SF6 and is destroyed after the chemiluminescent reaction. Applications of this system for the monitoring of water and wastewater and the detection of pesticides in agricultural and food products will be discussed.

Since the late 70's there has been a steady effort to channel microfabrication technology for analytical instrumentation applications by 1) using technology to fabricate chemical sensors 2) adapting existing processes from the semiconductor industry for the microfabrication of parts 3) identifying materials other than silicon for special applications where semiconductors cannot be used. Our research activity at Perkin-Elmer has been oriented toward adapting existing tools and processes for the microfabrication of parts with silicon and other materials and to apply them to the microfabrication of assemblies to be used in analytical instrumentation. Through examples, we will explain what types of processes are applicable to our industry. For instance, we have been systematically studying etching and bonding techniques. We will share some of our experiences in terms of wet and dry etching of various materials and we will show how chemical inertness can be achieved through chemical vapor deposition and plasma assisted chemical transport. Finally, the design of a microfabricated device to inject minute quantities of liquid directly in a chromatographic column will also be described. This device is original and gives us the possibility to inject at least two orders of magnitude less of sample than with a conventional syringe without need for a splitter. We will present some of the analytical results obtained with this device and we will show how chromatographic results can be improved through the use of microfabrication.
EXPLORING SCIENTIFIC DATA WITH CHEMOMETRICS. Robert R. Meglen, Center for Environmental Sciences, Campus for the University of Colorado at Denver, 1200 Larimer Street, Denver, Colorado 80204.

In recent years the role of the analytical chemist has changed from simply providing chemical characterization services to an expanded role in interdisciplinary problem solving. The chemist is becoming more involved in experimental design and interpretation of results. While the microprocessor revolution and modern instrumental advances have increased the quantity of data gathered, the electronic windfall provides the chemist with little assistance in increasing the quantity of information generated. Data are not information. However, recent advances in the field of chemometrics exploit multivariate statistical techniques and computer assisted exploratory data analysis to facilitate the conversion of data into information. The techniques use graphical methods as instruments of reasoning to enhance the interpretation of many measurement - many variable systems. These techniques greatly improve the assimilation and examination of data from large complex data bases. This presentation describes how these techniques may be used to enhance information generation and improve the interpretive powers needed for complex problem solving. Examples of how one may use chemometric techniques to combine and interpret data from different scientific disciplines will be given.

LABORATORY INFORMATION MANAGEMENT SYSTEMS: A MODULAR APPROACH. Richard D. Beatty and Leigh A. Richardson. Telecation Associates, P.O. Box 1118, Conifer, Colorado 80433.

With the volume of information handled in today's laboratory, the need for computers is obvious. However, the approach to implementing the use of computers is not always so obvious. To deal with differing and changing needs, TELECATION ASSOCIATES has developed a series of modularized solutions to laboratory computerization. Using this approach, laboratory computerization can grow from a basic data entry and report generation program to a full PC-based, networked Laboratory Information Management System by simply adding modules. All modules address specific laboratory problems: report generation, QC/QA management, instrument interfacing, invoicing, archiving, chain-of-custody maintenance, even use of multiple work stations. Modules may be used separately or together. When used together, modules interact by passing data from one module to another.

This concept of using modular software packages as the building blocks of a customized Laboratory Information Management System will be presented. Techniques for interfacing laboratory instruments to a PC/LIMS network will be discussed. Low cost alternatives to networking for electronic data transfer will also be addressed.

APPLICATION OF SPREADSHEET PROGRAMS TO INSTRUMENT REPORT GENERATION. Marc L. Salti and Cindy Andereau, Perkin-Elmer Corporation, 761 Main Ave., Norwalk, CT, 06859

Analytical chemists are increasingly burdened with the generation of routine reports on the analyses they perform. Analytical chemistry is moving towards the gathering of larger and larger amounts of information, as the techniques used for analysis become more sophisticated and automated. The reporting facet of the analyst's responsibilities is increasing out of proportion with the number of analyses being performed due to an information explosion.

Reporting a large amount of data is a significant task, as is the interpretation. Although efforts at automation of the interpretive task are in their infancy, automation of the reporting task can be accomplished with the tools available to analytical chemistry today: the small laboratory/personal computer and a "spreadsheet" program.

The multitude data acquired in an EPA wastewater analysis presents a large amount of information to the analyst, but it is not usually in the form required. Often, this data may come from several instrumental sources, requiring collation into a final report. For most analyses, the analyst not only has to interpret the data, but must also generate an application specific, detailed report. This is the case particularly in the area of regulatory compliance analyses. For such analyses, a large amount of time must be devoted to the generation of a strictly specified report.

With the use of a commercially available spreadsheet program, report generation for USEPA Contract Laboratory Program Inorganic Analyses will be automated. A spreadsheet "model" will be created, into which instrument generated data files will be ported. This model will have an automated "Macro" to read the data files and generate the report. Calculations can be performed on the data, the program can graphically represent the data (e.g., the form of quality control charts), and simple decision making can be performed. This approach will be used to automate much of the reporting required by the CLP program. In this application, there is a rigorously defined format with little interpretation involved in the report, so it is ideally suited to automation.
COMPUTERIZED SYSTEM FOR STUDYING GAS PHASE CHEMICAL KINETICS.
Juan L. Bonilla and Larry G. Anderson, Department of Chemistry, University of Colorado at Denver, Denver, CO 80204.

A discharge flow-resonance fluorescence system has been set up for the study of hydroxyl radical reactions with organic compounds. An IBM PC has been interfaced to the system to control the reaction conditions, and to collect and analyze data. The IBM PC has been equipped with Tecmar LAB MASTER and RADIO boards to permit interfacing to the experiment. Digital-to-analog converters were set up to control flows for the different reaction gases. Digital output lines were used to open or close valves in the flow controllers and to change the position of reactant introduction into the system. Analog-to-digital converters were used to monitor the flows, temperatures, pressure and position of reactant introduction. The LAB MASTER has five 16-bit timer/counters which were set up to count the amplified pulses generated by the photomultiplier, for a selected time interval. These photomultiplier pulses provide a measure of the fluorescence intensity, which is proportional to the hydroxyl radical concentration in the system. Although the discussion focusses on this specific gas phase kinetics system, the principles that will be discussed are generally applicable.

COMPUTER-AIDED DESIGN, SIMULATION, AND TESTING OF AUTOMATED ANALYTICAL INSTRUMENTS. James P. Avery, Vincent P. Heuring, Renjeng Su, Michael Seiler, Daniel Hunter, John Blanco, and Janet Anstett, Department of Electrical and Computer Engineering, University of Colorado, Campus Box 425, Boulder, Colorado 80309-0425.

The development of automated analytical instruments has traditionally involved a good deal of cut-and-try experimentation, with the resulting high engineering costs and inability to easily change designs as more information on the system becomes available. Previous design methods have also suffered from difficulties in including previously designed components. We describe work in progress on the development of an integrated system for the description, design, simulation, and programming of analytical instruments. Using concepts from control theory, robotics, computer language theory, and finite state machine analysis, we are implementing a methodology for design that produces a language for programming the instrument as well as the simulation model that can be used to test the assays. The goal is to produce systems capable of quickly and effectively designing and testing analytical instrumentation concepts.

INSTRUMENTATION AND SIGNAL PROCESSING FOR A UV ABSORBANCE DETECTOR AT MULTIPLE SITES ON A LIQUID CHROMATOGRAPHY COLUMN. Kenneth A. Duell, Kathy L. Rowlen, James P. Avery, John W. Birks. Department of Electrical and Computer Engineering, Department of Chemistry, and Cooperative Institute for Research in Environmental Sciences (CIRES), University of Colorado, Campus Box 425, Boulder, Colorado 80309.

The instrumentation and signal processing techniques for a multiple site on-column detector are presented. The detector system consists of a UV source that illuminates a 15 cm, reverse phase, quartz column. Attached to the column at 1 cm intervals are discrete photodiodes that measure on-column absorbances. The 14 photodiodes are rapidly scanned by a computer during separation. Sequential column scans produce a multidimensional chromatogram that provides information unobtainable by end detectors alone. A whole column detector can track peak crossovers and can determine peak parameters at the earliest moment to allow real time optimization of the separation process. Due to light scattering effects by the stationary phase, electronic differences in individual diodes, and the effective detection cell seen by each diode, several techniques for calibrating the array of diodes are required. The emphasis of this talk will be on the techniques of extracting information from the multidimensional chromatogram and calibrating the detector system by digital signal processing.

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A system has been developed to study the solubility and physical durability of fibers in a synthetic physiological fluid. The system provides for the continuous, constant flow of fluid through cells containing cleaned, debris-free fibers. After interaction with fiber, fluid is collected in bottles and chemically characterized by ICP and A.A. Since collection bottles are periodically changed over the course of the experiment, a plot of concentration versus time provides an estimate of solubility rates. For this study, dissolution rates were based on silica solubility, SiO₂ being the primary network-forming component of the fibers. The fibers are characterized before and after leaching to determine changes in chemistry and key physical parameters. The information gathered allowed the fibers to be ranked according to their durability relative to chrysotile (asbestos). This paper includes the results of a six month trial on a set of 10 manmade fibers and chrysotile fiber. Results indicate that alkali-borosilicate compositions and one lime-silicate composition were the most active, solubility rates being at least 6000 times greater than that of chrysotile. Refractory aluminosilicate fibers, and alkali-free aluminosilicate fibers and other alumina containing fibers were found to have much lower solubilities, still greater than chrysotile by a factor of at least 160.

Lead contamination of potable waters almost always results from contact of the water with lead services, interior plumbing, joints in copper pipe made with leaded solder, lead goosenecks, or brass devices (fixtures, meters). Elevated lead concentrations in raw or finished water is relatively rare. The trends in lead solubility in response to various water quality parameters can be modeled with reasonable success for many systems in terms of the formation of various carbonate, hydroxy-carbonate, and orthophosphate solids, plus aqueous complexation by mainly hydroxide and carbonate ligands. In addition, the levels observed in samples from consumers' taps are affected by factors such as analytical variability, pipe length and diameter, "standing" time of the water, sample size, the original location of that slug of water in the plumbing system, etc. Even in water systems of "constant" water quality, there is significant temporal variability at each site. The contributions of the factors governing the lead levels are critically evaluated, and a new statistical approach with targeted monitoring is proposed. How these factors relate to corrosion control, monitoring programs, exposure assessment, cost/benefit analysis, and the new USEPA lead regulations are discussed.

In 1987, the U.S. Geological Survey's national-water quality laboratory in Denver, Colorado, analyzed a large number of natural water samples for total chromium by flame atomic-absorption spectroscopy with chelation-extraction. This method involves a complicated oxidation-reduction step that has resulted in poor precision and accuracy. A method was needed to replace this chelation-extraction method, compliment an inductively coupled argon optical-emission spectroscopic (ICP-OES) technique, improve throughput, and achieve a detection limit of 1 μg/L. Studies were undertaken to determine if the direct-current plasma optical-emission spectroscopic (DCP-OES) technique was a viable alternative to meet these needs. The DCP-OES method proved to be fast, precise, and almost free of interferences. A detection limit of 1 μg/L was obtained using this technique, precision was typically less than 2 percent relative standard deviation, and accuracy of results were generally within 2 percent of the true value. The 425.4-nm (nanometer) wavelength was chosen for this technique because of its sensitivity. However, calcium emission from the 422.7-nm wavelength raises the background at this wavelength. Therefore, a two-point background correction was used to compensate for this rise. Lithium chloride was added to samples and standards to minimize enhancement or suppression effects or both caused by alkali and alkaline earth metals. Glycerin also was added to samples and standards as a viscosity modifier to normalize transport efficiency. Comparison of results with the ICP-OES and chelation-extraction techniques for Standard Reference Water Samples and natural water samples will be presented.
Several hundred requests for concentration determinations of As, Bi, Ge, Hg, Sb, and/or Se are received each year by the analysts working in the AA/ICP area at Coors. Most of these are for trace level concentrations and have been handled using the ICP technique with the normal aqueous aerosol sample introduction, graphite furnace atomic absorption, plug flow hydride atomic absorption and cold vapor atomic absorption methods. To improve analysis speed, detection limits, and analytical accuracy, a continuous flow hydride/cold vapor device for use with the ICP spectrometers has been evaluated in the Coors laboratory. Conditions that allow simultaneous multielement concentration determination of As, Hg, Sb, and Se were defined and optimized using the system as a sample introduction device on a Jarrell-Ash Model 1100 ICAP spectrometer. Three sigma detection limits obtained for these elements were 30, 100, 30 and 200 parts per trillion in solution, respectively. Similar studies using the ARL 3510 sequential system indicate Bi and Se detection limits are 500 parts per trillion. Sample pretreatment procedures, pre- and post-digestion spike data, and duplicate data will be presented for the determination of concentrations of these elements in several materials including water, waste oils, copper rods, alloys, silica, and hydroxyapatite. Using these data as indicators, the continuous flow hydride system has been commissioned for routine analytical use with the ICP spectrometers.

A sequential extraction procedure, based on published procedures, was developed for the partitioning of trace metals into six fractions, on the basis of sources and reagents used; (1) exchangeable metals, water-soluble fractions, and carbonate fractions, and carbonate minerals -- 1 M NaOOCCH$_3$ at pH 5.0; (2) manganese oxides -- 0.1 M NH$_4$OH·HCl in 0.01 M HNO$_3$; (3) organic matter -- NaOCl at pH 9.5; (4) amorphous iron oxides -- 0.25 M NH$_3$·HCl·0.25 M HCl; (5a) sulfides -- KClO$_3$ + concentrated HCl; (5b) followed by boiling in 4 M HNO$_3$; and (6) residuals -- HF and HClO$_4$. Each extractant was analyzed for As, Cd, Cu, Fe, Mn, Sb, and Zn. Sequential extractions performed on fresh, frozen, and freeze-dried samples of bottom sediments from Whitewood Creek determined the largest concentrations of As are recovered during the initial sulfide extraction (step 5a), whereas the largest concentrations of Fe are recovered during the amorphous iron-oxide extraction (step 4) and the final sulfide extraction (step 5b). Extractions performed on amorphous iron-oxide precipitates indicated that Fe and As are recovered in the amorphous iron-oxide extraction (step 4). Data from this extraction procedure suggest that As is not associated with amorphous iron oxides in the bottom sediments, but rather is associated with a crystallized iron oxide or occurs as a sulfide. Data for Cd, Cu, Mn, Sb, and Zn are inconclusive.

A model wetlands ecosystem has been built at the Big Five Tunnel, Idaho Springs, CO, to determine the feasibility of treating mine drainage to increase pH and remove metals. Three 200 square foot sections were constructed, filled with locally available substrates and planted with sedges, cattails, and bullrushes from surrounding areas. The system outputs were monitored monthly for pH, conductivity, Eh, dissolved oxygen, and metal content. Samples from six wells installed in each section were analyzed twice during the winter. Results show an increase in pH of the water in all three sections with the substrate composed of mushroom compost having a greater effect than the substrate composed of manure, peat, and wood products. Metal removal was occurring during the winter months even though the plants were dormant. It is anticipated that increased rates of metal removal will accompany the increased biological activity of warm weather. The contributions to metal removal of the microbial populations and the plant communities will be assessed then. Several operational problems must be solved if large scale drainage treatment is to be considered. PVC pipes occasionally clogged with precipitated iron oxyhydroxide and had to be cleaned; and large scale transplanting of native wetland vegetation could not be accomplished.
A number of changes in federal, state, and local laws dealing with hazardous waste, its creation and disposal, have created a need to look at the quality of today's groundwater. The quality of the final analysis result is only as good as the integrity of the sample taken from the field. A number of components including trained personnel, reliable transportation, dedicated pumps and bailers, quality controlled sample bottles, and calibrated field instruments, all come together to create a highly efficient groundwater sampling team. Closely followed decontamination techniques, purging procedures, water level measurements, preservation and sampling processes all result in a groundwater sample of the highest integrity. Documentation and data management also begin when the sample is first taken. All of these factors, along with the important ones of quality assurance and quality control, will be explored in this paper. The end result is a groundwater sampling team that provides the laboratory analyst with a sample of the highest integrity and a start toward a quality result.


Lewisite is hydrolyzed rapidly and quantitatively in water to the stable, watersoluble, and highly toxic derivative, 2-chlorovinylarsonic acid (CVAA). Consequently, the amount of pre-existing Lewisite that was present in a sample can be determined by analyzing for CVAA. A new method is described to directly analyze for trace amounts of CVAA in aqueous matrices by reverse phase high performance liquid chromatography with ultraviolet and electrochemical detection. The application of this method to the analysis of CVAA in soil and ground water is demonstrated. Separations in this study were carried out on a C-18 bonded silica column using an isocratic mobile phase consisting of 3% acetonitrile/97% 0.1 M ammonium acetate buffer (pH 5.0). CVAA was detected spectrophotometrically at 225 nm (Log ε = 3.63) and electrochemically using a glassy carbon working electrode at +980 mV vs. Ag/Ag Cl. CVAA peak identity was corroborated by oxidative derivitization (H2O2) to 2-chlorovinylarsonic acid. The minimum detectable concentration of CVAA was 20 ppb.


Broad-spectrum measurements of pesticides and associated breakdown products in natural water at nanograms per liter concentrations commonly need to be performed to define occurrence, distribution, and transport mechanisms. Continuous-flow liquid-liquid extraction, where the water sample is passed through a mixer/settler that contains 200 ml of methylene chloride, can be used as an analyte preconcentration technique to achieve appropriate detection limits, because large volumes of water may be extracted. The objective of the present investigation was to determine the recoveries of nine pesticides and breakdown products at concentrations of 10 to 1,000 ng/L by continuous-flow liquid-liquid extraction (4- to 120-L water samples), 4-L continuous liquid-liquid extraction, and 1-L shake-flask extraction to evaluate the efficiency of continuous-flow liquid-liquid extraction. In each recovery determination, spiked water samples containing the analytes were extracted with methylene chloride, and the methylene chloride was concentrated to 0.5 ml prior to instrumental analysis using a gas chromatograph equipped with a mass selective detector. Although continuous-flow liquid-liquid extraction did not recover the polar analytes, such as 4-chlorophenol, from water as efficiently as the continuous liquid-liquid and shake-flask extractions, the nonpolar analytes, such as permethrin, were predictably and quantitatively recovered. Continuous-flow liquid-liquid extraction appears to be an efficient sample preparation technique for the analysis of nonpolar pesticides at nanograms per liter concentrations in water.
IMPROVED DETECTION LEVELS FOR NITROGEN AND SULFUR IN PESTICIDES AND NITROGENOSUS GASES USING A CAPACITIVE CONDUCTIVITY AND THE HALL 1000 DETECTOR. Don Clay, David Williams, Robert Wenske, Tracer Instruments, Austin, Texas 78725-2100.

The popularity of capillary columns and especially wide bore capillary columns is growing rapidly, requiring better detectors which can perform well with the narrow peaks resulting from these columns. The Tracer HALL 1000 detector was designed to maintain the integrity of capillary column separations and allow the full benefits of capillary performance to be realized by the chromatographer.

Enhancements in this new HALL Electrolytic Conductivity Detector include minimized internal cell volume, a new vent design, and a new base design which incorporates an inert connection between the column and reactor and easier replacement of the reaction tube. In addition, the electronic and solvent modules have been packaged into a standalone detector that is easily adapted to any gas chromatograph.

Representative chromatograms will be shown demonstrating capillary performance with emphasis on Nitrogen and Sulfur containing pesticides and herbicides. The linear dynamic range and detectability of the detector in the different modes will be presented. Comparisons of packed and capillary performance demonstrating improvements in linearity due to the greater inertness of capillary systems, and lower detectability due to sharper peak shapes with capillary columns will also be presented for some compounds.

INVESTIGATION OF THE ANALYSIS OF CARbamATE PESTICIDES IN DRINKING WATERS. B. J. Wildman, A.E. Sims, P.D. McDonald, and A.D. Sarchilli. Waters, Division of Millipore, 34 Maple Street, Milford, MA 01757.

In recent years, public and political concern to maintain aquifers and surface waters as safe drinking water supplies has increased. The Environmental Protection Agency (EPA), in response to these demands, is continually evaluating various analytical techniques for pesticides, herbicides and other toxic compounds in raw source waters. Agricultural chemicals commonly enter drinking water surface sources from agricultural runoff and aquifers by leaching. It is believed the EPA plans to regulate carbamate pesticides soon as stated in the July 8, 1987 issue of the Federal Register and require their analysis under the Safe Drinking Water Act (SDWA). The analysis of carbamate pesticides is achieved by reverse phase high performance liquid chromatography (HPLC) with post-column derivatization and fluorescence detection. Various columns and gradient conditions and their effect on the resolution and analysis time of carbamate species will be presented. The use of post-column reagent delivery systems and evaluation of various light sources and excitation and emission wavelengths for fluorescence detection will be discussed. New approaches utilizing solid sorbent extraction techniques and large injection volumes to achieve low level analysis will be shown.


The movement of applied pesticides through soil and into groundwater, or as surface runoff, is being studied in a series of paired watersheds—one of each set producing corn by conventional techniques, the others under conservation or "No-Till" methods. Three soil types are under investigation in PA, DE and MD. Water samples are obtained via measured surface runoff through calibrated flumes, wells, suction lysimeters and pan lysimeters. Atrazine and dicamba move rapidly in Delaware sandy soil only if rains immediately follow application. A 2-8 fold increase in atrazine and simazine leaching in no-till plots on silty clay loams in Pennsylvania was observed. Maryland studies report slightly higher leaching rates in the No-Till systems, with rates for both leaching and runoff influenced by the time interval between application and rain events.

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ANALYSIS OF AIRCRAFT TURBINE ENGINE FUELS FROM WASTEWATER CONTAINING HIGH CONCENTRATIONS OF SURFACTANTS. William D. Schulz, Eastern Kentucky University and Howard T. Mayfield, Air Force Engineering and Services Center, Tyndall AFB.

Live fire training is conducted at nearly all U.S. Air Force Bases. It is necessary to train fire crews but the live fire training facilities (FTF) create problems in terms of toxicity and treatability of the wastewater which is generated in training exercises. The concentrations of excess fuel components (usually JP-4) and the fire suppression agent, aqueous film forming foam (AFFF) in the wastewater, are high enough so that the wastewater is detrimental to normal treatment facilities. AFFF is a very effective fire suppression agent consisting of several surfactants and "solubilizing agents" for the surfactants. The AFFF and JP-4 components are mutual analytical interferences. Work with synthetic models for the wastewater has shown that AFFF seriously alters the liquid-liquid extraction recovery of fuel components and internal standards. The amount of fuel equilibrated with AFFF containing water also affects the concentration of AFFF components in the water. A solid phase extraction (SPE) technique has been developed for fuel component analysis sample concentration and cleanup. The SPE technique removed interferences and resulted in increased fuel component recovery, including higher alkanes which were undetectable by liquid-liquid extraction. Analysis was by "bonded phase" capillary chromatography with FID and MS detection. Recovery was determined for model JP-4 fuel components and authentic FTF samples were characterized.

RADON 222 DETERMINATION USING A LOW SENSITIVITY INTRINSIC GERMANIUM DETECTOR. Claude R. Beverly, Martin Marletta Energy Systems, P.O. Box 1410, Paducah, KY 42001, US DOE Contract No. DE-AC05-84OR21400.

A comparison has been made of a 4" x 4" NaI(Tl) gamma spectrometer and a nominal 10% high purity germanium spectrometer for gamma ray determination of radon collected in activated charcoal adsorption canisters. Despite the obvious higher absolute detection efficiency of the sodium iodide detector, the small germanium detector has been shown to be fully adequate for radon measurements employing a 600 second counting cycle. The lower background and more stable energy boundaries of the germanium detector afforded better counting precision than the sodium iodide detector. Measurements were conducted using samples spanning a radon concentration range from 0.6 pCi/liter to 40 pCi/liter. No difficulty was experienced in determination of even the lowest activity samples.


The PCB composition of water and sediment in the Hudson and St. Lawrence rivers has been observed to vary with distance from the pollution source. This phenomenon has been investigated in the laboratory using a sediment release reactor which produces a steady stream of water containing dissolved PCB over a period of months. Kinetics of release from the polluted sediment have been measured. Unpolluted clay has been mixed with the reactor water and the scavenging of dissolved PCB from the water measured. A pattern of PCB congeners attributable to the sedimentary process has resulted, which resembles the modified PCB pattern encountered in both river systems. Hence the observed modified PCB patterns have been explained by the physicochemical processes of dissolution and reprecipitation from the polluted water column. PCB pattern comparisons were made on personal computers with one program developed in-house and two packaged programs: Lotus 123 and SIMCA.
A study was carried out to assess the differences in geochemical composition of sediments among three depositional basins of Lake Ontario. The concentrations of ten major elements (Si, Al, Fe, Ca, Mg, Na, K, Ti, Mn, and P) and eight trace elements (Cu, Ni, Co, Cr, V, Pb, Zn, and As) determined in surface sediment and sediment cores were used to characterize spatial and temporal variability of sediments in the Western, Central and Eastern Basins of Lake Ontario. Generally, the results indicated low spatial variability of sediment geochemistry in individual basins. However, concentrations of few elements originating mainly from anthropogenic inputs varied significantly from one basin to the other. The temporal distribution of elements determined by concentration profiles in sediments was affected by different sedimentation rates in individual depositional basins. Concentrations of elements originating mainly from anthropogenic inputs reflected remedial actions implemented in the lake's drainage basin. Results of the study provide background information for the establishment of stations to monitor contaminants in the sediments, to determine the efficacy of point and non-point source remedial measures, and to implement a proper management strategy plan for Lake Ontario's ecosystem.

The role of particle-mediated interactions in controlling the distribution and transport of PCBs was investigated. The suspended particulate matter and particle flux were sampled several times over the annual cycle. A continuous flow centrifuge was used to obtain suspended material. Settling particulate matter was collected using sediment traps. The particulate matter was size-fractionated and individual PCB congeners were measured in order to examine interaction specificity with respect to both PCB and particle properties. In general, congener prominence patterns indicated a resemblance to Aroclor 1254. In comparison to the dissolved phase, suspended material was enriched in the higher chlorinated congeners. However, sediment trap material was enriched over suspended material in lower chlorinated congeners, possible reflecting resuspension and retention of higher chlorinated congeners in bottom sediment. Particle-water partition coefficients ranged from $10^{4.3}$ to $10^{7.5}$ and were correlated to octanol-water partition coefficients ($K_{OW}$). Normalization to particle organic matter content reduced the variation in partition coefficients, but values were lower than predicted by widely used relations to $K_{OW}$. Fluxes of PCBs were dependent on particle mass flux, particle type, and partition coefficients. Applications to environmental fate assessment will be discussed.

The detailed aquatic behavior of non-polar organic contaminants may be studied using PCBs as surrogates of organic compounds having similar physical-chemical properties such as aqueous solubility (S), vapor pressure (P), Henry's Law constant (H) and octanol-water partition coefficients ($K_{OW}$). As an illustration, PCB cycling in Lake Superior will be presented in detail. The vast majority of PCBs enter the lake via the atmosphere, are rapidly cycled through the water column and deposited in the benthic region. Sediment trap data on mass, OC and PCB fluxes coupled with results obtained using deep-diving submersibles show that PCBs are rapidly delivered to the benthic region on settling particles high in OC, but are released when particles decompose. Sediment trap fluxes exceed sediment accumulation rates by 50 to 100x. This paper will examine the controls on contaminant residence times in large lakes.
Mass spectrometry, particularly when coupled with gas chromatography, is a marvelous technique for the analysis of organic compounds in the environment. No other technique couples specificity with sensitivity as does mass spectrometry. It is probably fair to say that much of the recent environmental legislation passed by the United States Congress would not have been possible without mass spectrometry. This talk will support, if not prove, this thesis by several examples drawn from work in our laboratory. These examples will include the measurement of polychlorinated dioxins and furans by electron capture negative ion mass spectrometry. The goal of these studies has been to determine the fate of combustion-produced dioxins and furans which are released to the atmosphere. Other work has traced the leakage of a hazardous waste dump site in the City of Niagara Falls, New York. In this case, the combination of electron impact and negative ion mass spectrometry were used to identify several unique markers from this dump and to trace their movement in Lake Ontario. Other examples will be presented as time and data allow.

Modelling the Physical Chemistry of Humic Substances in Acid Waters and Soils.
Edward Tippling. Freshwater Biological Association, Ambleside, Cumbria, LA22 OL9, United Kingdom.

The surface horizons of acid soils usually consist predominantly of organic matter, a significant fraction of which is present as extractable humic substances (HS). Often, appreciable amounts of HS dissolve into the soil water and find their way to streamwaters. Because of their ion-binding properties, these HS may control the activities of important components of acid environments, most notably protons and aluminium species. The objective of the research described in this paper is to formulate and test a mechanically-based model of HS that can be used to predict the chemical behaviours of acid waters and soils. At the core of the model is a simplified description of competitive ion-binding by discrete sites on humic macromolecules, based on concepts developed by J.A. Marinsky and co-workers. The model has been successfully applied to Al-binding in acid waters, and is currently being extended to acid soils. As well as ion-binding, the quantitative description of humic 'solubility' is also being pursued.


Dissolved organic carbon (DOC) was measured in two lakes, Lake Fryxell and Lake Hoare, and twelve inflow streams in the Dry Valleys of South Victoria Land, Antarctica. Stream DOC concentrations were low (0.3-0.8 mg/L), reflecting the lack of vegetation in the watersheds. DOC concentrations in the permanently ice-covered lakes were greater than in the streams and increased with depth. In Lake Fryxell, for example, DOC ranged from 3.3 mg/L at 5 m, just below the ice, to 25 mg/L at 18 m, just above the sediments. The DOC profile is similar to the profiles of inorganic species for which transport is controlled by diffusion from the sediments, suggesting that degradation of algal-derived organic material in the lake sediments is an important DOC source in these lakes. Two fractions of the DOC, fulvic acid and hydrophilic acids, were isolated from several depths in both lakes. For all depths, these two organic acid fractions comprised 55-80% of the DOC and fulvic acid was greater than or equal to the hydrophilic acids. These fractionation results are similar to those of temperate lakes, where DOC is dominated by allochthonous inputs derived from plants and soils of the watershed. However, in these Antarctic lakes allochthonous DOC inputs are very small because the watersheds are barren of any vegetation. These results imply that organic acids, especially fulvic acid, comprise the majority of DOC even in lakes where the DOC is derived from autochthonous algal productivity.


Recent field investigations have demonstrated the successful use of an XRF screening analysis for metal contamination at various hazardous waste sites.

Using minimal sample preparation and unique field sampling methods the results were comparable to laboratory results using conventional analytical methodology such as AA and ICP. Multi-elemental analysis was performed on soil samples with particular interest in lead and arsenic levels. Detection limits achieved for some elements were 10 ppm. The XRF results were used in mapping the extent of contamination at various hazardous waste sites containing metal contamination.
For many types of samples the amperometric back titration method is preferred because accuracy is directly related to chemical stoichiometry, sample color and turbidity do not interfere, and interfering side reactions by free iodine cannot occur. With continued attention to minimizing chlorine release to surface waters concentrations lower than 0.1 mg/L Cl\textsubscript{2} must often be monitored. Precision and accuracy for the method as specified in standard methods documents are limited by buret reading resolution, end point detection sensitivity, and buret droplet volume increments. Without improvements on these limitations, analysis of experimental end point data shows that errors of 100\% can occur for 0.10 mg Cl/L samples. Examination of the kinetics related to iodine solution stability and related experimental results show that use of a five-fold lower titrant concentration with corresponding increases in end-point reading resolution is achieved. Use of a 3-electrode cell improves sensitivity. An improved buret has been designed which minimizes titrant delivery and droplet increment errors. With these enhancements reliable chlorine concentration measurements to below 0.03 mg Cl/L can be made.

Further improvements can be obtained using in situ generation of iodine by analytical coulometry. Coulombic efficiency for the iodine generation for typical wastewater was experimentally determined to be 99.9\%. With proper calibration a direct digital readout in mg/L Cl\textsubscript{2} is obtained. Iodine titrant solution preparation, maintenance, standardization volume measurements and volumetric buret design considerations are eliminated. Precision and accuracy are acceptable down to the micrograms/liter range.

A POTENTIOMETRIC TITRATION METHOD FOR SULFATE IN CONTAMINATED GROUND WATERS.

In a recent ground-water study, samples from wells downgradient of an anaerobic hog-processing waste lagoon could not be analyzed accurately for sulfate using standard automated methylthymol blue or turbidimetric methods. The interference consisted of a sudden drop in baseline for some sampling events, and peak heights of incorrect proportionality to those of standards, which was discovered through sample spiking. The method developed was a hybrid of several potentiometric methods. Phosphate is removed by precipitation with lanthanum, and cationic interferents are removed by strong acid ion exchange. Titrations are performed in a 1:1 methanol:water medium adjusted to a pH of approximately 5. Ionic strength is adjusted with potassium nitrate, lead nitrate is used as the titrant, and a lead sulfide ion-selective electrode is used to follow the titration. The precision of the method was \pm 2 mg/L in the concentration range of 10-110 mg/L. Recovery of external reference standards averaged 99\%, with an average std. dev. of 2 mg/L. Spike recoveries averaged 105\% with a std. dev. of 1\% in samples containing up to 30 mg PO\textsubscript{4}/L. Recoveries from 25-30 mg SO\textsubscript{4}/L field standards averaged 98\% with a std. dev. of 1\%.

DETERMINATION OF TOTAL AND WEAKLY BOUND CYANIDE. Michael J. Doyle, Robert J. Joyce, Dionex Corporation, 1228 Titan Way, Sunnyvale, CA 94088-3603, (408) 737-0700

Ion exclusion chromatography combined with amperometric detection has been shown to be an effective method for the determination of unbound cyanide in wastewater matrices. The method separates cyanide from interfering sulfide and thiocyanate as well as allowing low ppb detection of cyanide in chlorinated and non-chlorinated wastewater. The use of photochemical dissociation has been found to be very effective in the recovery of total cyanide from various environmental water samples. A method is presented which combines photochemical dissociation with chromatographic separation and amperometric detection for the determination of total cyanide. In addition, new developments in a method which combines a ligand exchange technique with a chromatographic separation are presented for the determination of "cyanides amenable to chlorination".
The variability in performance of 7 wet/dry atmospheric deposition samplers were compared for 1 year. Weekly samples were analyzed for pH, specific conductance, common ionic chemical constituents, and sample mass. The criteria used in siting collectors for the National Trends/National Atmospheric Deposition Program networks were purposely compromised to determine the effect of such criteria on the validity of samples collected at sites which have siting violations. Compromise of three criteria was evaluated: (1) Nearness to a line source (a moderately traveled road), (2) The nearness of items of sufficient bulk to disturb wind patterns and (3) the presence of items within a 30° cone about the sampler. The presence of items in the cone and the nearness of items that would disturb wind patterns affected the catch efficiency of the sampler. The nonnormal distribution within the data set necessitated the application of the nonparametric Friedman test to assess comparability of sample chemical composition and volume between and within samplers. Statistically significant differences existed for most comparisons, however, the test does not permit quantification of their magnitudes, although general trends may be determined. Differences in analyte concentrations between samplers were small.

TRACE METALS IN PRECIPITATION: STANDARDIZATION OF COLLECTION METHODS
Barbara J. Keller, Illinois State Water Survey, 2204 Griffith Dr. Champaign, IL 61820, 217/333-2026.

Absorption/desorption characteristics of three types of collection vessels were compared using deionized water and acid blanks as well as natural and synthetic precipitation samples. Vessels evaluated were: 1) the white high density polyethylene (HDPE) buckets used in the National Atmospheric Deposition Program/National Trends Network (NADP/NTN), 2) a nylon-reinforced polyethylene bucket liner, and 3) an HDPE funnel and bottle combination.

Stabilization of the samples was also a major focus of the project. Collection of samples in the HDPE buckets followed by filtration and acidification was evaluated with sampling frequencies ranging from event to weekly. Also evaluated was in-situ filtration followed by acidification. Results showed in-situ filtration is the preferred method, but problems with high particulate samples and filter freeze-up at low temperatures prevent its routine use in sampling networks. Final recommendations include: 1) subevent to daily sampling frequencies, 2) use of the HDPE funnel and bottle collection vessel to collect wet-only samples, and 3) immediate filtration through 0.4 μm polycarbonate filters followed by acidification to pH <2.


The Computer Controlled Automated Rain Sampler (CCARS) is a combination rain gauge and sequential sampler for precipitation chemistry measurements. The primary objectives of the design are low cost and versatility of operational mode. The three major components of the device are the measuring valve (rain gauge), sequential distribution valve, and on-board computer which also serves as the data recorder. The measuring valve uses an electromagnetically operated plunger and optical sensors to divide rain events into adjustable rainfall increments (nominal 0.01 in.). The distribution valve, using a stepping motor and a rotating channelled disk, delivers pre-programmed volumes to nine sequential stages. The computer records rain and stage increment timing and can be programmed to sample on a time or volume basis; these features make the concept attractive for future monitoring application. In one such application, daily samples could be collected with only weekly site service required. Some 50 CCARS units were operated during the Cloud Chemistry and Cloud Physics Organization (3CPO) precipitation scavenging and model evaluation experiment in May and June 1988.
The dry-side bucket of the wet/dry automated collector of atmospheric deposition has been used in the past, and especially before 1980, as a sampling surface for the estimation of dry deposition fluxes. It was recognized that the plastic buckets were inappropriate for the collection of reactive gases, such as SO$_2$ and NO$_x$, and based on considerations of aerodynamic theory there were doubts about their effectiveness in collecting submicrometer aerosols. Nevertheless, because samples were easily obtained using this technique, because the data obtained from these samples appeared to be reasonable, and because no other monitoring technique was available, the dry-side bucket was used in some monitoring programs. Field intercomparison studies conducted during the early 1980's showed that even though particulate SO$_4^{2-}$ was collected with a high degree of precision by the dry bucket, when the results were compared to data obtained by micrometeorological techniques, they appeared to overestimate the SO$_4^{2-}$ flux by a factor of two. More recent studies have confirmed that, in addition to collecting submicrometer anthropogenic SO$_4^{2-}$ aerosol, the bucket also collects large aerosol particles, including those larger than 20 µm. Thus, the dry-side bucket is inappropriate for monitoring of the fine aerosol particles involved in long-range transport.

**DRY DEPOSITION OF LARGE PARTICLES, BASED ON NADP DRY BUCKET MEASUREMENTS.**


Dry deposition samples were collected in polyethylene buckets at all NADP sites from the network's inception in mid-1978 until June 1984, when the collection of the dry samples became optional. At the peak of sample collection in June 1984, 151 sites collected dry bucket samples. Although buckets lack many of the characteristics required for ideal dry deposition measurements, they may provide the best data available for large particle elements over large areas of the U.S. An investigation was carried out recently to show what degree of screening is necessary to remove contaminated samples from the data set. After removal of samples containing water and apparent contaminants, the data were separated into four data sets representing winter and summer seasons in eastern and western regions of the U.S. Mean dry fluxes of Ca, Mg, K, and Na were computed for each of the four data sets. The dry flux of Ca, which accounted for more than half of the dry deposited mass of these four elements, averaged 35 mg/m$^2$-wk in the eastern U.S. and 30 mg/m$^2$-wk in the west. Averaged over the whole country, summer and winter deposition rates of Ca were about equal. The spatial and temporal patterns for Mg were much like those of Ca. K dry deposition was greatest in the east, and in summer, while that of Na was just the opposite, with the highest rates in the west in winter.

**SAMPLING AND ANALYSIS OF HIGHER MOLECULAR WEIGHT TOXIC ORGANIC COMPOUNDS IN THE ATMOSPHERE AND IN DEPOSITION.** Thomas J. Murphy, Chemistry Department, DePaul University, 25 E. Jackson Blvd., Chicago, IL 60604.

A number of relatively non-volatile toxic organic compounds may be found in the vapor and/or particulate phases in the atmosphere, and in atmospheric deposition samples. They include such compounds as the PAHs, toxaphene, Dieldrin, PCBs and 2,3,7,8-TCDD. They can be transported long distances through the air and may have adverse effects at sites remote from their source. There are a number of problems in identifying and quantifying these compounds in environmental samples. These include: the low concentrations frequently present (1 ng/m$^3$ or less); the very large number of target compounds present in most samples; and the chemical reactivity of some of them. Thus sampling times are long, clean-up and isolation is time-consuming, and identification and quantitation are low through-put, operator-intensive procedures. Also, the limitation of our gaining an understanding of the atmospheric chemistry of these compounds is often the lack of appropriate samplers, rather than analytical methodology or detection limits. The present state of sampling and analyzing for these compounds will be discussed. The limitations of the sampling and analytical methodology need to be carefully considered when designing a program to sample this class of compounds in atmospheric samples, if the program is to be successful.
REAL-TIME MONITORING OF THE ATMOSPHERE USING FLOW INJECTION ANALYSIS.

Steven H. Hoke and Victor R. Rivera. U.S. Army Biomedical Research and Development Laboratory, Fort Detrick, Frederick, MD 21701-5010.

Some materials used for rocket propulsion are perchlorate-based and form HCl as one of the combustion products. Personnel associated with rocket firings can be exposed to short-term, relatively high concentrations of HCl. HCl can be present as a gas, as an aqueous aerosol, or as HCl adsorbed on solid particulate matter. In order to permit assessment to the health risks, all forms of atmospheric HCl need to be monitored on a real-time basis. This HCl monitor incorporates impinger and flow injection analysis principles. Approximately 1000 cc/min of air are drawn through a miniature impinger where the HCl is extracted into an aqueous phase. This aqueous phase is sampled continuously with a peristaltic pump. The pump delivers the sample to a flow cell containing a chloride electrode. The potential from the electrode is followed on a strip chart recorder. The response time of this monitor is about 3-5 sec and it can be calibrated in under 3 min. It appears to respond to all forms of HCl from 1 to 2000 ppm.


The National Atmospheric Deposition Program/National Trends Network (NADP/NTN) has been collecting precipitation samples throughout the United States since 1978. In 1985 the Mountain Cloud Chemistry Project (MCNP) began collecting cloud water samples in the Appalachian/Adirondack Mountains. The Illinois State Water Survey is in the unique position of analyzing the samples from these two complimentary networks for all of the major inorganic anions and cations. The purpose of this study was to investigate the chemical relationship between cloud water and precipitation samples. Annual averages for 1986 for both the MCNP and the NADP/NTN were compared and differences noted. In addition, average concentrations for the major constituents were compared for three selected sites. These sites are Whiteface Mountain, NY; Shenandoah National Park, VA; and Mt. Mitchell, NC. Finally, specific MCNP sampling events that coincided with a weekly collection period for the NADP/NTN for each of the three selected sites were used to examine the ratio of cloud water concentrations to the resulting precipitation concentrations. On the average, cloud water concentrations appeared to be at least 3-4 times higher than precipitation concentrations for NH₄⁺ and 2 times higher for SO₄²⁻, pH and most of the other major ions.


In May 1986 a series of measurements were begun at Mt. Gibbs (2000m MSL) and Mt. Mitchell (Commissary Ridge, 1760m MSL) in the Black Mountains of NC in order to characterize and quantify cloud deposition to these high elevation ecosystems. Frequency of cloudiness observed in 1986 exhibited a diurnal pattern with a maximum during early hour Early morning cloud events had low moisture content and were more acidic (volume-weighted mean pH 3.34) than longer cloud events associated with upper level disturbances. A modified Lovett's cloud water model (Atmos. Environ. 18, 361-371) was used to calculate deposition. Yearly deposition estimates for H, NH₄⁺, NO₃⁻, and SO₄²⁻ calculated from two well characterized events (known liquid water content and cloud droplet size distribution) were 1.5, 9.4, 38.5 and 87.6 kg/ha/yr (Stognier & Saxena, Environ. Poll. : In Press), respectively, in comparison to indirect measurements obtained from throughfall for both cloud and rainfall deposition of 1, 8, 20 and 80 kg/hr/yr. Between 40-70% of the deposition of NO₃⁻ and SO₄²⁻ measured in throughfall was due to cloud interception or dry deposition. Model sensitivity to wind speeds above ground level is part of the reason for the discrepancy between the calculated and indirect measurement of deposition. The need for carefully designed experiments incorporating direct measurements of throughfall canopy windfield and associated evaporation from needle surfaces for model validation will be discussed.
Preliminary Results of the Rocky Mountain Deposition Monitoring Project, Denise Link, USEPA, Denver, CO, Margie Bohn, Western Conifers Research Cooperative, Corvallis, OR, Larry Svoboda, USEPA, Denver, CO, and Richard Olson, Western Conifers Research Cooperative, Corvallis, OR.

The Rocky Mountain Deposition Monitoring Project (RMDMP) collects precipitation on a weekly basis at eight high elevation sites in the southern Rocky Mountains of Colorado and Wyoming. The purpose of the project is to characterize the spatial and temporal patterns of wet deposition and determine the effect of elevation on precipitation chemistry in the Rocky Mountain region. A network of five study areas has been established consisting of two wet deposition collectors located in the same alpine area separated by 2000 to 3000 feet of elevation. The RMDMP sites are operated as part of the National Atmospheric Deposition Program. Although average weekly precipitation amounts are consistently higher at higher elevations, deposition of sulfate does not seem to increase significantly with altitude. At a study area located near Steamboat Springs, CO, there is evidence to suggest that higher sulfate loading occurs at the lower site. The dominant ions are sulfate and nitrate. These ions are present in sufficiently large quantities to account for all of the free acidity.

Accumulation of Al, Cd, Cu, Pb and Se in the Tissues of Two Species of Fish from Lakes with Different pH Values, R. A. Stripp, M. Heit, and D. C. Bogen, U.S. Department of Energy, New York, NY 10014, and J. Bidanset, St. John's University, Jamaica, NY 11439

The effects of lake acidity on the accumulation of potentially toxic elements in the tissues of fish have been studied. The fish were collected in three lakes located in the North Branch of the Big Moose River drainage system of the New York State Adirondack Park Preserve. The lakes were circumneutral Moss Lake, pH 6.5 - 6.8; variable pH Lake Rondaxe, pH 5.8 - 6.7; and acidic Darts Lake, pH 4.9 - 5.4. The two species of fish collected from each lake were the omnivorous Catostomus commersoni (white sucker) and the more carnivorous Perca flavescens (yellow perch). The fish tissues analyzed were bone, gill, kidney, liver, and muscle. The elements measured by electrothermal atomic absorption spectrophotometry included Al, Cd, Cu, Pb, and Se.

Our results show that concentrations of Pb and Cd were significantly higher (P<0.05) in the bone, muscle, kidney, and liver tissues of the fish collected in the acidified lake. In addition, the yellow perch from the acidified lake contained significantly higher concentrations of Se in the muscle and liver. These fish were also significantly smaller than the fish collected from the other lakes. Aluminum concentrations were elevated in the gill tissues of both species from the acid lake relative to fish collected in the variable pH and circumneutral lakes. Copper concentrations were highest in the fish collected from the neutral lake. Possible mechanisms contributing to these differences in concentration will be discussed.


The stability of wet-deposition samples in a wet/dry collector with a 13-liter collection bucket lined with a polyethylene bag was determined for periods as long as 1 week. Individual storms with precipitation accumulations of 0.13 centimeter or more were subsampled daily. About 20 milliliters were removed and preserved for subsequent chemical analysis. Subsamples of each aliquot were preserved as follows: (1) addition of 15 microliters of ultrapure nitric acid for Ca²⁺, Mg²⁺, Na⁺, and K⁺ determinations; and (2) addition of 10 microliters of chloroform for Cl⁻, NO₃⁻, and SO₄²⁻ determinations. Subsamples were not preserved for pH and specific-conductance determinations; the pH and specific conductance were determined within 1 hour after the aliquot was removed from the sample. The cation and anion determinations were performed on a weekly basis. Preliminary data indicated that pH changes for individual samples were sometimes as large as 0.5 pH unit during the week. Concentration changes for cations and sulfate were minor unless dust, caused by high winds, was present during the storage period. Preliminary chloride and nitrate data indicate that concentration changes of 1 milligram per liter occurred during the

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A two year study by the Illinois State Water Survey, funded by the Baltimore Gas and Electric Company (BG&EE), has compared weekly and event precipitation sampling with a second year emphasis on organic acid contributions. The samples were collected at a BG&EE electric power substation. Over 90 precipitation events were recorded with 64 collections of sufficient volume to complete a comprehensive analysis. Event precipitation samples were sent to the Water Survey lab in the original collection bucket, as well as in high density polyethylene (HDPE) bottles. One 20 mL aliquot was removed at the site and preserved with chloroform and one 20 mL aliquot was sent unpreserved. Upon receipt, all precipitation samples were processed as described in the National Atmospheric Deposition Program/National Trends Network (NADP/NTN) procedural handbook and then refrigerated until analysis. A chemical profile included the major anions and cations, plus pH, conductance, and weak organic acid anions. Key findings revealed that in 100% of the samples, the organic acid levels were higher in the preserved aliquots. Mean acetate and formate concentrations of 0.46 mg/L and 0.54 mg/L, respectively, were determined. Field pH readings at the time of collection (mean of 3.95) agreed well with the lab preserved pH readings (mean of 3.93). The lab pH of the uppreserved bucket samples varied as much as 0.67 units higher (mean of 0.15 units) than the original readings made in the field. Differences in field versus laboratory pH measurements are discussed in relation to organic acid decomposition and dissolution of base metal cations.

WITHIN-EVENT VARIATION IN RAINFALL COMPOSITION. Frederic C. Laguerre, Department of Chemistry, University of Nebraska at Omaha, Omaha, NE 68182-0109

A within-event, sequential precipitation sampling apparatus has been constructed allowing the collection of rainfall fractions at regular rainfall depth intervals of 0.1 mm. The device uses a fraction collector, and separately measures rainfall pH, conductivity and temperature in an on-line flow fashion. Rainfall fractions are analysed for chloride, nitrate, sulfate and oxalate using a Dionex QIC and Fast-Anion column.

On at least one occasion, a plume was observed that resulted in increased concentrations of chloride and oxalate, and in conductivity. An hypothesis for a tetrachloroethylene (TCE) dry cleaning solvent origin of this plume has been developed. It has been reported that TCE reacts with hydroxide radical, forming oxalyl chloride, which in turn hydrolyzes forming oxalic acid and hydrochloric acid (C.J. Howard, 1976, J.Chem.Phys. 65,4771; R.B. Norton et al 1983, Geophys.Res.Lett. 10,517). Research is continuing at the present time to confirm this hypothesis.

ENDOR ON PRIMARY REACTANTS AND MODEL COMPLEXES OF PHOTOSYNTHESIS. Klaus Möbius, Martin Plato, Wolfgang Lubitz, Friedhelm Lendzian and Eberhard Tränkle, Departments of Physics and Chemistry, Free University Berlin, Arnimallee 14, D-1000 Berlin 33, West Germany

The X-ray crystallographic study of reaction center (RC) single crystals of the photosynthetic bacteria Rps. viridis and Rps. sphaeroides confirm the existence of bacteriochlorophyll (BChl) dimers which were postulated earlier to be the primary electron donors P960 and P870. Apart from the spatial structure of these dimers a knowledge of the electron density distribution in various electronic states is indispensable for an understanding of their functional properties.

For P970⁺ and P960⁺ the electron spin density distributions were obtained by ENDOR via the hyperfine couplings. The comparison between the EPR/ENDOR data of P870⁺ and P960⁺ in RC's and of monomeric BChl a⁺ and BChl b⁺ shows that the primary donors are supermolecules with more or less asymmetric spin density distributions over the dimer halves.

Theoretical spin and charge densities were calculated by an all-valence electron SCF method, RHF-INDO/SP, using coordinates from refined X-ray data. These calculations yield asymmetry ratios similar to those observed. Consequences of the asymmetries in the charge distribution with respect to the observed unidirectionality of the electron transfer will be discussed.
ENDOR DETERMINED STRUCTURES OF SUBSTRATES AND ENZYME REACTION INTERMEDIATES. M. W. Makinen, Department of Biochemistry and Molecular Biology, The University of Chicago, 920 East 58th Street, Chicago, Illinois 60637

The conformations of methyl esters of L-alanine and of 5- and 6-fluoro-tryptophan acetylated at the amino group with 2,2,5,5-tetramethylpyrroline-1-oxyl-3-carboxylic acid have been determined by electron nuclear double resonance (ENDOR). The electron-nucleus distances within each spin-labeled derivative are calculated from anisotropic hyperfine coupling constants in the point-dipole approximation and show less than 5% discrepancy from X-ray data. Resonances are assigned to the α- and β-protons and the methyl ester group and are confirmed through deuterium substitution. These assignments with fluorine resonances serve as accurate structural probes of molecular geometry. Molecular conformations that are sterically compatible with the ENDOR distance constraints are determined by computer based torsion angle search calculations. Two distinct conformations of tryptophan derivatives are observed, the relative populations of which can be altered by change of solvent from polar to apolar. The molecular geometry of spin-labeled L-tryptophan bound in the active site of the acyl enzyme form of α-chymotrypsin has been also determined. In the acyl enzyme the ENDOR data show significant geometrical changes of the substrate through binding that are distinctly different from the molecule free in solution. The structural definition of the spin-labeled tryptophanyl moiety provides an important basis through which the stereoelectronic control of the enzyme catalyzed reaction can be understood. (Supported by NIH GM 21900).

ENDOR OF METALLOPROTEINS AT X-BAND AND O-BAND MICROWAVE FREQUENCIES. M. Werst and H. M. Hoffman

One of the common difficulties in the ENDOR studies of many metalloproteins is that the resonances of non-protonic elements in the site of interest frequently are obscured by the more intense proton ENDOR signal. This makes it difficult and often impossible to detect, assign and analyse the ENDOR response from other nuclei. The proton pattern is centered at the proton Larmor frequency, \( v_p \), which is proportional to the microwave frequency: at X-band and g-2, \( v_p \sim 14 \text{MHz} \). The overlap problem can be eliminated by performing the ENDOR measurements at Q-band (35GHz). At Q-band, g-2 corresponds to a magnetic field of 12500G and the proton pattern is shifted to a center frequency of \( v_p \sim 50 \text{MHz} \). In contrast, the center-frequency of the \( ^{14}N \), \( ^{17}O \) and \( ^{57}Fe \) etc. resonances is determined by the hyperfine coupling constant and they remain at 0-30MHz. Q-band measurements have been made on the copper sites of cytochrome oxidase from different organisms, the type I copper sites, of copper blue proteins and the iron sulphur cluster of reduced aconitase. These studies which have revealed distinct signals due to \( ^{14}N \) and \( ^{57}Fe \) nuclei not previously seen at X-band will be discussed.

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et al.: 30th RMC Program and Abstracts

Octaethyl-porphyrinato cobalt (II) (CoIIIEP) with various axial ligands (pyridine, THF, MeOH) and a superoxo derivative CoIIIOEP,pyO$_2$ (py = pyri-
dine), have been studied in frozen solutions using orientationally-select-
ted (I) ENDOR spectroscopy. The use of isotopically labelled ($^{12}$H, $^{15}$N) sol-
vents allowed unambiguous assignment of the proton and nitrogen hyperfine
(tensors of the axial pyridine ligand for both CoIIIEP,py and CoIIIOEP,
pyO$_2$ species. For the low symmetry case of the oxygenated complex, the
additionally measured ENDOR coupling offer the possibility to examine
the cobalt hf coupling at specific molecular orientations with respect
to the magnetic field. These results, together with the corresponding EPR
data (principal values of g- and $^{59}$Co hf tensors) are interpreted to re-
veal changes in the electronic structure and axial coordination geometry
in formation of the superoxo complex. — Literature: M. Baumgarten,
W. Lubitz and C.J. Winscom;

SATURATION RECOVERY EPR AND MOLECULAR MOTION. B.H. Robinson and T.
Sugano. Department of Chemistry, University of Washington, Seattle, WA 98195

We have used the density matrix treatment including the dynamics of Brownian rotational
motion to model the spin response to the Saturation Recovery (SR) EPR experiment. The method
of approach was to consider the nitroxide spin label (the N spin 1/2 form was used). The
Hamiltonian was transformed to the frame rotating with the electron and all terms stationary in
that frame were retained. The SR EPR experiment is in principle a simple experiment: the field is
set at $H_0$, a partially saturating pulse, with amplitude $h_p$, is applied for time $T_1$; after this pulse
the recovery signal is obtained with the observer of amplitude $h_0$. The FID components are
removed (experimentally and theoretically). The remaining components (whose amplitudes are
proportional to the observing amplitude, $h_0$) are terms on the order of $T_1$. The resulting signal
is a sum of exponentials, which depend on the dynamics, $H$, $h_0$, $T_1$, and observer phase. Our
theoretical studies develop a method that allows us to understand the dependence of the recovery
on the dynamics and (exploiting the dependence of the recovery curves on spectrometer conditions)

to develop methods to extract the dynamics information from the recovery curves. Supported in
part by grant DMB-87-06175 from the National Science Foundation.

Sensitivity enhancement in slow motion studies by monitoring longitudinal spin
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Slow molecular dynamics are commonly encountered in a wide class of materials such as
biological tissues, polymers and mesophases and a strong demand exists for experimental techniques
able to ascertain knowledge of such viscous behaviours. Magnetic spectroscopies are widely used to
face the related problems and several methodologies have been proposing in literature. None the less to
date a number of flaws limits either the versatility or the practical implementation of the technique. To
quote, we recall that inhomogeneous broadening affects saturation-transfer experiments, while
time-resolved spectrometers are not commercially available and highly sophisticated in their set-up.
We describe two non-linear CW magnetic spectroscopies with the following features: i) high sensitivity in
slow-motion studies, ii) virtual independence from inhomogeneous broadening, iii) simple
experimental set-up. The first one, namely the D0ubly Modulated E.S.R. ( DOMESR ), employs with
respect to the customary ESR set-up a subsidiary static field modulation at frequency $v_m$ in addition
to the usual one at frequency $v_1$. When sweeping $v_1$, narrow dips are encountered any time the ratio
$v_2/v_1$ is a rational number. A suitable analysis puts into evidence that the linewidth of such dips is
essentially affected by longitudinal relaxation processes. The second spectroscopy, namely the
LONGitudinally Detected E.S.R. ( LODESR ), excites the spin system by using two MW radiations
with frequencies $v_1$ and $v_2$ respectively and detects the oscillations at the frequency $v_1 - v_2$ of the
longitudinal component of the magnetization. It is proven that the width of the spectral profile is related
to the longitudinal relaxation time. Novel experimental results, strongly confirming the sensitivity to
slow dynamics, are described in detail in an appropriate microscopic lineshape theory.
Recently a powerful new means of performing electron-electron double resonance was developed. It is based upon new two-dimensional Fourier Transform ESR methods, and may be referred to as 2D-ELDOR. This method has now been successfully employed for the study of spin relaxation and motional dynamics. Examples will be given for using 2D-ELDOR to quantitatively measure Heisenberg exchange rates, $\omega_{Hei}$ and $\omega_{12}$ spin relaxation rates $W_p$ in several media. In a detailed study of the smectic phase of the liquid crystal 8S a dramatic dependence of $W_p$ on temperature and orientation of the director is found. This data is utilized to obtain the fundamental spectral densities to analyze for the motional dynamics. Unusual results, suggesting an important application of 2D-ELDOR to study liquid crystalline phase transitions will be discussed. The particular advantages of 2D-ELDOR over older methods, such as cw-ELDOR and ELDOR echoes will be discussed.

EPR CHARACTERIZATION OF METALLOPROTEINS RESPONSIBLE FOR THE OXIDATION OF ARSENITE TO ARSENATE. Russ Hille and Gretchen Anderson, Department of Physiological Chemistry, Ohio State University, Columbus, OH 43210

The several proteins responsible for the bacterial conversion of arsenite to arsenate have been investigated by electron paramagnetic resonance spectroscopy. These proteins include the enzyme arsenite oxidase (initially reported by Williams et al. (1986) Fed. Proc. 45, 1660), the Type I (blue) copper protein azurin and cytochrome c553. On the basis of nitrogen- and helium-temperature EPR, the arsenite oxidase is found to be a molybdenum-iron/sulfur protein, and is responsible for the initial oxidation event. Reducing equivalents thus obtained are transferred to azurin, which in turn reduces the cytochrome c553. The ultimate acceptor of these equivalents is presumably molecular oxygen (via the terminal cytochrome oxidase of the organism). The kinetic and thermodynamic interactions of the components of this small electron chain are discussed. Among the important conclusions of this work is the demonstration of the first physiologically well-defined role for an azurin protein.

SPECTROSCOPIC STUDIES ON THE ACTIVE SITE OF GALACTOSE OXIDASE
James W. Whittaker and Mei M. Whittaker, Department of Chemistry, Carnegie Mellon University, Pittsburgh, Pennsylvania 15213.

Isolation of homogeneous and stable redox modifications of the fungal copper enzyme galactose oxidase has made possible detailed spectroscopic characterization of each of the forms for the first time. The form of the enzyme which has previously been extensively studied by EPR spectroscopy has been characterized as a catalytically inactive species which can be converted to a fully active form by mild oxidants. The active form of the enzyme has been shown to contain a unique, EPR-inaccessible cupric center which appears to be spin-coupled to a free radical site associated with an oxidized ligand. The magnitude of the antiferromagnetic exchange coupling between the metal and radical sites has been estimated to be $-2J > 200$ cm$^{-1}$ by SQUID susceptibility studies. By uncoupling the spins, it has proven possible to convert the enzyme extensively to a form in which the ligand radical signal can be studied by a combination of EPR, optical absorption and CD spectroscopies, contributing to mechanistic insights for this novel Cu active site relating to its substrate and ligand interactions.
Nitrous oxide reductase (NOR, 8 Cu/M₉ 140,000) is a novel copper protein isolated from denitrifying bacteria. Four spectroscopically distinct forms of the enzyme were observed, furthermore a protein from a mutant strain unable to reduce nitrous oxide (2 Cu/ M₉) could be isolated. Spectroscopic data including UV/VIS, Resonance Raman and EPR suggest a novel type of copper chromophore. The most active form (I, purple) exhibited an intense band at 540 nm (14 m²mol⁻¹cm⁻¹), upon reduction in the absence of dioxygen NOR I was converted to the blue form III with a broad maximum at 660 nm (6.1 m²mol⁻¹cm⁻¹). At X-band NOR I showed an axial type of EPR signal with g_I 2.16, g_II 2.03. A hyperfine pattern of seven nearly equidistant lines (A_I 3.83 mT) was resolved between 5-110 K. The blue form III revealed a broad and featureless EPR signal at 9.32 GHz with g_I 2.16, g_II 2.06. The EPR signal of the mutant protein (NOR V) had features also observed in the spectrum of NOR I. In the g_II region only four lines with A_I 3.55 mT could be resolved at X-band. Although only 30-40% of the copper determined by AAS were EPR-detectable we did not observe a g_I 4 signal at half-field. In further investigations to elucidate the individual Cu sites in the different forms of NOR we applied EPR spectroscopy at higher (34 GHz) and lower (2.4-3.5 GHz) frequencies. Furthermore, small ligands such as CO, NO, N₃⁻ or CNN⁻ were used to perturb the coordination sphere of the Cu centers. On the basis of these experiments a structural model for the active site of NOR is presented.

We report progress in the development of a low frequency imaging electron resonance (ESR) spectrometer for in vivo oxymetry. Hardware modifications have involved a redesign of the demodulation system replacing a superheterodyne with a homodyne system. We have implemented an amplification system with high dynamic range further stabilizing the system against mouse motion. More detailed evaluation of the role of feedback stabilization can be demonstrated under these circumstances. The addition of a computer controlled data acquisition system has added to the flexibility of the system for data acquisition and made possible the implementation of two-dimensional spectral-spatial imaging algorithms. Progress in this area will be detailed. Spectra taken under the new operating conditions will be demonstrated with its improved signal to noise ratio in modest data acquisition times (tens of seconds). Improved oxymetry will be demonstrated.

Magnetic resonance experiments of high temperature superconductors will be discussed with special attention given to EPR studies. Historically, magnetic resonance studies have been important in determining the properties of superconductors. The microwave induced Josephson effect and magnetic phenomena, Meissner effect and vortex states are important considerations in EPR experiments. It is possible to detect intrinsic paramagnetism and conduction electrons in superconductors. Paramagnetic doping can be used to probe the influence of paramagnetism on superconductor properties. The EPR spectrum of the paramagnetic impurity may be sensitive to the superconducting transition and reveal information about the superconducting state. A review of these types of experiments on Y-Ba-Cu-O and La-Sr-Cu-O high Tc superconductors will be presented.
The microwave absorption of the YBa$_2$Cu$_3$O$_{7-x}$ high temperature superconductor has been studied by electron spin resonance (ESR). The responses are related to the development of the superconducting phase by examination of samples after each of three heating stages in the sample preparation process. An apparently axially symmetric g = 2 signal (g$∥$ = 2.24, g$⊥$ = 2.05) is seen which is assigned to dipole broadened Cu$^{2+}$ impurity phases Y$_2$BaCu$_2$O$_{5}$, BaCuO$_2$ and possibly others. In early stages of the sample preparation process the g = 2 signal is observable to 4 K while at later stages it disappears below the superconducting transition temperature, T$_c$. A low field non-resonant absorption is also seen for samples cooled in a K$_6$ field which has a derivative maximum, (d$x^"$/d$\psi$)$_{max}$, which is approximately characteristic of YBa$_2$Cu$_3$O$_{7-x}$ and it disappears above T$_c$. It is due to magnetic flux trapping by superconducting current loops in clusters of weakly coupled Josephson junctions. The field at which (d$x^"$/d$\psi$)$_{max}$ occurs decreases with successive stages in the sample preparation process: this suggests that the area of the superconducting clusters is increasing during the preparation process. This low field microwave absorption is also extremely sensitive to small amounts of a superconducting phase and it is estimated that nanogram quantities can be detected.


Flux exclusion by a type II superconductor in a constant magnetic field will induce magnetic field inhomogeneities. If material with an EPR spectrum is placed in close proximity to the superconductor, EPR imaging can be used to measure the spatial distribution of the induced magnetic field inhomogeneity. The magnetic susceptibility of a powder sample of the high-temperature superconductor YBa$_2$Cu$_3$O$_{7-x}$ was measured with a vibrating sample magnetometer and had an exponential temperature dependence of 5*10$^{-10}$ (T/400) emu/gm between 5 and 75 Kelvin at an applied field of 3250 G. An 800 micron i.d. capillary was filled with the superconducting powder and placed in the center of a 3 mm i.d. quartz EPR tube. Powdered fusain coal (g$^2$, peak-to-peak line-width of 2.2 GHz at 77 K) filled an annular volume between the capillary and EPR tube. Two-dimensional EPR imaging was done at X-band using a projection reconstruction technique with a constant field gradient of 100 G/cm. Images were taken at temperatures between 30 and 115 K with the image plane and static field perpendicular to the capillary axis. The theoretical spatial pattern of image distortion (cos(2*theta)/r**2) was observed, and its amplitude increased at lower temperatures as expected. Computer simulations showed good agreement with experiment. This research was supported in part by NIH Grant RR-01811 and the Servants United Foundation.

MICROWAVE ABSORPTION IN HIGH-T$_c$ SUPERCONDUCTORS. Robert N. Schwartz, Daniel Rytz, and Kevin W. Kirby. Hughes Research Laboratories, 3011 Malibu Canyon Road, Malibu, California 90265.

The X-band microwave response in the g=2 region and near-zero magnetic field in the new high-T$_c$ superconducting materials La-Sr-Cu-O, Y-Ba-Cu-O, and Bi-Sr-Ca-Cu-O will be reported. The results of measurements on both single crystalline and polycrystalline samples will be presented. These studies indicate that the electron paramagnetic resonance (EPR) of the local moments associated with magnetic rare-earth ions provide an atomic probe of the electronic structure in both the normal and superconducting state. In addition, our studies suggest that the non-resonant microwave magnetosorption near-zero magnetic field provide a sensitive as well as convenient tool for detecting and characterizing the superconducting state.
An electron paramagnetic resonance investigation has been conducted on single crystals of the superconductor $\text{YBa}_2\text{Cu}_3\text{O}_{7-\delta}$. An asymmetric resonance absorption is observed at a magnetic field corresponding to $g = 2.045$. It is found that the characteristics of this EPR spectrum do not change upon passage through the superconducting transition temperature but that some change occurs upon reorientation of the crystal with respect to the Zeeman field direction. The signal is tentatively assigned to divalent copper which is thought to be present in an occluded non-superconducting impurity phase. In addition, no low field absorption of a non-resonant nature, characteristic of the granular compressed powders of this material, was observed at temperatures either above or below $T_c$. Finally, a weak spectrum attributed to divalent manganese has been observed and tentatively identified as belonging to the superconductor phase.


ESR instrumentation has been efficiently used to study magnetic field dependence of the non-resonant microwave absorption in ceramic and single crystal high-T$_c$ superconductors. The onset of superconductivity is accompanied by a giant signal (absorption dip) centered at zero magnetic field. The signal develops hysteresis and exhibits relaxation when the magnetic field is stepped. Single crystals of $\text{YBa}_2\text{Cu}_3\text{O}_x$ show successively three distinct types of signals as the temperature is lowered from $T_c$ to 2.4K. They differ in widths, angular dependences and hysteretic properties. The relative intensities of the signals are affected by annealing treatments in oxygen or vacuum. The relevance of these findings to the nature of the new superconductors will be discussed.

ENDOR STUDIES OF FLAVINS AND FLAVOPROTEINS. Harry Kurreck, Norbert Bretz, Norbert Helle, Norbert Henzel, and Ellen Weilbacher. Institut für Organische Chemie, FU Berlin, Takustr. 3, 1000 Berlin 33, West Germany.

(a) ENDOR in fluid solution: ENDOR studies have been performed on a variety of substituted and/or isotopically labeled (protein-free) flavin radicals. Conclusions about the influence of different substituents on the spin density distributions within the isooxazine ring system could be drawn. (b) ENDOR in reversed micelles: Only the cationic species of the different protonation states of flavin radicals exhibit considerable stability. In order to study anionic or neutral radical states of the flavins special techniques, such as electrolysis and chemical modifications, have to be applied. Here it is shown that ENDOR investigations of flavin radicals in reversed micelles offer a very promising approach to overcome the stability problems met with flavin radicals. (c) ENDOR in solid solution: ENDOR experiments on the radical states of flavoproteins are restricted to studies in the solid state since the cofactors are immobilized through binding to the biopolymer. Powder-type ENDOR spectra have been obtained from the radical states of a variety of flavoproteins. From these spectra anisotropic and isotropic hyperfine data could be extracted. It is shown that information about enzyme/substrate interactions is accessible since these interactions cause spin density redistributions which are reflected in changes of the hyperfine data.
The study of sulfur containing heterocyclic aromatic compounds is important since they occur frequently in natural resources, such as coal, that are used by man. Sulfur atoms in their aromatic environments were investigated using Electron Paramagnetic Resonance (EPR) and Electron Nuclear Double Resonance (ENDOR) Spectroscopy. Sulfur containing molecules examined include Thiophene, Tetraphenylmethane, and Dibenzoanthracene. These compounds as well as others were adsorbed onto a silica-alumina catalyst surface, where the corresponding radical species were generated. ENDOR provided adequate resolution of hyperfine structure, which allowed calculations of the elements of the A tensor through computer simulations. An interesting aspect of this problem is that some sulfur containing compounds display considerable anisotropy in their g tensors as well as in their A tensors. This presented a problem of magnetic field dependence of certain peaks. To examine this problem, two-dimensional ENDOR techniques were developed where the amplitude of the signal could be plotted versus both magnetic field and nuclear excitation frequency. Analysis of the ENDOR results has allowed us to better characterize these molecules as well as the catalyst surfaces upon which these molecules are supported. (Work partially supported by U.S. DOE DEFG 22-84PC70782.)


The anisotropic hyperfine splittings of some polycyclic aromatic hydrocarbon (PAH) radical cations have been measured from simulations of their ENDOR spectra. An optimization procedure has been developed in response to the difficulty of simulating these ENDOR spectra and other complicated spectral systems efficiently. The procedure makes use of the simplex method of optimization. Because the simplex method does not require the calculation of derivatives of the objective function with respect to the spectral parameters, it is more flexible than many of the commonly used methods of spectral optimization such as least squares fitting, and is therefore applicable to a wide variety of spectra without modification. The optimization procedure is applied to the simulation of the powder-like ENDOR spectra of PAH radical cations including pyrene and coronene cation radicals, and is shown to produce better results than had previously been obtained by trial and error fitting with a considerable savings in the time needed for simulation. (Work partially supported by U.S. DOE DEFG 22-84PC70782.)

CORRELATION BETWEEN THE HYPERFINE COUPLING CONSTANTS OF DONOR NITROGENS AND THE STRUCTURES OF THE FIRST COORDINATION SPHERE IN COPPER COMPLEXES AS STUDIED BY 14N ENDOR - N$_2$S$_2$ COMPLEXES-. Masamato Iwaizumi, Ryo Miyamoto and Yasunori Ohba. Chemical Research Institute of Non-aqueous Solutions, Tohoku University, Katahira, Sendai, Japan 980.

Hyperfine interactions of the coordinating nitrogens in some Cu(II) complexes with N$_2$S$_2$ donor sets have been examined by ENDOR spectroscopy. The hyperfine coupling parameters obtained from so called single-crystal-like ENDOR of frozen solutions or powder samples diluted with diamagnetic complexes were compared with those for Cu(II) complexes with N$_2$, cis-N$_2$O$_2$, trans-N$_2$O$_2$ and NO$_3$ donor sets obtained in the previous work (Inorg. Chem., 15, 1546 (1986)). The magnitudes of the 14N coupling parameters for the N$_2$S$_2$ donor set are well explained by assuming that the sulfurs give stronger crystalline fields and stronger covalent bonding effects than nitrogen and oxygen. The 14N hyperfine coupling constants reported for some blue copper proteins, in which copper is coordinated by nitrogens and sulfurs, seem very anomalous compared with those obtained in the present work. Based on consideration of the correlation observed between the 14N hyperfine coupling parameters and the donor sets, it is shown that the copper ions in the blue copper proteins have abnormally hybridized unpaired electron orbitals.
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THE ANODIC OXIDATION OF P-AMINODIPHENYLAMINE: AN EPR AND ELECTROCHEMICAL STUDY

Roxanne Male and Robert D. Allendoerfer, Department of Chemistry, SUNY University at Buffalo, Buffalo, NY 14214-3094

The detection of the p-aminodiphenylamine radical cation (PAD•⁺) by EPR during the anodic oxidation of PAD and the assignment of the hyperfine coupling constants found in its EPR spectrum using simultaneous electrochemistry and electron paramagnetic resonance (SEEPH) techniques will be described. The PAD•⁺ radical arises from a comproportionation equilibrium and is only observed as a transient intermediate during the oxidation of PAD which eventually produces an aniline oligomer which itself has the narrow, single line EPR spectrum characteristic of partially oxidized polyanilines.

ESR STUDY OF THE INTERACTION OF CuL⁺ WITH ISOLATED MEMBRANES AND THE FREE RADICAL FROM RDR IN INTACT HL60 CELLS. Jana Narasimhan, Dawn Singleton, William E. Antholine, Christopher R. Chitambar, and David H. Petering, National Biomedical ESR Center and Department of Hematology - Oncology, Medical College of WI 53226 and Department of Chemistry, University of Wisconsin - Milwaukee, Milwaukee, WI 53201.

The tyrosyl free radical signal attributed to ribonucleoside diphosphate reductase, RDR, disappears under our conditions after treatment for 24 hours of human promyelocytic leukemia HL60 cells (0.6 x 10⁶ cells/ml) with 10μM 2-formylpyridine monothiosemicarbazonato copper II, CuL⁺. These HL60 cells treated with CuL⁺ are viable (>75%), but cell growth is substantially inhibited 24, 48, or 72 hours after addition of CuL⁺. The tridentate complex CuL⁺ also forms adducts with both thiol- and histidine-like Lewis bases, as detected by ESR, from presumably amino acid residues of peptides or proteins associated with isolated membranes from HL60 cells. The ESR signal for the cysteine-like adduct is decreased 15 minutes after addition of CuL⁺ to isolated membranes (10 μg/m protein per ml of packed membranes). The thiol concentration in isolated membranes, as determined by the DTNB assay, is higher in the absence than in the presence of 100μM CuL⁺. A hypothesis is developed whereby CuL⁺ inhibits the activity of RDR and cell growth by preventing uptake of iron in addition to or instead of direct interaction with RDR. The initial reaction of CuL⁺ involves oxidation of glutathione and cysteine amino acid residues of proteins associated with isolated membranes. The radical signal after addition of CuL⁺ models the decrease of the radical signal when iron is replaced by gallium transferrin. Supported by NIH Grants GM35472, CA22184, CA41740, and RR01008. D.S. received credit under the Off Campus Experiential Learning Program at Alverno College.

SIMULATION OF ESR SPECTRA FOR A CUPRIC BISTHIOSEMICARBAZONE COMPLEX IN ORIENTED ARTIFICIAL MEMBRANES. Marta Pasenkiewicz-Gierula, William E. Antholine, and James S. Hyde, National Biomedical ESR Center, Medical College of Wisconsin, Milwaukee, WI 53226.

An exact simulation of multi-frequency ESR spectra should yield all magnetic and motional parameters, but various approximations may be more realistic in the early stages. One of these is the recognition that because nitrogen superhyperfine couplings are nearly isotropic, they can be very easily introduced after a simulation that omits ligand nuclear parameters has been completed. A stick diagram is convoluted with the spectrum obtained without superhyperfine structure. A comparison of simulated spectra with experimental spectra for 3-ethoxy-3-oxobutylaldehyde bis (N⁴, N⁴-dimethylthiosemicarbazonato) Copper II, CuKTSM₂ in paraffin oil, as a function of temperature suggests that the overall line shape and line position throughout a range of motion from the rigid limit through the near rigid limit to fast motion can be accounted for by motion. There is little change in the ESR parameters. Simulated spectra for CuKTSM₂ using Moro and Freed's slow motion theory followed by inclusion of isotropic nitrogen superhyperfine couplings, with experimental spectra for CuKTSM₂ in oriented L-α-dimyrystophosphatidylcholine fit well for the magnetic field both parallel to and perpendicular to the membrane normal. Spectra, for which the magnetic field is both parallel to the membrane normal and perpendicular to the parallel axis of CuKTSM₂, can be simulated only if "wobbling" and an ordering potential are included. It is concluded that the structure and dynamics of membranes can be better understood through use of simulations that take into account the membrane potential that restricts the motion of CuKTSM₂. Supported by NIH Grants GM35472 and RR01008.
Electron spin echo envelope modulation (ESEEM) spectroscopy has proven to be a powerful method for studying hyperfine and quadrupolar interactions of nuclei coordinated to paramagnetic electron centers. Important areas of application include the study of nitrogen coordination in metalloproteins; surface adsorbate interactions of supported transition metals; and the electron density distribution on organic paramagnetic radicals important in photochemistry and in photoexcited triplet states. Analysis of the ESEEM patterns for $5\frac{1}{2}$, $1\frac{1}{2}$ spin systems in randomly oriented solids is usually performed using frequency spectrum analysis. ESEEM spectra are simulated by calculating the superposition of the two powder pattern quadrupolar spectra obtained when the isotropic hyperfine coupling adds or subtracts to the Zeeman field. Such simulations will accurately predict ESEEM frequencies but will usually not even give qualitatively correct modulation depths in the ESEEM waveform or reproduce the correct linewidths in the ESEEM spectrum. These depend on the anisotropic hyperfine interactions and are therefore important spectroscopic parameters which can reveal additional chemical information about the coordination complex. This provides the impetus for numerical studies of the ESEEM spectrum and time domain waveforms in which the pseudodipolar as well as the isotropic hyperfine and quadrupolar interactions are retained. Some preliminary numerical results of this study will be presented in this poster. In particular, we explore the importance of the relative magnitudes of the Zeeman, isotropic and pseudodipolar hyperfine, and quadrupolar interactions in determining the modulation depth of the ESEEM waveform. We also explore the ESEEM waveform and frequency spectrum in the presence of anisotropic hyperfine interactions with only a partial cancellation of the Zeeman field by the isotropic hyperfine coupling.

CLOSED-FORM EXPRESSIONS FOR ANISOTROPIC MAGNETIC RESONANCE INTENSITIES, D.B. Fulton and J.A. Well, Department of Chemistry, University of Saskatchewan, Saskatoon, Saskatchewan, Canada S7N 0WO.

We previously reported a technique for calculating magnetic resonance intensities (and energies) via perturbation theory (1,2), which yields general, closed-form expressions for EPR or NMR transition probabilities for anisotropic systems of arbitrary symmetry. Our technique is complementary to numerical diagonalization since it reveals which scalar forms, involving the spin-Hamiltonian's parameter polyads, contribute appreciably. Herein we describe some applications of this technique. We present expressions for "forbidden" transitions of single-spin and two-spin systems, which are compared with intensities calculated by exact numerical diagonalization of the spin-Hamiltonian and with experimental intensities. In our two-particle expressions we allow the quantization axis of one particle to be a function of the state of the other particle, which explains dramatic effects on intensities observed in some systems. We also show the mathematical equivalence of the one-particle and two-particle cases.


A CONVOLUTIONAL ANALYSIS METHOD FOR EPR POWER SATURATION AND RELAXATION TIME MEASUREMENTS. Randy L. Tyson and Michael K. Bowman, Chemistry Division, Argonne National Laboratory, 9700 S. Cass Ave., Argonne, IL 60439 USA

Most EPR spectra are represented as the convolution of an inhomogeneous broadening function with a homogeneous spin-packet lineshape. Such spectra are tedious to simulate in the field (i.e. frequency) domain. In addition, progressive saturation measurements are complicated by lineshape changes taking place as a result of saturation. We present a method of analyzing lineshapes and progressive saturation data in the time domain. Fourier transformation of normal first or second derivative EPR spectra yields a time domain signal which is the product and not the convolution of broadening functions. Least-squares fitting for lineshapes proceeds rapidly yielding $T_1$ directly. Progressive saturation data yield the saturation parameter directly. Examples of convolutional analysis on EPR spectra of a nitroxide and on chlorophyll micelles are shown. Convolutional analysis is much simpler and more accurate for digitized EPR spectra than the traditional methods.

This work was supported by the U.S. Department of Energy, Office of Basic Energy Science, Office of Basic Energy Sciences, under Contract No. DE-AC02-76CH00016.
EPR SPIN-HAMILTONIAN PARAMETERS FOR CRYSTALLOGRAPHIC SITE SYMMETRIES.
Dennis G. Mc Gavin, Chemistry Division, Department of Scientific and Industrial Research, Private Bag, Petone, New Zealand.

The EPR spin-Hamiltonian parameters appropriate for all crystallographic site symmetries for a paramagnetic ion are given in chart form. The symmetry classes are arranged to reveal the hierarchy of site symmetries from highest to lowest. Within each class, conventional cartesian axis directions are shown diagrammatically, including all alternative axis conventions for cubic and trigonal classes. Information given for each class includes the forms of the electronic Zeeman interaction matrix $\mathbf{n}$ and the second-degree zero-field interaction tensor $\mathbf{D}$ (traceless), and a list of non-vanishing coefficients of Stevens' operators. In most cases the parameter sets are not unique: parameters whose sign is not fixed are indicated, as are parameters which may transform linearly amongst themselves. Full details of the linear transformation equations are tabulated in J. Magn. Reson., 74, 19-55 (1987).

GENERATING FUNCTIONS FOR ANGULAR MOMENTUM TENSOR OPERATORS. Harvey A. Buckmaster, Department of Physics, The University of Calgary, Calgary, Alberta T2N 1N4, Canada and Sam A. Marshall, Department of Physics, Michigan Technological University, Houghton, MI 49931, U.S.A.

There exist many tabulations of angular momentum tensor operators $T_k^L(J)$ in both symmetric and asymmetric formats. Unfortunately, typographic errors mar these tabulations. Recently, Marshall et al.* have described a program to compute these tensor operators $T_k^L(J)$ for $k \leq 10$ which enables users to create a realizable compilation. The availability of this program has enabled us to develop generating functions for $T_k^{L-1}(J)$ where $1 \leq k \leq 6$ which simplifies the computational time required. Expressions for both the symmetric and asymmetric formats are given.


TEMPERATURE- AND TIME-STABILITY STUDY OF THE DEHYDRATION MECHANISMS IN CA-MONTMORILLONITE. Jadwiga Kudrynska, Thomasz Dulczmal, and Harvey A. Buckmaster, Department of Physics, University of Calgary, Calgary, Alberta, Canada T2N 1N4

The aging of hydrated Ca-montmorillonite clay samples doped with Mn$^{2+}$ impurity ions has been investigated using 9 GHz CW EPR. It is shown that these clay samples are unstable in air when characterised by their EPR g-value and linewidth $\Delta E_{pp}$ parameters and are extremely sensitive to the storage pressure. The EPR linewidth temperature dependence was investigated in the 20°C to 180°C interval. Up to the 120°C, random tumbling of Mn(H$_2$O)$_{24}^{2+}$ complexes narrows the EPR spectral lines. Above 120°C, where the dehydration process decreases the interlayer spacing to below 1.2 nm, rotational modulation relaxation is responsible for significant further line narrowing. Storage and measurement of samples below atmospheric pressure shifts this process to lower temperatures.


Electron paramagnetic resonance measurements at 10K have been made on synthetic zircon irradiated with x-rays at 77K. Several previously unknown unstable paramagnetic centres are observed. These centres are not produced by irradiation at room temperature. Two of these centres show large zirconium hyperfine structure from the 11.2% Zr-91 isotope (I = 5/2). With the magnetic field aligned along the c-axis (the unique axis) these centres can be characterised by the following: centre(A) $g = 1.7818$, $A(Zr-91) = 92.4$ Gauss; and centre(B) $g = 1.8227$, $A(Zr-91) = 31.2$ Gauss. The angular dependence of the resonances shows that centre(A) has four magnetic sites and suggests a defect $\text{ZrSiO}_4\text{Mn}^{2+}$ has almost all sites equivalent indicating tetragonal symmetry. The intensity ratio of centre(A): centre(B) is approximately 1:1 and appears to be independent of
Cu²⁺ doped Na-A, K-A, Ca-A and Na-X zeolites were studied using the electron spin echo modulation (ESEM) method. In both hydrated and dehydrated samples ⁷¹Al modulation has been observed. The time domain ESEM traces were Fourier transformed (FT) and analyzed in the frequency domain. All FT-ESEM spectra of the hydrated samples showed a single peak at the Larmor frequency of ⁷¹Al, indicating that the Zeeman interaction is dominant and that the ⁷¹Al quadrupole and hyperfine interactions are relatively small. Considerable changes in the spectrum appear upon dehydration. Several frequencies, significantly different from the Larmor frequency appear and the spectrum depends on the major cation present. Calculated spectra showing the effects of the various parameters of the ⁷¹Al nuclear Hamiltonian on the FT-ESEM powder spectrum are presented. These spectra were calculated using Mims' general equations for the echo intensity, where the eigenvalues and eigenvectors were obtained using exact diagonalization of the nuclear Hamiltonian. Both hyperfine and nuclear quadrupole interactions were taken into account. Comparison of such calculated spectra with the experimental spectra provided the isotropic hyperfine interaction constant and the quadrupole coupling constant for the dehydrated zeolites.

EPR STUDIES OF MAGNETIC ANISOTROPIES OF LAYERED PEROVSKITES
[C₆H₅(CH₃)₂NH₃]₂CuX₄: Baldev R. Patyal, Department of Physics, and Roger D. Willett, Department of Chemistry, Washington State University, Pullman, WA 99164-4630.

Title compounds [C₆H₅(CH₃)₂NH₃]₂CuX₄ (X = Cl, Br) form a series of two dimensional ferromagnetic insulators. EPR studies of these compounds have provided a novel method of extracting the anisotropic exchange D, the antisymmetric exchange D and the interlayer exchange J. Single crystal EPR data has been taken on several compounds in the series mentioned above. Results will be presented and their agreement with static measurements will be compared.

DYNAMICS OF DNA: AN EPR SIGNATURE
A. Spallenstein, E.J. Hustedt, P.B. Hopkins and B.H. Robinson, Chemistry, University of Washington, Seattle, WA 98195

The structural heterogeneity of duplex DNA suggest that the dynamics may play an important role in the processes of transcription recombination. Experimental studies of base sequence effects has been inhibited by the lack of a technique which focuses on a specific location in a given sequence. EPR is well suited to detecting sequence dependent DNA dynamics but requires a method for the site-specific introduction of a paramagnetic probe. Such a probe must be non-perturbative to the native DNA structure yet correlated to the motions of the bases. We have recently synthesized a spin-labeled derivative of thymidine, T⁺, capable of being incorporated into oligomers via (automated) phosphoramidite synthesis. Characterization of the self-complementary DNA dodecamer 5'-d(CCGGAATT*CGCG) by NMR, UV-melting and CD demonstrates that this probe is non-perturbing. A hydrodynamic model for this dodecamer as a rigid cylinder are consistent with experimental EPR spectra indicative of a probe highly correlated with the motion of the base pair. Differential line broadening of imino proton resonances due to the presence of the EPR probe supports of the model of a localized probe. The probe T⁺ was incorporated into the hexadecamer 5'-d(GCGGAATT*CGCGCGC) which can self associate forming a nicked polymer of indefinite length. The EPR spectra of this material are indicative of a probe, immobilized well beyond that which could be accounted for by a 16-mer in solution. The EPR spectra do not show any rapid short-range internal motion, but rather are sensitive to the cumulative motions of many base pairs. Supported in part by NSF grant DMB-87-06175.

We have undertaken a theoretical investigation of the possible origins of the Electron Spin Echo Envelope Modulation (ESEEM) signal in $^{13}$C (98%) enriched pristine trans-polyacetylene. The Magnitude Fourier Transform of the 3-pulse ESEEM signal for $^{13}$C shows that the modulation occurs at multiple harmonics of the $13.5$ GHz Larmor frequency. The theoretical development is within the framework developed by Mims for a 3-pulse ESEEM signal. The interaction of the defect with the nuclei as defined by the local ENDOR signals seen for polyacetylene cannot account for the ESEEM results obtained. However, the experimental pattern of peaks at regular intervals can be explained by assuming that the spin defect has small but significant dipolar couplings to a large number of neighboring $^{13}$C (a matrix ENDOR effect). This phenomenon is only possible because of the extensive 1-dimensional delocalization of the spin defect. Our calculations modeling the ESEEM signal for a 1-dimensionally delocalized spin defect coupled to the $^{13}$C on neighboring chains give multiple harmonic patterns similar to the experimental results. Supported in part by NSF grant DMB-87-06175.

ISOPO EFFECTS ON SPIN LATTICE RELAXATION RATES IN PRISTINE TRANS-POLYACETYLENE: AN SR EPR STUDY. R. St Denis, E.J. Hustedt, C. Mailer and B.H. Robinson, Department of Chemistry, University of Washington, Seattle, WA 98195

We have examined the spin lattice relaxation rates, $1/T_{1p}$, for pristine trans polyacetylene (t-PA) prepared by the Shirakawa method. The data were obtained by SR EPR and compared to rates obtained by ESE. We have examined both the native form, (CH)$_3$, and the isotopically substituted forms, (CD)$_3$, (CD)$_2 CD$, and (CD)$_2 CH$, as a function of temperature. The relaxation rates for (CD)$_3$ and (CD)$_2 CD$ are consistent with a simple model which assumes that the defect relaxes in a manner analogous to relaxation of conduction electrons in simple metals. With the constraint that the spin density's modulation (i.e. diffusion) of the defect is restricted to one dimension. The presence of protons leads to an anomalous relaxation which is not explained within the framework of a simple Redfield relaxation matrix argument, and seems to be too fast to be accounted for by proton spin diffusion. The measured relative susceptibility of the EPR-visible species as a function of temperature shows no evidence for a departure from simple Curie-Weiss law for a single species. Supported in part by NSF grant DMB-87-06175.

AN AUTOMATED METHOD FOR PROPER MODULATION PHASE NULLING IN EPR AND ITS APPLICATION TO VARIABLE-FREQUENCY MODULATION ST EPR SPECTROSCOPY. F. Auteri, T. Conturo, A.H. Beth, C. Mailer and B.H. Robinson, Department of Chemistry, University of Washington, Seattle, WA 98195

Modulation of the DC magnetic field is universally employed in the acquisition of EPR spectra, including both linear and Saturation Transfer (ST) EPR. Modern two-channel lock-in analyzers produce two components which are set at angles $\phi$ and $\phi+90^\circ$ with respect to the modulation reference. Experimentally it is often desired to choose $\phi$ such that the quadrature signal is minimized, so that the in-phase signal exhibits the maximum signal to noise ratio. This is called phase nulling. We present a computational method for phase nulling the EPR signal, based on a least-squares based criterion for a minimized quadrature signal. The resulting formulae for the proper phase angle, $\phi$, and the standard error in $\phi$ are non-iterative and can be easily programmed to rapidly and automatically phase null EPR signals after acquisition. This method has application to ST EPR: variety of modulation frequencies can be phase nulled independently at each frequency. The application to ST EPR will be demonstrated. Supported in part by NSF grant DMB-87-06175.

RARE GAS MATRIX ISOLATION ESR AND ENDOR SPECTROSCOPY, Allan J. McKinley, Juliusz G. Radziszewski, and Josef Michl, Department of Chemistry, The University of Texas at Austin, Austin, Texas 78712-1167, (512) 471-1783

A system has been constructed to perform ESR and ENDOR spectroscopy of reactive species isolated in rare gas matrices. The design of the system and recent applications from our laboratory will be presented.
An EPR study of $SO_4^{2-}$ radicals in x-irradiated single crystals of $K_2LiH_2(SO_4)_4$ was performed in the temperature range of 77 - 300 K, at X-band. At least four inequivalent sets of four tetragonally arranged $SO_4^{2-}$ radicals were found in this material, which was expected to be a ferroelastic. For one set, the $g$-matrix was determined. The temperature dependence of one principal $g$ and of line intensity data confirmed the presence of a phase transition at 110 K.

MAGNETIC RESONANCE EXPERIMENTS ON SODALITES IN SODALITES, E.de Boer, University of Nijmegen, Toernooiveld 1, 6525 ED Nijmegen, The Netherlands, G. Geismar, University of Duisburg, Bismarckstrasse 90, D-4100 Duisburg, FRG.

Sodalites belong to the family of zeolites and consist of coupled $SiO_4$ and $AlO_4$ tetrahedra. The Si and Al atoms are located at the vertices of a truncated octahedron ($\beta$-cage). The general formula is Nax$[SiO_2 AlO_2]_i X_2$, where $X = Cl$, Br or I. When subjected to alkali vapour ionic sodium clusters, Na$^+$, and neutral metal clusters are formed. These clusters have been characterized by ESR and ESE (electron spin echo) measurements. The ESEEM (electron spin echo envelope modulation) spectra exhibit a doublet peak centred at about 3.70 MHz at 0.33 Tesla. ESEEM experiments on Na$^+$ in Gasodalite proved that these modulations are caused by sodium ions. Quantitative ESR experiments revealed that only one out of 10$^4$ $\beta$-cages are occupied by a sodium cluster. Therefore the modulations are attributed to anisotropic dipole and quadrupole interactions between the unpaired electron of the cluster and sodium nuclei in neighbouring cages. Two-dimensional motion $^{13}$Na experiments on the non-activated sodalites furnish the quadrupole parameters. The quadrupole interaction is smaller than the sodium Zeeman interaction, so that the ESEEM spectra show peaks at the sodium Zeeman frequency. The experiments suggest that the halide anions diffuse out of the $\beta$-cages on formation of the ionic clusters. The absorption spectrum of hydrated Cl-sodalite indicates mobility of the sodium atoms and/ or the water molecules.

EPR OF Gd$^{3+}$-DOPE SINGLE CRYSTALS OF Li$_{1-x}$Yb$_x$F$_4$, Lucjan E. Misia$^k$. Sushil K. Nier$^{*}$, and Pawel Nikolajczak$^{*}$, *Physics Department, Concordia University, 1455 de Maisonneuve Blvd. West, Montreal, Quebec H3G 1MB, Canada, **Department of Experimental Physics, Maria Curie-Sklodowska University, 20-051 Lublin, Poland.

Extensive X-band EPR measurements have been carried out on Gd$^{3+}$-doped single crystals of Li$_{1-x}$Yb$_x$F$_4$ ($x$ values anywhere from 0 to 1), covering the temperature range 4.3-290 K. The spin-Hamiltonian parameters (SHP) are evaluated by the use of a rigorous least-squares fitting procedure. The systematics of the SHP are studied both as functions of $x$, and of temperature, Newman's superposition model has been applied to the calculation of SHP. The temperature variation of SHP's has been explained to be predominantly due to spin-phonon interaction, and partially due to thermal expansion of the crystal lattice. Finally, the Gd$^{3+}$-Yb$^{3+}$ exchange interaction, averaged over the nearest and next-nearest neighbors, has been estimated, in Li$_{0.2}$Yb$_{0.8}$F$_4$, to be 3.8 GHz, using the molecular-field model and the $g$ shift in the paramagnetic host.
et al.: 30th RMC Program and Abstracts


The crystals of the olivine minerals, tephroite (Mn$_2$SiO$_4$) and fayalite (Fe$_2$SiO$_4$) containing manganese(II) and iron (II and trace of III) respectively, were synthesized. The fayalite and tephroite-composition glasses were prepared from these crystalline materials by splat-quenched technique. The electron paramagnetic resonance (EPR) of these glasses and powdered crystals were measured at room temperature. The g-factors of Mn$^{2+}$ in both glassy and crystalline environments ($g = 2.004$) were found to be the same, although the EPR linewidths (for glass, $AH = 290$ Gauss; for crystals, $AH = 287$ Gauss) suggested less clustering of paramagnetic Mn$^{2+}$ ions in the glass. The EPR parameters of Fe$^{2+}$ in synthetic fayalite glass ($g = 2.01$ and 6.00; $AH = 150$ G and 1375 G, respectively for the high and low field resonances) and powders and crystals ($g = 3.31$ and $AH = 900$ G) were, however, found to be different. The possible coordination states and the probable sites occupied by these metal ions in the two environments are discussed.


Three luminescence bands, centered approximately at 290, 450 and 650 nm, from high-purity synthetic silicas stimulated by 50 eV synchrotron photons has been quantitatively measured. Samples were divided into two sets. One set was irradiated by 137Cs gamma rays and another set was virgin samples. Then all the samples were exposed under 50 eV light from synchrotron. 50 eV photons stimulate more intense luminescence in pre-irradiated silicas than in virgin silicas. Increasing the exposure time to UV light on the same spot increases the luminescence intensity for both set of samples. The rate of increase of intensities of the luminescent bands decreased with increasing exposure. These results show that defects created either by gamma-ray radiation or by UV light enhance dynamic luminescence processes in silica. Electron Paramagnetic Resonance spectroscopy was used to determine the concentrations of paramagnetic centers, e.g. E$_{2}^{+}$ centers, introduced by gamma rays or UV light. We found that E$_{2}^{+}$ centers increase linearly with the increasing dose of 50 eV photons in virgin samples. We believe that more intense luminescence in pre-gamma-ray irradiated samples under 50 eV light exposure is due to more E$_{2}^{+}$ centers introduced into those silicas by the gamma-ray irradiation. The increase of luminescence intensity from same spot with UV exposure time are also attributed to the introduction of the E$_{2}^{+}$ centers by 50 eV photons in silicas. Possible defect-enhanced luminescence mechanisms will be discussed through electron-hole interactions with defect state in the bandgap.

MULTIFREQUENCY ESR AND ENDOR OF Cu(II) AND Ti(III) IN PERFLUORINATED IONOMERS. Shulamith Schlick, M. C. Alonso-Amigo, Lars Sjoqvist and Anders Lund. Department of Chemistry, University of Detroit, Detroit, MI 48221-9997 and Department of Physics, University of Linkoping, S-58183 Linkoping, Sweden.

The ligations of Cu(II) and Ti(III) in perfluorinated ionomers swollen by water and methanol has been studied as a function of cation concentration, temperature and solvent content. ESR spectra were measured at X- and S-bands. The specific ligation of the cations is very sensitive to the amount of solvent. In a wide range of cation concentrations isolated and aggregated ions have been detected. The interaction distance is ca. 5 Å for the aggregated ions and larger than ca. 10 Å for the isolated ions. ENDOR spectra of hydrogen, deuterium and fluorne nuclei associated with the paramagnetic Ti(III) center was measured in the temperature range 4-20 K. The swelling solvent was C$_{2}$D$_{6}$ and C$_{2}$D$_{6}$. Matrix ENDOR signals from all above nuclei were detected. Preliminary simulation of the F-matrix ENDOR line indicated the Ti-F distance of about 3 Å. Anisotropic splittings from the methyl protons were detected and a distance of 4.2 Å between the methyl protons and Ti(III) has been deduced. Deuterium splitting from the OD group of methanol was also detected. This is the first application of ENDOR spectroscopy to the study of ionomers. Extension of the method presented here to other systems is suggested.

Supported by NSF awards DMR-8718947 ROW (Polymer Progra) and INT-8610709 (US-Sweden Cooperative Research).
Semiconducting phthalocyanine type films are being used as vapor sensitive chemiresistor components of chemical vapor microsensors. These films function as chemical sensors by changing their conductivities as a function of the quantity of gas absorbed by the film. The mechanism of the change of conductivity is not well understood, but is known to depend upon the amount of gas absorbed and the morphology of the phthalocyanine molecules which make up the film. The molecular structure of the film is controlled to a large extent by the method of preparation. We have used the Langmuir-Blodgett technique to prepare ligand-substituted and transition-metal ion substituted phthalocyanine films. EPR spectroscopy gives a precise measurement of the order parameter of each film by detecting the transition-metal ion EPR signal. LB films of oxovanadium tetrakis(cumylphenoxy)phthalocyanine are found to be ordered similar to Cu(II) ion substituted LB films of the same phthalocyanine ligand which have an order parameter of -0.45 [M. D. Pace, W. R. Barger, and A. W. Snow, J. Magn. Reson. 75, 73 (1987)]. The significance of this order to film performance as a chemical microsensor component will be discussed.

A TWO-CHANNEL SUPERHETERODYNE SPIN-INDUCTION S-BAND SPECTROMETER FOR QUANTITATIVE ESR STUDIES. Cafero Franconi, J. Holowacz, and E. M. Staderini, Medical Physics Division, University of Rome at Tor Vergata, Via O. Raimondo, 00173 Rome, Italy.

We have developed a 2 GHz version of a true two channel, spin induction superheterodyne spectrometer, an X-band prototype of which has already been described (C. Franconi et al., J. Magn. Res. 59, 349, 1982), for assessing a low cost automated type of ESR readout device to be used as an analytical tool in the spin label methods of assay of biological species and in free radical dosimetry. Some useful features of this fixed RF frequency scheme are: a calibrated spectroscopical scale, the detection of both components of the spin magnetization vector both in polar (Modulus and Phase) and in cartesian coordinates (Absorption and Dispersion), easy high and low RF power studies, and effective noise averaging. The choice of a low RF frequency adds automation potential and low cost, together with the capability of handling lossy samples of large volume. A method of processing both components of the spin magnetization is given, which can be of use in quantitative assays and in automation of the readout, together with a novel method of modulation-detection, which allows the direct line intensity reading and the detection of true lineshapes, that are of paramount importance in quantitative ESR spectrometry.

THE DESCRIPTION OF S-STATE ION EPR SPECTRA USING SYMMETRY-ADAPTED GENERALIZED SPIN HAMILTONIANS. Harvey A. Buckmaster and Ramananda Chatterjee, Department of Physics, The University of Calgary, Calgary, Alberta, Canada T2N 1N4.

This paper provides a comprehensive review of the concept of a generalized spin Hamiltonian (GSH) and its application to describe the electron paramagnetic resonance (EPR) spectra of S-state ions in host lattices with various symmetries. The formulation of a GSH using double and triple spin angular momentum tensor operators and its decomposition into single tensor operators is discussed in detail. It is shown that it is advantageous to reformulate those GSH terms in this decomposition which describe the zero field splitting (ZFS) in terms of tesseral spin angular momentum tensor operators. It is then straightforward to include those ZFS terms which are allowed by various symmetries. Such GSH are called symmetry-adapted GSH(SAGSH).

These tensor operators are classified according to their functional argument as either polar or axial. Their properties under time-reversal, parity and Hermitian conjugation are developed. It is found that $00_0(S)_{0}^{0} = C_0(S)$ and $0S_0(S)_{0}^{0} = S_0(S)$ so all ZFS terms with $k$ both even and odd permitted by symmetry considerations are allowed contrary to accepted current opinion. Moreover $C_k(S) = C_0(S)$ and $S_k(S) = S_0(S)$ so these terms are also self-adjoint. This means that the SAGSH are also appropriate for the S-state ion gerdinum $Gd^{3+}(4f^{7})$ as given to familiarize the reader with this formulation. The implications of Kramer's theorem are also discussed.
Fast free-radical chemical reactions with rates of 0.1 to 50 MHz can be followed by polarization transfer in FT-EPR experiments. An M_g polarization pattern is set up across the EPR spectrum by two or more microwave pulses so that the polarization of each unpaired electron is related to its initial resonance frequency. Between 0.1 and 40 µs data, the EPR spectrum is recorded. The remains of the initial polarization pattern is used to correlate the final EPR frequency of each unpaired electron with its initial frequency. Any chemical reaction involving the free radical such as addition, decomposition, or electron transfer shows up as a characteristic pattern in the correlation spectrum. Reaction rates are measured by a number of variations of the classic Jeener-Ernst polarization transfer NMR experiment. Sequences will be described which maximize kinetic rate information and minimize data acquisition time. Experiments on electron transfer between chlorophyll and its radical cation will be described. Polarization transfer experiments yield rate constants on the order of 10^8 liters/mole/sec. Chlorophyll is an interesting case as the EPR spectrum consists of a single inhomogeneously broadened line.

This work was supported by the U.S. Department of Energy, Office of Basic Energy Sciences, Division of Chemical Sciences under contract W-31-109-Eng-38.

Pulsed EPR provides the opportunity to alter the spectral responses of a paramagnetic center by applying a series of microwave pulses to the sample. The pulses cause refocussing or coherent averaging of magnetic interactions and so-called "spin gymnastics". The objective is to produce a spectrum which exhibits the one spectral, relaxation or kinetic parameter one wishes to measure. Experiments in which trains of two or more microwave pulses have been used in the high-resolution study of paramagnetic defects in crystalline silicon dioxide will be discussed. Hyperfine and quadrupole parameters, as well as spin-spin, spin-lattice and cross-relaxation rates and motional effects have been measured for various Al, Ti and Ge centers. Modified three-pulse (Jeener-Ernst) sequences have been used to look for slow atomic motions in complicated EPR spectra.

This work was supported by the Natural Science and Engineering Research Council of Canada and by the U.S. Department of Energy, Office of Basic Energy Sciences, Division of Chemical Sciences under contract W-31-109-Eng-38.

A few years ago, photoacoustically detected magnetic resonance (PADMR) technique was proposed as a new detection method of ESR signals. When solid samples are irradiated with modulated microwave, a part of absorbed energy is converted into heat by nonirradiated relaxation process. The heat was propagated in the solid and transmitted periodically to the gas surrounding the surface of the solid. Since the periodic flow of the heat generates the fluctuations of pressure, these can be detected by a microphone. The thermal diffusion in the solid sample produces a time lag in the heat transmission. Therefore the time lag reflects the difference in the position of paramagnetic species in the solid.

In this study, we measured the time lag of paramagnetic species in multilayer solid samples by a Fourier transfer correlation PADMR technique.
We have built a loop-gap resonator for the optical detection of EPR (ODMR) at 5.0 GHz. The optical excitation of the probe and the detection of the phosphorescence are possible in three different perpendicular directions. The frequency of the cavity is adjustable over a range of about 500 MHz. The resonator can be used in the liquid helium temperature range. Compared to the previously used slow wave helix the larger B1 field homogeneity allows larger probe volumes and therefore leads to a considerable signal-to-noise improvement.

Using the well known ODMR spin locking sequence (π/2, τ, π/2) we have investigated the decay of the spin coherence on dibromobenzene (DBB) X-traps which are induced 26 cm below the host triplet exciton band by deuterated dichlorobenzene (DCB-d2) guest molecules in the chemically mixed molecular crystal DCB-d2/DBB. Raising the temperature from 1.5 K up to 4.2 K results in a thermally activated shortening of the T1D decay time. The obtained activation energy ΔE/κ = 13 cm−1 for that process supports our model of an energy funnel in which every guest molecule distorts four host molecules. The dephasing is then caused by hopping between neighboring DBB molecules within the funnel separated by energy barriers of 13 cm−1.

Following the development of bimodal inductors for ESR spectroscopy working at X-band (C. Francoini, Rev. Sci. Instr. 41, 148, 1970; C. Francoini, NATO Grant n. 294 Report, 1971) and of the reentrant cloverleaf model at L-band (C. Conciauro et al., J. Mag. Res. 2, 363, 1973) we have developed and given the fundamental tests to S-band hybrid spin inductors, developed to accommodate large volume, lossy biological samples. The Loop-Line Resonator (LLR) is a single or multiple thin wire loop, following the single coil resonator developed for the reflex detection scheme, which is brought to resonance at 2 GHz by a near 1/4 section of transmission line, either on air or on a fused quartz substrate, whose shortened end is used for an Inductive coupling to the RF circuit. Results are presented for 2 GHz crossed coil systems. The Crossed Line Resonator (CLR) consists of two 1/4 sections of transmission line lying on perpendicular planes, inside which the sample is placed facing the high RF current shorted ends, which can be considered as the ground plane. Results are presented for CLRs working at 2 GHz. Optimization criteria are discussed for both inductors accommodating biological samples of various size, shape and nature, including alanine dosimeters.

Analysis of the electron spin echo envelope modulation in disordered solids can provide information about interactions which may exist between a paramagnetic site and neighboring magnetic nuclei. It is possible to extract, from the modulation, information on both nuclear hyperfine and nuclear quadrupole couplings. At the usual X-band microwave frequencies, the envelope modulation may be very shallow or unobservable for weakly coupled nuclei. However, the depth of the modulation arising from such weak interactions can be increased if the experiment is performed at a lower magnetic field. This fact, among others, was the motivation for the construction of an S-band (2.4 GHz) electron spin echo spectrometer. A detailed description of the spectrometer and its operation will be presented and results from preliminary experiments reported. (Work supported in part by U. S. DOE DEFG 22-84PC70782; Illinois DOE and Natural Resources, Coal Development Board, through CRSC; and U. S. NIH RR01811.)
SPECTRAL-SPATIAL EPR IMAGING OF PORTIONS OF SPECTRA. Sandra S. Eaton, Department of Chemistry, University of Colorado-Denver, Denver, CO 80204, Martin M. Maltempo, Department of Physics, University of Colorado-Denver, Denver, CO 80204, and Gareth R. Eaton, Department of Chemistry, University of Denver, Denver, CO 80208.

Spectral-spatial EPR imaging gives the EPR spectrum as a function of position in the sample. This technique permits imaging of samples in which the spectrum varies with position in the sample due to the presence of multiple paramagnetic species or because of spatial variation in line width or hyperfine splitting. The spatial resolution can be improved by imaging a portion of the spectrum. In spectral-spatial imaging, EPR spectra are obtained at a series of magnetic field gradients. When only a portion of the spectrum is imaged, incomplete information is obtained for peaks that are outside the borders of the image. Techniques for minimizing the impact of artifacts due to these peaks will be discussed.

EPR LINESHAPE AND RELAXATION FUNCTIONS FOR MOBILE SPINS ON FINITE 1-D CHAINS OF CHLOROPHYLL. Michael K. Bowman, Chemistry Division, Argonne National Laboratory, 9700 S. Cass Avenue, Argonne, Illinois, 60439

It is well known that mobile spins on ideal one-dimensional (1-D) chains have correlation functions characterized by long tails resulting in the characteristic 1-D EPR lineshape. We have developed formulas for the EPR lineshape and the 2-pulse electron spin echo relaxation functions under conditions appropriate for mobile spins on the 1-D chains in chlorophyll micelles. The spins are restricted to 1-D chains of several hundred chlorophyll spin echo relaxation functions molecules in length. The EPR lineshape is the convolution of a Lorentzian and Gaussian broadening function although the EPR lineshape is strongly motionally narrowed at high spin mobility with respect to an isolated chlorophyll radical. The spin echo decay is exponential over 90% of the decay. The form of both the lineshape and the spin echo decay function arises because on a finite chain, the spin correlation function does not decay to zero but rather exponentially approaches a finite value. Detailed lineshape and relaxation studies have yielded both the size of the 1-D domains and the spin mobility and electron transfer rates in chlorophyll micelles.

This work was supported by the U.S. Department of Energy, Office of Basic Energy Sciences, Division of Chemical Sciences under contract W-31-109-Eng-38.

SPIN-LABEL-SPIN-PROBE STUDIES OF SODIUM DODECYL SULFATE MICELLES. Christopher Stenland and Barney L. Bales, California State University, Northridge, CA. 91330.

We have embarked upon a program to study bimolecular encounters at the surface of micelles using the spin-label-spin-probe technique. The model to be studied is a micelle-solubilized nitroxide spin label interacting with paramagnetic ions via the spin exchange and the magnetic dipolar interactions. The first stage of such a study is to assess the relative importance of the exchange and dipolar mechanisms because the interpretation of the ESR line shape and linewidth changes induced by the interactions depends critically upon this assessment. In these first experiments, doxyl stearic acids and their methyl esters solubilized in aqueous sodium dodecyl sulfate solutions were employed as "labels" and cations Cu++, Ni++, Gd++, Mn++, and Co++ served as "probes". Control experiments with nonmagnetic cations show that only minor line shape and linewidth changes are introduced due to perturbations in the system. Comparison of the results due to the various ions suggest that spin exchange interactions dominate the line broadening rather than magnetic dipolar interactions thus the line broadening may be interpreted in terms of a bimolecular collision rate. Work supported by the U. S. Army Research Office.
A rapid and continuous method for measuring phospholipase A\textsubscript{2} activity using electron spin resonance (ESR) spectroscopy and a spin-labeled phospholipid as a substrate has been developed. The substrate, 1-palmitoyl-2-(4-doxylstearoyl)-sn-glycerol-3-phosphocholine, gives rise principally to a broad ESR line in aqueous solution due to strong spin-spin interactions, probably resulting from its micellar formation. Upon addition of bee venom phospholipase A\textsubscript{2}, the water-soluble product, 4-doxylstearic acid, is released which brings about a sharp three-line spectrum. Thus, the kinetics of phospholipase A\textsubscript{2} activity can be followed by monitoring the increase in the ESR signal amplitude of the three-line spectrum, which is linearly proportional to the amount of 4-doxylstearic acid produced; no separation of the product from the substrate is needed during the measurement. The rate of hydrolysis of 1 nanomole min\textsuperscript{-1} can be accurately measured within a 5-minute period of time in a sample volume of 100 µl. This new method should be useful for assaying phospholipase A\textsubscript{2} activities in various biological systems.

**STUDY OF PHASE SEPARATION IN SEGMENTED POLYURETHANES AND OF MISCELLIBILITY IN POLYMER BLENDS USING NITROXIDE SPIN LABELS.** Shulamith Schlick, Raymond D. Harvey and Wen-Pin Chang. Department of Chemistry, University of Detroit, Detroit, Michigan 48221-9987.

The goal of this research is to develop methods for the study of phase separation in complex polymers and of miscibility in polymer blends on a molecular level. The phase separation was studied in polyurethanes (PU) based on the aromatic isocyanate 4,4'-diphenylmethane diisocyanate (MDI), polymeric glycols such as poly(propylene glycol) (PCL) or poly(oxytetramethylene glycol) (PTMG), and 1,4 butane diol (BD) as chain extenders. The extent of phase separation was studied as a function of the molecular weight of the polyurethane, in the range 600 to 3000. The PU was labelled by reacting the isocyanate group with TEMPO; an endchain label was thus obtained. The miscibility was measured in PU crosslinked in the presence of spin labelled polyvinyl chloride (PVC). ESR spectra of the spin label as a function of temperature are very sensitive to the local morphology and can be analyzed in terms of "fast" and "slow" components. The heterogeneity of the local environment is also reflected in the lineshapes of motionally averaged spectra detected around 400 K. Spectra can be simulated by a Gaussian distribution of $g_{iso}$ and $A_{iso}$ values. The widths of these distributions can be used as indicators for the degree of phase separation in segmented PU and for the degree of miscibility in the blends.

Supported in part by the Army Research Office award DAAO3-86-G-0059.

**IN VIVO ANALYSIS OF NITROXIDE RADICALS INJECTED INTO SMALL ANIMALS BY L-BAND ESR TECHNIQUE.** S. Ishida, H. Kumashiro, N. Tsuchihashi, T. Ogata, M. Ono, and H. Kamada. Fukushima Medical College, Fukushima 960, Japan and Faculty of Engineering, Yamagata University, Yonezawa 992, Japan.

We developed an L-band ESR system equipped with a loop-gap resonator having an electric shield in the loop. Using this system, in vivo ESR measurements were successfully performed for nitroxide radicals of TEMPO, 4-amino-TEMPO, CPTO, and 3-carbamoyl-PROXYL administered into rats and the fate of those nitroxide radicals were studied. The measurements were carried out for the head of rats received intravenous injection of nitroxide radicals (1 ml of 0.01 M for CPTO or 3-carbamoyl-PROXYL, 0.2 ml of 0.05 M for TEMPO or 4-amino-TEMPO). It was found that the ESR signals from these radicals decreased with time and the values of half-life were determined as 430 s, 230 s, 49 s, and 31 s for 3-carbamoyl-PROXYL, CPTO, TEMPO, and 4-amino-TEMPO, respectively.
To examine the effect of several metal-nitroxy1 linkages on the magnitude of the electron-electron interaction, EPR spectra were obtained for two spin-labeled isoquinolines and nine spin-labeled pyridines bound to copper(II) bis(hexafluoracetylacetonate), cobalt(II) tetra(p-trifluoromethylphenyl) porphyrin, vanadyl bis(hexa-
fluoracetylacetonate), and chromium(III) tetraphenylporphyrin chloride. The values of the metal-nitroxy1 electron-electron coupling constant, J, for the isoquinoline complexes were about a factor of 10 smaller than for complexes of spin-labeled pyridines with the same linkage between the heterocyclic ring and the nitroxy1. The values of J are strongly dependent on the conformation of the linkage. Addition of a carbonyl group to the metal-nitroxy1 linkage caused the value of J to decrease by a factor of 10 to 70. When the ortho isomer could not form a chelate ring, the value of J for the copper complex of the ortho isomer was about twice as large as for the para isomer. A saturated (CH$_2$)$_2$ linkage to the 2-carbon of the nitroxy1 ring resulted in about the same strength of exchange interaction as an unsaturated (CH=CH) linkage to the 3-carbon.

Transition metal hexafluoracetylacetonate, Mn(hfac)$_2$, M = Cu, Ni, 
Mn, form linear chain compounds in which the radicals bridge two different metal ions through their two equivalent oxygen atoms. The compounds behave as one dimensional ferromagnets (copper) or ferrimagnets (nickel, manganese). Cu(hfac)$_2$(NITR) remains paramagnetic down to 1 K, indicating that the interchain interactions are weak, but Ni(hfac)$_2$NITR and 
Mn(hfac)$_2$NITR undergo three-dimensional order at ca 4 and 7 K respectively. The EPR spectra of Mn(hfac)$_2$NITR and Cu(hfac)$_2$NITR at room temperature show the characteristic one-dimensional behavior with apparent spin diffusion effects, which again is an indication of small interchain coupling, but at low temperature sizeable g shifts are observed, determined by short range order effects. The orientation of the g shifts in single crystals provided the directions of the easy, intermediate, and hard axes. These results were confirmed also by magnetic anisotropy data collected with an ac susceptibility apparatus.

Two-pulse electron spin echoes were obtained for copper transferrin and lactoferrin with carbonate or oxalate as the obligatory anion and for vanadyl transferrin and lactoferrin with carbonate as the anion. Comparison of the echo modulation in D$_2$O/glycerol-d$_3$ and H$_2$O/glycerol solutions indicated that the exchangeable protons in the vicinity of the metal were similar for the copper and vanadyl complexes. Deep nitrogen modulation was not observed for either vanadyl transferrin carbonate or vanadyl lactoferrin carbonate or for the model compounds vanadyl bis(hexa-
fluoracetylacetonate)L, L = imidazole or pyridine.
The spin label substrate tryptamine was used as a structural probe of the active site of rat brain Monoamine oxidase (MAO) A and bovine liver MAO B. When the reaction was monitored by electron spin resonance (ESR), line broadening effects indicative of binding with an apparent relation to substrate specificity of both enzymes was observed. The spectrum indicates relatively fast and nearly isotropic motion of the spin label. The dissociation constant and the number of binding sites are determined. The environment surrounding the catalytic sites and the mobility of the label are both characterized and discussed.

This work was supported by NIH Grant # RR 08247 and NSF Grant # RI 855438.

ESR DATING: PLEISTOCENE FOSSIL MOLLUSCS FROM SAN NICOLAS ISLAND, CALIFORNIA. 

The electron spin resonance (ESR) clock operates over geologic time as traps in a crystal structure filled with electrons and holes produced by natural ionizing radiation from the decay of uranium, thorium, and potassium (and their daughter products) and from cosmic rays. The number of these filled traps is measured with an ESR spectrometer. Their rate of formation is determined by measuring the concentrations of the radioactive elements in the sample and in the host matrix that contains the sample, or by imbedding dosimeters in the host matrix. An age is then computed by dividing the number of filled traps by their rate of formation. The technique has been applied to the dating of Pleistocene fossil molluscs from three marine terraces on San Nicolas Island, California. The results compare favorably with ages determined by the U-series method.

GAMMA-IRRADIATED FOODS: IDENTIFICATION AND DOSIMETRY BY ELECTRON PARAMAGNETIC RESONANCE SPECTROSCOPY. Marc F. Desrosiers, Center for Radiation Research, National Bureau of Standards, Gaithersburg, MD 20899

Electron paramagnetic resonance (EPR) spectroscopy was used to measure the production of free radicals induced by 60Co γ-rays in shrimp exoskeleton, mussel shells, chicken and fish bones. The EPR spectrum for irradiated shrimp shell was dose dependent and appeared to be derived from more than one radical. The bones of chicken and fish also gave characteristic EPR signals when exposed to γ-irradiation. It was found that the radiation-induced EPR signal in bone and shell could easily be distinguished from the endogenous EPR signal. Long term (4 months) stability studies at 20ºC showed no decay of the radiation-induced EPR signal. For bone measurements, a linear relationship was observed between the radiation-induced EPR signal intensity and the absorbed dose (1-5 kGy; 1 or 3 kGy are the FDA proposed upper limits). It was concluded that EPR measurements of bones and shells can be used to determine whether the attached meat has been irradiated and also at approximately what dose. The measurements indicate the feasibility of postirradiation dosimetry (PID) of meats when bones or shell are present.

FREE RADICAL COMPLEX OF ORGANOTIN WITH AMINOPHENOLS. AN ESR SPECTROSCOPIC STUDY OF A NOVEL ORGANOTIN RADICAL COMPLEX OF 2-AMINO-4-TERTIARY BUTYL PHENOL. Sandip K. Sur and J. P. Colpa. Department of Chemistry, University of Oregon, Eugene, Oregon 97403, USA; Department of Chemistry, Queen's University, Kingston, Canada K7L 3N6.

The thermal and photochemical reactions of organotin compounds with the 2-amino-4-tertiary butyl phenol have been observed by CW-ESR spectroscopy and by time-resolved CDEP measurements at room temperature. The stable hypervalent radical adduct generated from the ground state reaction of the aminophenol with hexaphenyl ditin has been characterized by ESR (g = 2.0025) visible and near-IR absorption spectroscopies. The radical adduct exhibits a broad charge transfer band at ~578 nm. Tin is probably coordinated in this radical adduct to the oxygen and nitrogen of the aminophenol. The ESR spectrum exhibits satellites from tin hyperfine couplings (A, 117.19 ~ 56.8 Gauss). A least-squares fitting of the isotropic ESR spectra as used to obtain the spin Hamiltonian parameters.
DYNAMICS OF NITROXIDE SPIN LABEL IN THE SLOW MOTION REGIME STUDIED BY SR EPR: ISOTROPIC DIFFUSION NEGLECTING PSEUDOSECULAR EFFECTS. T. Sugano and B.H. Robinson, Chemistry, University of Washington, Seattle, WA 98195

The effects of motion on a nitroxide radical can be directly observed by Saturation Recovery (SR) EPR. The recovery curves may be analyzed in terms of a multi-component form; each component may be characterized by a single exponential with a characteristic relaxation rate and amplitude. Using the density matrix formulation and including simple isotropic rotational motion we directly compute the SR EPR data. The theory produces the result as a sum of exponentials. We have considered only secular terms, and are able to develop simple formulae for interpreting the many rate constants in terms of the eigenvalues of the motional operator. The multi-component nature of the spin response can best be resolved by a series of experiments which take advantage of the experimental spectrometer parameters of observe field position, pump field position, pump time, pump power and observer phase. The simulations, when combined with robust data analysis methods, provide a methodology capable of interpreting the data in terms of the fundamental dynamics of the system. Supported in part by NSF grant DMB-87-06175.

ANALYSIS OF SR EPR DATA: EXTRACTING MOTIONAL DYNAMICS FROM MULTI-EXPONENTIAL RELAXATION CURVES USING TFA AND LP METHODS. T. Sugano, E.J. Hustvedt, R. St Denis, C. Maier and B.H. Robinson, Department of Chemistry, University of Washington, Seattle, WA 98195

The SR EPR signal from a nitroxide spin label undergoing motion is theoretically predicted to be a multi-exponential curve: the exponential decay rates of the individual components are directly related to only the dynamic process of the spin labeled molecule. The amplitudes of each component, however, while remarkable insensitive to the motion, are characteristic functions of the various instrumental parameters. Taking advantage of these facts, we have applied factor analysis to analyze SR EPR data. The probe of non-uniqueness of principal components factor analysis, has been solved by the use of target factor analysis (TFA). SR-EPR measurements have been performed on model compounds. Factor analysis of the acquired data set has generated two components. Comparing the values of the computed simulations of SR-EPR data, the (known) rotational correlation time has been recovered. The data analysis is compared to the method of linear prediction (LP) and a standard least-squares bi-exponential fitting. The results of the data analysis by TFA and LP prediction indicate both methods may be applied complementary and that a hybrid LP/TFA method can be developed to enhance sensitivity. Supported in part by NSF grant DMB-87-06175.

THE INTERPRETATION OF DATA FROM PULSED ELDOR SPECTROSCOPY. T. Sugano and B.H. Robinson, Chemistry, University of Washington, Seattle, WA 98195

The theory for the SR EPR signal is extended to the cases of pulsed ELDOR. In this type of experiment the field position at which the pulse is applied is different from that at which the observer is set. One can use this to remove some components in the relaxation recovery curves. The total response is treated as a sum of single exponentials. The direct computation of all the relaxation components of the associated SR EPR and pulsed ELDOR experiments is computed as a function of different rotational rates for the case of isotropic Brownian rotational motion. A single component dominates the pulsed ELDOR recovery curves when the pump and observing field setting correspond to different manifolds. This single dominant component may be related to \( T_{1N} \), the nuclear spin-lattice relaxation rate, developed via a first order time dependent perturbation (or Redfield) treatment, which shows that such a component can be understood as nearly being the \( T_{1N} \) given by simple arguments. We have found that this treatment may be extended into the ultra-slow rotational regime and is not limited to rotational rates around 10 MHz. Supported in part by NSF grant DMB-87-06175.

RESOLUTION ENHANCEMENT OF ESE-DETECTED ESR SPECTRA DUE TO ALKYL RADICALS IN IRRADIATED SOLID ALKANES
Tsuneki Ichikawa, Faculty of Engineering, Hokkaido University, Sapporo, 060, Japan

The electron spin echo-detected ESR spectra of alkyl radicals in \( \gamma \)-irradiated solid alkanes were measured at 77K as a function of the time of longitudinal relaxation, \( t \). The longitudinal relaxation was mainly caused by the spectral diffusion induced by the modulation of isotropic hyperfine coupling constants. The resolution of the spectra increased with increasing \( t \), because the spectral diffusion causes the narrowing of each hyperfine line. The observed spectra compared well with the theoretical ESR spectra calculated by utilizing a spectral diffusion model in which the spectral shape of each hyperfine line at \( t = 0 \) is equivalent to the distribution of the diffusion time in the spectral space.
RAPID SINGULAR VALUE DECOMPOSITION FOR TIME-DOMAIN ANALYSIS OF MAGNETIC RESONANCE SIGNALS BY USE OF THE LANCZOS ALGORITHM, Glenn L. Millhauser\textsuperscript{1}, Alison A. Carter, David J. Schneider\textsuperscript{2}, Jack H. Freed* and Robert E. Oswald, Department of Pharmacology, N.Y.S. College of Veterinary Medicine and *Department of Chemistry, Cornell University, Ithaca, N.Y. 14853, IBM Corporation, Data Systems Division, Dept. 48B/MS 428, Neighborhood Road, Kingston, N.Y. 12401, \textsuperscript{1}Address after September 1, 1988 Department of Chemistry, University of California, Santa Cruz, CA 95064.

Spectral decomposition techniques, such as LPSVD (Linear Prediction with Singular Value Decomposition) or HSVD (Hankel SVD), provide the most complete analysis of time-domain signals but often at the cost of prohibitive computational time and memory. We have developed a new approach for the spectral decomposition problem which is based on the Lanczos Algorithm (LA). In the past the LA has provided an effective means for solving slow-motional magnetic resonance spectra as well as other complicated problems in chemical physics. Lanczos-based Singular Value Decomposition (SVD) is outlined and we show how this fits into the HSVD scheme. We have applied the technique to several test time-series and we find that reliability is not diminished in the test cases. Traditional SVD methods require computational time of $O(N^3)$ and storage of $O(N^2)$. We show that our Lanczos approach requires computational time and storage of $O(N^2)$ and $O(N)$, respectively. For short time-series, this results in an increase in the computational efficiency by more than an order-of-magnitude. For longer time-series the computational savings will be even greater. The findings reported here may be the first step towards a spectral decomposition algorithm that requires only slightly more computer time than a Fast Fourier Transform.

NATURE OF THE DOMINANT DEEP TRAP IN AMORPHOUS SILICON NITRIDE. David T. Krick and P. M. Lenahan. The Pennsylvania State University, 227 Hammond Building, University Park, PA 16802. J. Kanicki, IBM Thomas Watson Research Center, P. O. Box 218, Yorktown Heights, NY 10598.

The importance of silicon nitride in microelectronic devices is well established. This dielectric is used in both nonvolatile memories and amorphous hydrogenated silicon thin film transistors. We report experiments into the nature of the dominant deep trap in amorphous silicon nitride films. We use both electron spin resonance (ESR) and capacitance versus voltage (CV) measurements to monitor the changes in the spin and charge states of this defect, respectively. We observe a strong correlation between changes in the density of paramagnetic silicon "dangling bond" centers and changes in the space charge density in nitride films subjected alternately to optical illumination and charge injection. Our results provide, for the first time, direct experimental evidence associating a specific point defect with the trapping behavior in amorphous silicon nitride. We also demonstrate directly and for the first time the amphoteric nature of this silicon "dangling bond" defect center.

NOVEL EXPERIMENTAL SCHEMES OF ELECTRON SPIN ECHO SPECTROSCOPY. Arthur E. Schweiger. Laboratory for Physical Chemistry, ETH-Zentrum, 8092 Zurich, Switzerland.

Pulsed EPR and ENDOR have proved to be exceedingly useful methods for exploring the structure and dynamics of paramagnetic species. In the last few years, a variety of new pulse techniques have been proposed to increase resolution, sensitivity and orientation selectivity, to reduce or to eliminate the instrumental deadtime, to disentangle complicated spectra, to shorten the acquisition time, to reconstruct hyperfine lines in disordered systems and to determine the number and distance of nuclei surrounding a paramagnetic center. This contribution presents some of the novel experimental schemes developed at our laboratory, in particular for solid state investigations. The standard electron spin echo and ENDOR pulse sequences have been supplemented by introducing - jumps of the static magnetic field along the laboratory $x$, $y$ or $z$ axis - large microwave or radiofrequency flip angles - hybrid schemes consisting of soft and hard microwave pulses - phase cycling and pulse swapping techniques - new detection schemes - optimized polarization transfer path ways.
Electron spin echo envelope modulation (ESEEM) spectroscopy has been used to measure weak nitrogen hyperfine and $^{14}$N quadrupole coupling in $^{14}$N and $^{15}$N labeled pyridine axially coordinated to bis(benzoylacetonato)copper ($\text{Cu(benzac)}_2$) in frozen solution. Continuous wave-EPR spectra of polycrystalline samples are a summation of all possible individual single crystal molecular orientation contributions. The anisotropy $g$ and hyperfine tensors are known, distinct sets of molecular orientations can be associated with a given resonant field. Using ESEEM, the set of molecular orientations in resonance may be selected by choice of magnetic field. The resulting ESEEM spectra reflect the angular dependence of the hyperfine energies of ligand nuclei. These spectra were simulated by locating a nitrogen in the axial position 2.5 angstroms from the plane of the Cu(11). The contact hyperfine interaction was found to be 1 MHz for $^{15}$N and 0.7 MHz for $^{14}$N. These parameters are consistent with an unpaired electron located in the copper d$_{x^2-y^2}$ orbital.


PFSEPR is a low power, technically straightforward pulse technique to resolve underlying hyperfine couplings from inhomogeneously broadened EPR lines. Saturating, "hole-burning" microwave pulses are followed in time by a magnetic field sweep to monitor the spread of saturation away from the original "hole". Satellite holes systematically occur and are related to electron-nuclear hyperfine couplings and to partially forbidden $\Delta m_I \neq 0$ EPR transitions. PFSEPR uses the standard microwave source of commercial spectrometers; there is no complex double resonance or high power microwave equipment. PFSEPR has an order of magnitude more sensitivity than CW ENDOR and the spectral resolution of high resolution EPR. Satellite holes have been observed due to hyperfine couplings of protons, deuterons, and liganding nitrogens of heme complexes [Falkowski et al, J. Mag. Res. 68 (1986) 453-468]. More recently PFSEPR features with large splittings from copper in stellacyanin and CuA of cytochrome c oxidase have been observed, where such metal hyperfine coupling is not resolved directly by EPR [Fan et al., J. Mag. Res. 76, (1988) 74-86]. The copper PFSEPR splittings and intensities have been related to electron-nuclear energy levels. Work is in progress to resolve nitrogen hyperfine couplings from copper complexes and to elucidate the metal-proton distance dependence of PFSEPR from protons that are weakly dipolar-coupled to metal centers.

**OPTIMIZATION AND IMPLEMENTATION OF BROADBAND COMPOSITE PI/2 AND PI PULSES IN ESR**. Richard H. Crepeau, Antonije Dulcic, Jeff Forrester and Jack H. Freed, Baker Laboratory of Chemistry, Cornell University, Ithaca, NY 14853-1301

In NMR much progress has been made in the use of composite pulses both for selective and broadband excitation. In pulsed ESR there also exists the need for composite pulses to achieve uniform excitation over a broad range of resonant frequencies in loopgap resonators and cavities operating with limited power or $B_1$. The restrictions to microwave frequencies and pulse lengths on the order of 10 nsec has prevented a similar exploitation of composite pulses since the previously reported pulse sequences are difficult to achieve with existing microwave hardware. By first solving for the spin distribution resulting from an arbitrary pulse sequence and then optimizing this result for a desired spin distribution, we have determined the optimum performance within the range of our computation methods. By restricting to experimentally obtainable pulse compositions and typical cavity response characteristics, we then show that near optimum results may still be obtained. The experimental implementation and characterization of the effectiveness of these pulse sequences in our pulsed 2D-ESR spectrometer is underway. We will report on design, implementation and new results obtained with these pulse sequences.

Nuclear modulation of the electron spin echo envelope has proven to be a useful tool in characterizing the environment of paramagnetic centers in disordered solids. Unfortunately the modulation observed from distant nuclei, especially protons, is often quite weak when the experiment is performed at the customary X band frequency. In order for modulation of the echo envelope to be observed, electron spin transitions to mixed nuclear states must occur. In general, this mixing results when the hyperfine field at a nucleus is comparable in magnitude but not colinear with the total effective field at the nucleus. For weakly coupled protons this condition is only marginally satisfied at X-band. Theory predicts that for such weak couplings the depth of the modulation is approximately proportional to the inverse of the square of the magnetic field strength. Thus an enhancement of the nuclear modulation depth is achieved by performing the experiment at lower magnetic field. Moreover, the tighter spacing of nuclear levels in lower magnetic fields causes pulse excitations to span more nuclear states. To these ends and others, we have constructed an S-band ESE spectrometer. An overview of the instrument and illustrative results will be presented here; a detailed description of the instrument and performance will be presented in a companion paper (Brown et al., this conference). (Work supported in part by U.S. DOE DEFG 22-84PC70782; Illinois DOE and Natural Resources, Coal Development Board, through CRSC; and U. S. NIH RR01811.)

TIME DOMAIN ENDOR STUDIES OF DISORDERED SOLIDS: P. J. Tindall, M. Bernardo, and H. Thomann, EXXON Corporate Research Laboratory, Route 22 East, Annandale, N. J. 08801

Spectral simplification, resolution enhancement, and sensitivity enhancement are well known advantages of multiple frequency techniques used in NMR. The ability to coherently excite and coherently transfer longitudinal or transverse magnetization among sub-levels of the spin system eigenstates is fundamental for the success of most of these experiments and is only possible with time domain pulsed excitation. In contrast to NMR, the most widely applied multiple resonance technique in ESR, the ENDOR experiment, has traditionally been performed in the frequency domain. However, recent advances in instrumentation have now made time domain ENDOR more feasible. The time domain analog of the CW-ENDOR experiment is magnetization transfer (MT) ENDOR using the Davies pulse sequence. MT-ENDOR has the advantage that the ENDOR enhancement does not depend on the ratio of the electron and nuclear T1 rates as it does in CW-ENDOR. Furthermore, time domain excitation also makes possible more complex double resonance experiments which depend on coherence transfer, such as CT-ENDOR and spinor ENDOR recently demonstrated by Kehring et al. The general applicability of these techniques to disordered solids will be governed by electron T1 and T2 (phase memory) times which are typically shortened by disorder effects. Fortunately, in many cases of interest, relaxation times for hydrocarbon radicals in condensed hydrocarbons are sufficiently long for successful magnetization and coherence transfer experiments even at room temperature. Experiments on transition metal ion complexes and metal clusters are possible at liquid He temperatures. Some recent time domain ENDOR results on isolated coal macerals, polyacetylene, and frozen solutions of transition metal ion complexes will be presented.
A critical overview of the present state-of-the-art of ICP-MS will be presented. Basic operating principles of the ICP, the ion extraction interface, ion optics, mass analyzer, and detector will be described. Recent research indicates possible instrumental ways to improve the performance of ICP-MS in areas such as stability, precision, and susceptibility to overlap and matrix interferences. Modification of ICP operating conditions permits determination of isotope ratios for elements such as K and Ca that are normally obscured by background peaks. These modified conditions also permit adjustment of the major ion composition of the ion beam to study mass-dependent space charge effects that have been proposed to be responsible for matrix interferences. The performance of ICP-MS as an element and isotope-selective detector for chromatographic separations will also be discussed. This combination permits speciation studies and use of separations for convenient removal of interfering species. Finally, emission lines from halogens in the vacuum ultraviolet can be observed efficiently through an optical sampling orifice like that used for ICP-MS. Chlorine and bromine can be determined at µg L⁻¹ levels by this technique.

Potassium has useful chemical properties for the study of geochemistry in ground water aquifers. Potassium has been proposed as an injectable tracer to determine the chemical interactions taking place at the water/rock interface. These experimental requirements suggest the use of inductively coupled plasma-mass spectrometry in the isotope ratio mode, employing isotopically enriched potassium, as the injectable tracer. This technique offers both the required sensitivity and the ability to make isotope ratio measurements. Naturally occurring potassium has a major isotope at mass 39 and minor isotopes at masses 40 and 41. Conventional inductively coupled plasma-mass spectrometry using an atmospheric pressure argon plasma, has its major isotope at mass 40; therefore, a direct spectral overlap exists for potassium measurement at mass 40, and since the ArH⁺ molecular ion has appreciable abundance, potassium isotope measurements at 41 are also precluded. As a result, it is not possible to make accurate isotope ratio measurements for potassium with a conventional argon plasma ionization source. Results of experiments with a conventional premixed air/acetylene flame ionization source are described.

The inductively couple argon plasma is noted for its ability to excite and ionize virtually every element in the periodic table. The recent availability of mass spectrometers which are capable of sampling ions from an ICP, coupled with the now historic capabilities of ICP-AES offer new potential for multielement determinations of geological materials.

Sample preparation consisting of an acid digestion using HF, HClO₄, HCl, and HNO₃ is useful for many materials including rocks, plants, coal etc. where resistate minerals, a Na₂O₂ sinter is used for a more complete digestion.

Solutions ranging in total salt content from 0.5 to 2.5% from the digestion are presented to separate ICP-MS and ICP-AES instruments. The ICP-MS provides basic coverage for 38 elements in a concentration range between 0.01 and 100 µg/g and ICP-AES for 22 elements plus those elements already illustrated in the sample. Of the 60 elements, 35 elements are detectable at one tenth crustal abundance.
The critical role of sample introduction in ICP/MS is becoming increasingly apparent as studies with controlled solvent and analyte loading in the plasma are carried out. With sample introduction strategies it is of particular interest to compare the interactions of the plasma with aerosols and vapors in both atomic emission and ion sampling modes. Extensive studies have shown that the overall effect of the interaction of the sample with the plasma is quite different in ICPAES and in ICP/MS. In this paper some key aspects of sample introduction strategies for ICP/MS will be discussed. The fundamental processes occurring during the aerosol/solvent vapor transport process will be described, as will the net influence of these variables on basic plasma properties. The influence of different solvent types on basic analyte transport properties will also be discussed, as will the effect of spray chamber temperature variations and possible use of a condenser to remove solvent vapor.

ANALYTICAL APPLICATIONS OF ETV-ICP-MS TECHNIQUE.
Ewa Pruszkowski and Richard D. Ediger.
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ICP-MS is recognized and widely used technique for elemental analysis. However, some matrices such as saline solutions, mineral acids, and biological fluids can present problems for the ICP-MS with a conventional introduction system. Therefore, experiments were conducted with the electrothermal vaporization-ICP-MS. The system described in this paper can handle small sample volumes, viscous samples, and reduce some polyatomic interferences, since removal of solvent or matrix can be achieved in temperature pretreatment steps. Benefits of the ETV-ICP-MS technique will be shown for the analysis of brines, acids, and biological fluids.


ICP-MS can be used successfully for the determination of trace elements (Y, REE, U, Th, Tl, and Pb) in geological materials following digestion with mineral acid mixtures. Accuracy was shown to be affected by non-spectroscopic interferences produced, in part, by the high salt composition of sample solutions. Doherty introduced a two-element (Ru-Re) internal standardization correction procedure to compensate for non-spectroscopic interference effects. Accuracy can be limited by the possible presence of analytes in acid-insoluble mineral phases. Although sample fusion is expected to be more effective in sample decomposition, the resulting solutions need to be diluted in order to minimize nebulizer problems and the effect of non-spectroscopic interferences, resulting in a degradation of determination limits. This paper examines the application of the Hildebrand high-salt nebulizer to the ICP-MS determination of Y, REE and other traces in solutions of fused rock samples. Analytical results for certified reference materials are presented and are discussed in terms of precision and accuracy. The effect of the high salt content of fused sample solutions are discussed in terms of signal drift, determination limits, non-spectroscopic interferences and the applicability of the internal standardization correction procedure.
NEW CHALLENGES FOR MINE WATER RESEARCH. J.W. McLaren, D. Beauchemin, K.W.M. Siu and S.S. Berman, Chemistry Division, National Research Council of Canada, Ottawa K1A 0R9 CANADA.

Since the installation of commercially available ICP-MS instrumentation (Perkin-Elmer SCIEX ELAN) in our laboratory in May 1984, methods have been developed for the determination of a large number of trace elements in a wide variety of marine materials including both seawater and freshwater samples, marine sediments, and biological tissues. The object of current research is to extend the already impressive capability of ICP-MS using two approaches: the development of new chemical procedures to increase the number of elements determined in saline waters, and the coupling of HPLC and ICP-MS to address important problems of trace metal speciation.

The certification of a new estuarine water reference material (SLEW-1) required the development of an ICP-MS method for the determination of arsenic and antimony, neither of which can be determined in saline waters either directly (as was possible for the river water reference material SLRS-1) or indirectly by the previously developed separation by adsorption on silica-immobilized 8-hydroxyquinoline. The new method involves a reductive coprecipitation with iron and palladium, and is also suitable for the determination of a number of other metals.

The chemical speciation of arsenic in the dogfish muscle reference material DORM-1 was determined by using ICP-MS in combination with ion pairing chromatography. It was established that the major species is arsenobetaine, which constitutes about 85% of the total arsenic.


Three different methods utilizing the broad capabilities of inductively coupled plasma-mass spectrometry (ICP-MS) were employed to analyze natural waters and associated suspended sediments. Natural water samples were filtered through a 0.4 micron polycarbonate filter and acidified to a pH of about 2. Suspended sediments in two size fractions, 0.2 to 63 micron and <0.2 to 0.001 micron were freeze dried and digested using microwave techniques. A semi-quantitative method was used to determine about 80% of the naturally occurring elements with accuracy of +/-15% in approximately 2 minutes. Analyte isotopes were chosen on the basis of their natural abundance and lack of isobaric interferences. Calibration curves based on a blank and a 6-element mixed standard were used to estimate the concentrations of 63 analytes. Quantitative determinations for 20 analytes were routinely conducted in less than 2 minutes. Selected analyte concentrations were verified using a stable isotope dilution technique. Results corresponding to all three methods for several natural water samples and their associated suspended sediments will be presented. Spike recovery results for the digested suspended sediments analyzed using the quantitative method ranged from 90 to 110 percent.

ABSTRACT NOT AVAILABLE
In recent years, the determination of low levels of the rare earth elements (REE) has become increasingly important. The unique chemical and physical properties of the Lanthanide group have resulted in their commercial exploitation particularly for the super conductor industry. The analysis of the REE by traditional techniques is often inadequate for modern requirements. IDMS can only be used for polysirotic elements and is a relatively slow technique. The complex emission spectra of optical emission ICP mean that a separation of the REE from their matrix is essential. ICP-MS by contrast offers low detection from limits for all 14 REE, simple spectra and a relatively fast analysis time. The only real problem with REE analysis by ICP-MS is the formation of light REE (and Ba) oxides which cause an interference on the middle and heavy REE. The magnitude of the oxide interference is typically insignificant at less than 1%. However in samples with a very high LREE:HREE ratio e.g. in REE minerals, or in samples with a high Ba content, oxide levels (and therefore corrections) may be significant. The use of doubly charged ions in REE analysis will be illustrated with reference to the analysis of some deep sea sediments containing particularly high Ba and low REE levels.

APPLICATION OF STABLE ISOTOPE TRACERS TO NUTRITIONAL STUDIES.
S.R. Kortyshahn, Gretchen Hill, Departments of Chemistry and Human Nutrition, University of Missouri-Columbia, MO 65211 and John R. Garbarino, U.S. Geological Survey, 5293 Ward Road, MS408, Arvada, CO 80002.

$^{70}\text{Zn}$, $^{65}\text{Cu}$ and $^{58}\text{Fe}$ were administered to rats in a pilot project for anticipated human nutrition studies. Purposes included verification of experimental design from a biological perspective and development of suitable analytical procedures. Isotope ratio determinations were used to detect deviations from normal abundances and thereby yield information on the behavior of test elements in treated animals. The three elements presented very different analytical problems. For Zn, isotopic ratios in solutions of rat feces could be measured after appropriate dilution with good precision (0.5-1%) and good apparent accuracy. For copper, apparent deviations from normal abundances which were concentration dependent were measured in animals which had received no isotope treatment. After chemical separation (APCD-MIBK extn.), behavior improved but ratios for untreated animals still differed significantly from normal abundances indicating the need for a further analytical study. Fortunately, these errors were small relative to deviations in treated animals and the measured ratios were useful. For iron, interferences from $\text{Aro}^+$ and $\text{AroH}^+$ on $^{56}\text{Fe}$ and $^{57}\text{Fe}$ prevented accurate isotopic ratio determination whether or not a chemical separation was used.

TRACE METAL DETERMINATIONS IN NBS BOVINE SERUM USING ICP/MS ISOTOPE DILUTION.

The ICP/MS has been applied to the determination of $\text{Mo}$, $\text{Mg}$, and $\text{Sn}$ in NBS Bovine Serum, SRM 1598, using stable isotopic dilution (IDMS). The ability of IDMS to eliminate inaccuracies due to variations in absolute signal intensities will be described. Aspects of accurate isotope ratio measurement, both instrumental and chemical, will be discussed. Chemical separations as well as problems relating to the chemical stability of sample solutions will be presented.

The isotopic ratios were measured in the scan mode. Samples of pure, natural abundance elements were run frequently throughout these analyses in order to correct for instrument mass bias in the measured ratio and drift with time. Blanks were low, representing 0.2% of the sample or less. Elemental concentrations determined ranged over three orders of magnitude (from ppm (Mg) to ppb (Mo, Sn) level). Spike levels of a few percent were reproducible, and gave precisions of 0.2% or better.
HIGH PRECISION MEASUREMENTS OF ISOTOPE RATIOS FOR IRON IN HUMAN BLOOD, John Erve, B.T.G. Ting and Morteza Janghorbani, Department of Medicine, University of Chicago, Chicago IL 60637

We have previously developed a complete analytical scheme for measuring stable isotope ratios for iron in human blood using the ICP-MS. We have now studied the overall precision and accuracy of these measurements. Our error analysis indicates that instrumental variation accounts for less than .5% of total error. In this presentation we will discuss 1) our chemical wet-ashing procedure, 2) the stability of the ICP-MS, and 3) calibration procedure. Results to date indicate that these measurements can be made with a precision and accuracy of better than 1%

DETERMINATION OF URANIUM IN ENVIRONMENTAL SAMPLES BY ICP-MS*

James F. Grohs and Mark H. Hollenbach
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ICP-MS enables the rapid determination of uranium in environmental samples. Because a substantial fraction of uranium is observed as \( {U}^6 \), it is imperative that the instrument be set up such that the percentage of oxide formed is constant throughout analysis or compensated for in some other manner. This can be accomplished in the following ways:

- Maintain precise control over the instrument operating conditions.
- Add \( {U}^6 \) to \( {U}^4 \) in the element equation.
- Use an internal standard with an oxide-forming behavior similar to that of uranium.

Results obtained using these techniques will be discussed.

*Work performed under the auspices of the U.S. Department of Energy, DOE Contract No. DE-AC07-86ID12584.

REACTION OF NITROGEN OXIDES WITH BLACK CARBON: AN FT-IR STUDY
Dwight M. Smith, William F. Welch and Abdul R. Chughtai, University of Denver, Denver, CO 80208; Brian G. Wicke and Karin A. Grady, General Motors Research, Warren, Michigan 48090.

Qualitative and quantitative studies of the reaction of black carbon with the oxides of nitrogen, including \( \mathrm{N}_2, \mathrm{~N}_2\mathrm{O}, \mathrm{~N}_2\mathrm{O}_4, \mathrm{~N}_2\mathrm{O}_5 \), and \( \mathrm{N}_2\mathrm{O}_3 \), have been carried out using Fourier Transform Infrared spectroscopy (FTIR). The reaction of black carbon with nitrogen dioxide and not a reaction with \( \mathrm{N}_2 \), is predominantly responsible for the formation of species resulting in the IR absorption region at 1660 cm\(^{-1}\), 1565 cm\(^{-1}\), 1540-1535 cm\(^{-1}\), 1325 cm\(^{-1}\), 1300 cm\(^{-1}\) and 1277 cm\(^{-1}\) confirmed isotopically in our earlier work published elsewhere (1). For candle soot exposed simultaneously to oxygen atoms and nitric oxide at 298 K, the absorbed nitrogen oxide species appears also to be from nitrogen dioxide, formed by oxidation of nitric oxide at the oxygen-atom covered soot surface.

The interaction of water with coal is of interest not only because of its technological implications but also, in a fundamental sense, because of its exemplification of water's structure near the interface. It has been speculated that water in coal exists as chemisorbed, physisorbed, micro- and macro-pore water, interparticle and intraparticle held water, though no conclusive experimental evidence is yet available for these models. A two-prong approach was adopted to understand the coal-water interactions. In the first approach, the dynamics of water in a lignite coal were examined via water's vibrational spectra at 100 K < T < 300 K. The systematic temperature dependence of water's stretching, bending and librational modes frequency, width and intensity shows discontinuities at 183±5 and 263±5 K. This result suggests the presence of two types of freezeable water in coal. In the second approach, the isothermal desorption kinetics of water from the lignite coal were examined at a pressure of 0.013 Pa in the temperature range 325 K to 435 K. The FTIR spectral data was analyzed by generating difference spectrum and curvefitting. The results indicate the presence of four types of water in this coal with distinctly different activation energies. Efforts were also made to dewater the coal by using surface active heavy crude oil fractions.

*Work supported by DOE (DE-FC22-88PC88861)
The recently developed technique of gas chromatography-matrix isolation-Fourier transform infrared spectroscopy (GC/MI/FTIR) has been applied to the analysis of environmental samples contaminated with polychlorinated dibenzo-p-dioxins (PCDD's) and dibenzofurans (PCDF's). In this technique, the effluent of a capillary gas chromatograph is frozen in an argon matrix at ~13K, and is analyzed using micro-sampling FTIR optics. Reference GC/MI/FTIR spectra of the 15 laterally substituted PCDD's and PCDF's (those having the highest toxicity equivalency factors [TEF's]) and the octachlorinated Species have been obtained. In addition, spectra have been recorded for several brominated dioxins and furans. Details of the experimental technique will be presented, and major features of the infrared spectra of these compounds will be analyzed. Applications of this technique to "real world" samples will also be discussed.

FT-IR/VCD OF POLYPEPTIDES

Sritana C. Yasui and Timothy A. Kelderling. Department of Chemistry (M/C 111), University of Illinois, P.O. Box 4348, Chicago, Illinois 60680.

Vibrational circular dichroism (VCD) is a new spectroscopic technique of great potential for stereochemical analysis. The abundance of vibrational transitions gives VCD an advantage over electronic CD. Even though the same is true for infrared absorption, it lacks the stereosensitivity found in VCD. The magnitude of VCD (the difference in absorbance of chiral molecules to left and right circularly polarized infrared light) is typically $10^{-4}$ to $10^{-5}$ times the ir absorbance. The improvement in VCD measurement by its adaptation to Fourier transform infrared spectrometers has yielded very high quality and high resolution spectra and can take advantage of excellent sampling accessories and computerized data manipulation. The application of VCD to the conformational analysis of polypeptides will be discussed. In addition, selected protein VCD data will also be presented.

ESTIMATION OF THE COMPOSITION OF COMPLEX MIXTURES VIA INFRARED SPECTROSCOPY. Howard B. Powell, Eastern Kentucky University.

As part of an investigation of use of infrared spectroscopy in quantitative determinations, the estimation of the nonvolatile components of an oil-based paint via infrared was studied. A series of synthetic paint mixtures were prepared. Thin films of these mixtures were supported on polyethylene and air dried. The infrared spectra of the films were obtained on both a Fourier-transform spectrometer and a dispersion spectrometer. In addition portions of the dried sample were ground to a fine powder and the spectra of the powder determined by diffuse reflectance. The spectra were subjected to a variety of quantitation techniques including a commercial computer program. The results of these determinations will be compared with each other and with other techniques used in quality control of paints. Several commercial samples of paints using the same
EPR investigations have revealed that NH₄Ln(SO₄)₂·4H₂O (where Ln=Ca, Pr, Nd, Sm, and Eu) forms an isostructural series of crystals which show multiple phase transitions at 10 K < T < 300 K. The mechanisms responsible for the observed phase transitions are not understood at present. FTIR and differential scanning calorimetry (DSC) measurements were undertaken on NH₄Pr(SO₄)₂·4H₂O monocrystals at 100 K < T < 300 K in order to understand the observed phase transitions in these monocrystals. The observed FTIR spectra were analyzed using a least squares curvefitting computer program at each measurement temperature to better resolve the overlapping infrared bands. The room temperature IR spectrum was subjected to a factor group analysis, determining the band assignments of the sulfate, ammonium and water fundamentals. The analysis was consistent with the crystal structure, revealing two crystallographically inequivalent SO₄ and H₂O sites. The internal modes of the SO₄²⁻ ions show splitting into several components due to site and correlation field effects. The frequencies, linewidth and intensities of some of the internal modes of the SO₄²⁻ and NH₄⁺ ions exhibit anomalous temperature dependence around 230 and 150 K. The specific heat data obtained from DSC measurements also show anomalous behavior around the above mentioned temperature. The results will be compared with those obtained by EPR technique.

HIGH RESOLUTION INFRARED STUDIES OF THE CORIOLIS COUPLED v₆ AND v₈ BANDS OF FORMIC ACID, R.E. Bumgarner, Jong-In Choe and S.G. Kukolich, Chemistry Department, University of Arizona, Tucson, Arizona 85721

The infrared spectrum of formic acid (HCOOH) has been recorded at 0.01 cm⁻¹ resolution using the Kitt Peak FFT spectrometer. Over 400 lines in the v₆ and v₈ bands (v₆ = 1104.85 and 1033.47 cm⁻¹) have been assigned. In addition, about 20 lines in the v₈ Q-branch were resolved using a diode laser source. The data was combined with previous microwave and laser saturation data in a fit of excited state constants. Several unobtained sextic distortion parameters in the v₈ band were determined. The improved set of parameters has allowed some previously measured laser saturation data to be assigned. The relevance of these constants to formic acid far infrared laser action will be discussed.


The Detection limit of OCS at less than 30 parts per trillion(ppt) has been achieved using a tunable diode laser, InSb detector and second derivative signal averaging in the 2050 cm⁻¹ region. The major cause for noise at this stage is the fringing due to the beam interaction in the White cell. The fringes contribute 1 x 10⁻⁵ in absorbance units. The detector noise signal is 5 x 10⁻⁷ absorbance units which is equivalent to a detection of 1.5 ppt of OCS in the 40 meter path length of the White cell. Similar equivalent absorbances have been demonstrated using a HgCdTe detector in the 1300 cm⁻¹ region. The diode is swept at about 50 Hz through a range of about 0.01 cm⁻¹ and modulated at 1 kHz with a small square wave. The 2f signal is pass through a lock-in amplifier set to the minimum time constant (about 100 microseconds). The output of the lock-in is then averaged at the 50 Hz sweep frequency. Averaging of unmodulated signals has also been performed with the noise in this case being a factor of 10 worse than the second derivative signal with the majority of the noise being fringes. When second derivative modulation techniques are applied to the signal, a washing out of some of the fringes is achieved.
NIR ANALYSIS: WHY ALL THE FUSS ABOUT THIS SPECTRAL REGION?

Donald J. Burns, 54 Campus Hollow Road, Putnam Valley NY 10579.

Near Infrared Analysis (NIRA) is finally being accepted by spectroscopists. This region of the spectrum has been known since Herschel left his thermometer just beyond the rainbow created by his prism, but it took another 1 3/4 centuries (along with some fancy mathematical algorithms) to realize its full worth. Today we have several instrument/computer packages which seem to answer the chemist's dream:

- They can be "taught" what to look for in a sample.
- They often require no sample preparation, and are non-destructive.
- They are fast (usually requiring 20-30 seconds).
- They are versatile (samples can be solid or liquid, generally anything containing C-H, O-H, or N-H bonds is a good candidate).
- They are inexpensive and easy to operate (requiring no consumables and little operator training (except for the initial calibration)), and
- They are safe (using no dangerous reagents or radiation).

This presentation will provide a background for those papers which follow. You will see how some "bad" features of the 1000-5500 nm region can be turned into advantages. By the end of the symposium, you will have been exposed to the basics, some modern data treatments, and several applications, enabling you to assess the potential of NIRA in your area of expertise, and possibly becoming the company hero.

MATHEMATICAL TRANSFORMATIONS OF NEAR INFRARED (NIR) SPECTRA

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There are many algorithms available to the analyst which can mathematically enhance near infrared (NIR) spectra. These treatments can correct for scattering difference between samples, enhance spectral resolution (deconvolution or Fourier self-deconvolution) or reduce noise by spodization of Fourier transformed spectra. Ideally, mathematical treatments should not affect peak position or relative intensity while correcting for scattering and improving resolution with minimum addition of spectral artifacts.

This presentation will compare and contrast the ability of various mathematical treatments to correct for scattering differences and enhance spectral resolution.


The Hadamard Transform Spectrometer using a liquid crystal spatial light modulator has no moving parts. Previously, this instrument had been successfully used in the visible spectral region. The Hadamard technique can provide the following advantages for dispersive near-infrared spectrometer.

a) Multiplex Advantage
b) Co-addition of spectra
c) Spectral subtraction

The question to be answered is "Can this instrument be used to one's advantage in the near-infrared?" This will be discussed and answered with spectra to be presented.

References

FOURIER ANALYSIS OF NEAR-IR SPECTRA OF WHOLE GRAIN AND GROUND WHEAT.

W.I. McClure, N.C. State University; Russell Tkachuk, Canadian Grain Commission; A.M.C. Davies, Oxford Instruments, England; and Gao Wenyu, Huazong Agricultural College, Peoples Republic of China.

This is the first application of Fourier analysis to the near infrared (NIR) spectra of wheat. Traditionally, researchers have performed both qualitative and quantitative analyses of NIR spectra of wheat in the wavelength domain. This study involved the transformation of Log (1/R) spectra of wheat to the Fourier domain for qualitative and quantitative manipulations. We will demonstrate advantages in using Fourier analysis including the use of Fourier coefficients for estimating protein, the use of Fourier and "derivative Fourier" coefficients for spectral searching and matching, as well as band enhancements of the spectra of ground and whole-kernel wheat. We will show, for example, the Fourier self-deconvolution of whole grain wheat contains considerably more information than the eye can observe from the plots and that the "hidden" information is useful for both quantitative and qualitative work.

THEORY OF THE ASSOCIATION BETWEEN COTTON FIBER QUALITY PARAMETERS AND NEAR INFRARED SPECTROSCOPY. Joseph G. Montalvo, Jr., USDA, ARS, Southern Regional Research Center, P.O. Box 19687, New Orleans, LA 70179.

Two models are presented to predict and to explain the underlying cause of the association between cotton fiber quality parameters and near infrared spectroscopy. The cotton fiber is a hollow cylinder whose wall is composed chiefly of cellulose; a high quality fiber has a thick wall and a small cross-sectional perimeter. Important fiber quality parameters include: wall thickness, wall area, weight fineness (weight of a unit length of fiber), cross-sectional perimeter and specific surface (external surface area per gram of cotton). The two models are considered on the basis of the interaction of the fiber with NIR light. The approach in the fiber wall model is to select geometric and spectral factors in the measurement system which optimize the absorption of light by cellulose in the fiber wall. In the fiber surface model, the approach is to select geometric and spectral factors in the measurement system so that the scattering of light by the fiber is independent of absorption. Indeed, the fiber wall model predicts three quality parameters should be associated with NIR: wall thickness, wall area and weight fineness. The fiber surface model predicts two other quality parameters should be associated with NIR: perimeter and specific surface. The theory is compared with experiment.

MONITORING COATING LEVELS OF PHARMACEUTICALS USING NEAR-INFRARED SPECTROPHOTOMETRY. Paul J Brimmer, Pacific Scientific, Instrument Div, 2431 Linden Lane, Silver Spring MD 20910.

Coatings on pharmaceuticals are designed to assure the integrity of the tablet ingredients, and to affect the delivery of the active ingredients. The amount of coating can drastically affect these functions, and must be carefully controlled in the manufacture of these materials. The methods currently in use to monitor coating levels are time consuming (usually on the order of a few hours) and are destructive methods.

Near-infrared (NIR) spectrophotometry offers an alternative method of monitoring coatings on pharmaceuticals. NIR has the advantage of high precision, fast analysis time, and little or no sample preparation is required. By using sample cells which present a large area of each sample to the spectrophotometer, pharmaceuticals ranging from 1 mm diameter spheres to coated tablets can be monitored without sample pretreatment.

Near-infrared monitoring of coating levels on several pharmaceutical beads and tablets will be discussed.
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NIRA STRUCTURAL INVESTIGATIONS OF NYLON YARNS. James E. Rodgers, III and Shirley Lee. Monsanto Chemical Company, P. O. Box 12830, Pensacola, FL 32575

Near Infrared Reflectance Analysis (NIRA) has gained increasing importance in the textile industry. The NIRA technique has been used extensively in the measurement of the heatset temperature of nylon yarns. Heat significantly influences the molecular packing of nylon, which results in changes in the fiber's chemical and physical properties. Several investigators have reported heatset temperature empirical equations for nylon yarns which consist primarily of wavelengths in the 2050nm to 2300nm range, with 2130nm being common to all equations. Studies of the NIRA spectra obtained from Suessen heatset nylon 66 samples have yielded additional information on the critical wavelengths for the heatset temperature equations, their structural assignments, and the probable rationale for the morphological changes in the yarn that are being observed by the NIRA technique. NIRA derivative spectra indicate that a slope change is occurring in the reflectance values from 2100nm to 2130nm. This slope change correlates to the crystallinity changes in the yarn with changing heatset temperature. Based on our band assignments, we propose that C-H stretch in Van der Waals plane, not the N-H stretch in the hydrogen bonding plane, is responsible for the NIRA technique's ability to predict the heatset temperature of heatset nylon 66 yarns.

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QUALITY ASSURANCE FOR TEXTILES USING THE NIR METHOD. Subhas Ghosh, Donna Di Ianni, Tammy Ebersole, and James Hassick. Institute of Textile Technology, P. O. Box 391, Charlottesville, Virginia 22902.

Near infrared reflectance spectroscopy has been found to be a useful quality control method in high speed textile processes. In this method, solid textile samples can be tested rapidly without destroying its integrity. Several applications have been developed to perform quantitative analysis of textile materials to determine: (1) cotton fiber maturity, (2) the degree of mercerization of cotton fabric, (3) dyeability of polyester fibers, and (4) analysis of polyester/cotton blends. NIR method has replaced time consuming and costly wet chemical procedures. X-ray diffraction studies were made to provide an understanding of the methods used in the measurement of textile properties using NIR spectroscopy. Excellent agreements were obtained between the conventional laboratory measurements and the NIR method with r² ranging from 0.90 to 0.99.

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NEAR INFRARED ANALYSIS OF PAPER AND PAPER COATINGS. Frank A. PetThomas, Pacific Scientific, 2431 Linden Lane, Silver Spring MD 20910

Near infrared spectroscopy (NIRS) has provided analytical methods of analysis for an array of different materials. Analysis in the NIR region of the spectrum focuses upon high instrument precision, fast analysis time, and limited or no sample preparation. Paper products are not only blends of different woods but are manufactured into a variety of physical forms.

Paper products have lent themselves to the development of many unique methods of quantitative analysis. Analysis of paper products for percent moisture, percent lignin (aromatic alcohols), as well as hardwood and softwood ratios have been performed. These parameters ultimately affect the ability to manufacture finished goods.

Many paper products are coated with waxes or polymers in the finishing process. NIR can provide the quantitative analysis for coating thickness. This abstract highlights the ability of NIR to provide quantitative methods of analysis for paper and paper coatings.
It is very difficult to quantify the amounts of actual compounds present in Portland cements by direct assay of those compounds. What is normally done instead is to measure the amount of metals present, along with sulfur as SO₃, and to calculate the amount of the actual compounds present based on the stoichiometry of the reactions assumed to exist at the conditions of manufacture. These compounds are called "potential compounds" in the literature of cement technology.

In this work, results from the analysis of Portland cements used in Delaware roads and bridges by atomic absorption and gravimetric analysis were used to calibrate FTIR transmission spectra of KBr pellets of the cements using multivariate regression techniques similar to those employed by the United States Department of Agriculture in the near infrared reflectance analysis of wheat.

There is an almost unlimited number of opportunities for problems to arise that can hinder formal production in a manufacturing complex as large and technically sophisticated as the Oak Ridge Y-12 Plant. When a process is not functioning properly (rejected parts due to corrosion) or becomes environmentally unsound (hazardous waste disposal), the problem-solving capabilities of the Plant laboratory are often utilized. This paper gives a brief overview of several types of problems and discussions as to how ion chromatography was utilized as a problem-solving tool. Discussion on the following topics will be presented: chloride in methanol fuel, anions in various types of environmental samples, thiocyanate in urine, perchlorate in exhaust hood ducts, anions in acrylic spray paint, cyanide in photographic wastes, and anions in various matrices that cause corrosion problems.


The flexibility, selectivity and sensitivity of conventional SCIC is widely known. However, the presence of stainless steel in the flow path limits the types of eluant that can be used and also interferes with metal sensitive samples and shortens the lifespan of IC columns. A discussion on how a metal-free system overcomes these disadvantages and still maintains SCIC advantages will be presented. The focus will be on the improved performance and increased sensitivity of the metal-free system for cations and transition metals.

The determination of cyanotransition metallates is of importance to the mining and metal finishing industries. The labilites of some of these complexes has hindered the development of methods for their determination. A gradient anion chromatographic separation coupled with spectrophotometric detection offers a simple yet versatile method of quantitation. The problem of complex lability has been solved by the appropriate choice of chromatographic conditions, including the addition of cyanide to the eluant. Eight complexes of interest have been determined, with detection limits of 10 to 50 ppb by direct injection.

INTEGRATED SEPARATION SCHEMES IN ION CHROMATOGRAPHY: SEQUENTIAL AND SIMULTANEOUS DUAL MODE ANALYSIS. W. R. Jones, P. Jandik, A.L. Heckenberg, P. Alden. Waters, Division of Millipore, 34 Maple Street, Milford, MA 01757.

Integrated separations or coupled ion chromatography is an analytical technique which either captures or transfers the void volume of unretained ionic species from one separation mode and injects that void volume sample onto a different separation mode better suited for that class of ionic species. Examples of coupled IC are simultaneous cations/anions and simultaneous weak acid anions/strong acid anions with a single injection. The hardware employed for simultaneous analysis is a six-port automatic column switching valve operated via timed events. This valve acts as the transfer point between two IC systems. For sequential analysis using a single analytical pump and detector, more valving is required to achieve the same end. This powerful analytical technique allows for more ionic information per sample injection, on-line sample preparation, and minimization of matrix interferences. A review of current applications, new developments along with guidelines to their usage will be discussed.


The increasing range of ion chromatography has led to the development of a number of new columns and separation mechanisms. The selection of an appropriate separation column may be determined by considering factors such as analyte concentration, pKa's of the analyte, detection system available and sample matrix. This paper will review a number of new column formats for anions exchange which permit improved efficiency, sample loading characteristics and resolution. These new techniques and columns allow the chromatographer to analyze samples that previously presented separation problems. Ion exclusion separations of a number of inorganic and organic ions have been shown to be highly selective for complex sample matrices. The advantages and areas of utility of these columns will be reviewed. Polyvalent anions such as EDTA, Polyphosphate, and Polyphosphonates separated by gradient anion exchange techniques have been shown to be very useful. The scope of new separations and sample matrices for these applications will be covered. Ethanolamine separations using cation exchange with conductivity detection have been developed and their application to a variety of sample types will be shown. Similarly cation exchange mechanisms for transition metals and lanthanides will be addressed. Overall this paper will outline the important factors used to modulate retention for the various separations and provide guidelines for the selection of appropriate columns for given analytes.
A Comparison of Anion Chromatography and Reverse Phase Ion-Pair Chromatography for the Determination of Perchlorobenzenesulfonic Acid in Groundwaters


Perchlorobenzenesulfonic acid and its anion (both referred to as pCBSA) have been identified in groundwater in and around the Stringfellow Site, located at Glen Avon, CA. This species is a byproduct of DDT synthesis and has been utilized as an indicator of offsite contaminant migration. In order to efficiently determine pCBSA in large numbers of samples, two HPLC methods have been evaluated and compared. The first consists of ion-pair HPLC with a Dionex NS-1 column and an acetonitrile/water mobile phase containing a quaternary ammonium pairing agent. An alternative procedure consists of anion chromatography with a Dionex AS4-A column and aqueous sodium carbonate eluent. Spectrophotometric detection at 225 nm is employed in both cases. Either procedure is acceptable for routine use, with one or the other being preferred under certain circumstances. Results of detection limit and spike recovery studies are presented.

The Use of Post Column Derivatization in Ion Chromatography


In Ion Chromatography the primary detector of choice is conductivity. In a complex sample, low level quantitation of a few ions may be compromised by matrix interferences and chromatographic resolution. UV/Vis detection is a means to enhance specificity but a majority of anions and cations are not UV/Vis active. Post column derivatization is a technique used to give these ones UV/Vis absorption characteristics for selective and sensitive detection. The analysis of polyphosphates, polyphosphonates, and other polyvalent anions has always been difficult. Gradient elution techniques have solved the chromatographic resolution problems but created problems for conductivity detection. Post column derivatization using Fe(NO3)3 yields a product with absorption characteristics at 320nm. This detection scheme has been applied to various chemical, personal care, and beverage formulations. Similarly, transition and lanthanide metal cations can be complexed post column with various selective color reagents to yield a product that can be quantitated at the 10-25 ppb level. These methods have been successfully applied to wastewater, brine, food, fermentation broths, and nuclear fuels. In conclusion, post column derivatization is simple and offers the chromatographer another means to develop IC methods that allow for the selective and sensitive detection of specific ions in a complex sample. Post column derivatization is low cost and compliments conductivity detection.

Optimization Techniques for Anion Exclusion Chromatography

David W. Togami, David J. Hometchko, Interaction Chemicals, Inc., 1615 Plymouth Street, Mountain View, CA 94043.

Anion exclusion chromatography has been shown to be an extremely useful method for the separation of organic and inorganic acids of pKa greater than 1. Optimization techniques for anion exclusion chromatography can allow users to realize maximum potential performance for their analyses. One example is the use of an eluent additive to increase sensitivity of detection for an analyte. These and other parameters will be discussed. Applications examples of optimized separations will be shown.

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Conventional stainless steel column systems often compromise performance due to dissolution of metals into the eluant. Two new metal-free column systems have been developed which utilize high-strength polymeric or glass components. Both systems have been designed to maintain the high-pressure integrity required for both traditional IC and HPLC applications. A wide variety of IC and HPLC packings are available in cartridge format. These cartridges fit within a reusable holder which simplifies column replacement and interchange. Glass cartridges of 3mm ID offer the advantage of a visible packed bed for rapid diagnosis of column contamination or void formation. In addition, the reduced internal diameter as compared with standard 4-6mm ID columns, provides increased mass sensitivity with many detection systems. Polyprep polymeric columns of 4mm ID provide increased column capacity and increased volume flow rates for applications requiring low linear solvent velocities. Several SCIC applications will be presented to demonstrate the utility of these new systems.

A CHROMATOGRAPHIC METHOD FOR STRETFORD PROCESS MONITORING IN WU THERMAL POWER PLANTS

Margaret A. Walkin and Jim Ray. Wescan Instruments, 3018 Scott Blvd, Santa Clara, CA 95054.

Streftord Process Chemistry is used in geothermal power plants to oxidize hydrogen sulfide in the gas stream to elemental sulfur. The principal chemical reactions are:

1. Absorption and dissociation of hydrogen sulfide into alkali.
2. Bisulfide oxidation with metavanadate to form elemental sulfur and reduced vanadium.
3. Vanadium reoxidation by dissolved molecular oxygen in the presence of anthraquinone disulfonic acid (ADA).

In addition to the above reactions many side reactions can occur. These have been associated with operating problems such as formation of soluble sulfur species; chemical consumption of ADA; and precipitation of vanadium. As a result reliable analytical methods are essential for process control. Because many Streftord components are ionic, ion chromatography is a natural tool for such an analysis.

This paper will discuss ion chromatography methods for determination of sulfur species; measurement of ADA and its isomers; determination of vanadium in the +4 and +5 oxidation states; as well as the analysis of other Streftord components.

ION CHROMATOGRAPHIC DETERMINATION OF LOW LEVEL ANIONS FOLLOWING HYDROFLUORIC ACID DIGESTION.* Raymond M. Herrill, Sandia National Laboratories, P. O. Box 5800, Albuquerque, New Mexico 87185

Low concentrations of anions have been determined in samples of material dissolved in hydrofluoric acid using ion chromatography. Since HF is a weak acid, we separate the strong acid anions from fluoride by ion chromatography exclusion (ICE). The anions are then injected onto an anion separator column and determined in the normal method. The technique is facilitated by use of a computer which automatically performs the necessary mechanical operations during the course of the analysis. The procedure is particularly applicable to the analysis of glasses and other materials easily dissolved in HF. Using this technique, chloride as low as 0.4 ppm has been determined in solutions which contained greater than 20,000 ppm fluoride. *This work performed at Sandia National Laboratories supported by the U. S. Department of Energy under Contract DE-AC04-76DP00789.

DETERMINATION OF FLUORIDE IN SEMICONDUCTOR PROCESS CHEMICALS BY ION CHROMATOGRAPHY WITH ION SELECTIVE ELECTRODE DETECTION - Robert T. Talasek, Texas Instruments, P. O. Box 655012 H/S 46, Dallas, Texas 75265

Determination of low levels of halide impurities in many semiconductor process chemicals have become a critical issue in recent years, and the development of suppressed ion chromatography with conductivity detection has been a key factor. However, the detection of fluoride by this method is hindered by a large number of interferences and by poor detection limits. Through the addition of a fluoride selective electrode in series with the normal conductivity detection, fluoride levels as low as 5 ppb can be quantitated without interfering with the analysis of other anions by suppressed conductivity detection. The application of this technique to a number of important samples will be discussed.
HIGH PERFORMANCE ION CHROMATOGRAPHY OF ANIONS: G. Vautour, M.C. Mehra and V. Mallet, Département de chimie et biochimie, Université de Moncton, Moncton, NB, E1A 3E9 Canada.

High performance ion chromatography of inorganic and organic anions can be performed much more efficiently on shorter ion exchange columns with a properly selected mobile phase. Relative efficiencies of water soluble substituted monocarboxylic aromatic acids as potential eluents have been examined on a silica based mini anion exchange column (50 x 4.6 mm) for Cl⁻, Br⁻, NO₂⁻, NO₃⁻, SCN⁻, SO₄²⁻, SO₃²⁻, SeO₃²⁻ and SeO₄³⁻ in aqueous and environmental samples. In addition chromatographic behavior of organic anions drawn from weak carboxylic acids has, as well, been examined on the same column using sulfobenzoate as mobile phase. The experimental conditions for multianion analyses have been optimized using a conductivity detector. The experimental data concerning specific separations of analytical interest shall be presented and discussed.

SINGLE COLUMN ION CHROMATOGRAPHIC DETERMINATION OF CHROMATE IN SLUDGES AND SOILS. H. C. Mehra and W. T. Frankenberger, Jr. Dept. of Soil and Environmental Sciences, University of California, Riverside, California 92521.

Single-column ion chromatography (SCIC) was investigated as a routine, rapid, precise and selective analytical method for the micro-determination of chromium (VI) in sewage-sludge and soil water extracts. Chromatographic parameters were optimized for chromate determination with the simultaneous detection of Cl⁻, NO₃⁻, and SO₄²⁻. A low-capacity resin based column was used for the separation and the anions were quantified by conductimetric detection. p-Hydroxybenzolic acid (5 mM) at pH 8.5 was used as eluent. The limit of detection defined as S/N = 3 is 0.90 µg ml⁻¹ of chromium. Resolution of CrO₄³⁻/SO₄²⁻ was 2.8, while relative standard deviation of 1.98% for chromate was obtained. Peak areas are a linear function of Cr(VI) concentration. Analysis of SCIC agrees closely with values obtained by inductively coupled plasma emission and visual spectrophotometry.


Single Column Ion Chromatography (SCIC) does not use post column chemistries to modify background conductance. This allows for more flexibility in the choice of counter-ions used for eluents in anion exchange separations. Depending on whether the eluent counter-ion has a higher or lower ionic equivalent conductance than the eluting sample anions will determine the suitability of an eluent for indirect or direct detection. Indirect detection means that the eluting sample anions are negative peaks while in direct detection the peaks will be positive. In an isocoordinative gradient the eluent strength is increased while the overall background conductance is kept constant. This is achieved by changing the cation associated with the eluent from a high to a lower conducting species. This technique can be applied to virtually all eluents found in use for single column ion chromatography. Through derivation of a formula used in predicting eluent background conductivity and the equivalent conductances of the ionic components of the eluent, the gradient strength ratio can be calculated. From simple calculations it is found that the strongest isocoordinative gradients are achieved with direct detection eluents.

This paper will focus on the comparison of direct and indirect eluents with the various selectivities associated with the different counter-ions.

In the column and detector overload is often an issue. The disparate levels of ions in the sample matrix can interfere with the total analysis causing analytes of interest to be obscured. This is particularly a problem in the analysis of brines which contain very high levels of halides relative to other anions. The requirement for analysis of both anions and cations in a sample makes it difficult if not impossible to analyze in a single injection on a simple chromatographic system. The prevailing routine methods for the analysis of anions, monovalent cations, and divalent cations in a sample requires three different systems if time and sample throughput are of importance. A new approach which uses a system that will analyze for monovalent cations and divalent cations in parallel will be discussed. This system consists of two columns and two eluents but only one pump, one injector, and one detector. The two eluents and columns can be alternated with the use of a switching valve depending on whether monovalent or divalent are of interest. Since optimum sample preparation usually requires dilution in different eluents for anions and cations, better sensitivity and selectivity can be achieved using two individual systems. Anions are done separately on another system so that in utilizing this new approach only two chromatographic systems are required. New ion chromatography columns and eluents which will reduce the problems observed with the analysis of inorganic ions will also be discussed.


Amperometric (electrochemical) detection of inorganic ions is both sensitive and selective. In recent years the number of working electrode materials and experimental conditions has increased. Suitable ranges of working potentials were determined for silver, platinum, copper, nickel and glassy carbon electrodes. Through the correlations of chromatographic conditions and cyclic voltammetric results the ideal conditions for sensitive and specific detection of inorganic ions has been achieved. The major advantage of using the results of chromatography and cyclic voltammetry is the former provides a mechanism for the separation of the analyte from possible matrix interferences whilst the latter provides optimum selectivity for detection.

ANALYSIS OF SELECTED HERBICIDES AND THEIR METABOLITES BY CHEMICAL IONIZATION TANDEM MASS SPECTROMETRY. Colleen E. Rostad, Wilfred E. Pereira, and Thomas J. Leiker. U.S. Geological Survey, P.O. Box 25046, Mail Stop 408, Denver Federal Center, Denver, Colorado 80225

Several commonly used herbicides and their metabolites were investigated using chemical ionization tandem mass spectrometry. The selected compounds included simazine, atrazine, deethylatrazine, deisopropylatrazine, tertbutylazine, metolachlor, alachlor, 2-chloro-2',6'-diethylacetanilide, 2-hydroxy-2',6'-diethylacetanilide, and 2,6-diethylaniline. Each compound was subjected to positive chemical ionization using isobutane, which increased the sensitivity 4 to 8 times over methane chemical ionization. Argon was used as the collision gas for collision activated dissociation (CAD). The CAD of each compound occurred under a variety of conditions by varying collision gas pressure and collision energy. For some of the compounds, increasing the intensity of the fragmentation conditions caused the same group of specific daughter ions to increase. For other compounds, the daughter ions changed under different CAD conditions. Structural similarities of some compounds were reflected by common daughter ions. All five selected triazine compounds produced some daughter ions in common. The acetanilide-related compounds produced few daughter ions in common.

Three modern chromatographic techniques are employed to investigate the neurochemical potency of components of Aroclor 1254. Preparative adsorption chromatography on Florisil (1200 g) activated at 450 °C separated Aroclor 1254 (10 g) into two fractions (I and II). Congener specific gas chromatography with electron capture detection on an Apiezon L coated soda glass capillary (50 m) was employed to determine the PCB composition of each fraction; this analysis was confirmed using the Hewlett-Packard Mass Selective Detector (MSD) in the scanning mode. Polychlorinated dibenzofuran (PCDF) and dioxin content of II was determined after further purification using the MSD in the selected ion monitoring mode. High performance liquid chromatography with electrochemical detection was employed to determine catecholamine neurotransmitters in rat pheochromocytoma (PC-12) cells in culture. Dose dependent changes in both release of dopamine into media and, at higher concentrations, reduced cellular concentrations were observed for Aroclor 1254 and I and II. The assay responds to pg levels of compounds and hence may be used for assay in conjunction with analytical scale chromatographic methods.

The gas chromatograph—mass spectrometer: Considerations for purchase and start-up. Diane Elchi Lawver and Patricia L. McGlothlin, City of Colorado Springs, Department of Utilities, 2855 Mesa Road, Colorado Springs, CO 80904

The purchase of a Gas Chromatograph/Mass Spectrometer is one of the largest instrument expenditures of water analysis laboratory will make. Because of the range of instruments available and variations in prices, careful consideration must be given to the needs of the utility laboratory. To assist in the initial shopping for the GC/MS, we prepared a questionnaire to help keep questions consistent and provide a record of answers for subsequent evaluation. The questions asked concerned the manufacturers, type of analysis performed, length of time in service, frequency of use, manufacturer support and service, and site preparation requirements for a GC/MS. On-site visits were then conducted directly with the GC/MS analyst and actual observations of the instruments in their workplace setting were made. Meetings with supervisory personnel provided information on administrative issues such as initial capital expenditures, operating expenses, personnel qualifications, and salary requirements. The start-up of our instrument has been completed for the list of volatile organic compounds that can be analyzed using Method 524. This goal was achieved with very little down time and maximum acceleration through the learning curve. Sharing our experience gained during the process should provide useful information to any water laboratory contemplating such a purchase.

The human eye, a unique spectrometer. John Quenzel, Robert L. Spraggin, Manville Technical Center, Denver, CO

Old techniques and methodologies can be very useful for solving modern analytical problems. If possible, blending old techniques and newer instrumentation is ideal for solving sophisticated modern analytical problems. If however all instrumentation were removed from your arsenal, how would you attack a complex organic analytical problem involving process chemistry? The problem was to determine the presence and amount of a specific process chemical without the use of analytical instrumentation. The methodology once developed, would be used by plant operators for controlling levels of this process material. A colorimetric procedure was developed based on trial and error methodology. The color produced is developed over a period of time (60 hrs.) and is proportional to the concentration of the process chemical. Interferences are discussed, as well as methods for calculating process levels of this material in the presence of interfering substances.
8-diketone complexes of barium, yttrium, and copper have been studied by mass spectrometry to assess the potential of using such compounds as reagents in metal organic chemical vapor deposition of high temperature superconductors of the composition YBa$_2$Cu$_3$O$_7$. The mass spectra and properties of the barium complexes are particularly interesting because previous mass spectral and chromatographic studies have shown that some of these complexes are oligomeric in nature, and not very volatile. It has been suggested that at least some oligomerization occurs in the source of the mass spectrometer. The mass spectrometry of the barium, yttrium and copper complexes was investigated using electron, chemical, and fast atom bombardment ionization. For barium complexes of 2,2,6,6-tetramethyl-3,5-heptanedione under negative chemical ionization conditions, the predominant ion corresponds to $\text{M}+\text{H}^+$ even at low probe temperatures, while with electron ionization the major ion corresponds to $\text{M}+\text{H}^+$. The possibility of enhancement of molecular ion formation by addition of excess (protonated) ligand to the ion source under chemical ionization conditions was studied. Although the ligand itself serves well as an ionization reagent, it does not change the distribution of the peaks in the mass spectrum. The possibility of ligand and metal exchange occurring between complexes in the ion source has also been examined.

PHARMACOKINETIC STUDY OF LIDOCAINE IN BURN VICTIMS USING GC/MS. Lynette D. Lohrmeyer, *Duane Bloodow, and Keith L. Clay. University of Colorado Health Sciences Center, Department of Pharmacology, 4200 E. 9th Ave., Denver, CO, 80262 and *University of Colorado, Boulder, School of Pharmacy, Boulder, Colorado 80309.

In severely burned individuals, a shift of plasma proteins occurs which results in significantly lower plasma albumin concentrations. In concert with lower albumin, there is an increase in the plasma alpha-1 acid glycoprotein content. These shifts are of therapeutic importance since many drugs are highly protein-bound and this binding can affect the response to a given dose. We have developed a GC/MS procedure to measure the pharmacokinetics of lidocaine, a highly protein bound drug, commonly used in this group of patients. By measuring the bioavailability and disposition of lidocaine, it is possible to measure the net effect of the shift of plasma proteins, thus contributing to the therapy management of these patients. The pharmacokinetic parameters of interest are measured by the simultaneous administration of an iv. dose of lidocaine and an oral dose of a stable isotopically labelled variant. A second stable isotopically labelled variant is then used as internal standard to quantitate the amount of lidocaine in the plasma as a function of time after dosing. For oral administration, we synthesized the D$_2$-lidocaine variant with the deuterium atoms on the glyceryl methylene carbon. For the internal standard, we synthesized lidocaine with three deuterium atoms in each of the ethyl groups to give a D$_8$ variant. In the positive ion EI mode, the mass spectrum of lidocaine consists almost exclusively of an ion at m/z 86 which contains the elements of the diethylaminomethane moiety. This ion is shifted to m/z 88 in the lidocaine variant administered orally and to m/z 92 in the internal standard. The sensitivity of the assay is sufficient to allow plasma lidocaine measurement for three half-lives with 1 ml of whole blood per sample.

EVALUATION OF TECHNIQUES FOR THE QUANTITATIVE ANALYSIS OF D-COMPOUNDS IN URINE. Susan L. Togna, P.V. Venkatesh. Departments of Pediatrics and Pharmacology, University of Colorado Health Sciences Center, Denver, CO 80262

We recently described the first case of human b-mannosidase deficiency (1) and found that, in addition to the absence of b-mannosidase enzyme activity in tissues, the patient excreted excessive mannose (1-4)-N-acetylglucosamine in urine. At the time of the earlier report, we were unable to quantitate the disaccharide concentration in urine. However, because of the ease of using urine samples to screen for a wide variety of metabolic disorders, we developed a general method for the analysis of disaccharides in urine. Three different approaches were evaluated. All the methods began with the general isolation of all sugars from the urine. The first approach was to derivatize the sugars as their TMS ethers and to add together the contribution from both the natural a and b forms. Another approach involved the reduction of the sugars to their alditols and further derivatization using either acetic anhydride, TMS reagent of MeI + dimethylsulfonium anion. All the methods were evaluated for overall sensitivity and quantitative analysis on disaccharide standards and the b-mannosidosis patient’s urine were carried out. Results from these studies will be presented. (1) Togna, B.A. Wenger, et al., 315:120145 (1986).
APPLICABILITY OF CONVENTIONAL METHODS FOR ANALYSIS OF TRACE LEVEL ORGANIC CONTAMINANTS IN NATURAL WATERS

Organic contaminants in natural waters are frequently present at trace levels. This study evaluates several analytical methods for recovery and identification of 22 target compounds from distilled water and natural river water matrices, at concentrations of less than 1 ug/l. Extraction methods studied were purge and trap, closed-loop-stripping, and liquid extraction. Gas chromatography was used for compound separation. Mass spectrometry (MS), flame-ionization (PID), electron capture, electrolytic conductivity, photo-ionization and nitrogen phosphorus detectors were used for identification and quantitation. Recovery results were interpreted with respect to the compound’s Henry’s Law Constant and water solubility. Although there was some overlap, each extraction method was variable with respect to percent recovery, precision, and compounds detected. Recovery and precision for the distilled versus river water was comparable, with the exception of several positive interferences resulting from the presence of target compounds in the river water. The universal detectors (MS, PID) performed similarly in the simple distilled water matrix, but in the complex river water the MS provided more reliable identifications. The class specific detectors had greater sensitivity for some compounds but yielded less information about the total water sample, and the reliability of identification in the natural water matrix was less than that provided by MS.

APPLICATIONS OF A NEW HELIUM DISCHARGE IONIZATION DETECTOR. Don Clay, David Williams, Tracor Instruments, Austin, Texas 78725-2100.

Tracor Instruments has introduced a concentration/sensitive universal detector for gas chromatography which uses far UV photons to ionize and detect sample components. The Discharge Ionization Detector is of a two chamber design with an upper chamber containing the discharge electrodes and a lower chamber containing the sample detection electrodes. The two chambers are connected by an optically aligned port beneath the discharge electrode and share a common vent out of the sample chamber. The output of the DID is directed to a standard FID type electrometer. The detector has been operated with micropacked columns, Megabore capillary PLOT columns, and 0.32 mm capillary columns, in addition to the standard packed columns.

This paper will present chromatograms showing separations of unique interest, precision of the method, and dynamic range of application. Representative chromatograms will be shown demonstrating analyses of fixed gases, environmental trace gases, e.g., ethylene oxide in air, separation and analysis of C10 and C11 hydrocarbons, and atmospheric analyses of a coal mine where flooding with CO2 and N2 for fire control was occurring.

NMR STUDIES OF MODIFIED METAL-EXCHANGED ZEOLITES. R. Johnson, B. Marshik and T. Apple. Department of Chemistry, University of Nebraska-Lincoln, Lincoln, Nebraska, 68588-0304.

$^1$H, $^{129}$Xe and $^{13}$C NMR studies were carried out on Rh-containing Y zeolites which were modified by dealumination and co-cation impregnation. Following formation of H-Y by NH$_4^+$ exchange $^1$H NMR spectra revealed a spinning side band pattern associated with detrital aluminum species formed by dealumination which accompanied deammoniation. Migration of Rhodium species during calcination was probed with $^{129}$Xe NMR. Calcination underflowing O$_2$ was performed from 300-550$^\circ$C. The effects of other cations on the migration of rhodium has been determined.

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ALUMINUM-27 MAS NMR SPECTROSCOPY OF LAYER ALUMINOSILICATES.
Donald E. Woessner, Mobil Research and Development Corporation, 13777 Midway Road, Dallas, Texas 75244-4312.

The $^{27}$Al isotropic chemical shift and nuclear electric quadrupole coupling parameters were determined for a wide variety of 2:1 clay minerals. These quantities were obtained from magic-angle spinning nuclear magnetic resonance spectra measured at $^{2}$H magnetic fields of 6.35 and 11.74 T using proton decoupling and high speed sample spinning (8.9 kHz at 6.35 T and 5.3 kHz at 11.74 T). The VAI chemical shift becomes progressively deshielded (more positive) with increasing VAI substitution and increasing total layer charge, following the same trend as noted by previous authors for $^{29}$Si. The $^{27}$Al nuclear electric quadrupole coupling parameter also increases with increasing VAI substitution and total layer charge. Both quantities are related to tetrahedral layer distortion. The VAI chemical shift is decreased by Mg substitution also, as noted previously for $^{29}$Si. The $^{27}$Al MAS NMR peak shows multiple Al electrostatic site environments in the octahedral sheet of gibbsite, beidellite, and other minerals. This peak is broadened by Mg substitution in the octahedral sheet. Quantitation of VAI/VAI using the 11.74 T spectra shows excellent agreement with structural formulas. The high spinning speed contributes to this agreement. The amount of VAI in montmorillonites is either small or undetectable. However, the published structural formulas of some clays do not represent the samples used in this study. High field, high-speed spinning $^{27}$Al MAS NMR measurements should be a direct and sensitive technique for distinguishing montmorillonite from beidellite.

CHANNEL DYNAMICS IN UREA/n-ALKANE CLATHRATES
Nicholas J. Heaton, RegiZte R. Vold and Robert L. Vold
Department of Chemistry, University of California-San Diego, La Jolla, CA 92093

Deuterium nuclear magnetic resonance has been employed to study the dynamics of urea in urea/n-alkane clathrates. Powder and single crystal spectra of the C$_5$H$_{14}$N$_2$/urea-D$_2$ compound can be interpreted by assuming that the urea molecules undergo 180° flipping motion about their carbonyl bonds at rates on the order of $10^6$ s$^{-1}$. The motion distinguishes two types of deuterium nuclei; those for which the C-D bonds lie approximately parallel to the jump axis and those where the C-D bonds are inclined at about 60° to this axis. These two types of deuterons make separate contributions to the powder spectra and have different relaxation rates. Zeeman and quadrupolar relaxation rates have been measured and are found to have very different orientation dependencies in agreement with theoretical predictions for 180° jump motion. The activation energy of 23 ± 2 kJ mol$^{-1}$ found for the flipping provides a measure of the hydrogen bond strengths in the clathrate. Four hydrogen bonds are broken during each jump so that the average hydrogen bond energy is estimated to be about 6 kJ mol$^{-1}$.

PROTON MAGNETIC RESONANCE STUDIES ON ZEOLITES AND RELATED CATALYSTS
Harry Pfeifer, Sektion Physik, Karl-Marx-University, Linnestr. 5, Leipzig, 7010 German Democratic Republic

Through magic angle spinning of fused glass ampoules containing dehydrated zeolites under vacuum, highly resolved solid state proton magnetic resonance spectra can be obtained exhibiting up to five different resonances$^1$. It may be shown theoretically and experimentally that the proton magnetic resonance shift of the Bronsted acid sites is a direct measure of their acidity, defined as the ease of proton transfer to an adsorbed base. The obtainable resolution of the $^1$H MAS NMR spectra of zeolites and related catalysts is comparable to that of IR spectroscopy (stretching vibrations of the OH groups$^2$). Hence the strength of the acidity of Bronsted acid sites may be differentiated by either IR or NMR. In the latter case, absolute intensities of the site concentrations are measurable. An example will be given of the possibility of separating quantitatively the influence of strength and concentration of Bronsted sites.

Cutin and suberin are the major structural polymers of plant cuticle, functioning in conjunction with lipid waxes and carbohydrate cell walls to provide effective barriers to the environment. Although the major monomeric components of cutin and suberin have been identified, the insolubility of these biopolymers has made their detailed physical characterization difficult. In this paper, we report on a high-resolution solid-state $^{13}$C NMR study designed to determine the structure of and characterize the dynamic properties of intact plant cutin and suberin. Additional information about the cuticle is obtained from NMR analyses of solid cutin and suberin residues from partial depolymerization treatments and from cutin-wax and suberin-cell wall assemblies. Cross-polarization magic-angle spinning $^{13}$C NMR spectra with dipolar decoupling have been used to identify and quantitate the magnetically distinct carbons of these solid biopolymers. By comparing these spectra with direct polarization results obtained with scalar decoupling, a quantitative comparison of mobile vs. immobile groups has been made. Cutin, in particular, is found to contain a large fraction of mobile aliphatic carbons. $^{13}$C and $^{1}$H spin-relaxation experiments ($T_1(C)$, $T_1(H)$ and $T_1(C)$) have been used to probe biopolyester motions in the kilo and MHz frequency regimes and have revealed the presence of specific crosslink structures which help to maintain cuticle integrity. Experiments involving the incorporation of specific $^{13}$C-enriched metabolites are also discussed.
MULTIPLE QUANTUM SPIN COUNTING IN STRONGLY DIPOLAR COUPLED
DIPOLAR SOLIDS USING A SINGLE QUANTUM PROPAGATOR, B.C. Gerstein, D.G.
Cory*, V.S. Veeman*, and M. Goldman+, 229 Speeding, ISU, Ames, IA,
50011, *University of Nijmegen, Nijmegen, The Netherlands, + CEA-CENS,
91191 Gif Sur Yvette Cedex, France

The concepts involving production and detection of multiple quantum
coherence in ensembles of dipolar coupled clusters of spins 1/2 systems
are reviewed. The development of pulse sequences which produce an
average Hamiltonian single propagator is discussed, including the
effects of finite pulse widths upon the formation of the propagator.
Results of spin counting of finite clusters of protons in model
compounds are presented.

ROTATIONAL ECHO DOUBLE RESONANCE

Terry Gullion, Vincent Bork, and Jacob Schaefer
Dept. of Chemistry, Washington Univ., St. Louis, MO 63130

Dephasing of $^{13}$C rotational echos in solids containing pairs of
dipolar-coupled $^{13}$C and $^{15}$N spins occurs when the sign of the C-N
interaction is reversed by $^{15}$N x pulse trains with periods less
than half the rotor period. Fourier transforms of the echos with
and without the x pulses lead to a $^{13}$C NMR difference spectrum
which arises only from those $^{13}$C's with $^{15}$N neighbors. This
rotational-echo double-resonance (REDOR) experiment is easier to
perform than $^{13}$C-$^{15}$N double-cross polarization because the
technically difficult Hartmann-Hahn match between weakly coupled
carbons and nitrogens is avoided. REDOR depends on the dephasing
cauised by local fields and so has an $r^{-3}$ dependence on the $^{13}$C-
$^{15}$N internuclear distance. Dipolar couplings of about 50 Hz have
been observed for some crystaline materials, allowing the
determination of $^{13}$C-$^{15}$N distances on a scale of 5 A.

TWO DIMENSIONAL NMR OF SOLIDS. K. W. Zilm, G. G. Webb, J. C. Duchamp, J. Szczyrba,
and M. H. Cozine. Department of Chemistry, Yale University, 225 Prospect St., New
Haven, CT 06520

Two dimensional NMR methods for solid samples often utilize heteronuclear or
homonuclear dipolar couplings to introduce the frequency modulation into the second
dimension. Separated local field experiments in combination with magic angle spinning
(MASSLF) have been shown useful in the measurement of bond distances and for following
molecular motion. Homonuclear solids NMR methods which mimic solution NOESY and COSY
experiments have proven useful in establishing connectivity between functional groups or
domains of a solid. Quantitative interpretation of results from such experiments of this
type is often difficult. In MASSLF experiments the apparent homonuclear decoupling
scaling factor needed to fit the dipolar coupled sideband patterns is always
significantly less than that predicted by average hamiltonian theory. This discrepancy
will be shown to be due to both motional averaging and the effect of the X-nucleus
dipolar coupling on the evolution of the protons during homonuclear decoupling.
Correlation experiments using homonuclear dipolar couplings can be complicated by the
interplay of the chemical shift anisotropy, homonuclear dipolar couplings and MAS, often
with unexpected results. Systems containing isolated spin 1/2 pairs will be presented in
which the scalar coupling in the solid is approximately equal to the isotropic chemical
shift difference, yet the MAS spectra and COSY spectra are first order in appearance. The
problems of establishing connectivity in solids will be discussed in light of these complications.
With MAS speeds inching toward 30 KHz, a variety of important possibilities and issues arise in solid-state NMR. One of the most direct benefits of high-speed MAS is the ability to reduce spinning sidebands and remove them from spectral regions of interest. This is especially beneficial with such quadrupolar nuclides as $^2$H,$^1$H, allowing the use of high fields with the corresponding reduction in the second-order quadrupole effect. Examples will be shown. The temptation to employ high-speed MAS as a high-resolution solid-state $^1$H NMR technique must be considered in relation to the nature of the $^1$H--$^1$H dipolar interactions in each sample. Direct comparisons of CRAMPS and MAS--only results show that when strong $^1$H--$^1$H dipolar interactions are present, as expected, the CRAMPS approach provides far superior results. The anticipated interference of high-speed MAS with CP efficiency is readily demonstrated, even in systems with strong dipolar interactions. In $^1$H--$^{13}$C CP experiments carried out as a function of MAS speed, the Hartmann-Hahn match curves differ dramatically for carbons with directly attached hydrogens relative to carbons without. Hence, the use of high-speed MAS to overcome spinning sideband problems in high-field CP-MAS experiments seems problematical.

EXPERIENCES WITH LOW TEMPERATURE NMR

Costantino S. Yannoni, IBM Research Division, Almaden Research Center, 650 Harry Road, K32/803D, San Jose, CA 95120-6099

We have been involved in doing low temperature NMR over the last few years, including magic-angle spinning, and more recently dynamic nuclear polarization.

Our experience with the methodology of these experiments will be described along with the results.

DEUTERIUM RELAXATION AND MOLECULAR DYNAMICS IN CLATHRATES

Robert L. Vold, Regitte R. Vold, Jong H. Ok and Alan D. Ronemus. Department of Chemistry, University of California--San Diego, La Jolla, California, 92093-0342.

Analysis of solid state deuterium lineshapes and relaxation behavior has been carried out for several organic inclusion compounds. Results obtained for 1:6 benzene-d$_6$:cyclohexane-1,3-dione show that benzene undergoes six-fold jumps about the hexad axis which in turn wobbles by about 10°. The rate of six-fold jumps has been followed over 6 decades and interestingly enough, the rate is slower than in pure benzene. The motion of biphenyl included in β-cyclodextrin is quite complex. It has been studied using both biphenyl-d$_{10}$ and biphenyl-4,4'-d$_2$ as guests, and the results show that internal rotation is the dominant motion affecting the spectrum of the o,m-deuterons above -60° C. Simultaneously, the p,p'-axis undergoes librational motion (E$_L$ = 14 kcal/mol) inside a cone with a half-angle of ca. 25°. At the temperature where the internal rotation stops, the librational amplitude is reduced to 10° and the rate is nearly temperature independent.

Overall, the results obtained in the course of the work illustrate the potential and limitations of deuterium lineshape analysis.
NMR OF "TETHERED" BIOLOGICAL SYSTEMS. A. W. Adam, Ronald W. Behling, and Tetsuo Yamanaka. AT&T Bell Laboratories, 600 Mountain Avenue, Murray Hill, New Jersey 07974.

Many biological interactions occur at quasi-solid/solution interfaces. These interactions, which result in the formation of "tethered" assemblies, are a recurring theme in biophysics. Examples include enzyme-substrate interactions, antigen-antibody binding, receptor-ligand interactions, and protein-DNA recognition.

This talk will address several strategies for observing "tethered" biological assemblies by NMR spectroscopy. Examples include determination of the conformation of acetylcholine in its receptor-bound state, and attempts to observe peptides that are covalently attached to solid supports.


High-resolution $^1$H NMR spectra on solid samples are obtained routinely with a severely modified NT-200 spectrometer, using CRAMPS (Combined Rotation and Multiple Pulse Spectroscopy). Line widths as small as 0.2 ppm are observed on powdered, crystalline samples, even for protons that have very strong dipolar couplings. A series of CRAMPS-based time-domain experiments has been developed for establishing proton-proton proximity and/or dynamics in solids. The applications that have received substantial attention include: the analysis of coal and solvent-treated coal, the adsorption of small bases on silica and silica-alumina surfaces, the silylation of silica surfaces, the distribution of hydroxyl groups on surfaces, and the deposition of catalytic materials on surfaces.

ABSTRACT NOT AVAILABLE

NMR IMAGING OF MECHANICALLY AND CHEMICALLY INDUCED DEFECTS IN INORGANIC SOLIDS. B. H. Suits and J. L. Lutz, Physics Department, Michigan Technological University, Houghton, MI 49931.

Results of NMR imaging measurements to study the spatial distribution of defects created mechanically in alkali halides and through thermal decomposition in sodium chloride will be presented. In both cases the effects of lattice distortions in the vicinity of defects on the electric field gradient give rise to a loss of intensity in the NMR lines. The cubic alkali halides have no quadrupole field in the undistorted state and the loss of intensity is principally due to movement of the quadrupole satellites away from the central line. Sodium chloride, however, has a significant axial quadrupole field in the undistorted crystal and hence the satellites themselves can be used for imaging. The relative sensitivity of the two cases and the prospects for obtaining spatially resolved information to quantify the types of defects present will be discussed. This work is supported in part by the U.S. ARO contract DAAL03-86-G-0065 and the U.S. ONR Contract N00014-86-K-0149.
NMR "microscopic" imaging holds great potential for true noninvasive, nondestructive, characterization and testing of materials. Unfortunately, progress in this area has been hampered by a paucity of suitable gradient hardware for this class of samples. The inherently short $T_2^*$ associated with materials require imaging gradients with fast rise times and high field strengths to detect the signal. Furthermore, high gradient strengths are needed to achieve "microscopic" digital resolution.

To address these requirements, we have developed high field self-shielded gradients ($I$) for large, horizontal bore magnets. The 6" (ID) gradient set achieves +/-20 gauss/cm in a rise time of 200 microseconds and can accommodate up to a 4.25" (ID) rf coil for imaging relatively large material samples. This is in contrast to microscopy accessories for vertical bore magnets, where the limited available imaging volume severely restricts the size of samples that can be examined. Self-shielded gradients on a GE CSI 2.0 T, 31 cm, imaging spectrometer are currently being used in applications involving characterization of oil cores, solid-solid and solid-liquid interfaces, as well as, microdefects and cracking in materials.


NMR imaging is now a well established technique, but its application to material science problems has been somewhat limited in the past. We will describe our use of NMR imaging to examining viscous polymer melts and plasticized rubbery solids containing suspended aluminum metal particles and other solids. Our objective is to image both the polymer matrix and the solid particles in these materials. When the polymer matrix is imaged, indirect information about the distribution of particles in the matrix is obtained. Other features, such as voids and cracks, can also be identified. Imaging of aluminum metal particles becomes feasible since the AI-27 line width is not strongly broadened by quadrupolar interactions, making it amenable to line narrowing by multiple-pulse techniques (M. Mehring, et al., Solid State Comm., 13, 1637 (1973)). Aluminum imaging by multiple-pulse and other techniques such as multiple-quantum excitation will be discussed. We are also imaging flowing suspensions by NMR to determine whether the particles remain uniformly suspended when complex flow patterns are involved. This information can be coupled with rheology investigations to improve the processing of such suspensions and, ultimately, to provide new on-line process monitoring methods. This research has been sponsored by the Strategic Defense Initiative Office / Innovative Science and Technology, and managed by the Office of Naval Research under contract No. N00014-86-C-0724.


Electron transfer between Ti(III) ion and [Ru(acac)$_3$] proceeds with a second order rate constant $k \approx 1 \text{ M}^{-1} \text{s}^{-1}$ via an outer-sphere mechanism, owing to the substitution inertness of the Ru(III) complex. However, the mononormophyric complex [Ru(3-CHO-acac)(acac)$_2$] reacts much more rapidly via a ligand-bridged inner-sphere mechanism where the formyl oxygen is believed to insert into the coordination sphere of the Ti(III) ion. Since the thermodynamic driving forces for the two reactions are nearly the same, the large increase in reactivity for the formylated complex is ascribed to the longevity of the ligand-bridged binuclear intermediate and significant electronic coupling between the metal redox sites mediated by the pseudo-aromatic ring. $^{11}$H and $^{13}$C NMR spectra of the paramagnetic $d^5$ Ru(III) complexes reveal large paramagnetic shifts with the central 3-C nucleus exhibiting the largest spin density. The signs and magnitudes of the paramagnetic shifts are consistent with a contact shift mechanism coupled through the $r$ system of the acac$^-$ and 3-CHO-acac$^-$ ring systems. X-band EPR spectra of nitric oxide adducts of [Ru(3-CHO-acac)(acac)$_2$] are presented in the g tensors allowing for a neglect of dipolar shifts as a dominant term in the observed NMR shifts. These features will be discussed in terms of the ability of the ligand to mediate electron transfer via the 3-formyl substituent.
AN NMR VIEW OF MAGNETIC SUPEREXCHANGE IN TRANSITION METAL COMPLEXES

Gordon C. Campbell, Patricia Shepard, and James F. Haw, Department of Chemistry, Texas A & M University, College Station, TX 77843.

The establishment of correlations between magnetic and structural properties in nondiamagnetic transition metal complexes is of central importance in fields ranging from chemistry to biology and materials science. We are currently applying CP/MAS NMR techniques to a variety of important nondiamagnetic solids -- the amount of magnetic and structural information available from this work is often greater than that from analogous studies on diamagnetic materials. This is especially true when variable-temperature (VT) operation is possible, since the magnetic properties of many of these compounds exhibit pronounced temperature dependence. Copper (II) carboxylates, for example, have a diamagnetic ground electronic states (S = 0) with thermally-accessible triplet states (S = 1). Changing sample temperature in the course of 13C CP/MAS NMR studies will be shown to allow the resolution of structurally-significant chemical shifts and the determination of magnetic parameters which are characteristic of the extent and mechanism of exchange coupling between metal centers. Other results will be discussed including 77Se VT CP/MAS NMR studies of Fe₄-Se₄ model ferredoxin compounds.

ROTATING-FRAME DYNAMIC NUCLEAR POLARIZATION. Robert A. Wind, Liyun Li, Herman Lock and Gary E. Maciel, Department of Chemistry, Colorado State University, Fort Collins, Colorado 80523.

It has been found that in solids containing fixed paramagnetic centers and magnetic nuclei the nuclear polarization in the rotating frame can be enhanced via a simultaneous irradiation at the nuclear Larmor frequency and near the electron Larmor frequency. This has been called the Rotating-Frame Dynamic Nuclear Polarization (RF-DNP) effect. In the seminar the following properties of this phenomenon will be discussed: (i) The dependence of the RF-DNP enhancement factor, PRF, on the microwave off-set frequency from the electron resonance frequency; (ii) The dependence of PRF on the amplitudes of both irradiation fields; (iii) The time-dependence of PRF after the on-set of both irradiation fields; and (iv) Prospects for using RF-DNP in combination with rare-spin NMR.

SOLITON LOCALIZATION IN POLYACETYLENE REVEALED BY ELECTRON-NUCLEAR SPIN COHERENCE STUDIES. Hans Thomann and Halyong Jin, Corporate Research Lab, EXXON Research and Engineering Company, Annandale, NJ 08801

Evidence for one dimensional (1D) neutral soliton spin diffusion is primarily derived from magnetic resonance experiments. The rapid 1D diffusion of the paramagnetic soliton along the polyene chain is presumed to induce strong local magnetic field fluctuations which dominate the power spectrum for spin relaxation. Spin relaxation studies of the power spectrum should therefore probe the soliton motion. However, a plethora of conflicting conclusions have been reported for both the magnitude and temperature dependence of the diffusion rate as well as for the 1D coherence length. This is attributable to the difficulty in separating the relative contributions of soliton spatial diffusion from other spin dynamics mechanisms that contribute to the power spectrum for spin relaxation. An alternate method of probing soliton spin motion is to directly monitor the evolution of electron-nuclear spin coherences induced by electron spin echo and electron-nuclear double resonance techniques. These experiments and their implications for spin transport models of (CH)$_x$ will be presented.
Solid State NMR of $^1$H and $^{13}$C was used to study fraction crystallinity in poly(paraphenylenephenylene), poly(2,6 dimethylparaphenylene oxide), poly(paraphenylene sulfide), poly(paraphenyleneseelenide), and a 1:1 blend of poly(thiophene) and poly(paraphenylene). Rotating frame relaxation times of hydrogen were inferred from both proton and carbon NMR, and found to agree in the two cases studied (PDMPF and PPS). Carbon intensities selected by carbon $T_2$ under dipolar dephasing, and under proton $T_1$, under conditions of cross polarization and strong decoupling are used to infer relative amounts of crystalline, interfacial, and non-crystalline portions of these polymers.

A HIGH Q TUNABLE PROBE FOR NMR STUDIES AT LOW TEMPERATURE
Luisita DeLaRosa and B.C. Gerstein, 229 Speding ISU, Ames, IA 50011

A loop gap coupled resonator probe, tunable over a range of 8 MHz, with a center frequency of 53 MHz, and Q = 300 at 78K, has been designed and tested for NMR measurements of nuclei with chemical shifts in the range of percent, rather than ppm. The principles of operation will be discussed, and the sensitivity to detection of supported Pt at 78K will be illustrated.

TEMPERATURE DEPENDENCE OF CHEMICAL SHIFT TENSORS OF MOLECULES IN SOLUTION. Thomas C. Parrar, John Decatur, and Michael Jablonski, Department of Chemistry, University of Wisconsin, Madison, WI. 53706.

The complete chemical tensor for a given nucleus provides much more information about the electronic structure of a molecule than the isotropic chemical shift, which is usually measured in a solution state NMR experiment.

We report here the measurement of the temperature dependence of the phosphorus, hydrogen, and fluorine chemical shift tensors for samples of $\text{PO}_3^-$ and $\text{PF}_3^-$ in solution. For the phosphite anion, the isotropic chemical shift is, surprisingly, almost independent of temperature. The parallel and perpendicular components of the chemical shift tensor, however, experience large changes as a function of temperature. The origin of the temperature dependence is discussed.


Solid-state NMR studies have been carried out on silica gel samples that have been derivatized with dimethyloctadecylchlorosilane (DMODCS), using $^1$H, $^2$H, $^{13}$C and $^{29}$Si. $^{13}$C studies were carried out with various combinations of MAS, CP, high-power $^1$H decoupling and single-pulse excitation and have included measurements of $T_1$, $T_10$ and $T_{CH}$. The effects of surface loading level by wetting solvents and DMODCS have been examined systematically. $^2$H line shapes have been examined in parallel. The results will be discussed in terms of the configurations and dynamics of the C18 chains on the surface.

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A STUDY OF CARBON AND HYDROGEN AROMATICITY IN COALS BY HIGH RESOLUTION SOLID STATE NMR AND FTIR SPECTROSCOPY. B. C. Gerstein, P. D. Murphy*, M. Pruski, and P. R. Solomon**. Ames Laboratory, DOE and Department of Chemistry, Iowa State University, Ames, Iowa 50011; *IBM Instruments, Orchard Park, Danbury, Connecticut; **Advanced Fuel Research, Inc., E. Hartford, Connecticut.

High resolution solid state NMR and fourier transform infrared spectroscopy has been applied to study carbon and hydrogen aromatics in 8 coals varying in rank from lignite to high-rank bituminous. Detailed studies of 13C and 1H relaxation parameters have been performed to provide quantitatively reliable NMR results. The extent to which the carbon and hydrogen aromatics as inferred from FTIR can be quantitated with the results as determined by NMR is discussed.

FIELD-CYCLING, ZERO-FIELD RF-EXCITATION SPECTROMETER. L. G. Butler, W. L. Jarrett, K. Guo, and M. I. Altbach, Department of Chemistry, Louisiana State University, Baton Rouge, LA 70803-1804

We use field cycling methods, developed by Hahn and Redfield in the 1960's, to acquire deuterium quadrupole coupling constants in the solid state. The zero-field rf excitation allows deuterium transition frequencies to be obtained with high resolution. The quadrupole coupling constants and asymmetry parameters provide chemical and structural information.

The spectrometer is homemade and exists in two versions. In one form, the sample is polarized in the field of an XL100 electromagnet, then mechanically transferred to a region of zero applied magnetic field where the quadrupolar rf excitation search frequency is applied. In a more recent manifestation, a small solenoidal electromagnet is rapidly de-energized; the sample is held fixed in a two-coil probe (high-field proton and zero-field quadrupolar).

The experimental sequence requires automation of numerous steps. The computer hardware/software combination that has proven most satisfactory is based on a Macintosh II computer, IEEE-488 interface bus, a CAMAC crate, and a graphical-based programming language (LabView). A take-home message is that 4th generation languages have dramatic advantages relative to the traditional FORTRAN/BASIC/Pascal triad, which are older than most graduate students.

ISOTROPIC AND ANISOTROPIC CHEMICAL SHIFT STUDY OF TERTIARY AMINE-FATTY ACID COMPLEXES. Charles D. Saravsky, Fouad S. Ezra, and Robert S. Honkonen. The Procter & Gamble Company, Miami Valley Labs, P.O. Box 398707, Cincinnati, OH 45239-8707

Solid mixtures of tertiary amines and fatty acids typically yield complexes with rather complicated structures and physical properties. Since single crystals are rare, structural data for these materials is scarce and vague. We have used isotropic C-13 NMR data to determine the stoichiometry and phase behavior of dimethylalkyl amine: fatty acid complexes. These results will be discussed. In addition, we are currently attempting to use the anisotropic chemical shift interaction to determine amine: carboxylate geometries. Progress in establishing individual C-13 shielding tensor element-structure correlations for these complexes, as well as for other model compounds, will be discussed in detail.


Humic acids from a peat soil, an agricultural soil and a lake sediment from the Philippines were fractionated by sorption chromatography on cross-linked dextran gels (Sephadex). The NMR spectra of these fractions have sharp, well-resolved bands which can be attributed to lignin-like structures, carbohydrates, and aliphatic groups. Similar bands have been observed in the NMR spectra of humic acid fractions from other environments, however, the chemical shifts of some of the lines vary from one humic acid to another. These lines appear to arise from well-defined, partially decomposed plant components, and are probably diagnostic of the types of plants that decomposed into these humic acids. The lines in the carbohydrate region are the best resolved and may prove to be the most useful in identifying the plant precursors of any particular humic acid fraction.
INTEGRATION OF SUPERCRITICAL FLUID EXTRACTION INTO ANALYTICAL METHODOLOGY.

Jerry W. King, Northern Regional Research Center, ARS, U.S. Department of Agriculture, 1815 N. University Street, Peoria, Illinois 61604.

The application of supercritical fluid (SCF) extraction to analysis problems requires an appreciation of the physicochemical principles which govern analyte solubility in dense gases. This lecture will focus on the use of fundamental concepts, such as the critical loci of mixing between a solute and a SCF, the solute’s solubility in the dense gas phase, and solute flux rates into a SCF, to optimize analytical extraction and fractionation conditions. Particular emphasis will be placed on the selection of the proper extraction pressure for enhancing solute solubility in the extraction gas and on the conditions that are required for monitoring specific analyte concentration levels. Limitations in extrapolating data between techniques (analytical SCF extraction, SCF chromatography, large-scale SCF extraction) will be discussed. The effect of the sample matrix characteristics (moisture level, particle size, sample heterogeneity) on extractability of the solute will be documented with experimental results. Numerous examples will be presented of analyte extractions from natural products, particularly the removal of trace components and oils from seed and meat products.

A comparison of Supercritical Fluid Chromatography and Gel Permeation Chromatography. Mark P. Italin, Union Carbide, 1 River Road, Bldg. 200, Bound Brook, NJ 08805 and David E. Knowles, Lee Scientific, 4426 South Century Drive, Salt Lake City, UT 84123.

Gel Permeation Chromatography (GPC) is typically used as an analytical technique to separate molecules by their differences in size and/or molecular weight. It is used to determine molecular weight averages, or to obtain information as to the molecular weight distribution of polymers. Supercritical Fluid Chromatography (SFC) is often used to expand the molecular weight range of gas chromatography analysis. In part of this molecular weight range both techniques can be applicable.

This presentation will show comparisons of the two techniques on polymers such as polycathinones, polyols, and petroleum additives. Data will be presented showing the benefits and limitations of each technique. Examples will be presented showing where SFC is now being used to provide more detailed information than is presented with GPC.

COLUMN TECHNOLOGIES FOR SENSITIVE AND QUANTITATIVE SUPERCRITICAL FLUID CHROMATOGRAPHY. R.K. Houck, M.L. Kumar, A. Rosselli, G.P. Williams, and D.B. Boyer, Suprex Corporation, SFC Research Center, 125 William Pitt Way, Pittsburgh, PA 15238

Applications of supercritical fluid chromatography (SFC) continue to expand rapidly. This is largely attributable to the high sensitivity and reproducibility offered by packed columns, as well their ability to generate improved resolution per unit time.

Many packed columns contain a significant number of bare Si-OH sites, even after phase bonding and deactivation. These active sites can be detrimental to reversed phase LC performance as well as SFC performance. The existence of active sites has led to the use modifiers in CO₂. A different approach to the same problem is to make the column itself more inert through the use of different packing materials to allow the analysis of polar molecules. Data will be presented on various SFC columns for the elution of hydroxy- and carboxylic acid-containing compounds which serve as test probes for column inertness. In addition, data will be presented to show the sensitivity and quantitation that can be achieved with these columns.

ABSTRACT NOT AVAILABLE
The increasing attention given to chemical residues in our environment has generated an extensive file of methods for their analysis. Nearly all of the accepted methods require extensive sample preparation. This step is usually a time-consuming liquid solvent extraction technique. As an alternative, Supercritical fluids have several properties that make them attractive as extraction solvents. Their strong solvating ability along with their low viscosities can result in quantitative extractions in much less time than the traditional liquid methods. Several researchers have reported ease of use with good recoveries from soils and plant materials.

We report the use of a commercially available Supercritical Fluid Extraction/Injection System for both Gas Chromatographic and Supercritical Fluid Chromatographic analysis. Results from its use on samples of soil, water, plant and animal tissues and various absorbent materials will be discussed. Where possible, comparisons will be drawn to the traditional method addressing time savings and quantitative considerations. Residues studied will include chlorinated pesticides, antibiotics, poly chlorinated biphenyls and carbamate pesticides.

SUPERCRITICAL FLUID CHROMATOGRAPHY WITH PACKED MICROBORE COLUMNS AND UV/FID DETECTION. P.J. Barthel and H.E. Schwartz, Applied Biosystems, 2045 Martin Avenue, Santa Clara, CA 95050

Packed microbore (1 mm i.d.) columns can offer practical advantages in SFC with regard detector compatibility (e.g. FID,MS), sample capacity, analytical precision and fluid consumption. In this paper chromatographic retention on silica, diol, cyanopropyl, octyl and polyisocyanate phases is examined under typical SFC conditions. Polar and nonpolar group selectivity are compared using various test probes. With packed columns, modifiers are often added to CO2 in order to reduce retention and/or to improve peak shape. However, very few modifiers (e.g. formic acid and water) can be used with FID detection. It will be shown that a water saturated CO2 mobile phase can reproducibly be used with FID detection. With other modifiers such as acetonitrile or isopropanol, the FID is no longer useful and alternate detectors have to be employed. Applications with UV detection and on-line UV/FID will be shown using a 5 ul high pressure flow cell. The utility of the Applied Biosystems dual syringe pump for combined step-compositional programming and pressure programming will be demonstrated.

WATER AS A STATIONARY PHASE MODIFIER IN SUPERCRITICAL FLUID CHROMATOGRAPHY. Fiona Geiser, Steven Yockovich, Marc Sims, Eugene J. Levy. Computer Chemical Systems, Inc. Rt 41 & Newark Road, Avondale, PA 19311

The addition of water to supercritical carbon dioxide has been reported to improve peak asymmetry and to decrease retention time of pyrethrum extract and of fatty acids. Water is a desirable SFC additive because of its compatibility with universal detectors such as FID, thereby enabling the analyses of nonchromophoric solutes. In earlier reports, a water-saturated silica gel precolumn was inserted between a syringe pump and an injector. Using a CCS 5000 SFC, we modified this arrangement by connecting the precolumn to an auxiliary 8-port valve which could be remotely actuated at any time during the chromatography. Permethrin, pyrethrum extract, and a commercial permethrin formulation were chromatographed on a variety of packed columns (1 mm x 180 mm). Highly activated stationary phases, such as cyano propyl, were found to exhibit a memory effect in which the chromatographic performance with and without water-saturated carbon dioxide remained the same unless adsorbed water on the stationary phase was removed by heating the column to 150 C. This effect suggests to us that water is modifying the stationary phase in a manner similar to that reported for normal-phase liquid chromatography.
Capillary supercritical fluid chromatography (SFC) is a recently developed technique for high resolution separation of heat labile, polar, and high molecular weight compounds. The gas-like and liquid-like properties of supercritical fluids give SFC the high resolution of capillary GC and the ability of high performance liquid chromatography (HPLC) to analyze high molecular weight compounds. SFC, however, provides much higher resolution than HPLC.

This presentation will discuss chromatographic conditions necessary for optimization of the separation by SFC of polyethylenes of mean molecular weights ranging from 595 to 1214 and a narrow distribution of the oligomers. Polystyrene oligomers used in this study ranged in molecular weight from 500 to 1800; the polystyrene oligomers also had a narrow molecular weight distribution. Advantages and disadvantages of density gradient of the mobile phase and temperature programming, both performed simultaneously and independently of each other, will be discussed. Other factors examined were the specificity of the column, speed of analysis, and solvents required to dissolve the polymers.

*Work supported by the U.S. Department of Energy under Contract W-31-109-Eng-38.

Capillary columns of 100 μm or less inner diameter are easily overloaded if the total (constant) volume of the internal loop is injected. Different injection techniques such as time controlled injection have been developed recently. We have taken another approach to the traditional split technique. Instead of using a non-variable restrictor at the column and at the split outlet, we have replaced the split restrictor by a micro valve which is connected to a stepping motor, which in turn is controlled by a microcomputer (Commodore C64). Either small (1:10) split ratios or very large (1:500) split ratios and change of split ratio can be programmed. The same device can also be used to control flow, pressure and density as the outlet restrictor in packed column SFC. We report here some first results of this new device.

The new Sulfur Chemiluminescence Detector (SCD) is a highly sensitive and selective gas or liquid chromatography detector for many reduced organosulfur compounds, including sulfides, disulfides, and thiols. SCD response is based on chemiluminescent reactions between molecular fluorine, produced from SF₆ using an electrical discharge, and organosulfur compounds having reduced S=O bonds. The chromatographic column effluent containing the analytes is mixed with F₂ in a reaction chamber maintained at pressures of 0.5 - 2 torr. The SCD exhibits a linear response of 10⁻⁵ to 10⁻¹, and a high degree of selectivity for reduced organosulfur compounds compared to most organic compounds (e.g., hydrocarbons, halogenated hydrocarbons, aldehydes, ketones, alcohols, etc.). Recently, the SCD has been successfully interfaced to a capillary column supercritical fluid chromatography using CO₂ as the mobile phase. This SFC-SCD interfacing was accomplished by inserting the capillary column through a heated (100° - 125°C) interface tube, and carefully positioning the integral restrictor end of the SFC column within the reaction chamber. This coupling resulted in direct transfer of the column effluent into the chamber, which minimized dead volume and provided good sensitivity, peak shape and resolution. Design and operation details of the SFC-SCD will be described, and some applications will be presented.

The redox chemiluminescence detector (RCD) has been established as a powerful and selective detector in gas chromatography for some time. The selectivity can be controlled through the gold catalyst temperature, which is necessary to oxidize certain classes of compounds with NO₂⁺ is detected. Under SFC conditions the RCD offers the same selectivity and sensitivity as those applied to GC. We compared RCD and flame ionization detector for SFC applications and will report some of our results and problems.
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ASSESSING THE ACCURACY OF ANALYTICAL DATA, John K. Taylor, Quality Assurance Consultant, 12816 Tern Drive, Gaithersburg, MD 20878.

Data of sufficient accuracy are required whenever it is to be used for decision purposes. Since inaccuracy is caused by both imprecision and bias, both of these factors must be evaluated in every quantitative measurement situation. A well designed and implemented quality assurance program facilitates the estimation of the overall accuracy of data. The evaluation of precision depends on replicate measurements and is facilitated by the measurement of suitable test samples. The results of which, ideally, are plotted on control charts. Bias may be evaluated by several approaches including the use of reference materials, spikes, and surrogates, and by participating in collaborative testing exercises. Details of the above will be discussed and procedures to optimize the information provided by each technique will be presented. The statistical tools most useful for interpreting precision and bias estimations will be reviewed. Attainable and attained accuracy of measurement will be discussed as they are related to data quality objectives.


The U.S. Geological Survey managed three external quality-assurance programs in 1987 for the National Atmospheric Deposition Program (NADP) and National Trends Network (NTN). (1) An intersite-comparison program assessed onsite specific-conductance and pH determinations. Solutions of known specific conductance and pH were mailed to the NADP/NTN site operators twice during 1987. Site operators determined specific conductance and pH of the intersite-comparison solutions using standard protocols. The NADP/NTN goal of ± 4 microsiemens per centimeter was met by 90 to 95 percent of the site operators, while 72 to 77 percent of the site operators met the NADP/NTN goal of ± 0.1 pH unit. (2) A blind-audit program was used to assess the precision and bias of NADP/NTN wet-deposition data. Blind-audit solutions were mailed to 10 NADP/NTN site operators, who then disguised the blind-audit solutions as natural wet-deposition samples and submitted them to the NADP/NTN central analytical laboratory. Neutralization processes appeared to cause a median decrease of 10 microequivalents per liter in the hydrogen-ion concentration. A paired T-test between blind-audit samples shipped in sample collection buckets and blind-audit solution remaining in the bottle indicated a significant (α = 0.01) increase in concentrations of calcium, magnesium, sodium, potassium, chloride, and ammonia. (3) Analytical results from four laboratories were examined with an interlaboratory-comparison program to determine if differences existed between laboratory analytical results and to provide estimates of precision for each laboratory. The difference between laboratory results was small for all analytes. Analyses of deionized-water blanks indicated a difficulty measuring analyte concentrations near reported detection limits.


The U.S. Environmental Protection Agency's Contract laboratory Program (CLP) was established to provide laboratory services in support of the Superfund program. Approximately 100 laboratories provide the state-of-the-art analytical services that result in the generation of environmental data of documented quality. During fiscal year 1987, in excess of 132,000 samples were processed through the CLP program. The legal and technical mandate of "data comparability, completeness, representativeness, accuracy and precision" require that a substantial effort be directed toward Quality Assurance activities. Superfund Quality Assurance is not limited to Laboratory QA/QC. A comprehensive and effective Quality Assurance/Quality Assessment program demands the coordination and cooperation of a network of individuals and agencies since all aspects of the data collection process must be addressed. These include project planners, samplers, laboratories, and data users in both the public and private sectors. These requirements result in an extremely complex Quality Assurance program. An overview of the current Superfund Quality Assurance Program, with special emphasis on laboratory QA/QC, will be presented and discussed.
The U.S. Geological Survey's water quality laboratory in Denver, Colorado, routinely analyzes natural waters for 22 elements by inductively-coupled plasma optical-emission spectroscopy and for 3 elements by direct-current plasma optical-emission spectroscopy. During 1987, the laboratory made more than 141,000 determinations by plasma-emission techniques. Acceptable quality of data is achieved by four procedures: (1) established analyst protocol, (2) internal quality control, (3) external quality assurance, and (4) interlaboratory evaluations. Analyst protocol includes calibration check standards every 5 to 10 samples and verification by the analysis of U.S. Geological Survey Standard Reference Water Samples (SRWS). If results obtained for these quality control standards are outside pre-established quality control limits, the affected samples are reanalyzed. The internal quality control program submits blind SRWS and blanks to plasma-emission analysts daily. If quality control limits are not met, the problem is identified and a corrective response is reported to internal quality control personnel. A U.S. Geological Survey laboratory in Ocala, Florida, supplies quality assurance samples. The Florida laboratory mixes and dilutes SRWS for blind submission to the Denver Laboratory. Weekly control charts are generated from this program. The Denver laboratory also participates in interlaboratory evaluation programs conducted by the U.S. Geological Survey and the U.S. Environmental Protection Agency. As a result of these intensive quality control and quality assurance procedures, virtually all plasma-emission analyses are accurate and precise.

INNOVATIVE SCIENCE AND QUALITY ASSURANCE IN WATER-RESOURCES RESEARCH.

Innovative science requires extensive thought, experimentation and risk. It also requires that others trust scientists conducting the work and accept the validity of the work. In recent years, there have been increased requirements to demonstrate the validity of science—that have resulted in a rigorous campaign for extensive quality-assurance practices to enhance data quality. While quality assurance is a necessary part of scientific endeavor, scientists need to determine the degree of quality assurance needed to validate their methods and results.

THE SAN JOAQUIN VALLEY DRAINAGE PROGRAM: A COMPARISON OF MULTILABORATORY DETERMINATION OF SELENIUM IN REFERENCE MATERIALS AND OTHER ENVIRONMENTAL SAMPLES. W. J. Walker and R. G. Burau, University of California, Davis, Davis, CA 95616.

ABSTRACT: Twenty nine laboratories participated in The San Joaquin Valley Drainage Program's (SJVDP) selenium round-robin test in order to assess their ability to determine selenium in water, soil, sediment, and biological tissue. Results showed that 17 of 21 laboratories reported values near the accepted values. Pooled laboratory results indicated that most samples were within the range of the accepted values. Water samples analyzed by hydride generation or fluorimetry, appeared to give better results than other methods. Different sample pretreatment procedures accounted for some of the variation among laboratories using similar selenium detection methods as well as for a given laboratory reporting high or low results.
The Nevada Nuclear Waste Storage Investigation (NNWSI) branch of the U.S. Geological Survey (USGS) is supporting the efforts of the Department of Energy (DOE) to identify a possible location at or near the Nevada Test Site as a nuclear waste repository. The USGS has developed and is implementing a quality assurance program to meet the quality and technical requirements of the DOE Waste Management Project Office's NNWSI Project quality assurance plan (WVO-196-17). A wide range of earth sciences test and measuring equipment is employed by USGS scientists in their efforts to define the hydrologic and geologic characteristics of the site. A variety of sometimes unique calibration procedures is used, with some instruments requiring laboratory calibration at regular intervals, while others are at irregular intervals determined by project needs. Instrument acquisition, calibration, maintenance, operation, and special handling requirements are described in detailed, formally reviewed documents called technical procedures. These written procedures, along with formal activity recording methods and records storage, calibration traceability, personnel certification, and periodic audits and surveillances, are employed to maximize the quality of the overall field data acquisition effort.

ORDER OUT OF CHAOS — OR CHAOS OUT OF ORDER? Sydney Abbey, Geological Survey of Canada (Retired), 479 Riverdale Ave., Ottawa, Ontario, CANADA, K1S 1S3

Because of the large number of constituents involved, the derivation of reliable values for the concentrations of nearly all constituents in reference samples of silicate rocks is generally achieved by means of inter-laboratory collaborative analysis. Unfortunately, the resulting data are usually highly incoherent, in the number of results reported for each constituent and in the wide divergences in the results reported by different laboratories for the same constituent. A review is presented, describing various computation procedures that have been proposed for resolving the discrepancies and arriving at good working values. Suggestions are made for possible combinations of the different procedures. Using proposed “tests of validity”, the results obtained from those procedures are compared with one another, and also with results obtained by means of the author's own “select-laboratories” method.

VARIATIONS IN THE CONCENTRATION OF THE TRACE CONSTITUENTS EXTRACTED FROM SEDIMENT STANDARDS USING SEVERAL ACID DIGESTION PROCEDURES. Ralph V. Poulsen, Frank E. Polniak. ACZ INC. Laboratory Division, 1475 Pine Grove Road, Steamboat Springs, Colorado 80477

Analytical chemists have a multitude of choices of acid digestion procedures for the extraction of trace metals from sediment and soil samples. Many of the procedures are similar in the types of acids required, but will extract various metals with greatly different efficiencies.

ACZ INC. has performed thousands of acid digestions on soil and sediment samples over the past five (5) years. With each group of twenty (20) samples or less, one (1) NBS Standard Reference Material-River Sediment No. 1645 has been analyzed. Acid digestions procedures most commonly employed include EPA Method 3050 from EPA SW846, USGS Method 1-5485-78 Extraction Procedure, and the U.S. Bureau of Mines "Total Dissolution of Metals and Minerals Samples in Plastic Pressure Vessels, Investigation 8480".

Each of the above acid digestion procedures will extract metals of interest from the NBS sediment standard at varying efficiencies. Percent recovery for the USGS procedure will vary from 50% to 100% depending on the metal while the U.S. Bureau of Mines total dissolution procedure will consistently provide recoveries of 100%.
Cellulosic membrane filters are used by the U.S. Geological Survey in the field to filter water samples that are to be analyzed for dissolved chemical constituents. An experiment was conducted to quantify the amount of selected constituents leached from various brands of filters and to measure the effectiveness of rinsing the filters in the field prior to sample collection. Constituents of interest were leached from the filters using American Society of Testing Materials Type I Reagent Water using two procedures: (1) soaking individual filters for 24 hours, and (2) sequentially filtering three aliquots of 100, 100, and 200 milliliters.

Analysis of replicate aqueous leachates derived by soaking six widely-used brands of filters identified significant variance in concentrations of nitrogen and phosphorous species; values ranged from 1 to 162 micrograms per liter. Lesser variance and lower concentrations of selected trace elements were detected; values ranged from less than 1 to approximately 40 micrograms per liter for these constituents. Concentrations of major cations ranged from about 10 to 1,000 micrograms per liter.

Analysis of leachates derived from sequential filtration indicated that most of the leaching of nitrogen and phosphorous occurred in the first 100 milliliter filtrate. However, some filters yielded appreciable amounts of these constituents in the subsequent 100 and 200 milliliter filtrates. No other constituents were analyzed.

These experiments indicate that the ambient constituent concentrations of dilute-solution samples, such as rainfall samples may be significantly enriched by chemical leaching from some types of filters.

During the winter of 1987-1988, a pilot scale underground coal gasification project was conducted at a site near Hanna, Wyoming. One of the technical objectives of the project was evaluation of the environmental impact, therefore quality assurance/quality control procedures were emphasized for groundwater sampling and analysis activities so that data of known quality could be provided to both researchers and the Wyoming Department of Environmental Quality. Under the umbrella of Western Research Institute's corporate QA program, a project specific QA program was planned around three distinct project phases: baseline, gasification, and post-gasification. Generally accepted quality control practices were implemented both for field sampling (i.e. field blanks, field duplicates, rinseate samples chain-of-custody documentation, etc) and for analysis (i.e. calibration requirements, reference material analysis, spike recoveries, laboratory duplicates, etc). Examples will be given of how these practices directly impacted the interpretation and use of the data.

Quality-assurance planning is an important aspect of all water-quality investigations. Such planning is necessary in order to define clearly the practices needed to ensure that: (1) The investigative activity is addressing the problems to be resolved, (2) the methods being used will provide all of the data needed, and (3) the data generated are valid. Sometimes, however, quality assurance is inadequately addressed in either the planning or the investigative process, which may lead to a subsequent failure in meeting the objectives of the investigation. There are many factors that may lead to the failure of quality-assurance planning, several of which are:

1. Incomplete understanding by the project leader of the purpose and objectives of quality assurance activities.
2. The concept that quality-assurance activities are not worth the money or time, with a subsequent inadequate funding level for quality-assurance activities.
3. Failure to identify the decision maker and the decisions to be made as a result of the project findings.
4. Incomplete understanding of the statistical requirements for proper data assessment.
5. Failure to define acceptable limits of error for the results of chemical analyses or for analysis of the data.
6. Inadequate documentation of the quality-assurance planning or data or both.
7. The "Leave me alone, I know what I'm doing!" syndrome.

Not all of these factors are present in all investigations, of course, but the presence of even one could be sufficient to cause the failure of the quality-assurance process for a given investigation.
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Soil samples were collected from six sites in the high-elevation spruce-fir ecosystem in the eastern U.S., corresponding to intensive research sites in the NAPAP Forest Response Program. Fifty-five soil horizons are represented; soil organic matter by loss-on-ignition ranged from two to ninety-three percent across all horizons. Samples were split into those maintained at field moisture content and those air-dried prior to analysis. Analyses included: soil pH (de-ionized water and 1 N KCl), exchangeable bases and acidity, and extractable metals, phosphorus and sulfate. Within-sample variance was very small suggesting that the soils were well mixed. Significant differences between field-moist and air-dried samples were apparent for pH (by water) in 90 percent of the horizons, with air-dried samples having higher pH in 45 cases. Differences were also apparent in the other variables. The bias is thought to be linked to procedural differences and changes in soil chemistry. We found wet soil samples to be tremendously difficult to work with; however, the difficulty does not seem to introduce additional analytical error. For those who support wet-soil analyses as more accurate measures of soil parameters (particularly pH), this study indicates that differences created by air-drying soil samples is relatively consistent (for the horizons we analyzed) and can be corrected.

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Standardization for the measurement of gaseous organic compounds, according to the U.S. Environmental Protection Agency's Reference Method 18, is accomplished by using calibration gas cylinders or by preparing known concentrations from liquids in Tedlar bags. An alternative method exists for the accurate preparation of standard gas concentrations from pure liquids. The method involves the use of a rigid container that can be constructed of glass, aluminum, or stainless steel. To prepare a standard gas concentration, the vessel is evacuated. While under vacuum, a known mass of the organic(s) of interest is injected, through a septum, into the vessel. The vessel is then pressurized to the desired level and after mixing, the standard is ready for use. The advantages of this method of standard preparation as compared to the Tedlar bag method include: the determination of very accurate gas volumes from pressure measurements, very accurate mass values for injected organics because all liquid enters the evacuated vessel and the rapid and accurate preparation of up to six component organic mixtures. This technique has been used, under field conditions, to analyze audit gas concentrations on the order of 1 ppm/v.

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Since its inception in 1984, the Hazardous Waste Research and Information Center (HWRIC) has developed an extensive program of sponsored research to assess the magnitude of and provide solutions for the hazardous waste problems of Illinois. One HWRIC funded project measures the occurrence of toxic substances in air in both urban and rural areas and attempts to identify the sources of these contaminants. This information will be used to develop source/receptor models to predict the movement of contaminants released to the atmosphere. Analysis of water and sediment samples from contaminated lakes and rivers is a fundamental part of other HWRIC projects. These analyses provide the data required to assess the toxicological effects of the measured contaminants and to facilitate the selection of effective methods for site remediation and restoration. The flow of contaminants from a former landfill site and the potential for contamination of nearby groundwater is also being studied. Finally, an educational program to alert the public to hazardous substances routinely used in the home, resulted in a drive to collect unwanted products for disposal and the distribution of literature that provides information on less hazardous substitutes.

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Three dimensional Fluorescence Spectra (EEM) of surface water samples are representative of the fluorophoric composition of materials either dissolved or suspended in these samples. EEM spectra having humic character show broad fluorescence from 300 to 800 nanometers with excitation peaks at wavelengths longer than 300 nanometers and emission peaks at wavelengths longer than 500 nanometers. Water from the Calcasieu River, Louisiana has characteristics of fluorophoric patterns found in Humic materials. An analysis of these patterns as compared with various Humic fractions shows many similarities. Samples from local surface water sites at the Denver Federal Center had less macromolecular character, but were readily characterized.

In the USP XXI, approximately 32 monographs use chloroform-solution infrared identification tests. The infrared spectra of fifteen of these compounds were available in our files. Of these, 11 spectra showed a negative peak at 3620 cm⁻¹. The common structural feature among these 11 compounds was the presence of at least one amine moiety in each. The reagent-grade chloroform that had been used was labeled to contain 0.75% ethanol as a preservative. When the spectra were redetermined in ethanol-free chloroform, the negative peak was no longer observed. We undertook a more rigorous study of the predictability and quantitative aspects of this phenomenon. The intensity of the negative peak appears to depend on the concentrations of the ethanol and the compound. The negative peak did not show in some amides or in compounds without the amine moiety. The cause of the negative peak will be discussed.

A colorimetric method for the determination of Selenium in feed premixes is described. The premix is digested in a sulfuric acid - perchloric acid - sodium molybdate mixture; diluted; filtered; subjected to cation exchange chromatography to remove potentially interfering copper, iron, and manganese cations; pH adjusted; treated with hydroxylamine and ethylene-diaminetetraacetic acid; complexed with 3,3'-diaminobenzidine; pH adjusted; extracted into toluene; and absorbance measured at 420 nm. Typical selenium concentrations are between 50 and 200 μg/g, and up to ten samples per day can be run. Recoveries both with and without cation exchange; effectiveness of the ion exchange column in removing cations; operating curve; and a detailed procedure are reported.
A KINETIC MODEL FOR PHOTODECOMPOSITION OF SOLUTIONS OF AMINO ACIDS AND SUSPENSIONS OF GOETHITE + ADSORBED AMINO ACID. Kirkwood M. Cunningham and Marvin C. Goldberg, U.S. Geological Survey, Box 25046, Mail Stop 424, Denver Federal Center, Denver, CO 80225. Ferrous iron and acetaldehyde are produced during the near-UV photolysis of aqueous suspensions of goethite and the adsorbed amino acid d,L-alanine in the presence of bicarbonate buffer. These products are thought to result from 1) surface redox reactions between photoexcited Fe$^{2+}$ in the goethite surface and adsorbed carboxylate and carbonate, and 2) subsequent radical-radical and radical-molecule reactions of the initially formed species. Product yields are a function of photolysis time, pH, and oxygen concentration. A kinetic model was devised to describe this complex system qualitatively using known or estimated rate constants in numerically integrated differential equations for a dozen of the most important species. Simplifying assumptions were made to accommodate the heterogeneous nature of the system. The experimentally observed effects of pH, photolysis time and oxygen concentration were generally reproduced within the limits of the model and input data. Carbonate ion was found to play an important role as both radical source and sink in the modeled reaction.

LIQUID CHROMATOGRAPHIC DETERMINATION OF THE AMOUNT OF EPIMERIZATION OF CHLOROTETRACYCLINE RESIDUE TO 4-EPI-CHLOROTETRACYCLINE RESIDUE IN ANIMAL FEED. Elizabeth E. Martinez and Wilbert Shimoda. Food and Drug Administration, Bldg. 20, Denver Federal Center, P.O. Box 25087, Denver, Colorado 80225-0087

A liquid chromatographic (LC) method was developed to determine the amount of epimerization of Chlorotetracline-HCl (CTC) in animal feed. The extraction procedure involved double extraction with pH 2.0 McIlvain's buffer. The amount detected is 100 ppm and the detection limit is 3 ppb with 10 μL injections of CTC and 4-epi-CTC. The calibration curve is linear between 5-80 ppm for both CTC and 4-epi-CTC combined. A previous method will quantitate multiresidue levels of TC, OTC and CTC from animal feeds. These recoveries were lower for CTC than TC or OTC. As a consequence this method was developed to show that epimerization does take place and it does have an effect on the total recovery of CTC from animal feed; especially in high acid solutions.

A REVISED LIQUID CHROMATOGRAPHIC METHOD FOR THE DETERMINATION OF GENTIAN VIOLET IN ANIMAL FEED. Elizabeth E. Martinez and Wilbert Shimoda. Food and Drug Administration, Bldg. 20, Denver Federal Center, P.O. Box 25087, Denver, CO 80225-0087

A revised liquid chromatography method for the determination of Gentian Violet (GV) in animal feed is described. The quantitation level was between 2.5 and 10.0 ppm. The reliable limit is 10 ppb and the method will quantitatively analyze samples down to 1.0 ppm. The calibration curve shows linearity between 1-40 ppm. The GV is extracted from feed using methanol-1N HCl (99+1). This method was developed from a study by National Center for Toxicological Research. The method was revised to use methanol-water (9+1) instead of benzenemethanol as the eluting solution. Sephadex LH-20 column is used in the cleanup procedure, separation on a Nova-Pak C18 column and detection at 588 nm. Recoveries of three sets of five samples at concentration of 2.5, 5.0 and 10.0 ppm were 64.4, 91.4 and 92.2 %, respectively. Gentian violet was confirmed by thin-layer chromatography (TLC).
DETERMINATION OF SOME BETA-LACTAM ANTIBIOTICS IN MILK AND KIDNEY TISSUE BY HPLC-ELECTROCHEMICAL ANALYSIS. Robert K. Munns, Jose E. Roybal, Jefferay A. Hurlbut and Wilbert Shimoda. Food and Drug Administration, Bldg. 20, Denver Federal Center, P.O. Box 25087, Denver, CO 80225-0087

A rapid method for determining beta lactam Penicillin residues in milk has been developed. An HPLC-postcolumn UV-hv-reactor system with an electrochemical detector can separate and determine Penicillin G, metacillin, cephamtin and cloxacin in milk. Milk is treated with acetonitrile and the supernatant is concentrated. Lipids are removed with ethyl ether and, after further concentrating, the aqueous fraction is saturated with a salt solution and the sample is partitioned with acetonitrile. Kidney tissue is treated similarly after blending with a buffer solution.

Detection of hydrolyzed forms of each of these beta lactam penicillins, amoxicillin and ampicillin are discussed.

DETECTION OF GENTIAN VIOLET, ITS DEMETHYLATED METABOLITES, LEUCOGENIANT VIOLET AND METHYLENE BLUE BY ELECTROCHEMICAL/HPLC. Jose E. Roybal, Robert K. Munns, Jeffrey A. Hurlbut and Wilbert Shimoda. Food and Drug Administration, Bldg.20, Denver Federal Center, P.O. Box 25087, Denver, CO 80225-0087

The liquid chromatographic conditions for the electrochemical (EC) detection of Gentian violet (GV), its demethylated metabolites, Leucogeniant violet (LV) and Methylene blue (MB) are reported. Separation of GV, its demethylated metabolites and LV was accomplished within 14 minutes using cyano column eluted isocratically with 60% methanol-buffer as the mobile phase. EC response for GV, LV and MB showed linearity over a range of 0.54 to 6.75 ng, 0.5 to 25.2 ng and 5.7 to 285 ng, respectively. The elution under these conditions, in increasing order, was LV, N^2 tetramethylpararosaniline chloride, N^1 tetramethylpararosaniline, pentamethylpararosaniline chloride and GV. MB and GV had essentially the same retention time under these parameters. The detection limit for GV, its demethylated metabolites and LV was determined to be 0.1 picomole. A detection limit of three picomoles was established for MB. Detector response, elution, separation, linearity and sensitivity of detection are discussed.

DETERMINATION OF CHLORAMPHENICOL IN VARIOUS MATRICES BY GAS CHROMATOGRAPHY ANALYSIS. Susan B. Torda. Food and Drug Administration, Bldg. 20, Denver Federal Center, P.O.Box 25087, Denver, CO 80225-0087.

Methods are described for the isolation of chloramphenicol in various matrices, such as tissue, milk and urine, with gas chromatography quantitation. A synthetic chloramphenicol glucuronide is added to tissue and urine for extraction, enzymatic hydrolysis and isolation as chloramphenicol. Cleanup involves mini-columns of Chromosorb 102 and basic alumina, or solvent-partitioning using CCl4 for lipid removal. Chloramphenicol is derivatized with Sylon HTP. Detection limits, recoveries and detailed procedures are included.

A study to determine pesticides in surface water was undertaken within a 20-mile reach of the San Joaquin River during the summer of 1987. The goal was to characterize the types of pesticides moving through the stream and passing between two pre-selected sampling sites. All water samples were collected using a depth-integrating water sampler operated from a bridge directly above the channel and lowered to the stream bottom. Liquid-liquid extraction and solid-phase extraction were compared with respect to ease of operation and effectiveness in terms of recoverable material. All extracts were analyzed by capillary column gas chromatography employing an ion-trap detector. Pesticides were identified by a combination of retention parameters and ion-trap mass spectra matched from a user generated library of enhanced mass spectra. Mass chromatograms also were used to confirm identity, as well as for low-level, selected-ion quantitation. The mass-spectral library consisted of 53 registered and applied pesticides, and included most of those used on farmland drained by the San Joaquin River flowing through the study area. Several individual pesticides were detected in many of the extracts at a concentration less than 50 ng/L. Lindane, several chemicals in the DDT family, and atrazine were found most frequently and in the highest concentrations. The efficiency and selectivity of solid-phase extraction and the utility of the ion-trap detector for rapid environmental-residue determinations will be presented in the context of these results.

ATOMIC SPECTROSCOPY DATA CENTERS AT THE NATIONAL BUREAU OF STANDARDS--CRITICAL COMPILATIONS OF ATOMIC TRANSITION PROBABILITIES AND ATOMIC ENERGY LEVELS. Jeffrey R. Fuhr, Wolfgang L. Wiese, Mark A. Suskin, William C. Martin, Jack Sugar, and Arlene F. Robey, National Bureau of Standards, Physics Bldg., Gaithersburg, MD 20899.

The NBS Data Centers on Atomic Transition Probabilities and Atomic Energy Levels publish critically evaluated data tables on selected spectra, as well as annotated bibliographies. The Data Center on Atomic Transition Probabilities has recently completed a critical compilation of atomic transition probabilities for the elements scandium through nickel. This work, to be published as Supplements 2 and 3 to the Journal of Physical and Chemical Reference Data (Vol. 17, 1988), will cover neutral and ionized species, as well as allowed and forbidden lines. The Atomic Energy Levels Data Center has recently published wavelength tables for Ni and Mo and plans to publish tables on Cr, Fe, and Sc later this year. This data center is also planning to publish evaluated energy levels for sulfur, molybdenum, and copper. Future plans include bibliographic and numerical databases for both data centers.

DETERMINATION OF SODIUM NITROFERRICYANIDE BY HPLC, C. P. Patel, M. V. Rebec, QAD-Analytical Services, Miles Inc., P. O. Box 70, Elkhart, IN 46515

An HPLC method, specific to determine the purity of Sodium nitroferricyanide (SNFC) in the presence of Potassium ferricyanide (PFC) and Sodium ferrocyanide (SFC) has been developed. The method is based on the separation of above chemicals using a 5 micron, spherical ODS packed column (4.6 x 250 mm) with a mobile phase composed of 720 mL of 2.7 mM potassium phosphate, pH 7.5 + 280 mL acetonitrile + 0.68 g of tetraethyl ammonium phosphate. The eluant is monitored at wavelength 220 nm. This approach has benefits over USP recommended titrimetric procedure because the latter could not be used to determine the relative levels of SNFC in presence of the other two. PFC and SFC could both be found in SNFC due to poor manufacturing and solution storage controls. The detector response for SNFC was found to be linear in the range of 10 to 100 ug/mL (20 mg to 200 mg) with standard error of estimate of 0.7 ug/mL. Day-to-day and within-day precision both were below 2 ug/mL at 95% confidence level.
The research objective was to characterize the reaction of superoxide anion (O$_2^-$) with the anti-neoplastic agent 6-mercaptopurine (6-MP) used in the treatment of leukemia. Electrochemical methods were used to generate O$_2^-$, to monitor O$_2^-$ reacted and to monitor the amount of oxygen released. The reactions utilized acetonitrile and dimethylsulfoxide aprotic solvents with 6-MP in millimolar amounts. Monitoring with cyclic voltammetry showed that O$_2^-$ disappeared immediately with the release of oxygen. The UV spectrum of an aliquot of reaction mixture in pH 4.5 buffer showed initially unchanged starting material. Slower follow-up reactions were seen as the reaction progressed using UV spectroscopy and polarography. The oxidation products, purine-6-sulfinate and purine-6-sulfonate were identified by these techniques. No evidence was found for the presence of hypoxanthine, 6-thiouric acid or 8-hydroxy-6-mercaptopurine which have been reported previously as metabolites of the biological oxidation of 6-MP. Our experiments, however, did not rule out 6-mercaptopurine disulfide as a possible intermediate or byproduct. Similar experiments utilizing 6-MP with oxidizing agents and bases were performed. These results are consistent with a proton induced disproportionation of superoxide yielding oxygen, hydrogen peroxide, and the corresponding negative ion of 6-MP. Thus superoxide acts as a base and in the case of thioacyl compounds produces more readily oxidizable negative ions. These results suggest that high levels of biological O$_2^-$ could alter the reactions of 6-mercaptopurine in the body. (Supported by NIH RR-8177-6)

The concentration of pertinent levels of oxygen in viable biological systems is one of the most important but elusive parameters in biology, because of the difficulties of making such measurements. A variety of ESR methods now make such measurements feasible. These approaches are based on the interactions of paramagnetic oxygen with nitroxides and/or the oxygen dependent metabolism of nitroxides. The types of measurements that are currently available and/or in significant stages of development in our laboratory include: 1) the measurement of oxygen concentrations inside cells by conventional ESR; 2) the measurement of the diffusion of oxygen by one and two dimensional rapid ESR imaging; 3) the measurement of the amount of hypoxic cells by conventional ESR; 4) the measurement of oxygen concentrations by 2D and 3D ESR imaging at 9 GHz; 5) the measurement of oxygen concentrations by spectral-spatial ESR techniques at 9 GHz; 6) the measurement of oxygen concentrations in vivo by surface coil studies of oxygen dependent metabolism of nitroxides. These related but different techniques have the potential to make ESR an important technique for many types of experimental and, perhaps, clinical studies of metabolism and disease. (This research was supported in part by NIH grants GM42550 and GM 55534 and used the facilities of the University of Illinois ESR Center which is supported by NIH grant RR01811)

Molecular reorientation for perdeuterated 2,2,6,6-tetramethyl piperidine N-oxide (PD-Tempone) and N-(4-butylnitrenilidine) 4-amino 2,2,6,6-tetramethyl piperidine 1-oxide (BTTMPO) and in toluene was analyzed in terms of the hydrodynamic free space model for molecular relaxation in liquids at 1, 4, 9, and 35 GHz. From an analysis of the temperature-dependent ESR line shapes in the motional narrowing and slow tumbling regions, the stickiness factors (S) were measured. For PD-Tempone in toluene the results are: at 1.171 GHz, S = 0.708, at 3.952 GHz, S = 0.500, at 9.084 GHz, S = 0.336, and at 35.11 GHz, S = 0.164, and for BTTMPO in toluene, the results are: at 1.097 GHz, S = 1.00, at 3.954 GHz, S = 0.851, and at 9.119 GHz, S = 0.707. The results showed that for a given system S is decreasing with increasing microwave frequency and S is higher for the elongated solute (BTTMPO) and lower for the spherical solute (PD-Tempone). For BTTMPO in toluene at 1.097 GHz, the stick limit (S = 1.00) is reached. When plotted against $\nu^{-2}$ it has a linear dependence in the frequency range of 1-4 GHz but started to curve downward at higher frequencies. The onset of linearity seems to be earlier for elongated molecule (BTTMPO) than it is for spherical molecule (PD-Tempone). The results are in agreement with theoretical predictions and molecular dynamics calculations and represent the first experimental ESR verification of the long time tails effect.

EPR spin probe studies of Dowex 44324 and Dowex 44339 ion exchange resins were carried out as a function of temperature from 77 K to 429 K. The spin probe used was 2,2,6,6-tetramethyl piperidine-1-oxide (Tempo), and both the resins were strong basic anion exchange resins with quartenary ammonium type structure. The magnetic parameters of Tempo in the resins were determined and found to be typical of systems with hydrogen bonds. EPR line shape results from 148 to 429 K revealed that Tempo was undergoing anisotropic rotational diffusion along z' = Y axis with N = 15 ± 1 at the higher temperature range (326-429 K) in both resins, while N = 2.7 in the lower temperature range (148-247 K). The rotational correlation times from 148 to 247 K varied from 2.3 x 10^4 to 1.0 x 10^2 s, indicating that the probe was highly immobilized. The activation entropies (E_a) in Dowex 44324 and 44339 over the two temperature ranges studied were 16.5 ± 0.3 and 13.8 ± 0.3 kJ/mol, respectively. The anisotropic interaction parameter x, which measures the coupling of rotation to translation, was found to be 0.02. The magnitude of E_a's and the smallness of x are typical for spin probes rotating in a clathrate-type environment. The EPR line shapes of Tempo in Dowex 44324 (mesh 20-50) and Dowex 44339 (mesh 200-400) were virtually identical indicating that no surface effects were observed in this range of resin size.

CONDENSATION, GELATION, AND DRYING OF SILICA SOL-GELS CHARACTERIZED BY 29Si NMR. Alexander J. Vega and George W. Scherer, Central Research and Development Department, E. I. du Pont de Nemours and Company, Experimental Station, Building 356, Wilmington, DE 19898, U.S.A.

Silica sols and gels were prepared by the hydrolysis and condensation of tetraethoxysilicate. The chemical and structural evolution were followed through nearly all the processing stages, i.e., hydrolysis, condensation, densification, gelation, aging, and drying. Nonspinning 29Si NMR shows the extent of crosslinking before and after gelation. After gelation a large portion of the silicate species remains as an internetwork liquid and new siloxane bonds continue to form for weeks. The state of intercapillary water and its interaction with the silica network in the incompletely dried gel has been studied. The asymptotic hydrogen content during drying under various conditions at temperatures below 100°C are in agreement with the concentration of hydroxyl groups obtained by 29Si NMR. The local structure of the hydroxyl groups in the dried gels is in many respects identical to that of colloidal silica particles, as shown by proton and heteronuclear 1H-29Si 2D NMR.

ZERO FIELD NMR ENTIRELY IN HIGH FIELD. Robert Tycko, AT&T Bell Laboratories, Murray Hill, NJ 07974.

A new technique that, in effect allows zero field NMR spectra of solids to be obtained entirely in high magnetic field will be described. The technique uses a combination of rapid sample rotation and synchronized rf pulses to remove the orientation dependence of nuclear magnetic dipole-dipole couplings while preserving the coupling information. The resulting NMR spectra show sharp lines with splittings that depend only on distances between nuclei, rather than the broad, powder pattern lines that are normally observed. Such spectra should be useful in structural studies of solids that are not single crystals. Experimental spectra of organic solids will be presented. A brief account of the theory behind the experiments will be given, explaining how sample rotation and rf pulses average the truncated, orientation-dependent couplings that occur in high field to the form of the untruncated, scalar couplings that occur in zero field. Advantages of the new technique, in terms of sensitivity, time resolution, and isotopic selectivity, will be discussed.


Double tuned circuits are frequently used in NMR probes as a simple means of exciting and detecting nuclei in a single coil device. General examples of different double tuned circuits will be examined in terms of efficiency and practical application to NMR probes. Examples will include circuits used in CP MAS and surface coil probes with comparison of calculated and experimentally determined data.
SOLID STATE ADVENTURES WITH ODD QUADRUPOLES. Evan Williams, Varian Associates D-298, 611 Hansen Way, Palo Alto, CA 94303.

Solid State nmr has concentrated to a large extent on two groups of nuclear spins, the dipolar spin 1/2 and the quadrupolar spin 1 nuclei. Thus, techniques such as MASS and CP/MAS are usually associated with spin 1/2 nuclei such as 13C and 29Si and powder pattern spectroscopy is associated with either spin 1/2 or spin 1 such as 2H. However, the bulk of quadrupolar nuclei do not have an integral spin. Exceptions to this statement are 1H, 6Li and 14N which have a spin of 1, 10B with a spin of 3, 139La with a spin of 5 and 50V and 176Lu which have spins of 6. The rest of the quadrupolar nuclei have non-integral (odd) spins between 3/2 and 9/2.

This paper will survey the field of solid state nmr of these odd quadrupoles. Key to the area is the need to understand the nmr techniques available to obtain meaningful spectra. The general area can be considered as two subsets, spinning and static. Spinning techniques include MASS, CP/MAS and VASS (in which the sample is spun at angles other than the magic angle.) Static experiments range from the well known solid echo through to 2D techniques such as nutation nmr. As the type of information sought is quite diverse, the discussion will range from a look at a range of these techniques. The discussion will be illustrated with data from research in progress.

NMR STUDIES OF INORGANIC POLYMERS.
James F. Haw, Richard C. Crosby, Shawn Maynard, Doug Gabler, and Richele Theodore, Department of Chemistry, Texas A&M University, College Station, TX 77843.

Our group has been using solid-state and solution-state NMR methods to investigate the synthesis, structure, morphology, and reactivity of selected classes of inorganic polymers. Much of this work involves polyphosphazenes which are based on chains of alternating phosphorus and nitrogen atoms. We are also studying preceramic polymers such as polysilanes which are precursors to silicon carbide.

NEW METHODS FOR THE STUDY OF CHEMICAL REACTIONS ON CATALYSTS.
James F. Haw, B. R. Richardson, I. S. Oshiro, Noel Lazo, and J. White, Department of Chemistry, Texas A&M University, College Station, TX 77843.

Novel experimental techniques are introduced which will be applicable to the study of many highly reactive catalyst/adsorbate systems. Some of these methods make use of a novel device called the CAVERN and in-situ variable-temperature CP/MAS NMR.

Using these methods, the oligomerization reactions of propene and other olefins on zeolite catalyst HY have been studied in detail. Propene is shown to be highly mobile in the zeolite at temperatures far below the onset of chemical reactivity. Alkoxo species formed between protonated alkenes and zeolite framework oxygens are found to be important long-lived intermediates in the reactions. Simple secondary or tertiary carboxations either do not exist as free ions in the zeolite at low temperature or are so transient that they are not detected by NMR even at temperatures as low as 163 K. There is, however, evidence for long-lived alkyl-substituted cyclopentenyl carboxations, which are formed as free ions in the zeolite at room temperature. These carboxations do not form until all of the propene is consumed and hence do not play a significant role in the oligomerization reactions.
CHARACTERIZATION OF NADPH-INDUCED NITROXIDE REDUCTION IN LIVER MICROSONES.

Hideo Utsumi, Masahiro Kashiwagi, Akira Shimakura & Akira Hamada, School of
Pharmaceutical Sciences, Showa University, Shinagawa, Tokyo, 142 JAPAN

Nitroxide radical is widely used as a spin-labeling reagent and may be
useful as a imaging reagent in MRI. Nitroxide is susceptible to various redox systems
in organism. In the present paper, we investigated NADPH-induced nitroxide reduction
in rat liver microsomes, using spin-labeled fatty acids and phospholipids.

The depth of active center of nitroxide reduction in microsomal membranes
was determined with 4 spin-labeled stearic acid derivatives which bear nitroxide
radical at 5, 7, 12, and 16 carbon position (abbreviated as 5-, 7-, 12-, 16SLS). ESR
spectrum of each SLS in microsomes showed that nitroxide radical must be located in
the depth as desired. The reduction rate was estimated by tracing the central peak
after the addition of NADPH. The rate depended strongly on the position of nitroxide,
and was related to the cytochrome P-450 content in microsomes but not to NADPH-
reductase. These facts suggest that the active center of nitroxide reduction should
be located in the lipophilic region in membranes.

To clarify the specific interaction of phospholipid with enzymal systems
taking part in nitroxide reduction, 4 different spin-labeled phospholipids, PC, PE,
PA and PG, was used which bear 7SLS at 2 position of glycerol. The NADPH-induced
nitroxide reduction was the fastest in PA, and no appreciable difference was observed
among PC, PE and PG, indicating that PA may predominantly locate around nitroxide
reduction systems in rat liver microsomal membranes.
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Map Legend
1 Radisson Hotel Denver
2 Brown Palace Hotel
3 Executive Tower Inn
4 Hyatt Hotel
5 Holiday Inn-Downtown
6 Marriott City Center