Rocky Mountain Conference on Magnetic Resonance

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32nd Rocky Mountain Conference

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PROGRAM
AND
REGISTRATION INF

JULY 29 - AUGUST 3, 1990

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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Speakers will be able to prepare their talks in the Birch Room Monday, Tuesday, and Wednesday from 7:00 a.m. to 6:00 p.m.

WELCOME

On behalf of my fellow organizers and volunteers, I am delighted to welcome you to the 32nd Rocky Mountain Conference on Analytical Chemistry. The Conference symposia continue to provide a respective forum for the exchange of scientific advances in many analytical fields. The Exhibition area gives conferees an opportunity to see and evaluate state-of-the-art analytical instrumentation and accessories, and to become familiar with the many services and supply sources which are necessary to the practice of analytical chemistry. Finally, the banquet and other social activities provide a great opportunity to get better acquainted with our scientific colleagues. We hope your visit to the Conference will be enriching in all aspects.

Sincerely,

Patricia L. Sulik, Ph.D

Patricia L. Sulik
Conference Chair

Conference Location

Technical sessions and the exhibition for the 32nd 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 the name badge for the 32nd Rocky Mountain Conference. Preregistration, using the form in the center of this booklet, is encouraged. The deadline for the receipt of the preregistration form and full remittance of conference fees is July 20, 1990. Conference fees are payable by check (denominated in $US, only) made payable to the Rocky Mountain Conference.

Registration Fees - 1990

Preregistration (received by July 20, 1990)	$50.00
Preregistration - one specified day	$30.00
Registration - on site	$65.00
Registration - one specified day	$35.00
Student registration	$15.00
Additional Vendor registration	$35.00
Unemployed or Retired registration	$15.00

Refunds

Requests for refunds of conference fees must be received by July 20, 1990.

Times

On-site registration for the 32nd Rocky Mountain Conference will be held in the Convention Lobby of the Radisson Hotel Denver during these times:

Sunday, July 29, 1990	5:00 p.m. - 9:00 p.m.
Monday, July 30, 1990	7:30 a.m. - 3:30 p.m.
Tuesday, July 31, 1990	7:30 a.m. - 3:30 p.m.
Wednesday, August 1, 1990	7:30 a.m. - 3:30 p.m.
Thursday, August 2, 1990	8:00 a.m. - 10:00 a.m.

Social Program

Registration Night Mixer
Sunday, July 29, 1990, 7:00-9:00 p.m., Exhibit Hall

Conference Mixer
Monday. July 30, 1990, 5:00-7:30 p.m., Exhibit Area

On Monday afternoon, July 30, immediately after the conference, please join us for a cocktail and hors d'oeuvre mixer at the Radisson Hotel. Mixer sponsored by Hewlett Packard.

Conference Banquet
Tuesday, July 31, 1990, 7:00-10:00 p.m., Majestic Ballroom

The Rocky Mountain Chapter of the Society of Applied Spectroscopy is pleased to present our banquet speaker Dr. John Brandt, Professor of Astrophysics at the University of Colorado's Laboratory for Atmospheric and Space Physics (LASP). Professor Brandt is a principal investigator on the recently launched Hubble Space Telescope Project. The orbiting spectrometer will provide a view of the edge of the universe never before seen by man. Murphy's law withstanding, by the date of the banquet Professor Brandt will share with us mankind's first spectroscopic glimpses of the beginning of time.

Tour

On Wednesday, August 1, there will be a guided tour (approximately 30 minutes) of the operating brewery at the Wynkoop Restaurant located in historic downtown Denver followed by dinner at the Wynkoop. The tour is free but space is limited, so please make your reservation early before June 15. Information will be available at the registration desk.

Exhibition

The Rocky Mountain Conference exhibition provides an opportunity to see and discuss the latest in analytical instrumentation, supplies, and service. Other activities in the exhibition hall include coffee breaks, mixers, and poster sessions.

Hours

Sunday, July 29	Mixer	7:00 p.m. - 9.00 p.m.
Monday, July 30	Exhibits	9:30 a.m. - 5:00 p.m.
Monday, July 30	Posters	2:00 p.m. - 4:00 p.m.
Monday, July 30	Reception	5:00 p.m. - 7:30 p.m.
Tuesday, July 31	Exhibits	9:30 a.m. - 5:00 p.m.
Wednesday, August 1	Exhibits	9:30 a.m. - 5:00 p.m.

Posters will be set up in the exhibition area Monday morning through Wednesday afternoon.

The following exhibitors have reserved space as of April 10, 1990:

Affiliated Scientific
Alpkem Corporation
American Microwave Technology
Applied Technical Products
Brinkmann Instruments, Inc.
CDS Instruments
Chemagnetics, Inc.
Dionex Corporation
Extrel Corporation
General Air Service
Instruments, SA
Mattson Instruments
Micro-Now Instruments
NIST
Oxford Instruments
Questron Corporation
Tekmar Company
Varian Instrument Group
Zymark Corporation
Allen Scientific Glassblowers
Analyte Corporation
Applied Research Labs/FISIONS
Bio-Rad, Digilab Division
Bomen, Inc.
Broker Instruments, Inc.
CEM Corporation
Doty Scientific
Finnigan MAT
General Cable Company
JEOL USA, Inc.
Medical Advances, Inc.
Nicolet Instruments
On-Site Instruments
Perkin Elmer Corporation
Sadder Research Labs
Thermo Jarrell Ash
Waters Div. of Milipore
Wilmad Glass

Additional financial support for the conference has been provided by Hewlett Packard and Leeman Labs.

For exhibit information, please contact:

Jim Parker R-38
Manville Technical Center
10100 West Ute Avenue
Littleton, Colorado 80127
Tel. (303) 978-5481
FAX (303) 978-5094

ADDITIONAL ACTIVITIES

Visitor **Information**

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) 592-5510.

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. 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 a.m. to 10:00 a.m. Thursday.

ThermoSPEC™ Software Seminar

8:30 a.m. to 5:00 p.m. Thursday, August 2, 1990

A workshop for experienced users of ThermoSPEC™ software for Thermo Jarrell Ash AAS and ICPES systems will be offered to Rocky Mountain Conference attendees. There is an additional $20 charge for this workshop which will include lunch. A structured learning session, led by Ron Manabe, will be held in the morning with open discussions following the lunch break. Space will be limited for this workshop and preregistration is recommended. The deadline for onsite registration is noon on Monday, July 30. Call (415) 327-5605 if additional information is needed.

Seminar Topics:

- * Version-to version updates
- * Use of command language
- * Ancillary integrated software (including Enable and SPC)
- * Turbo-ThermoSPEC™
- * Latest in preintroduction systems (chelation chemistry, ultrasonic)
- * User open forum
- * Group discussions
- * Formation of User Groups

Formal presentations will begin promptly at 9:00 a.m. on Thursday, August 2.

ThermoSPEC™ Seminar Registration Form

Name______________________________
Company___________________________
Address___________________________
____
Phone_____________________________

Make checks payable to Rocky Mountain Conference.

This seminar is available only to RMC attendees. The $20 seminar fee may be added to your RMC preregistration payment.

Please provide the following information concerning your current use of ThermoSPEC™ software so we may tailor the course to participants:

ThermoSPEC™ used on the following instruments:________________________

Data manipulation and reporting packages used:________________________

Data are exported to the following LIMS:____________________________

ACS EMPLOYMENT BOOTH ACTIVITIES

The Employment Committee of the Colorado Section of the American Chemical Society will sponsor a workshop on RESUME PREPARATION and CONDUCT DURING AN **INTERVIEW.**

The workshop will be conducted by Lauren Skinner, Lab-Support, on Tuesday, July 31, from 8:30 to 12:30. The workshop will consist of formal presentations by Jennifer, with follow-up discussions on an individual basis. For room location contact the registration desk or the Employment booth in the exhibits area.

The Employment Committee will also conduct an employment clearing house. Resumes will be available prior to, and during the meeting, for review by prospective employers. Facilities will be available for on-site interviews by employers and posting of positions available. Employers who are interested in using this employment booth should register at the Employment Committee Booth.

All job-seekers are invited to register at the Employment Booth by submitting a resume.

Douglas B. Manigold, Chairman
US Geological Survey
Road
Arvada CO 80002
236-5345
FAX (303)467-9598

Sonia Atwood
Marathon Oil Company 5293 Ward
P.O. Box 269
Littleton, CO 80160
794-2601
FAX (303) 794-1720

Helen Brandenburg
US Geological Survey
5293 Ward Road
Arvada, CO 80002
236-5345
FAX (303)467-9598

Ronald G. Thompson
Marathon Oil Company
P.O. Box 269
Littleton, CO 80160
794-2601 ext. 708
FAX (303) 794-1720

Interested employers and job-seekers can receive additional information on available jobs and on employment activities by calling the ACS Employment committee Hotline number which is 933-4375.

CEM WORKSHOP

CEM Corporation will conduct a workshop on Closed Vessel Microwave Sample Preparation.

The workshop will cover the latest in microwave hardware (high power unit, 200 psig vessels and pressure feedback controller). In addition to the hardware, we will cover Sample Preparation Applications for the system. These applications will include environmental, oils, tissues, metallurgical and geochemical for spectroscopic analysis and environmental samples for total nitrogen phosphorous. This workshop will be held Thursday, August 2, 1990 from 9:00 a.m. to 12:00 Noon.

Basic Electronics for Scientists

August 2-3, 1990 Fee: $350 Member; $400 Nonmember

This two-day intensive course will take the student from the basic physics of electronics and electrical circuits to the design and troubleshooting of transistor and op-amp circuits, power supplies and the control of electromagnetic actuators. No previous knowledge of electronics is assumed. The course will be both quantitative and experimental. You will work with a kit of components, making circuits and testing them with electronic instruments. You will become familiar with common electronic components and learn how to assemble them. The course will familiarize you with fundamental concepts useful in electronics, such as impedance , single-time constant circuits, feedback, and working models for semiconductor devices. These concepts will allow you to understand and use electronics with increased confidence.

The students should bring a digital multimeter or equivalent to the course, so that they will become familiar with the use of their own instrument. Some multimeters will be available for students who do not bring their own.

Faculty: Dr. James B. Calvert, P.E., is Associate Professor of Engineering at the University of Denver. He has prepared and presented courses in electronics and microcomputers there since 1979 and has over 20 years of University teaching experience. Dr. Calvert's research interests have been in ultrasonics, optics, atomic and molecular structure, quantum mechanics, analog integrated circuits and the history of technology. He is a registered professional engineer in the State of Colorado.

For Short Course registration by July 16, 1990 contact:

Joe Zirrolli
National Jewish Center
Dept. of Pediatrics, K923
1400 Jackson Street
Denver, CO 80206
Tel 303-398-1853
Fax 303-398-1694

or

Sonia Atwood
Marathon Oil Company
P. O. Box 269
Littleton, CO 80160
Tel 303-794-2601
Fax 303-794-1720

OUTLINE: ELECTRONICS

This is an intensive course in analog electronics for scientists who have to deal with measurements, data acquisition and recording, laboratory control, monitoring, as well as the design, maintenance and operation of experimental apparatus. The course does not depend on previously acquired knowledge and skills, but begins at the beginning. Its object is the development of the ability to use rational, widely applicable techniques based on knowledge and understanding.

The Course

I. The art of electronics. Troubleshooting and design. What's available today. How to become an electronics wizard in the eyes of your colleagues.

II. Circuits and impedance. Using thermocouples and pH electrodes.

III. Semiconductors. Transistors are easy to use and do it all.

IV. Operational amplifiers and the feedback concept. Make accurate voltage and current standards. Convert or buffer voltages and currents.

V. Optoelectronics - sources, detectors, measurements. Light can be used for isolation, noise immunity, data links and more.

VI. Power supplies. Make your own for special purposes, and get the exact source you want.

VII. Electromechanics - motors, relays and solenoids. Controlling and using high currents. Dealing with the power line. Overcoming power-frequency noise.

VIII. Electronic construction and troubleshooting techniques. How to establish an electronic shop. Electrical safety. Fun with electricity.

For Short Course registration, see form in the center of this booklet.

Basic Principles of Mass Spectrometry and Interpretation of Organic Mass Spectra

August 1-3, 1990 Fee: $400 Member; $450 Nonmember

This course will describe the principles of modern mass spectrometry and apply them to the identification of organic compounds. Sample introduction methods (GC, vapor, direct probe), ionization processes (positive, negative, FAB, chemical, electronic), mass analysis and detection will be discussed with emphasis on molecular ion analysis and simple fragmentation processes. The course will develop an approach to the determination of elemental composition and diagnostic fragmentation patterns, and the student will become familiar with the mass spectra characteristic of common organic compound classes, drugs, pesticides and pollutants. The course is based upon and uses as reference the text, Interpretation of Organic Mass Spectra. Third Edition by F. W. McLafferty, University Science Books, 1980, which will be provided.

Faculty: Dr. Joseph A. Zirrolli is a Research Associate in the Department of Pediatrics and Research Director of the Mass Spectrometry Center at the National Jewish Center for Immunology and Respiratory Medicine in Denver. He is a member of the American Society of Mass Spectrometry and the American Chemical Society.

For Short Course registration by July i, 1990 contact:

Joe Zirrolli
National Jewish Center
Dept. of Pediatrics, K923
1400 Jackson Street
Denver, CO 80206
Tel 303-398-1853
Fax 303-398-1694

or

Sonia Atwood
Marathon Oil Company
P. O. Box 269
Littleton, CO 80160
Tel 303-794-2601
Fax 303-794-1720

OUTLINE: MASS SPECTROMETRY

1. Basic Principles of Mass Spectrometry
    - 1.1 Introduction
        - -Historical Overview of MS
    - 1.2 The Mass Spectrometer System
        - -Analyzers
            - Magnetic
            - Quadrupole
            - Ion Trap
        - -Sources & Ionization Processes
            - Source Components
            - Electron Ionization
            - Chemical Ionization
                - Positive Ion
                - Negative Ion
            - FAB
        - -Detectors
            - Faraday Cup
            - Electron Multiplier
                - Discrete Stage
                - Continuous Dynode
        - -Inlets
            - Vapor
            - Direct Insertion (Solid Probe)
            - GC
            - LC
        - -Vacuum Systems
2. Interpretation of Organic Mass Spectra
    - 2.1 Introduction
        - -Electron Ionization, Positive Ions, Unimolecular Dissociations
        - -The Mass Spectrum
    - 2.2 Elemental Composition
        - -Natural Abundances of Stable Isotopes
        - -Rings Plus Double Bonds Rule
    - 2.3 The Molecular Ion
        - -Requirements
        - -Odd - Electron Ions
        - -Nitrogen Rule
    - 2.4 Basic Mechanisms of Ion Fragmentation
        - -General Characteristics
        - -Types
            - Sigma Bond Dissociation
            - Radical Site Initiation
            - Charge Site Initiation
            - Rearrangements
    - 2.5 Mass Spectra of Common Compound Classes
    - 2.6 Computer Assisted Identification of Unknowns
    - 2.7 General Discussion/Examples

Quality Assurance Practices for The Environmental Laboratory

August 2-3, 1990 Fee $350 Member; $400 Nonmember

This two-day short course is designed for laboratory analysts who require an introduction to quality assurance practices used in environmental measurements. The course starts with a discussion of basic statistical concepts required in QA, i.e., detection limits, confidence limits, determination of standard deviations; then the principles of quality assurance practices are explained and discussed in depth. These range from the preparation of duplicate and spiked samples, use of internal standards and standard reference materials, and instrument calibration to the role of the QA manager, training requirements and record documentation. Examples of the application of these procedures to actual environmental analyses; BOD, solids analyses, colorimetric procedures (nitrate, phosphate), ICP of metals, GC analyses; residual chlorine and fluoride determinations are then discussed.

In addition to laboratory analysts, engineers and project officers who use laboratory generated data in their programs and require a better understanding of how the data are obtained will benefit from this course.

Faculty: Steve Callio, B. S., M.S., is currently supervisor of the Soils and Solid Waste Group at Accu-Labs Research, Inc. in Wheat Ridge, Colorado. He has more than 14 years of experience in Environmental Analytical Chemistry with EPA and in private testing laboratories. He has been a member of EPA's CLP program. He has presented papers to the CLP caucus, EPA's Symposium on Solid Waste Testing and published with ASTM and Atomic Spectroscopy.

For Short Course registration by July 16, 1990 contact:

Joe Zirrolli
National Jewish Center
Dept. of Pediatrics, K923
1400 Jackson Street
Denver, CO 80206
Tel 303-398-1853
Fax 303-398-1694

or

Sonia Atwood
Marathon Oil Company
P. O. Box 269
Littleton, CO 80160
Tel 303-794-2601
Fax 303-794-1720

OUTLINE: QUALITY ASSURANCE

I. Basic Concepts

A. Statistical Concepts
B. Calculating Some Basic Statistical Measurements
C. A Basic Program To Calculate Mean and Standard Deviation From a Set Of Replicates
D. **Defensibility** Of Your Data
E. Common Sources Of Error In Environmental Analysis
F. Detection **Limit/Limit** Of **Quantitation**
G. Confidence **Limits/Control** Charts
H. Good Lab Practice
I. Cost Versus Benefits

Some Common QC Practices And What They Tell Us

A. Blanks
B. Duplicate Samples (Replicates)
C. Spiked Samples
D. Internal Standards & Surrogate Compounds
E. Standard Reference **Materials** (SRM's)
F. **Calibration/Standardization**
G. Balance Calibration
H. Thermometer Calibration
I. Record Keeping
J. External Studies
K. **Equivalency** Of Methods
L. Training Requirements
M. QA Manager
N. Cross Checking Of Calculations
O. Document Control
P. What To Do When Nothing Works. Some Examples Of Troubleshooting a Procedure When The QA Says Something Is Wrong.

Application Of Practices To Some Common Environmental Analyses

A. BOD - A Biochemical Test
B. Solids Analyses TSS, TDS Gravimetric Procedures
C. **Colorimetric** Procedures, i.e., N03, P04 - Formation of a Highly Colored Compound Followed by Molecular Spectra
D. AA & **ICP** Metals Analyses
E. Residual Chlorine
F. A Typical GC Analysis
G. Fluoride by Ion Selection Electrode

For Short Course registration, see form in the center of this booklet

Organizers of the 32nd Rocky Mountain Conference

Conference Chairwoman - Pat Sulik Rocky Mountain Instrumentation 456 S. Link Lane, Fort Collins, CO 80524, (303) 530-1169.

Conference Program Chairman - Steve Callio, Accu-Labs Research 11485 W. I-70 Frontage Road North Wheat Ridge, Co. 80033, (303) 423-2766.

Exhibits - Jim Parker, Manville Tech Center, Mail Stop R-38, PO Box 5108, Denver, CO 80217 (303) 978-5481.

Registration -
John Garbarino, USGS, Mail Stop 408, 5293 Ward Road, Arvada, CO 80002 (303) 236-3614.

Joe Broadus, USGS - NWQL, 5293, Ward Road, Arvada, CO 80002 (303) 236-5345.

Treasurer - Dave Ordemann, Adolph Coors Co., Mail No BC600, Golden, CO, (303) 277-2590.

Social Events - Bob Conway, PO Box 6167, Denver, CO 80206 (303) 793-1350.

Staff - John Fowler, USEPA-NEIC, Box 25277, DFC, Lakewood, CO 80226, (303) 236-5132.

Publicity -
Jan Gurnsey, 5531 Bitterbush Way, Loveland, CO 80537 (303) 669-9216.
Renee Hoatson, Rocky Flats, General Lab Bldg 881, PO Bos 464, Golden, CO 80402-0464, (303) 966-2436.
Short Courses - Joe Zirrolli, Dept of Pediatrics, K923, National Jewish Center,1400 Jackson, St. Denver CO 80206 (303) 398-1853.

Audio-Visual - Tom Leiker, USGS, 5293 Ward Road, Arvada, CO 80002, (303) 236-3616.

Mailing List - Carol Gies, Rocky Flats, General Lab Bldg 881, PO Box 464, Golden, CO 80401, (303) 966-7380.

Program Typist - Debbie Taylor, USGS, MS 408, 5293 Ward Road, Arvada, CO 80002, (303) 236-3600.

Symposia Chairwomen and Chairmen

Atmospheric Sciences - Dr. D. Stedman, Univ. Denver Chem Dept.. University Park, Denver, CO, 80208-0179, (303) 871-3530.

Atomic Spectroscopy - Dr. Thomas Niemcyck, Univ. of New Mexico, Chemistry Dept., Albuquerque, NM, 87131, (505) 277-5319.

Computer Applications, Robotics and Chemometrics -
Ms. Vanessa Fishback, Matrix Solutions, 600 1st Ave., Suite 306A, Seattle, WA, 98104.
Dean John Lanning, Univ., of Colo. at Denver, Box 144, 1200 Larimer St., Denver, CO, 80204, (303) 556-2557.
Rob Maruyama, Adolph Coors Analytical, Mail No. BC600, Golden, CO 80401, (303) 277-6499.

Chromatography & Supercritical Fluid Chromatography -
Steve Nyarady, Adolph Coors Analytical, Mail No. BC600, Golden, CO 80401, (303) 277-5917.
Bernd Wenclawiak, University of Munster, Wilhelm Klemm Str.10, D-4400, Munster, W. Germany, 01149251833610.

Chlorinated Hydrocarbons - Brian Bush, NY State Dept. of Health, Wadsworth Laboratories, Albany, NY 12201-0509, (518) 473-7582.

Electrochemistry -
Joe Christie, USGS, MS 973, Box 25406, DFC, Denver, CO 80225, (303) 236-2464.
Larry Jackson, USGS, MS 973, Box 25046, DFC, Denver, CO 80225, (303) 236-2473.

Electron Paramagnetic Resonance -
Gareth Eaton, Dept. of Chemistry, University of Denver, Denver, CO 80208, (303) 871-2980.
Sandra Eaton, University of Denver, Dept of Chemistry, Denver, CO 80208, (303) 871-3102.

Environmental Chemistry - Lynda M. Faires, USGS, MS 411, Box 25046, DFC, Denver, CO 80225, (303) 236-9362.

Poster Session - Carlos Arozarena, USGS, 5293 Ward Road, Arvada, CO 80002, (303) 236-5345.

ICP-MS - Howard Taylor, USGS, MS 408, 5293 Ward Road, Arvada, CO 80002, (303) 236-1928.

IR & FTIR Spectroscopy - A.R. Chughtai, Dept. of Chemistry, University of Denver, Denver, CO 80208, (303) 871-4404.

Ion Chromatography - Bill Williams, Manville Tech Center, PO Box 5108, Denver, CO 80217, (303) 978-5595.

Luminescence - Marv Goldberg, USGS, MS 424, PO Box 25046, DFC, Denver, CO 80225. (303) 236-4728.

Near IR Spectroscopy -
Donald Bums, Los Alamos National Labs, Mail Stop E-535, Los Alamos, NM 87545, (505) 665-4186.
Joseph Montalvo, USDA, ARS, SRRC, PO Box 19687, New Orleans, LA 70179, (504) 286-4249.

Nuclear Magnetic Resonance -
Bernie Gerstein, Iowa State University, 229 Spedding, Ames, IA 50011, (515) 294-3375.
Ed Hogaman, ORNL, PO Box 2008, 4500N, Oakridge, TN 37840, (615) 576-2751.
Hellmut Eckert, Dept. of Chemistry, Univ. of California Santa Barbara, Goleta, CA 93106, (805) 961-8163.
Alexander Vega, EI duPont, PO Box 80356, Wilmington, DE 19880-0356.

Quality Assurance - Bill Shampine, USGS, MS 401, Box 25046, DFC, Denver, CO 80225, (303) 236-1940.

ATMOSPHERIC SCIENCE SYMPOSIUM

Donald H. Stedman, Presiding

Monday morning, July 30, 1990

9:00 a.m. 1. Plenary Lecture. ATMOSPHERIC CHEMISTRY AND THE NATIONAL PARK SERVICE. Dr. William Malm. U.S. National Park Service.

10:00 a.m. 2. FURTHER DEVELOPMENTS OF THE SULFUR CHEMILUMINESCENCE DETECTOR (SCD) AS A REAL-TIME ATMOSPHERIC MONITOR. Richard L. Benner and Donald H. Stedman, Chemistry Department, University of Denver.

10:20 a.m. BREAK

11:00 a.m. 3. DEVELOPMENT OF A TECHNIQUE FOR DETERMINATION OF AMBIENT ATMOSPHERIC CONCENTRATIONS OF ALCOHOLS. Arturo Palomares. Larry G. Anderson, and John A. Lanning, Department of Chemistry, University of Colorado at Denver.

11:20 a.m. 4. DIURNAL VARIATIONS IN AEROSOL COMPOSITION AND CONCENTRATION. William E. Wilson. and Anthony Clark, U.S. Environmental Protection Agency, Atomospheric Research and Exposure Assessment Laboratory, Research Triangle Park, North Carolina, and University of Hawaii.

11:40 a.m. 5. DETERMINATION OF SPECIATED HYDROCARBON EMISSIONS FROM MOTOR VEHICLES BY LONG PATH ULTRAVIOLET SPECTROSCOPY. James E. Peterson and Donald H. Stedman, Chemistry Department, University of Denver.

12:20 p.m. LUNCH

Monday afternoon, July 30, 1990

1:30 p.m. 6. AMBIENT CO AND NO_x CONCENTRATIONS ASSOCIATED WITH COLORADO'S OXYFUELS PROGRAM. Larry G. Anderson , John A. Lanning. and Robert G. Meglen, Department of Chemistry and Center for Environmental Sciences, University of Colorado at Denver.

1:50 p.m. 7. CARBON MONOXIDE IN DOWNTOWN DENVER: APPLICATION OF A CHEMICAL MASS BALANCE FOR SOURCE APPORTIONMENT. Kamal A. Mohammed and Donald H. Stedman, Chemistry Department, University of Denver.

2:10 p.m. 8. ATMOSPHERIC CONCENTRATIONS OF FORMALDEHYDE AND ACETALDEHYDE DURING AN OXYFUELS PROGRAM. W. Kerry Grant, Larry G. Anderson, and John A. Lanning, Department of Chemistry, University of Colorado at Denver.

2:30 p.m. BREAK

3:00 p.m. 9. OBSERVATIONS FROM A MULTI-YEAR FINE PARTICLE AND VISIBILITY MEASUREMENT STUDY IN THE SOUTHWEST. Peter K. Mueller. Charles E. McDade, and Robert C. Nininger, Electric Power Research Institute, ENSR, and AeroVironment, Inc.

3:20 p.m. 10. DEVELOPMENT OF THE CHEMILUMINESCENT SELENIUM DETECTOR. T. Hosick and Donald H. Stedman, Chemistry Department, University of Denver.

3:40 p.m. 11. NICKEL CARBONYL CHEMILUMINESCENCE AS A MEANS OF CARBON MONOXIDE DETECTION. Anthony E. Allen. Mona Shahgholi, John A. Lanning, and Larry G. Anderson, Department of Chemistry, University of Colorado at Denver.

4:10 p.m. 12. PROGRESS TOWARDS DEVELOPING A NEXT GENERATION CO/CO_2 REMOTE SENSING DEVICE. Paul L. Guenther and Donald H. Stedman, Department of Chemistry, University of Denver.

4:30p.m. 13. SOLAR PHOTOLYSIS OF OZONE TO SINGLET D OXYGEN ATOMS, $O(^1D)$. Solomon T. Bairai. and Donald L. Stedman, Department of Chemistry, University of Denver.

ATOMIC SPECTROSCOPY SYMPOSIUM

Tuesday morning, July 31, 1990

9:00 a.m. 14. Keynote Address

THE NEW CORNUCOPIA: ARRAY DETECTORS AND PULSED DISCHARGES. Alexander Scheeline. Cheryl A. Bye, Steven W. Rynders and Duane L. Miller, School of Chemical Sciences, University of Illinois, 1209 W. California St., 79 RAL Box 48, Urbana, IL 61801.

9:50 a.m. 15. ANALYSIS OF SOILS & SEDIMENTS BY ICP EMISSION SPECTROMETRY WITH ULTRASONIC NEBULIZATION. Danton D. Nygaard, and Xiaoru Wang, Baird Corporation, 125 Middlesex Turnpike, Bedford, MA 01730.

10:15 a.m. 16. DETERMINATION OF TRACE METALS IN SLURRY SAMPLES USING AUTOMATED ULTRASONIC AGITATION. R.L. Hergenreder, G.R. Carnrick, W. Slavin and D. Bradshaw, Perkin-Elmer Corp., 761 Main Avenue, Norwalk, CT 06859-0219.

10:40 a.m. BREAK

11:00 a.m 17. THE FLEXIBILITY OF FLOW INJECTION AA. Susan McIntosh, and Randy Hergenreder, Perkin-Elmer Corp., 761 Main Avenue, Norwalk, CT 06859-0219.

11:25 a.m. 18. HYDRIDE GENERATION OR GRAPHITE FURNACE ATOMIC ABSORPTION SPECTROPHOTOMETRY: A COMPARISON OF TECHNIQUES FOR ANALYSIS OF HIGHLY MATRIXED SAMPLES. Maria W. Tikkanen. Roger Starek, and Robert Peile, Applied Research Laboratories/Fisons Instruments, Inc., 24911 Avenue Stanford, Valencia, CA 91355.

11:50 a.m. 19. AUTOMATION OF GFAAS ANALYSES FOR EPA CONTRACT LABORATORY SAMPLES. John E. Schmelzel. Gerald Delude, David Pfeil, and John Sotera, Thermo Jarrell Ash Corporation, 175 Jefferson Drive, Menlo Park, California 94025.

12:15 p.m. LUNCH

Tuesday afternoon, July 31, 1990

1:30 p.m. 20. RECENT DEVELOPMENTS IN AUTOMATED ANALYSIS OF GEOLOGICAL AND ENVIRONMENTAL MATERIALS BY ICP-AES, AND CHEMOMETRIC DATA INTERPRETATION. Dr. Marc L. Nouri and I.B. Brenner, ISA, Inc., 6 Olsen Avenue, Edison, New Jersey 08820. M. Borsier, Bureau Recherches Geologiques et Minieres (BRGM), B.P. 6009, 45060, Orleans, Cedex 2, France.

1:55 p.m. 21. ON-LINE ION EXCHANGE PRECONCENTRATION FOR DETECTION OF IODINE BY FIA ICP-AES, Scott P. Dolan and Stephen G. Capar. U.S. Food and Drug Administration, Washington, DC 20204. Akbar Montaser and Robert H. Clifford, George Washington University, Washington, DC 20052.

2:20 p.m. 22. SOLVENT-ANALYTE SEPARATOR FOR ATOMIC EMISSION AND MASS SPECTROMETRY. Hsiaoming Tan. R.H. Clifford, S. Nam, and A. Montaser, Department of Chemistry, George Washington University, Washington, DC 20052.

2:45 p.m. BREAK

3:10 p.m. 23. A NEW COMPACT HYDRIDE GENERATOR FOR AS, SE AND SB DETERMINATIONS IN ENVIRONMENTAL MATERIALS BY ICP-AES. INFLUENCE OF HYDROGEN, SHEATH GAS FLOW AND GENERATOR FREQUENCY ON ANALYTICAL PERFORMANCE. Dr. Ralph H. Obenauf and I.B. Brenner, ISA Inc., 6 Olsen Ave., Edison, New Jersey 08820.

3:35 p.m. 24. RAPID SCREENING ANALYSIS WITH A SEQUENTIAL ICAP PLASMA SPECTROMETER. John E. Schmelzel. Ann E. Grindle, and John Sotera, Thermo Jarrell Ash Corporation, 175 Jefferson Drive, Menlo Park, California 94025.

4:00 p.m. 25. A NEW ATTEMPT TO IMPROVE DETECTION CAPABILITIES OF ICP-AES FOR THE DETERMINATION OF AL IN BIOLOGICAL AND ENVIRONMENTAL MATERIALS. Dr. Didier Arniaud and I.B. Brenner, ISA, Inc., 6 Olsen Avenue, Edison, New Jersey 08820.

4:25 p.m. 26. APPLICATIONS OF ION EXCHANGE FOR MATRIX ELIMINATION PRIOR TO INDUCTIVELY COUPLED ARGON PLASMA ATOMIC EMISSION SPECTROSCOPY (ICAP-AES), Ron M. Manabe and John E. Schmelzel, Thermo Jarrell Ash, 175 Jefferson Dr., Menlo Park, CA 94025, John M. Riviello, Dionex, Sunnyvale, CA, Howard M. Kingston, Archava Sirraks, NIST, Gathersburg, MD.

CHROMOTOGRAPHY SYMPOSIUM

Stefan A. Nyarady, Chairman

Monday morning, July 30, 1990

8:30 a.m. INTRODUCTION

8:35 a.m. 27. LIQUID CHROMATOGRAPHIC ANALYSIS OF POLYNUCLEAR AROMATIC HYDROCARBONS WITH DIODE ARRAY DETECTION. Michael W. Dong and Daniel Clutter, The Perkin-Elmer Corporation.

9:00 a.m. 28. ANALYSIS OF CARBAMATE PESTICIDES BY LIQUID CHROMATOGRAPHY. Michael W. Dong and Daniel Clutter, The Perkin-Elmer Corporation.

9:25 a.m. 29. WHOLE COLUMN DETECTION: APPLICATION TO PREPARATIVE-SCALE LIQUID CHROMOTOGRAPHY. Kevin L. Kelly and John W. Birks, Department of Chemistry and Biochemistry and Cooperative Institute for Research in Environmental Sciences (CIRES), University of Colorado, Boulder.

9:50 a.m. 30. NEW SULFUR SELECTIVE DETECTOR FOR GAS AND SUPERCRITICAL FLUID CHROMATOGRAPHY. R.S. Hutte. N.G. Johansen, M.F. Legier, Sievens Research, Inc.

10:15 a.m. 31. GAS CHROMATOGRAPHIC CHARACTERIZATION OF OXIDATION PRODUCTS FROM A SURROGATE JET FUEL. William D. Schulz. Department of Chemistry, Eastern Kentucky University.

10:35 a.m. BREAK

11:00 a.m. 32. ADVANCED ION CHROMATOGRAPH DETECTS LOW MEA LEVELS. David B. Palladino. and Scott Lindsay, Brinkmann Instruments, Inc., and Texaco Refining & Marketing.

11:25 a.m. 33. ELECTRODIALYTIC GENERATION OF ELUENTS FOR CHEMICALLY SUPPRESSED ION CHROMATOGRAPHY. J. Stillian, K. Friedman, P.K. Dasgupta, and D. Strong. Dionex Corporation and Texas Tech University.

11:50 a.m. 34. SOME NEW SOLUTIONS TO SENSITIVITY/SELECTIVITY LIMITATIONS IN ORGANIC ELEMENTAL ANALYSIS BY OXIDATIVE PYROLYSIS/ION CHROMATOGRAPHY. Dutt V. Vinjamoori, Sharon J. Lemp, and Charles H. Condra, Monsanto Company.

CHROMATOGRAPHY - SUPER CRITICAL FLUIDS SYMPOSIUM

Monday afternoon, July 30, 1990

1:25 p.m. INTRODUCTION

1:30 p.m. 35. A PROCESS FOR THE EXTRACTION OF FLAVOURS FROM MILKFAT WITH SUPERCRITICAL CARBON DIOXIDE. Andre B. de Haan. J. de Graauw, J.E. Schaap, and H.T. Badings, Delft University of Technology, The Netherlands and Dutch Institute for Dairy Research, the Netherlands.

1:55 p.m. 36 SUPERCRITICAL FLUID SOLID PHASE EXTRACTION/SFC OF PESTICIDES, HERBICIDES AND RELATED COMPOUNDS IN COMPLEX SAMPLE MATRICES. Balasingam Murugaverl and Kent J. Voorhees, Department of Chemistry and Geochemistry, Colorado School of Mines.

2:20 p.m. 37. PACKED MICROBORE SUPERCRITICAL FLUID CHROMATOGRAPHY WITH FLAME IONIZATION DETECTION OF ABUSED VEGETABLE OILS. John E. France. Jerry W. King, and Janet M. Snyder. Northern Regional Research Center, Agricultural Research Service, U.S. Department of Agriculture.

2:45 p.m. 38. AUTOMATED SUPERCRITICAL FLUID INSTRUMENTATION: INDUSTRIAL R&D AND ENVIRONMENTAL APPLICATIONS. Eugene J. Lew. Timothy W. Ryan, Steven M. Lurcott, Sean O'Neill, and John Watkins, Computer Chemical Systems, Inc.

3:10 p.m. 39. VOLUMETRIC PROPERTIES OF MOBILE PHASES IN SUPERCIRTICAL FLUID CHROMATOGRAPHY WITH A PHC EQUATION OF STATE. Maurizio Fermaglia, Jacek Gregorowicz, and Ireneo Kikic. Instituto di Chimica Applicata e Industriale, Universita di Trieste, Italy.

COMPUTER APPLICATIONS/ROBOTICS/CHEMOMETRICS SYMPOSIUM

Rob Maruyama, Presiding

Tuesday morning, July 31, 1990

10:00 a.m. 40. ROBOTIC APPLICATIONS AS A FUNCTION OF LAB WORKER PARTICIPATION. G.L. Hoffman. T.J. Bushly, and C.J. Patton, U.S. Geological Survey, Arvada, Colorado.

10:25 a.m. 41. AUTOMATION OF POLYMER PHYSICAL TESTING INSTRUMENTATION. Daniel G. Moldovan. Dow Chemical Company, Freeport, Texas.

10:50 a.m. 42. THE USE OF AUTOMATED GRAVIMETRIC TECHNIQUES FOR ENHANCED ANALYTICAL PRECISION. Brian G. Lightbody, and Sally D. Dowling, Zymark Corporation.

11:15 a.m. 43. AUTOMATED CHEMISTRY WORKSTATIONS. THE FUTURE OF LABORATORY AUTOMATION. John Petracca. Source for Automation.

SYMPOSIUM ON ELECTROCHEMISTRY

Organized by Larry L. Jackson and Joseph H. Christie

Monday morning, July 30, 1990

9:00 a.m. 44. ELECTROCHEMICAL APPLICATIONS OF SOLUBLE POLYELECTROLYTES. S. James Schmittle, Ronald B. Sprinkle, and C. Michael Elliot. Colorado State University.

9:20 a.m. 45. SPATIALLY-RESOLVED ELECTROCHEMICAL DETECTION FOR HIGH PERFORMANCE LIQUID CHROMATOGRAPHY AT SEMICONDUCTING TITANIUM DIOXIDE WIRES. Garrett N. Brown. John W. Birks, and Carl A. Koval, University of Colorado.

9:40 a.m. 46. PULSED ELECTROCHEMICAL DETECTION IN LIQUID CHROMATOGRAPHY. William R. LaCourse and Dennis C. Johnson. Iowa State University.

10:00 a.m. 47. THE ELECTROCHEMICAL DETECTION OF PENICILLIN COMPOUNDS FOLLOWING THEIR SEPARATION BY HPLC. Lisa M. Koprowski and Lawrence E. Welch. Knox College.

10:20 a.m. BREAK

10:40 a.m. 48. FUNCTIONAL GROUP SELECTIVITY IN PULSED ELECTROCHEMICAL DETECTION. William R. LaCourse and Dennis C. Johnson, Iowa State University.

11:00 a.m. 49. KEYNOTE SPEAKER. CHARLES R. MARTIN

ENHANCING CONDUCTIVITIES IN ELECTRONICALLY CONDUCTIVE POLYMERS. Charles R. Martin. Colorado State University.

11:50 a.m. LUNCH

Monday afternoon, July 30, 1990

1:30 p.m. 50. INVESTIGATION OF ELECTRON TRANSFER KINETICS AT N-TYPE METAL DICHALCOGENIDE SEMICONDUCTOR/SOLUTION INTERFACES USING A MICROELECTROCHEMICAL CELL. Jason N. Howard and Carl A. Koval, University of Colorado.

1:50 p.m. 51. DETECTION OF HOT ELECTRONS AT A P-TYPE INDIUM PHOSPHIDE PHOTOELECTROCHEMICAL CELL UTILIZING ROTATING RING DISK ELECTRODE VOLTAMMETRY. Robert Torres and Carl A. Koval, University of Colorado.

2:10 p.m. 52. FABRICATION AND ELECTROCHEMISTRY OF MICROHOLE ARRAY ELECTRODES. Charles J. Brumlik and Charles R. Martin, Colorado State University.

2:30 p.m. BREAK

2:50 p.m. 53. ELECTROCHEMICAL SYNTHESIS OF ULTRATHIN FILM COMPOSITE MEMBRANES. Chao Liu. Mark W. Espenscheid, W-J. Chen, and Charles R. Martin, Colorado State University.

3:10p.m. 54. THE USE OF ELECTROPOLYMERIZED METALLOPORPHYRIN FILMS FOR THE SEPARATION OF NITROGEN HETEROCYCLES FROM HYDROCARBON PHASES VIA ELECTROCHEMICALLY MODULATED COMPLEXATION. Douglas E. Wedman and Carl A. Koval, University of Colorado.

3:30 p.m. 55. EFFECTS OF HYDROXIDE ON THE ELECTROCHEMISTRY OF POLYPYRROLE. Leon S. Van Dyke and Charles R. Martin, Colorado State University.

3:50 p.m. 56. INFRARED AND UV-VISIBLE STUDIES OF THE TRAPPED CHARGE WITHIN ELECTROPOLYMERIZED TRIS(VINYLBIPYRIDINE)RUTHENIUM(II). Scott C. Paulson and C. Michael Elliot, Colorado State University.

Tuesday morning, July 31, 1990

9:00 a.m. 57. OXYGEN REDUCTION AT THE PERFLUOROSULFONATE IONOMER FILM-MICROELECTRODE INTERFACE: TRANSPORT AND KINETICS. Arvind Parthasarathy and Charles R. Martin, Colorado State University.

9:20 a.m. 58. OXYGEN REDUCTION KINETIC CURRENTS AT PERFLUOROSULFONATE IONOMER FILM-COATED PLATINUM ELECTRODES: RESULTS PERTAINING TO HYDROGEN-OXYGEN PHOSPHORIC ACID FUEL CELLS. Del R. Lawson and Charles R. Martin, Colorado State University.

9:40 a.m. 59. BATTERY STUDIES IN NEUTRAL ROOM TEMPERATURE CHLOROALUMINATE MOLTEN SALTS. Jeffrey Boon, John Sanders, Larry Vaughn, and John S. Wilkes. USAF Academy.

10:00 a.m. 60. HIGH CYCLE LIFE RECHARGEABLE ALUMINUM BATTERIES. V. R. Koch and C. Nanjundiah, Covalent Associates, Inc.

10:20 a.m. BREAK

10:40 a.m. 61. POTENTIOMETRY OF POLAR DISSOLVED ORGANICS USING THE NICKEL ELECTRODE. Ben S. Hui and Calvin O. Huber. University of Wisconsin-Milwaukee.

11:00 a.m. 62. A COMPARISON OF HYDROGEN ELECTRODE AND pH GLASS ELECTRODE FOR pH MEASUREMENT. Naila Ashraf and K. L. Cheng, University of Missouri-Kansas City.

11:20 a.m. 63. APPLICATIONS OF ELECTROCHEMISTRY TO THE ANALYSIS OF GEOLOGIC MATERIALS. Larry L. Jackson and Joseph H. Christie, U.S. Geological Survey.

11:40 a.m. 64. SLOW SCAN CYCLIC VOLTAMMETRIC STUDY OF TRIVALENT GROUP V HINDERED CHLORO-COMPOUNDS. Carlos Arcos. Somchai Saelee, and Richard T. Keys, Department of Chemistry and Biochemistry, California State University.

SYMPOSIUM ON ENVIRONMENTAL CHEMISTRY

Organized by Lynda M. Faires

Monday morning, July 30, 1990

Edward T. Furlong, presiding

9:00 a.m. 65. INTRODUCTION OF INVITED SPEAKER, Edward T. Furlong.

INVITED SPEAKER IN ENVIRONMENTAL MASS SPECTROMETRY
SPONSORED BY FINNIGAN MAT.
ROBERT D. VOYKSNER

ENVIRONMENTAL APPLICATION OF HIGH PERFORMANCE LIQUID CHROMATOGRAPHY/MASS SPECTROMETRY. Robert D. Voyksner., Analytical and Chemical Sciences, Research Triangle Institute, North Carolina.

[redacted]

10:00 a.m. BREAK

10:30 a.m. 66. DETERMINATION OF LINEAR ALKYLBENZENESULFONATES AND THEIR CARBOXYLATED INTERMEDIATES BY DERIVATIZATION GAS CHROMATOGRAPHY/MASS SPECTROMETRY. Jennifer A. Field and Larry B. Barber, II, U.S. Geological Survey.

10:50a.m. 67. ANALYSIS OF TRIFLUOROETHYL DERIVATIVES OF SULFOPHENYLCARBOXYLATES BY GAS CHROMATOGRAPHY/ NEGATIVE ION CHEMICAL IONIZATION/ MASS SPECTROMETRY. Colleen E. Rostad and Jennifer A. Field, U.S. Geological Survey.

11:10a.m. 68. AZAARENES IN GROUND WATER FROM AN IN SITU OIL-SHALE RETORT SITE, ROCK SPRINGS, WYOMING. Larry B. Barber. II and Jerry A. Leenheer, U.S. Geological Survey.

11:30 a.m. 69. A SIMPLE GC METHOD FOR THE ANALYSIS OF ALKYL PHOSPHONATES IN WATER AND SOIL. Jesus R. Abril. Elizabeth D. Sexton, and Andrew W. Law, Colorado Department of Health.

12:00 noon LUNCH

Monday afternoon, July 30, 1990

Peter F. Rogerson, presiding

1:30 p.m. 70. MOBILE UNIT FOR FT-1R MEASUREMENTS OF VOC's. William G. Fateley, Marty Spartz, Mark Witkowski, Robert M. Hammaker, Jonathan Fateley, Kansas State University. Bill Fairless, Tom Holloway, Jodi Hudson, Don Gurka, U.S. Environmental Protection Agency. Dennis Lane, University of Kansas.

1:50 p.m. 71. RAMAN INDICATORS: A POSSIBLE METHOD FOR REMOTE SENSORS? Keith T. Carron and Ken I. Mullen. University of Wyoming.

2:10 p.m. 72. MONITORING STACK EMISSIONS OF URANIUM FROM AN ENRICHMENT PLANT. Claude R. Beverly. Martin Marietta Energy Systems.

2:30 p.m. 73. KINETIC ANALYSIS OF DISSOLUTION OF CROSSLINKED PROPELLANTS BY SOLVOLYSIS. A. S. Tompa, B. R. White, and A. C. Richardson, Naval Surface Warfare Center/Naval Ordnance Station.

2:50 p.m. BREAK

3:00 p.m. 74. FORMALDEHYDE ANALYSES BY HPLC AS 2,4,-DINITROPHENYLHYDRAZONE. Michael J. Diesing and Robert L. Spraggins. Manville Sales Corporation.

3:20 p.m. 75. FORMALDEHYDE MEASUREMENTS IN AIR, AS ITS OXAZOLIDINE DERIVATIVE. Timothy J. Wilhelm and Robert L. Spraggins, Manville Sales Corporation.

3:40 p.m. 76. CHEMICAL CHARACTERIZATION OF HUMIC ACID SUPERNATANT EXTRACTED FROM A PHILIPPINES AGRICULTURAL SOIL. Ann M. Nefcy and Robert L. Wershaw, U.S. Geological Survey.

4:00 p.m. 77. AN ANALYTICAL METHOD FOR DISTINGUISHING FORMS OF CARBON. Michael J. Diesing. John L. Quenzer, and Robert L. Spraggins, Manville Sales Corporation.

Tuesday morning, July 31, 1990

Mark J. Carter, presiding

9:00 a.m. SPECIAL SYMPOSIUM

ENVIRONMENTAL MONITORING IN THE 1990s
CHALLENGES AND OPPORTUNITIES
Organized by Mark J. Carter, Lynda M. Faires, and Jim Parker.

A panel with extensive business and technical experience will reflect on environmental monitoring and the rapid growth of its associated laboratory industry during the 1980s and predict future technical and regulatory requirements and new business opportunities during the 1990s.

TOPICS include:

- Will the rapid growth observed during the 1980s continue in the 1990s?
- What is the significance of the recent trend of waste generator companies to establish their own in-house laboratory capabilities?
- What new methods and techniques will the regulations of the 1990s require?
- Will the EPA be successful in standardizing its methodology and quality control requirements?
- Is national laboratory certification a reality, and what will the requirements be?

Each panel member will provide a perspective on the status and future trends of environmental monitoring in short, informal presentations. AH panel members will then respond to questions from the chair as well as open questions and discussion from the audience.

PANEL MEMBERS include:

Dr. Mark J. Carter, Panel Chairman, is Senior Vice President of Environmental Resource Associates. In the past 20 years in the industry, he has managed two laboratories for the USEPA as well as founded Rocky Mountain Analytical Laboratory. Dr. Carter will address the opportunities and challenges for environmental laboratories in the 1990s.

Dr. George Stanko is a Senior Scientist with Shell Development and has a major responsibility for the analytical support of Shell's environmental projects. He has also been a leading force within CMA and API to encourage the improvement of environmental analytical methodology. Dr. Stanko will speak on Shell's program to improve the quality and level of service of Shell's commercial analytical support services.

Robert Booth has recently retired as Laboratory Director of the EPA Environmental Monitoring Support in Cincinnati where he had principal responsibility for establishing analytical and quality control methodology for the EPA's water monitoring programs. Mr. Booth will speak on the EPA's recently established Environmental Monitoring Management Counsel which has the responsibility to standardize methodology and quality assurance procedures throughout the Agency.

Ms. Kathleen Carlberg is Vice President of ENSECO responsible for corporate-wide quality assurance programs. She is the leading force within the consortium of organizations to standardize quality assurance requirements nationwide and establish a uniform laboratory certification program. She will provide an update on the current activities in these areas.

Dr. Stuart P. Cram is Federal Programs Manager for Hewlett Packard's Analytical Products Group. Dr. Cram has extensive experience in the development of instrumentation, methods applications and marketing. He is currently responsible for the coordinated marketing of all instrumentation for environmental applications. Dr. Cram will speak on trends in new instrumentation.

Financial support for this symposium is being provided by Manville Corporation, Denver, Colorado.

12:00 noon LUNCH

Tuesday afternoon, July 31, 1990

Thomas R. Steinheimer, presiding

1:30 p.m. 78. INTRODUCTION OF INVITED SPEAKER, Thomas R. Steinheimer

INVITED SPEAKER. DONALD G. CROSBY

PHOTOTRANSFORMATION OF PESTICIDES IN NATURAL WATERS. Donald G. Crosby. Department of Environmental Toxicology, University of California at Davis.

2:30 p.m. 79. COMPARISON OF LARGE SAMPLE LIQUID-LIQUID AND SOLID-PHASE PRECONCENTRATION TECHNIQUES TO LOWER DETECTION LIMITS FOR PESTICIDES IN WATER. Gregory D. Foster. George Mason University. Paul M. Gates and William T. Foreman, U.S. Geological Survey.

2:50 p.m. 80. PESTICIDE OCCURRENCE AND TRANSPORT IN THE YAKIMA RIVER BASIN, WASHINGTON. Paul M. Gates. William T. Foreman, Stuart W. McKenzie, and Frank A. Rinella, U.S. Geological Survey. Gregory D. Foster, George Mason University.

3:10 p.m. 81. CHROMATOGRAPHIC DETERMINATION OF ORGANOCHLORINE PESTICIDES IN SERUM. Elizabeth D. Sexton, Yvonne K. Herman, and Lann A. Smith, Colorado Department of Health.

Wednesday morning, August 1, 1990

Lynda M. Faires, presiding

8:30 a.m. 82. NEW REAGENT AND CADMIUM REACTOR DESIGN FOR REDUCTION OF NITRATE TO NITRITE IN AUTOMATED, COLORIMETRIC DETERMINATION OF NITRATE USING A MINIATURE, AIR-SEGMENTED CONTINUOUS FLOW ANALYZER. Amy S. Ludtke and Charles J. Patton, U.S. Geological Survey.

8:50 a.m. 83. MICROWAVE PREPARATION OF ENVIRONMENTAL SAMPLES FOR TOTAL NITROGEN ANALYSIS. Rick Cousins. Greg LeBlanc, and Sara Littau, CEM Corporation.

9:15 a.m. 84. INTRODUCTION OF INVITED SPEAKER, Lynda M. Faires

INVITED SPEAKER. H. M. (SKIP) KINGSTON

NEW SAMPLE PREPARATION METHODS FOR ENVIRONMENTAL ANALYSIS. H. M. (Skip) Kingston, F. A. Settle, M. A. Pleva, P. J. Walter, L. B. Jassie, and A. Siriraks, National Institute of Standards and Technology, Inorganic Analytical Research Division, Gaithersburg, Maryland.

10:15 a.m. BREAK

10:40 a.m. 85. A CHELEX RESIN INTEGRATING SAMPLER FOR THE DETERMINATION OF TRACE ELEMENT UPTAKE (CD, CU, PB, ZN) FROM DRINKING WATER SUPPLIES. J. C. Meranger, B. Lo, National Health and Welfare, Environmental Health Directorate, Canada.

11:00 a.m. 86. APPLICATIONS OF ON-LINE CHELATION CONCENTRATION CHROMATOGRAPHY WITH INDUCTIVELY COUPLED PLASMA-MASS SPECTROMETRY FOR TRACE ELEMENT ANALYSIS OF ENVIRONMENTAL SAMPLES. Lynda M. Faires and Charles J. Patton, U.S. Geological Survey.

11:20 a.m. 87. THE USE OF ICP-MS FOR THE ANALYSIS OF ENVIRONMENTAL SAMPLES. Peter D. Blair, Robert Henry, and Thomas Rettberg, VG Instruments, Inc.

12:00 noon LUNCH

Wednesday afternoon, August 1, 1990

Lynda M. Faires, presiding

1:30 p.m. 88. THE TCLP-CREATING SUPERFUND SITES IN THE FUTURE? Robert L. Smith, Resource Materials Testing, Inc.

1:50 p.m. 89. SELENIUM INVESTIGATIONS AT THE KENDRICK RECLAMATION PROJECT AREA, CASPER, WYOMING. J. G. Crock. J. A. Erdman, and R. C. Severson, U.S. Geological Survey.

2:10 p.m. 90. RAPID ESTIMATION OF SATURATION-PASTE SELENIUM AND SODIUM IN WYOMING SOILS BY CONSTANT-RATIO WATER EXTRACTION. Kathleen. C. Stewart. David L. Fey, and Ronald R. Tidball, U.S. Geological Survey.

2:30 p.m. 91. CHEMICAL COMPOSITION OF IRON-RICH BED SEDIMENT FROM A STREAM AFFECTED BY ACID MINE DRAINAGE. Kathleen S. Smith. James F. Ranville, and Paul H. Briggs, U.S. Geological Survey, Colorado School of Mines.

2:50 p.m. 92. EFFECT OF DISSOLVED ORGANIC CARBON ON THE ELECTROPHORETTC MOBILITY OF IRON-RICH SUSPENDED SEDIMENTS IN A STREAM CONTAMINATED BY ACID-MINE DRAINAGE. James F. Ranville. Kathleen S. Smith, and Diane M. McKnight, U.S. Geological Survey, Colorado School of Mines.

3:10 p.m. 93. U.S. GEOLOGICAL SURVEY'S NATIONAL WATER-QUALITY ASSESSMENT-RESULTS OF THE LOWER KANSAS RIVER PILOT PROJECT. Dwight Q. Tanner and John K. Stamer, U.S. Geological Survey.

3:30 p.m. 94. GEOCHEMICAL AND BIOGEOCHEMICAL BASELINES AND TRENDS, KENAI PENINSULA, ALASKA. J. G. Crock. R. C. Severson, and L. P. Gough, U.S. Geological Survey.

13th INTERNATIONAL EPR SYMPOSIUM

Monday morning, July 30, 1990

Session I - Two Pumps, One Probe - H. Thomann, chairing
(joint with NMR Symposium)

8:20 a.m. OPENING REMARKS, S. S. Eaton

8:30 a.m. 95. DYNAMIC NUCLEAR POLARIZATION AT 140 GHZ. Thomas F. Prisner. Sun Un, Ralph T. Weber, Ken W. Fishbein, Ann E. McDermott, Matthew J. Seaman, Michael Whitmore, David J. Singel, and Robert G. Griffin, Francis Bitter National Magnet Laboratory, Massachusetts Institute of Technology, and Harvard University.

9.15 a.m. 96. CHARACTERIZATION OF THE INTERFACIAL REGION OF POLYSTYRENE-POLYCARBONATE BLENDS BY DYNAMIC NUCLEAR POLARIZATION ^{13}CCPMAS NMR. M. Afeworki and J. Schaefer. Washington University

10:00 a.m. BREAK

10:30 a.m. 97. A NEW ANALYSIS OF SOLITON DYNAMICS IN TRANS-POLY ACETYLENE: MOTIONAL EFFECTS OF DYNAMIC NUCLEAR POLARIZATION SPECTRA. B. H. Robinson and A. R. Coffino, University of Washington.

11:15 a.m. 98. EPR PARAMETERS MEASURED BY NMR. R. A. Wind. J. Blair, and J. B. Wooten, Colorado State University and Philip Morris Research Center.

Monday afternoon, July 30, 1990
Session II Two Pumps, One Probe - S. Eaton, chairing
joint with NMR Symposium)

1:30 p.m. 99. RADIO FREQUENCIES IN PULSED ESR. A. Schweiger, ETH Zurich.

2:15 p.m. 100. COORDINATION STRUCTURE OF ACTIVE SITES IN METALLOENZYMES AND PROTEINS BY PULSED ELECTRON NUCLEAR MULTIPLE RESONANCE. H. Thomann and M. Bernardo. Exxon Research.

3:00 p.m. BREAK

3:30 p.m. 101. DEVELOPMENT OF PULSED ENDOR AND APPLICATIONS TO ORGANIC RADICALS. P. Hofer. Bruker Instruments.

4:15 p.m. 102. HIGH DYNAMIC NUCLEAR POLARIZATION AT ROOM TEMPERATURE. A. Henstra, T, -S. Lin, J. Schmidt, and W. Th. Wenckebach. Leiden.

5:00 p.m. BUSINESS MEETING OF INTERNATIONAL EPR SOCIETY.

Tuesday morning, July 31, 1990
Session III - M. Rakowsky, chairing

8:30 a.m. 103. PLENARY LECTURE- STIMULATED NUCLEAR POLARIZATION STUDY OF SHORT-LIVED RADICAL SPECIES. R. Z. Sagdeev and E. G. Bagryanskaya, Institute of Chemical Kinetics and Combustion, USSR.

9:10a.m. 104. TWO-DIMENSIONAL FOURIER TRANSFORM ESR IN THE SLOW MOTIONAL REGIME. B. Patyal, R. H. Crepeau, J. H. Freed, Cornell University.

9:45 a.m. 105. DYNAMICS AND FOLDING OF VERY HELICAL PEPTIDES REVEALED BY ESR, TIME-DOMAIN ESR AND MOLECULAR DYNAMICS CALCULATIONS. A. P. Todd, S. M. Miick, W. R. Fiori, K. M. Casteel, J. C. Williams, G. L Millhauser. University of California, Santa Cruz

10:05 a.m. BREAK

10:35 a.m. 106. PROBING Cu(II) SITES IN ZEOLITES USING ESEEM INDUCED BY FRAMEWORK ^{27}Al. D. Goldfarb.K. Zukerman, and K. Matar, Weizmann Institute of Science

10:55 a.m. 107. ANALYSIS OF ^{14}N SUPERHYPERFINE INTERACTION TO Cu(II) BY MULTIFREQUENCY ESR AND COMPUTER SIMULATIONS. J. Bednarek and S. Schlick. University of Detroit.

11:15 a.m. 108. COMPUTER SIMULATION OF SPIN RELAXATION IN DILUTED LATTICES. S. K. Misra and O. Orhun, Concordia University

11:35 a.m. 109. LINESHAPE SIMULATIONS OF THE LOW FIELD MICROWAVE ABSORPTION OF A SUPERCONDUCTING $Bi_2Sr_2Cu_2O_x$ CRYSTAL. J. T. Masiakowski, M. Puri, M. Romanelli, L. Kevan. and R. N. Schwartz, University of Houston and Hughes Research Laboratories

Tuesday afternoon, July 31, 1990
Session IV - J. P. Homak, chairing

1:30 p.m. 110. FAST ESR-IMAGING. U. Ewert and J. H. Freed, Cornell University

1:50 p.m. 111. EPR SPECTRA OBTAINED FROM FIELD-CYCLED PEDRI IMAGES. D. J. Lurie. I. Nicholson, and J. R. Mallard, University of Aberdeen

2:10p.m. 112. STUDIES OF HYDROGEN BONDING COMPLEXES BY FLOW DNP. H.C. Dorn and K.H. Tsai, Virginia Polytechnic.

2:35 p.m. BREAK

Tuesday afternoon, July 31, 1990
Session V - Posters, S. S. Eaton, Chairing
3:00 - 4:00, authors present for posters labeled A
4:00 - 5:00, authors present for posters labeled B

A 113. MAGNETIC RESONANCE MEASUREMENTS OF MEDIUM EFFECTS ON HYDROGEN BONDING OF SOLVENTS WITH NITROXIDES. I. Bala'a, J.-A. K. Bonesteel, B. Borah, and R. D. Bates. Jr.. Georgetown University

B 114. ESR IMAGING OF THE DISTRIBUTION OF EXOGENOUS NITROXIDE RADICALS IN THE RAT HEAD BY AN L-BAND ESR SYSTEM. N. Tsuchihashi. S. Ishida, N. Mori, H. Kumashiro, T. Ogata, T. Kitajima, H. Kamada, and E. Yoshida, Fukushima Medical College and JEOL Ltd

A 115. SENSITIVITY AND RESOLUTION ENHANCEMENT FOR SPECTRAL SPATIAL ESR-IMAGING. U. Ewert and J. H. Freed, Cornell University

B 116. IMAGING FREE RADICALS IN VIVO IN THE RAT USING PEDRI. I. Nicholson, D. J. Lurie. M. A. Foster, and J. R. Mallard, University of Aberdeen

A 117. EPR IMAGING OF ELECTROCHEMICALLY GENERATED RADICALS. M. Sueki. R. W. Quine, S. S. Eaton, and G. R. Eaton, University of Denver

B 118. THE USE OF ELECTRONIC COUPLING ADJUSTMENT IN A CAPACITIVELY COUPLED SYSTEM TO REDUCE BOTH COUPLING VARIATION AND MICROPHONIC NOISE IN EPR SPECTROSCOPY OF LIVING ANIMALS. M. Peric. H. J. Halpern, and M. K. Bowman, University of Chicago and Argonne National Laboratory

A 119. TIMING AND CONTROL UNIT FOR CONVERSION OF CW EPR SPECTROMETERS TO PULSED OPERATION. R. W. Ouine and G. R. Eaton, University of Denver.

B 120. EPR/ENDOR 9 GHz SPECTROMETER SENSITIVITY ENHANCEMENT FOR SMALL SAMPLES USING DIELECTRIC RESONATORS. R. A, Isaacson and G. Feher, University of California, San Diego

A 121. ^{14}NENDOR OF THE W7 Di-NITROGEN CENTER FOUND IN BROWN DIAMOND. M E. Newton and J. M. Baker, National Biomedical ESR Center and Clarendon Laboratory.

B 122. ELECTRON SPIN TRANSIENT NUTATION: A NEW APPROACH TO UNRAVEL COMPLICATED EPR SPECTRA. A. Astashkin, A. Schweiger, and R. R. Ernst, ETH Zurich

A 123. AN ENDOR AND ESEEM STUDY OF THE LIGAND HYPERFINE AND QUADRUPOLE INTERACTION IN $Fe(CN)_6^{3-}$ DILUTED IN A KCl LATTICE. D. Wang and E. de Boer, University of Nijmegen

B 124. STRUCTURE AND CONFORMATION OF SPIN-LABELED METHYL L-PHENYLALANATE IN FROZEN SOLUTIONS BY ENDOR SPECTROSCOPY AND MOLECULAR MODELING. H. Joela and M. W. Makinen. University of Chicago

A	125.	PROTON ENDOR AND EPR SPECTRAL SIMULATION OF A NITROXYL RADICAL FORMED FROM N-2,4,6-TETRANITRO-N-METHYLANILINE. M. D. Pace and R. Weber, Naval Research Laboratory and Bruker Instruments
B	126.	SIMULTANEOUS ELECTROCHEMICAL - ELECTRON SPIN RESONANCE STUDIES OF CAROTENOID RADICALS AND DICATIONS: DETECTION OF AN ELECTRON TRANSFER PROCESS. M. Khaled, A. Hadjipetrou, and L. Kispert, University of Alabama
A	127.	EPR DOSIMETRY FOLLOWING A RADIATION ACCIDENT. M. F. Desrosiers. NIST
B	128.	NOVEL SPIN TRAPPING STUDIES OF NITROSOAMINE FREE RADICALS. M. F. Desrosiers and D. A. Wink, NIST
A	129.	EPR MEASUREMENTS ON SOME Mn(II)-DOPED TETRA ALKYLAMMONIUM COMPOUNDS. S. K. Misra, M. O. Steinitz, and M. Kahrizi. Concordia University and St. Francis Xavier University
B	130.	EPR STUDIES OF DEMINERALIZED ARGONNE PREMIUM COALS. L. A. Gebhard, B. G. Silbernagel, R. A. Flowers, and J. W. Larsen, Exxon Research and Lehigh University
A	131.	THE LOW TEMPERATURE OXIDATION OF ARGONNE PREMIUM COALS USING DYNAMIC, IN-SITU 9 GHz CW-EPR. J. Kudynska and H. A. Buckmaster. University of Calgary
B	132.	9 AND 34 GHz CW-EPR STUDIES OF MANGANESE IMPURITY IONS IN AN ALBERTA HV BITUMINOUS COAL. Y.-P. Zhang, J. Kudynska, and H. A. Buckmaster. University of Calgary
A	133.	EXPERIMENTAL STUDIES OF RADIAL DIFFERENCE aodo-ARGAND DIAGRAMMATIC LINESHAPE ANALYSIS. H. A. Buckmaster. T. H. T. van Kalleveen, and S. Esfandabadi, University of Calgary
B	134.	EPR-ENDOR SPECTRA OF THE V_k CENTER IN SINGLE CRYSTALS OF KCl. Y. N. Zhang and S. A. Marshall, Michigan Technological University
A	135.	EPR SPECTRUM OF Ag(I) AND Ag(III) IN SINGLE CRYSTALS OF KF. C. Yu and S. A. Marshall, Michigan Technological University
B	136.	AN ELECTRON PARAMAGNETIC RESONANCE STUDY OF POLYCRYSTALLINE Tin(IV) OXIDE DOPED WITH Cr(III) and Fe(III) IONS. J. C. Evans, C. R. Owen. and C. C. Rowlands, University of Wales
A	137.	AN EPR-ENDOR STUDY OF THE PHOTODEGRADATION OF POLY(dialkylsilane)s IN SOLUTION. A. J. McKinley, T. Karatsu, G. M. Wallraff, R. Sooriyakumaran, R. D. Miller, and J. Michl, University of Texas at Austin and IBM Research Laboratories
B	138.	ESR STUDY OF ACTIVE COPPER SITES IN THE CuThO CATALYSTS. A B. Kais. R. Bechara, C. F. Aissi, M. Guelton, and J.-P. Bonnelle, University of Sciences and Techniques de Lille I
A	139.	COBALT-59 NUCLEAR QUADRUPOLE AND LIGAND HYPERFINE COUPLING IN A LOW-SPIN SCHIFFS BASE COMPLEX. F. S. Jiang. R. B. Clarkson, and R. L. Belford, University of Illinois
B	140.	EPR STUDY OF CONFORMATION OF $M(TBSQ)_2L_n$ COMPLEXES IN SOLUTION. A. Ozarowski, B.R. McGarvev. C. Peppe, and D.G. Tuck, University of Windsor, Ontario.
A	141.	ELDOR-ENDOR SPECTROSCOPY: PULSED ELECTRON NUCLEAR ELECTRON TRIPLE RESONANCE. M. Bernardo. and H. Thomann, Exxon Research.

B 142. PULSED EPR, ELECTRON SPIN ECHO, AND PULSED ENDOR SPECTROSCOPY OF ARGONNE PREMIUM COALS. L. Gebhard, M. Bernardo, B.G. Silbernagel, and H. Thomann. Exxon Research.

Wednesday morning, August I, 1990
Session VI- In Vivo Detection of Free Radical Metabolites
R. P. Mason, Chairing

830 a.m. 143. ESR, NMR, AND GC/MS ANALYSIS OF HALOCARBON METABOLISM BY RAT LIVER IN VITRO AND IN VIVO. R. A. Towner and E. G. Janzen, University of Guelph

9:00 a.m. 144. SPIN-TRAPPING STUDIES WITH ISOLATED HEPATOCYTES EXPOSED TO TOXIC AGENTS: ETHANOL, ACETALDEHYDE, AND HALOGENATED COMPOUNDS. J. L. Pover. J. M. Rau, L. A. Reinke, and P. B. McCay, Oklahoma Medical Research Foundation.

9 30 a.m. 145. REACTION OF GLUTATHIONE WITH A FREE RADICAL METABOLITE OF CARBON TETRACHLORIDE. H. D. Connor. L. B. LaCagnin, K. T. Knecht, R. P. Mason, and R. G. Thurman, NIEHS and University of North Carolina

10:00 a.m. BREAK

10:30 a.m. 146. SPIN TRAPPING OF FREE RADICALS FORMED DURING IN VITRO AND IN VIVO METABOLISM OF 3-METHYLINDOLE. T. M. Bray and S. Kubow, University of Guelph.

11:00 a.m. 147. IN VIVO ESR SPIN-TRAPPING INVESTIGATIONS OF XENOBIOTIC METABOLISM BY RED BLOOD CELLS. K. R Maples. Lovelace Inhalation Toxicology Research Institute

11:30a.m. 148. BILIARY RADICAL ADDUCTS OF CCl_4 AND ETHANOL. R. P. Mason and K. T. Knecht, NIEHS

Wednesday afternoon, August 1, 1990
Session VII - D. Goldfarb, chairing

1:30 p.m. 149. AN EPR AND ODMR STUDY OF INTERCALATED LAYERED SEMICONDUCTOR LATTICES. E. Lifshitz, S. Sibley, and A. H, Francis. University of Michigan

1:50 p.m. 150. RADIATION INDUCED DEFECTS IN AMORPHOUS SILICON DIOXIDE: KINETICS OF DEFECT GROWTH. D. B. Kerwin and F. L. Galeener, Colorado State University

2:10 p.m. 151. INCLUSION COMPLEX FORMATION OF SURFACE IMMOBILIZED CYCLODEXTRINS USING THE SPIN PROBE METHOD. A. Hooper, M. P. Eastman, and R. G. Kooser. Knox College

2:30 p.m. DISCUSSION: ISSUES CONCERNING EPR SOFTWARE. R. Cammack, presiding.

Wednesday afternoon, August 1, 1990
Session VIII - Posters, S. S. Eaton, chairing
3:00 - 4:00, authors present for posters labeled C
4:00 - 5:00, authors present for posters labeled D

C 152. FIRST OBSERVATION OF PARAMAGNETIC NITROGEN DANGLING BOND CENTERS IN SILICON NITRIDE. W. L. Warren, P. M. Lenahan. and S. E. Curry, Pennsylvania State University

D 153. AN ELECTRON NUCLEAR DOUBLE RESONANCE AND ELECTRON SPIN RESONANCE STUDY OF SILICON DANGING BOND CENTERS IN SILICON NITRIDE. W. L. Warren and P. M. Lenahan. Pennsylvania State University

C 154. A ^{29}Si HYPERFINE STUDY OF P_b AND E' CENTERS AT AND NEAR THE Si/SiO_2 INTERFACE. M. A. Jupina and P. M. Lenahan, Pennsylvania State University

D 155. AN EFFICIENT SEMIANALYTICAL METHOD OF SIMULATION OF EPR POWDER PATTERNS AND SPECTRA. L. Gonzales-Tovany and V. Beltran-Lopez, Instituto Nacional de Investigaciones Nucleares and Universidad Nacional Autonoma de Mexico

C 156. LINESHAPES OF EPR SPECTRA OF POLYIMIDE RESINS. M. K. Ahn, T. C. Stringfellow, M. J. Fasano, K. J. Bowles, and M. A. Meador, Indiana State University and NASA Lewis Research Center

D 157. AN AUTOMATED METHOD FOR IDENTIFICATION AND QUANTITATION OF FREE RADICALS AND PARAMAGNETIC CENTERS FROM COMPLEX MULTI-COMPONENT EPR SPECTRA. P. Kuppusamy and J. L. Zweier, Johns Hopkins Medical Institutions.

C 158. EPRFIT: A COMPUTER MODELING PACKAGE FOR THE SIMULATION OF ISOTROPIC EPR SPECTRA INCLUDING INTRAMOLECULAR EXCHANGE-BROADENING. IBM-AT COMPATIBLE COMPUTER VERSION 1.00. J. A. Menapace, U.S. Air Force Academy

D 159. ON THE FUTURE OF EPR SPECTROSCOPY. C. Rudowicz, City Polytechnic of Hong Kong

C 160. TEMPERATURE DEPENDENCE OF THE BENZYL HYDROGEN HYPERFINE SPLITTING IN EPR SPECTRA OF THE 3,5-DINITROPHENYL BENZYL NITROXIDE RADICAL BETWEEN 195 AND 290 KELVINS. J. A. Menapace, J. E. Marlin, and G. E. Godec, U.S. Air Force Academy

D 161. $[Cr(V)O(EHBA)_2]^-$ LIGAND EXCHANGE AT CALCIUM SITES ON THE SARCOPLASMIC RETICULUM ATPase. C. Coan and J.-Y. Ji, University of the Pacific.

C 162. GENERATION OF SUPEROXIDE ANION RADICAL IN CHOLESTEROL OXIDASE REACTION. M. Sonoda, T. Hanada, Y. Nakajima, and Y. Sakagishi, Saitama Medical School

D 163. ESR STUDIES OF ASCORBATE METABOLISM IN THE HUMAN ERYTHROCYTE. R. J. Mehlhorn, Lawrence Berkeley Laboratory.

C 164. METABOLISM OF NITROXIDES BY MOUSE LYMPHOCYTES. P D Morse, II, J. M. Petruszak, and L. Reminger, Illinois State University

D 165. ATP BINDING TO BOVINE SERUM ALBUMIN (BSA). M. P. Bauer, P. Jakobs, and W. E. Trommer, University of Kaiserslautern

C 166. USE OF DOXYL-STEARIC ACID PROBES TO MONITOR CHANGES IN PLASMA MEMBRANE FLUIDITY FOLLOWING INITIATION OF THE FIRST MEIOTIC DIVISION IN RANA OOCYTES. G. A. Morrill, K. Doi, and A. B. Kostellow, Albert Einstein College of Medicine.

D 167. 3 mm-HIGH-FIELD EPR ON DONOR AND ACCEPTOR RADICAL IONS RELATED TO PHOTOSYNTHESIS. O. Burghaus, W. Lubitz, K. Mobius, and M. Plato, Free University, Berlin.

C 168. W-BAND EPR OF VARIOUS SYNTHETIC MELANINS: IDENTIFICATION AND DIFFERENTIATION. W. Wang, M. J. Nilges, S. Enochs, P. Gast, R. B. Clarkson, T. Walczak, H. M. Swartz, T. Sarna, and R. L. Belford, University of Illinois.

D 169. ON THE MOTIONAL PROCESSES IN THE ULTRA SLOW MOTIONAL REGIME, STUDIED BY SATURATION RECOVERY EPR AND PULSED ELDOR. D. Haas, R. StDenis, C. Mailer, and B. H. Robinson, University of Washington.

C 170. AN ESEEM SEQUENCE WITH AN IMPROVED MODULATION DEPTH. C. Gemperle and A. Schweiger, R. R. Ernst, ETH Zurich.

D 171. AN ESEEM STUDY OF Cu(II) BINDING TO CHIRAL BIOMIMETIC LIGANDS. D. Goldfarb. J.-M. Fauth, Y. Tor, and A. Shanzer, Weizmann Institute of Science.

C 172. FORMATION OF NEW COPPER (II) SPECIES DURING PROPYLENE OXIDATION ON COPPER (II)-EXCHANGED X ZEOLITE. J.-S. Yu and L. Kevan. University of Houston.

D 173. INTRAMOLECULAR EFFECT OF Cu(II) AND Co(II) ON NITROXYL RELAXATION TIMES. A. V. Kulikov. K. M. More, S. S. Eaton, and G. R. Eaton, University of Denver.

C 174. NITROXYL, T_1 AND T_2 VALUES IN SPIN-LABELED IRON(III) TETRAPHENYLPORPHYRINS. M. H. Rakowsky. K. M. More, A. V. Kulikov, S. S. Eaton, and G. R. Eaton, University of Denver.

D 175. PORTABLE ESR SPECTROMETER USING PERMANENT MAGNET CIRCUIT. A. Nakanishi. K. Konishi, N. Sugawara, and M. Ikeya, Sumitomo Special Metals Co. and Osaka University.

C 176. A MODULAR LOW FREQUENCY ESR SPECTROMETER. M. Spacher, R. G. Bryant, and J. P. Hornak. Rochester Institute of Technology and University of Rochester.

D 177. TEACHING MRI AND MRS USING COMPUTER ANIMATION. D. S. Browne, P. E. Ellsworth, W. A. Weigert, R. M. Agostinelli, and J. P. Hornak. Rochester Institute of Technology.

C 178. ESR STUDIES OF TRIPLET STATE IN DIACETYLENE MONOMER MATERIALS. S. Shih. A. Hu, and J. H. Chen, National Tsing Hua University.

D 179. HIGH FIELD ESR AT 140 GHz. T.F. Prisner. S. Un. R.T. Weber. A.E. McDermott, and R.G. Griffin, Massachusetts Institute of Technology.

C 180. EPR-ENDOR OF THE COMPOUND I RADICAL IN SITE-DIRECTED MUTANTS OF CYTOCHROME c PEROXIDASE. Y. Liu, C.P. Scholes, L.A. Fishel, J.M. Mauro, M. Miller, and J. Kraut, SUNY Albany and University of California - San Diego.

D 181. ULTRA LOW FIELD EPR MEASUREMENTS ON LITHIUM PHTHALOCYANINE RADICAL. M. Moussavi. C. Jeandey, M. Beranger, and D. Duret, CEA LETI, Grenoble.

Wednesday evening - open house at University of Denver
EPR Laboratory

Thursday morning, August 2, 1990
Session IX - G. R. Eaton, chairing

8:30 a.m. 182. PLENARY LECTURE - EPR, ENDOR, AND ESEEM SPECTROSCOPY OF NICKEL(III) IN HYDROGENASES. R. Cammack. King's College, London.

9:15 a.m. 183. DETECTION AND CHARACTERIZATION OF EXCHANGEABLE PROTONS BOUND TO THE NICKEL SITE OF *DESULFOVIBRIO GIGAS* HYDROGENASE: A ^{1}H AND ^{2}HQ-BAND ENDOR STUDY. C. Fan. M. Teixeira, J. Moura, I. Moura, B.-H. Huynh, J. LeGall, H. D. Peck, Jr., and B. M. Hoffman, Northwestern University.

9:40 a.m. 184. THE COPPER SITE IN CYTOCHROME c OXIDASE AND NITROUS OXIDE REDUCTASE. P. M. H. Kroneck and W. E. Antholine, University of Konstanz and Medical College of Wisconsin.

10:05 a.m. BREAK

10:30 a.m. 185. EFFECT OF ZERO FIELD SPLITTING ON ESEEM OF MANGANESE. A. R. Coffino, C. Bender, and J. Peisach, Albert Einstein College of Medicine.

10:50 a.m. 186. SUBSTRATE COORDINATION TO THE [2Fe-2S] CLUSTER OF SPINACH DIHYDROXY ACID DEHYDRATASE. K. Nakagawa, M. H. Emptage, D. Houseman, and B. M. Hoffman, Northwestern University and E. I. duPont de Nemours.

11:15 a.m. 187. PROGRESS IN EPR OXIMETRY OF VIABLE BIOLOGICAL SYSTEMS. H. M. Swartz, J. Glockner, P. Gast, and R. Clarkson, University of Illinois.

11:40 a.m. 188. TOWARDS A QUANTITATIVE EPR OXYMETRY IN TISSUES OF A LIVING ANIMAL: MEASUREMENT STABILITY AND THE IN VIVO CORRECTION FOR CONFOUNDING EFFECTS. H. J. Halpern, M. Peric, E. Barth, Y. J. Lin, B. A. Teicher, and M. K. Bowman, University of Chicago, Harvard University and Argonne National Laboratory.

Thursday afternoon - Bruker user's meeting. Please contact Dr. Art Heiss if you wish to participate.

NOTE: Poster presenters are requested to display their posters from Monday morning to Thursday morning to permit time for browsing.

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INDUCTIVELY COUPLED PLASMA-MASS SPECTROMETRY

Howard E. Taylor, Chairman

Monday afternoon, July 30, 1990

1:00 189. CHARACTERIZATION OF POLYATOMIC SPECIES IN INDUCTIVELY COUPLED PLASMA-MASS SPECTROMETRY BACKGROUND SPECTRA. Richard D. Ediger, Perkin-Elmer Corp.

1:50 190. RECENT ADVANCES IN ICP-MS TECHNOLOGY. Peter D. Blair. Robert Henry, David Gregson, Neil Bradshaw, and Chris Tye, VG Instruments, Inc.

2:15 191. CHARACTERIZATION OF THE DELSI-NERMAG MASS SPECTROMETER INTERFACED TO A VERSATILE ICP SYSTEM. Akbar Montaser. H. Tan, I. Ishii, and S. Nam, George Washington University.

2:40 BREAK

3:00 192. UTILIZATION OF INDUCTIVELY COUPLED PLASMA-MASS SPECTROMETRY AS AN ELEMENT SPECIFIC DETECTOR FOR SEDIMENTATION FIELD-FLOW FRACTIONATION. John R. Garbarino. Howard E. Taylor, U.S. Geological Survey, and Diedra Hotchin, Ronald Beckett, Chisholm Institute of Technology.

3:25 193. APPLICATIONS OF LASER ABLATION-ICP-MS TO GEOLOGICAL SAMPLES. Fred E. Lichte. Joseph H. Christie, and Allen L. Meier, U.S. Geological Survey.

3:50 194. DATA QUALITY CONSIDERATIONS IN THE APPLICATION OF ICP/MS LEAD ISOTOPE RATIO DATA TO ENVIRONMENTAL ENFORCEMENT. Michael E. Ketterer. U.S. Environmental Protection Agency.

4:15 195. COMPARISON OF INFLUENCE OF OPERATING PARAMETERS UPON PERFORMANCE OF AN ULTRASONIC NEBULIZER AND A PNEUMATIC NEBULIZER IN ICP MASS SPECTROMETRY. Arthur W. Varnes. BP Research.

IR/FTIR SYMPOSIUM

A.R. Chughtai, Chairman

Monday morning, July 30, 1990

8:15 a.m. 196. SPECTROSCOPIC AND SOLUBILITY CHARACTERISTICS OF OZONATED, NITRATED AND SULFONATED SOOTS. Abdul R. Chughtai. Jabria A. Jassim, and Dwight M. Smith, University of Denver.

8:40 a.m. 197. GUEST SPEAKER: Professor Dwight M. Smith. Former Chancellor of the University of Denver.

THE REACTIVITY OF OXIDANTS WITH SOOT. I. A COMPARATIVE STUDY OF O_3 AND NO_2/N_2O_4. Abdul R. Chughtai and Dwight M. Smith. Department of Chemistry, University of Denver.

9:40 a.m. BREAK

9:55 a.m. 198. GC/TRACER ANALYSIS OF BEERS. Jav R. Powell. Bio-Rad, Digilab Division.

10:20 a.m. 199. FT-IR CHARACTERIZATION OF CHRONIUM(III) ACETATE IN AQUEOUS SOLUTION. Janes E. Tackett, Marathon Oil Company.

10:45 a.m. 200. STRUCTURAL INTEGRITY ASSESSMENT OF CONCRETE SLABS BY NDE AND FT-IR METHODS. T.V. Rebagay and D.A. Dodd, Analytical Systems Laboratories, Westinghouse Hanford Company.

11:05 a.m. 201. ADVANTAGES OF FT-RAMAN SPECTROSCOPY IN THE BIOLOGICAL SCIENCES. Jay R. Powell, David A.C. Compton, and Norman A. Wright, Bio-Rad, Digilab Division.

11:30 a.m. 202. DESIGN AND PERFORMANCE OF A NEW INFRARED MICROSCOPE. W.D. Perkins. Perkin-Elmer Corp., D.W. Schiering and E.F. Young, Perkin-Elmer Corp.

11:55 a.m. 203. GAS OUANTIATION MADE EASY. Philip L. Hanst. Infrared Analvsis. Inc.

SYMPOSIUM ON LUMINESCENCE

Marvin C. Goldberg, Chairman

Tuesday morning, July 31, 1990

8:25 a.m. INTRODUCTORY REMARKS. Marvin C. Goldberg.

9:00 a.m. 204. MEASUREMENT OF THE SIZE AND SHAPE OF FULVIC ACID BY FLUORESCENCE DEPOLARIZATION SPECTROSCOPY. Marvin C. Goldberg. U.S. Geological Survey, Lakewood, Colorado.

9:30 a.m. 205. PHOTOINITIATION OF PEROXYOXALATE CHEMILUMINESCENCE: APPLICATION TO FLOW INJECTION ANALYSIS OF CHEMILUMOPHORES. Robert E. Milofsky. John W. Birks, University of Colorado, Boulder.

10:00 a.m. BREAK

10:30 a.m. 206. PHYSICOCHEMICAL INTERACTIONS OF THE AMINOBENZOIC ACID ISOMERS WITH SODIUM ACETATE IN SOLID-MATRIX ROOM-TEMPERATURE LUMINESCENCE SPECTROSCOPY. S.M. Ramasamy and R.J. Hurtubise, University of Wyoming, Laramie.

11:00a.m. 207. TRACING THE MOVEMENT OF TRANSPOTED MATERIALS IN THE SOUTH PLATTE RIVER BY EEM LUMINESCENCE SPECTROSCOPY. Marvin C. Goldberg. U.S. Geological Survey, Lakewood, Colorado.

11:30 a.m. 208. MEASUREMENT OF EEM SPECTRA IN NATURAL WATERS. Karen K. Francis and Marvin C. Goldberg, U.S. Geological Survey, Lakewood, Colorado.

NEAR-IR SYMPOSIUM

Donald A. Bums, Chairman

Monday afternoon, July 30, 1990

1:40 p.m. 209. NEAR-IR: WHERE THE ACTION IS. Donald A. Burns. Los alamos National Laboratory.

2:05 p.m. 210. THE USE OF MULTIVARIATE STATISTICAL CALIBRATION METHODS IN NIR: IS MORE ALWAYS BETTER? Steven M. Buco. Statistical Resources.

2:30 p.m. 211. EFFECTS OF SCATTERING ON NEAR-INFRARED ANALYSIS OF PULP AND PAPER. Paul Brimmer. NIRSystems.

2:55 p.m. BREAK

3:10 p.m. 212. INTERACTION BETWEEN NEAR-INFRARED LIGHT AND COTTON TO MEASURE FIBER MATURITY AND FINENESS. Joseph G. Montalvo. Jr.. Sherman E. Faught, and Stephen M. Buco, Southern Regional Research Center.

3:35 p.m. 213. STATIONARY HADAMARD TRANSFORM NIR INTERFEROMETRY. J.D. Tate. Joseph V. Paukstelis, Robert M. Hamaker, and William Fateley. Department of Chemistry, Kansas State University.

4:00 p.m. 214. RECENT TRENDS IN ON-LINE NEAR-IR SPECTROSCOPY. Lawrence McDermott and Isaac Landa, LT Industries.

NMR SYMPOSIUM

Two Pumps. One Probe
Session I
H. Thomann, Chair

Monday morning, July 30, 1990

8:20 a.m. Opening remarks, S. S. Eaton

8:30a.m. 215. DYNAMIC NUCLEAR POLARIZATION AT 140 GHZ. Thomas F. Prisner, Sun Un, Ralph T. Weber, Ken W. Fishbein, Ann E. McDermott, Matthew J. Seaman, Michael Whitmore, David J. Singel, and Robert G. Griffin, Francis Bitter National Magnet Laboratory, Massachusetts Institute of Technology, Department of Chemistry, Massachusetts Institute of Technology, Department of Chemistry, Harvard University.

9:15 a.m. 216. CHARACTERIZATION OF THE INTERFACIAL REGION OF POLYSTYRENE-POLYCARBONATE BLENDS BY DYNAMIC NUCLEAR POLARIZATION ^{13}C CPMAS NMR. M. Afeworki and J. Schaefer. Washington University

10:00 a.m. BREAK

10:30a.m. 217. A NEW ANALYSIS OF SOLITON DYNAMICS IN TRANS-POLYACETYLENE: MOTIONAL EFFECTS OF DYNAMIC NUCLEAR POLARIZATION SPECTRA. B. H. Robinson and A. R. Coffino, University of Washington.

11:15 a.m. 218. EPR PARAMETERS MEASURED BY NMR. R. A. Wind, J. Blair, and J. B. Wooten, Colorado State University and Philip Morris Research Center.

12:00 noon LUNCH

1:30 p.m. 219. RADIO FREQUENCIES IN PULSED ESR. A. Schweiger, ETH Zurich.

2:15 p.m. 220. COORDINATION STRUCTURE OF ACTIVE SITES IN METALLOENZYMES AND PROTEINS BY PULSED ELECTRON NUCLEAR MULTIPLE RESONANCE. H. Thomann and M. Bernardo, Exxon Research.

3:00 p.m. BREAK

"Spin Dynamics (I)"
C. Bronniman, Chair

Monday afternoon, July 30, 1990

3:30 p.m 221. PRECISE DETERMINATION OF INTERPARTICLE DISTANCE THROUGH MAS-NMR SIDEBAND INTENSITY ANALYSIS. Po-Jen Chu. Department of Chemistry, Texas A&M University.

4:00 p.m. 222. HYDRODYNAMIC EFFECTS IN A CRITICAL BINARY MIXTURE. Serge Lacelle, Franco Cau, Luc Tremblay, and Stephane Lavallee, Departement de chimie, Universite de Sherbrooke, Qc, CANADA, J1K 2R1.

4:30 p.m. 223. 2-D NMR STUDIES OF POWDERED AND ORIENTED MATERIALS WITH SAMPLE REORIENTATION. Craig D. Hughes, Mark H. Sherwood, D. W. Alderman, and David M. Grant, Chemistry Department, University of Utah.

5:00 p.m. 224. COMPUTER AIDED NMR MULTIPLE-PULSE SEQUENCE DESIGN FOR QUADRUPOLAR NUCLEI: AN ARTIFICIAL INTELLIGENT APPROACH. Po-Jen Chu. Department of Chemistry, Texas A&M University.

"Vendor"
B. C. Gerstein, Chair

Monday evening, July 30, 1990

7:30 p.m. 225. SOLID-STATE NMR ON THE CMX SPECTROMETER. Victor J. Bartuska, Joseph A. DiVerdi, Allen R. Palmer, Dean W. Sindorf, and Robert A. Wind. Chemagnetics, Inc.

7:50 p.m. 226. CHARACTERIZATION OF HIGH PERFORMANCE SHIM SYSTEM BY FIELD MAPPING. D. F. Hillenbrand and P. M. Starewicz. Resonance Research, Inc.

8:10 p.m. 227. CROSS POLARIZATION AT HIGH SPINNING SPEEDS. T. M. Barbara, A. Brooke, H. D. W. Hill, and P. H. Williams. Varian Associates.

8:30 p.m. 228. SOLID STATE NMR PROBE TECHNOLOGY. D. Doty. Doty Scientific.

8:50 p.m. 229. NEW DEVELOPMENTS IN SOLID STATE NMR. D. Burum. Burker Instruments, Inc.

"General"
R. Honkonnen, Chair

Tuesday morning, July 31, 1990

8:00 a.m 230. NMR OF HEME PROTEINS. Eric Oldfield. 505 South Mathews Avenue. Urbana, IL 61801.

8:30 a.m. 231. ^{17}ONMR STUDIES OF OXIDES A EXTREMES OF TEMPERATURE. Jeffrey A. Reimer. Stuart Adler, and Marjorie Went, Department of Chemical Engineering, University of California.

9:00 a.m. 232. PRESSURE, TEMPERATURE, AND COMPOSITIONAL EFFECTS ON SILICATE LIQUID STRUCTURE AND DYNAMICS: THE VIEW BY NMR SPECTROSCOPY. Jonathan F. Stebbins. Ian Farnan, and Xianyu Xue, Department of Geology, Stanford University.

9:30 a.m. 233. APPLICATIONS OF SECOND-ORDER EFFECTS IN SOLID-STATE NMR. Philip J. Grandinetti. M. A. Eastman, Y. Wu, R. Jelinek, and A. Pines, Lawrence Berkeley Laboratory and University of California.

10:00 a.m. BREAK

10:30 a.m. 234. HETEROGENEITY OF CROSS RELAXATION IN SOLID STATE NMR. Xiaoling Wu and Kurt W. Zilm, Department of Chemistry, Yale University.

11:00a.m. 235. THE NUCLEAR OVERHAUSER EFFECT IN SOLIDS. Jeffery L. White and James F. Haw, Department of Chemistry, Texas A&M University.

11:30 a.m. 236. 1D AND 2D SOLID STATE NMR OF HOMONUCLEAR SPIN SYSTEMS USING MAGIC ANGLE SPINNING. James C. Duchamp, Xiaoling Wu, and Kurt W. Zilm, Department of Chemistry, Yale University.

12:00 noon LUNCH

"Polymers"
M. Ahn, Chair

Tuesday afternoon, July 31, 1990

1:30 p.m 237. NMR STUDIES OF FLUORINATED POLYCARBONATES. John Grutzner. Satoshi Usui, Brett Cowans, Young Lee, and Jim Caruthers, Department of Chemistry, Purdue University.

2:00 p.m. 238. SOLID STATE ^{13}C CPMAS-NMR STUDY OF AN A/B BOCK COPOLYMER OF POLYSTYRENE AND POLY(METHYL METHACRYLATE). E. O. Stejskal. S. S. Sankar, R. E. Fornes, W. W. Fleming, T. P. Russell, and C. G. Wade, Department of Chemistry, North Carolina State University.

2:30 p.m. 239. DRUG-DNA COMPLEXES - STRUCTURE AND DYNAMICS BY SOLID STATE NMR. Pei Tang, Chi-Long Juang, Rodolfo A. Santos, Wei-Jyun Chien, and Gerard S. Harbison. Department of Chemistry, SUNY Stony Brook.

3:00 p.m. 240. LOCAL CHAIN MOTION OF POLYMERS WITH BACKBONE AROMATIC RINGS - THE RELATION OF RING FLIPPING TO SUB-TG MECHANICAL RELAXATION. P. Mark Henrichs, Exxon Chemical Company, Baytown Polymers Group.

3:30 p.m. BREAK

4:00p.m. 241. SOLID STATE ^{15}N NMR OF NYLONS. Lon J. Mathias, Douglas G. Powell, Allison M. Sikes, and C. Greg Johnson, University of Southern Mississippi.

4:30 p.m. 242. ESTIMATING DOMAIN SIZES FOR CHEMICAL AND PHYSICAL HETEROGENEITY IN SOLIDS USING PROTON SPIN DIFFUSION. Gordon C. Campbell and David L. VanderHart, National Institute of Standards and Technology, Polymers Division.

5:00 p.m. 243. SOLID-STATE NMR CHARACTERIZATION OF FUNCTIONALIZED, GRAFTED POLYSTYRENE/POLYPROPYLENE POLYMERS. Joel R. Garbow, Physical Sciences Center, Monsanto Company.

"Solids"
Session I
T. Apple, Chair

Wednesday morning, August 1, 1990

8:00 a.m 244. ^{19}F AND ^{31}P MAS-NMR OF Sb-DOPED FLUOROPATITE PHOSPHORS: DOPANT SITES AND SPIN DIFFUSION. James P. Yesinowski, Liam B. Moran, and Jefferey Berkowitz, Department of Chemistry, Michigan State University.

8:30 a.m. 245. A MULTINUCLEAR (^{19}F, ^{1}H, ^{87}Sr) SOLID-STATE NMR STUDY OF THE FLUORIDATION OF Ca- AND SUBSTITUTED-APAT1TIC SURFACES. A. T. Kreinbrink, C. D. Sazavsky, J. R. Wietfeldt, D. G. Nelson, R. S. Honkonen, P. S. Marchetti, and G. E. Maciel, Miami Valley Laboratories, The Procter and Gamble Company.

9:00 a.m. 246. NDE BY NMR IMAGING OF AEROSPACE MATERIALS. Charles G. Frv and Arthur C. Lind, McDonnell Douglas Research Laboratories.

9:30 a.m. 247. SOLID STATE SILICON-29 MAS NMR STUDY OF NEW HIGH PERFORMANCE CERAMIC. K. R. Carduner, M. J. Rokosz, S. S. Shinozaki, and Y. Yasutomi, Ford Motor Company.

10:00 a.m. BREAK

10:30 a.m. 248. DEUTERIUM NMR LINESHAPES AND RELAXATION BEHAVIOR OF INTERCALATION COMPOUNDS. Ta-Hsien Lin, Robert L. Vold, and Regitze R. Vold, Department of Chemistry, University of California, San Diego.

11:00 a.m. 249. HIGH RESOLUTION NMR OF QUADRUPOLAR NUCLEI IN MOLECULAR SIEVES. Bradlev F. Chmelka, Y. Wu, M. E. Davis, P. J. Grobet, P. A. Jacobson, and A. Pines, Department of Chemistry, Pines Research Group, University of California, Berkeley.

11:30 a.m. 250. DIPOLAR NMR SPECTROSCOPY OF NON-OXIDIC GLASES. Hellmut Eckert, David Lathrop, Deanna Franke, and Robert Maxwell, Department of Chemistry, University of California, Santa Barbara.

12:00 noon LUNCH

"Fossil"
Session II
R. Botto, Chair

Wednesday afternoon, August 1, 1990

8:00 a.m. 251. PULSED ENDOR STUDIES OF COALS. H. Thomann, M. Bernardo, P. Tindall, and B. G. Silbernagel, Exxon Research and Engineering Company.

8:30a.m. 252. A BLOCH DECAY AND CPMAS ^{13}C NMR STUDY OF THE ARGONNE PREMIUM COALS: EFFECTS OF HIGH-SPEED SPINNING ON THE CPMAS EXPERIMENT. J. A. Franz and J. C. Linehan, Pacific Northwest Laboratory.

9:00 a.m. 253. EPR STUDIES OF DEMINERALIZED AGRONNE PREMIUM COALS. L. A. Gebhard, B. G. Silbernagel, R. A. Flowers, and J. W. Larsen, Exxon Research and Engineering Company.

9:30 a.m. 254. DISTORTION-FREE ^{13}CNMR IN COAL BY MEANS OF ^{1}H ROTATING-FRAME DYNAMIC NUCLEAR POLARIZATION AND ^{1}H-^{13}C CROSS POLARIZATION. R. A. Wind. Department of Chemistry, Colorado State University.

10:00 a.m. BREAK

10:30 a.m. 255. MULTIDIMENSIONAL ELECTRON MAGNETIC RESONANCE OF COAL. R. B. Clarkson, W. Wang, K. M. Motsegood, and R. L. Belford, Department of Chemistry and Illinois EPR Research Center, University of Illinois.

11:00 a.m. 256. QUANTITATION OF PROTONS IN THE ARGONNE PREMIUM COALS BY SOLID-STATE ^{1}HNMR. L. dela Rosa, M. Pruski, and B. C. Gerstein, Institute of Physical Research and Technology and Department of Chemistry, Iowa State University.

11:20 a.m. 257. THE SOLVATION OF COALS BY PITCHES AND MODEL COMPOUNDS AT HIGH TEMPERATURES. Richard Sakurovs. CSIRO Division of Coal Technology.

LUNCH

"Catalysis"
Session I
H. Eckert, Chair

Wednesday afternoon, August 1, 1990

1:30 p.m 258. MAGNETIC RESONANCE STUDIES OF MeAlPO-5. Z. Levi, D. Goldfarb. Department of Isotope Research, The Weizmann Institute of Science, 76 100 Rehovot, Israel.

2:00 p.m. 259. VARIABLE-TEMPERATURE IN-SITU SOLID-STATE NME INVESTIGATIONS OF REACTIONS OF ZEOLITE CATALYSTS. Eric J. Munson, Jeffery L. White, Marsha J. Lambregts, Noel D. Lazo, and James F. Haw, Department of Chemistry, Texas A&M University.

2:30 p.m. 260. IN SITU NMR STUDIES OF ZEOLITE CATALYSIS. Michael W. Anderson and Jacek Klinowski, Department of Chemistry, UMIST, P.O. Box 88, Manchester M60 1QD, UK.

3:00 p.m. 261. DEVELOPMENT AND USE OF THE CARR-PURCELL PULSE TRAIN FOR DIPOLAR SPECTROSCOPY: THE GEOMETRY AND REORIENTATIONAL MOBILITY OF BENZENE CHEMISORBED ON Pt/η-Al_2O_3. M. Engelsberg, C. S. Yannoni, C. Dybowski, and M. A. Jacintha, IBM Almaden Research Center.

3:30 p.m. BREAK

4:00 p.m. 262. ^{129}Xe NMR OF METAL-EXCHANGED ZEOLITES. Cathy Tway and Tom Apple. Department of Chemistry, University of Nebraska, Lincoln.

4:30 p.m. 263. MULTINUCLEAR NMR INVESTIGATIONS OF HETEROGENEOUS CATALYSTS. Cecil Dvbowski. Matthew Smith, Mary Jacintha, Mark Hepp, and C. J. Tsiao, Navin Bansal, Department of Chemistry and Biochemistry, University of Delaware.

5:00 p.m. 264. QUADRUPOLAR NUCLIDES IN CATALYTIC ENVIRONMENTS. Paul D. Ellis. John C. Edwards, H. Douglass Morris, and Shelton Bank, Department of Chemistry, University of South Carolina.

"Polvmer II and Coal II"

R. Wind, Chair

Wednesday afternoon, August 1, 1990

1:30 p.m 265. THE RELAXATION OF ELECTRON ZEEMAN AND ELECTRON DIPOLAR FIELDS IN DILUTE PARAMAGNETIC SOLIDS. M. K. Bowman.

2:00 p.m. 266. WIDE-LINE ^{2}H NMR STUDY OF PERDEUTERATED PYRIDINE IMBIBED IN A PREMIUM COAL. J. S. Frve and G. E. Maciel.

2:30 p.m. 267. EPR SPIN PROBE STUDIES OF POROSITY IN SOLVENT SWELLED COALS. R. Spears and L. D. Kispert.

3:00 p.m. 268. CHARACTERIZATION OF COAL MACERALS BY NMR SPECTROSCOPY AND IMAGING. R. E. Botto. C.-Y. Choi, S. L. Dieckman, N. Gopalsami, A. R. Thompson, and C.-J. Tsiao, Argonne National Laboratory.

3:30 BREAK

4:00 p.m. 269. A STUDY OF THE MORPHOLOGY OF POLYPHOSPHAZENES USING SOLID-STATE NMR. Sharon A. Tavlor. Jeffery L. White, Nicholas C. Elbaum, and James F. Haw, Department of Chemistry, Texas A&M University.

4:30 p.m. 270. SOLID STATE ^{2}H NMR SPECTROSCOPY OF ORIENTED Li AND Na DNA FIBERS. G. H. Meresi. R. R. Vold, R. L. Vold, D. R. Kearns, R. Brandes, A. Rupprecht, and W. K^hnlein,, Department of Chemistry, University of California, San Diego.

5:00 p.m. 271. SOLID SAMPLE ^{13}C NMR STUDIES OF POLYIMIDES. Myong K. Ann. Mary Ann Meador, and Kenneth J. Bowles, Department of Chemistry, Indiana State University.

"New Developments"

Lex Vega, Chair

Thursday morning, August 2, 1990

8:00 a.m. 272. NUCLEAR ACOUSTIC RESONANCE. Robert G. Leisure. Department of Physics, Colorado State University.

8:30 a.m. 273. ON THE GROWTH OF MULTIPLE-SPIN COHERENCES IN THE NMR OF SOLIDS. Serge Lacelle. DEpartement de chimie, UniversitE de Sherbrooke, Sherbrooke, Qc, Canada J1K 2R1

9:00 a.m. 274. DIPOLE MEASUREMENTS WITH COMPENSATED CARR-PURCELL SEQUENCES. Terry Gullion, Jacob Schaefer, David Baker, Martin Lizak, and Mark Conradi, Department of Chemistry, Washington University, St. Louis, MO.

9:30 a.m. 275. ROTATIONAL RESONANCE IN AN RF FIELD FOR NMR OF ROTATING SOLIDS. Zhehong Gan and David M. Grant, Department of Chemistry, University of Utah.

10:00 a.m. BREAK

10:30 a.m. 276. MULTINUCLEAR NMR STUDIES OF SAMPLES BASED ON ALUMINATE AND SILICATE STRUCTURES. Steven F. Dec, Charles E. Bronnimann, Abdullatef I. Hamza, John J. Fitzgerald, and Gary E. Maciel, Department of Chemistry, Colorado State University.

11:00 a.m. 277. ADVANCES IN HETERONUCLEAR CORRELATION APPROACHES FOR SOLIDS. Charles E. Bronnimann and Gary E. Maciel, Department of Chemistry, Colorado State University.

11:30 a.m. 278. STEPPED FREQUENCY NMR SPECTROSCOPY OF QUADRUPOLAR NUCLEI. Robert L. Vold, Regitze R. Vold, and Michael A. Kennedy, Department of Chemistry, University of California, San Diego.

QUALITY ASSURANCE SYMPOSIUM

Bill Shampine, Chairman

Wednesday morning, August 1, 1990

8:25 a.m. WELCOME AND INTRODUCTORY REMARKS

8:30 a.m. 279. CHEMICAL STABILITY OF WET-DEPOSITION SAMPLES SUBSAMPLED DAILY FOR ONE WEEK. Timothy C. Willoughby, LeRoy J. Schroder, and John D. Gordon; U.S. Geological Survey

9:00 a.m. 280. APPLICATION OF STATISTICAL QUALITY-CONTROL METHODS TO AN EXTERNAL QUALITY-ASSURANCE PROGRAM OF THE NATIONAL ATMOSPHERIC DEPOSITION PROGRAM/NATIONAL TRENDS NETWORK. John D. Gordon, LeRoy J. Schroder, and T.C. Willoughby; U.S. Geological Survey

9:30 a.m. 281. GRAPHICAL METHODS FOR EVLUATING ANALYTICAL DATA FROM REFERENCE SAMPLES. H. Keith Long: U.S. Geological Survey

10:00 a.m. BREAK

10:30 a.m. 282. QUALITY ASSURANCE WITHIN THE ALASKAN LIMNOLOGY PROGRAM THROUGH STATEWIDE STANDARDIZATION OF FIELD AND LABORATORY METHODOLOGIES. Jim Edmundson and Jeffrey P. Koenings; Alaska Dept. of Fish and Game

11:00 a.m. 283. EXTERNAL QUALITY-ASSURANCE PROGRAM FOR U.S. GEOLOGICAL SURVEY ANALYTICAL LABORATORIES. Thomas J. Maloney: U.S. Geological Survey.

11:30 a.m. LUNCH

Wednesday afternoon, August 1, 1990

1:00 p.m. 284. QUALITY ASSURANCE REQUIREMENTS FOR SUPERFUND RI/FS ACTIVITIES IN REGION V. James H. Adams: U.S. Environmental Protection Agency, Region 5

1:30p.m. 285. U.S. ARMY TOXIC AND HAZARDOUS MATERIALS AGENCY INSTALLATION RESTORATION QUALITY ASSURANCE PROGRAM. Kenneth T. Lang: U.S. Army Toxic and Hazardous Materials Agency

2:00 p.m. BREAK

2:30 p.m. 286. QUALITY ASSURANCE IN THE SAN JOAQUIN VALLEY DRAINAGE PROGRAM, CALIFORNIA. Marvin L. Yates. U.S. Geological Survey, William J. Walker, and Richard G. Burau; University of California, Davis

3:00 p.m. 287. THE SAN JOAQUIN VALLEY DRAINAGE PROGRAM QA/QC PROGRAM: A COMPARISON OF ANALYTICAL METHODS USED FOR THE DETERMINATION OF As, Se, B, Mo, AND Cr IN SEVERAL ENVIRONMENTAL MATRICES. William J. Walker. Richard G. Burau, University of California, Davis; Marvin L. Yates, U.S. Geological Survey.

3:30 p.m. 288. QUALITY ASSURANCE PRACTICES IN A UNIVERSITY SETTING. Robert L. Sutton and Eric R. Allen Environmental Engineering Sciences Department University of Florida

4:00 p.m. 289. MERCURIC CHLORIDE INTERFERENCE IN LOW LEVEL NUTRIENT ASSAYS. Deborah A. Hunter. Division of Environmental Studies, University of California-Davis.

4:00 CLOSING REMARKS

GENERAL POSTERS
Carlos Arozarena, Presiding

Posters will be set up Monday morning through Wednesday afternoon.
Authors will be available Monday afternoon between 2:00 p.m. and 4:00 p.m.

290. A COLORIMETRIC DETERMINATION OF SELENIUM IN ANIMAL FEED PREMIXES. Jeffrey A. Hurlbut. Roger G. Burkepile, and Carolyn A. Geisler, U.S. Food and Drug Administration, Denver, Colorado.

291. AN UPDATE TO THE EXTERNAL QUALITY ASSURANCE AND ITS IMPACT ON LABORATORY PERFORMANCE IN THE ACID RAIN PROGRAM. Nabil M. Arafat and Keijo I. Aspila, National Water Research Institute, Ontario, Canada.

292. IMPROVED SELENIUM RECOVERY FROM TISSUE WITH MODIFIED DRY ASHING. William G. Brumbaugh and Michael J. Walther, U.S. Fish and Wildlife Service, Columbia, Missouri.

293. CHEMISTRY OF EPISODIC RAINFALL-RUNOFF FROM INERT MICROCATCHMENTS IN THE ADIRONDACK MOUNTAINS, NEW YORK, 1987-88. Paul F. Schuster and Michael M. Reddy, U.S. Geological Survey, Arvada, Colorado.

294. A RAPID METHOD FOR DETERMINING METHYLENE BLUE AND ITS METABOLITES IN MILK BY HPLC. Robert K. Munns. David C. Holland, Jose Roybal, and Jeffrey A. Hurlbut, Food and Drug Administration, Denver, Colorado.

295. A RAPID METHOD FOR DETERMINING GENTIAN VIOLET IN ANIMAL FEED BY HPLC WITH ELECTROCHEMICAL DETECTION. Jose E. Roybal. Robert K. Munns, Jeffrey A. Hurlbut, and Roger G. Burkepile, Food and Drug Administration, Denver, Colorado.

296. HANDLING GREAT LAKES DATA; LAKE ERIE, AND EXAMPLE. (A SIMPLE APPROACH USING MAINFRAME TO PC DATA TRANSFER). Fernando Rosa. Environment Canada, Ontario, Canada.

297. SEQUENTIAL-PARTIAL EXTRACTIONS OF PINAL CREEK AQUIFER MATERIAL NEAR GLOBE. ARIZONA, FOR SULFATE AND PHOSPHATE. Alonza H. Love and Walter H. Ficklin, U.S. Geological Survey, Denver, Colorado.

298. LC SEPARATION AND UV/FLUORESCENT DETECTION OF CARBOXYLIC ACIDS UTILIZING 1-AROMATIC-2-BROMOETHANONES. Jeffrey A. Hurlbut and Linda D. Himmelbauer, Chemistry Department, Metropolitan State College, Denver, Colorado,

299. SUPERCRITICAL FLUID EXTRACTION FROM MEDITERANEED BROWN ALGA DILOPHUS LIGULATUS. Pascale Subra. Roland Tufeu, and Yves Garrabos, L.I.M.H.P., Villetaneuse, France.

300. SOLUBILITY OF CHLOROPHYLLIAN PIGMENTS IN SUPERCRITICAL CARBON DIOXIDE AND ETHANE. Pascale Subra and Roland Tufeu, L.I.M.H.P., Villetaneuse, France.

LATE ADDITION TO LUMINESCENCE SYMPOSIUM

Tuesday morning, July 31, 1990

8:30 a.m. EXPENDING THE SENSITIVITY AND DYNAMIC RANGE OF AN AUTOMATED LIPOSOME IMMUNO ASSAY FOR DETECTION OF TRACE ANALYTES. Laurie Locascio-Brown. Anne L. Plant, William T. Yap, Steven J. Choquette, Richard A. Durst, NIST, Gaithersburg, Maryland.

NO ABSTRACT AVAILABLE

2

FURTHER DEVELOPMENTS OF THE SULFUR CHEMILUMINESCENCE DETECTOR (SCD) AS A REAL-TIME ATMOSPHERIC MONITOR. Richard L. Benner and Donald H. Stedman. Chemistry Department, University of Denver, Denver, CO 80208-0179.

The Sulfur Chemiluminescence Detector (SCD) has been gaining wide acceptance for gas chromatographic use. As a real-time atmospheric sulfur detector the SCD offers many advantages over other detection schemes as well. The additional sensitivity, selectivity, and fast response times allow the SCD to be used in atmospheric studies that are not possible with other technology. For example eddy correlation flux measurements, cumulus scale ventilation studies, and sulfate aerosol measurements in remote areas are possible and are the focus of our efforts. Results obtained in our laboratory concerned with the development of the SCD for use in these areas will be presented.

DEVELOPMENT OF A TECHNIQUE FOR DETERMINATION OF AMBIENT ATMOSPHERIC CONCENTRATIONS OF ALCOHOLS

Arturo Palomares, Larry G. Anderson and John A. Lanning, Department of Chemistry, University of Colorado at Denver, 1200 Larimer Street, Denver, CO 80204.

A sensitive and selective method is necessary for determining the atmospheric concentrations of alcohols. Currently, gas chromatographic-flame ionization techniques are used for measuring emissions of methanol from samples collected in a water bubbler. These techniques do not provide the sensitivity or selectivity that is desired for atmospheric measurements. As the use of alcohols as an alternative fuel increases, ways to measure their atmospheric concentrations will be necessary. Derivatization of alcohols and their determination by high performance liquid chromatography appears to have considerable potential. The advantages and disadvantages of determining ambient concentration levels of alcohols by this technique will be discussed.

4

DIURNAL VARIATIONS IN AEROSOL COMPOSITION AND CONCENTRATION.

William E. Wilson. Atmospheric Research and Exposure Assessment Laboratory, United States Environmental Protection Agency, Research Triangle Park, NC 27711, and Anthony Clark, University of Hawaii, Honolulu, Hawaii 96822

Host measurements of aerosol composition and concentration have been based on samples collected over periods of 24 hours. However, diurnal mixing processes of the atmosphere produce a shallow nighttime layer 1n which dry deposition can change aerosol concentrations. More vigorous daytime mixing coupled with photochemical production of secondary aerosol leads to significant changes in aerosol concentration and composition. These changes can be noticed in six-hour measurements but become clear in one-hour or continuous measurements. Information from the literature and results from recent one-hour composition studies conducted in Philadelphia and Denver will be analyzed. Strong diurnal variations in concentrations of sulfate, carbon soot, lead, and acidity will be described. Implications of these strong diurnal variations for visibility-aerosol relationships, source apportionment, and exposure assessment will be discussed.

5

DETERMINATION OF SPECIATED HYDROCARBON EMISSIONS FROM MOTOR VEHICLES BY LONG PATH ULTRAVIOLET SPECTROSCOPY.

James E. Peterson Chemistry Department;
University of Denver; Denver, Colorado 80208-0179

A description is given of a long pathlength ultraviolet spectrophotometer developed to remotely monitor tailpipe emissions from on road vehicles. Distribution of photochemically significant hydrocarbon species in the sampled vehicle exhaust is presented. Correlation with time-averaged proportional volume data from Warren Spring Laboratory studies and concurrently collected carbon monoxide/dioxide data are discussed.

6

AMBIENT CO AND NO CONCENTRATIONS ASSOCIATED WITH COLORADO'S OXYFUELS PROGRAM

Larry G. Anderson and John A. Lanning, Department of Chemistry, and Robert G. Meglen, Center for Environmental Sciences, University of Colorado at Denver, 1200 Larimer Street, Denver, Colorado 80204.

The Colorado Oxyfuels Program assumes that emission data collected under laboratory conditions combined with AIRSHED modeling accurately predict changes in ambient concentrations of CO and NO associated with the use of high oxygen fuels. The predicted ambient concentrations contain large uncertainties due to variable emissions data, differences between laboratory and actual driving conditions, variable meteorology and restrictions of modeling accuracy. We have evaluated ambient concentrations of CO and NO_x for the period 1981-1989. Diurnal variations along with daily, weekly and monthly averages of CO and NO_x have been subjected to statistical analyses. The presentation will discuss a preliminary assessment of the effects of the Colorado Oxyfuels Program on ambient concentrations of CO and NO_x.

7

CARBON MONOXIDE IN DOWNTOWN DENVER: APPLICATION OF A CHEMICAL MASS BALANCE FOR SOURCE APPORTIONMENT.

Kamal A. Mohammed, Donald H. Stedman. Chen. Dept, Denver Univ, Denver, CO, 80208.

During the spring of 1990, a study carried out in downtown Denver, measured the concentrations of carbon monoxide (CO) and other gases. Average concentrations of CO over 6-hr periods are measured, and apportioned among its sources, which are wood burning and automobiles. A chemical mass balance is applied to apportion the observed CO among its sources. Hydrogen (H_2), in excess of background levels, is used as a tracer of CO from automobiles. Chloromethane (CH_3Cl) served as a tracer of wood burning. The methods for obtaining all measured gases, and the results of this study will ba described.

8

ATMOSPHERIC CONCENTRATIONS OF FORMALDEHYDE AND ACETALDEHYDE DURING OXYFUELS PROGRAM

W. Kerry Grant, Larry G. Anderson and John A. Lanning, Department of Chemistry, University of Colorado at Denver, 1200 Larimer Street, Denver, Colorado 80204.

The Colorado Oxyfuels Program has mandated the use of high oxygen fuels for the high pollution period each winter since January, 1988. The Program has been expanded from two months to four months and from 1.5% oxygen by weight to 2.0% oxygen by weight. The oxygen content of fuels is predominantly obtained through the addition of methyl tertiary butyl ether (MTBE). Laboratory emissions data published by the State of Colorado indicate the use of MTBE will lower the emission of CO but increase the emission of formaldehyde. We have measured atmospheric concentrations of formaldehyde and acetaldehyde at the Auraria campus, adjacent to downtown Denver, each winter before, during and after the formal Oxyfuels Program. The formaldehyde and acetaldehyde concentrations, and the formaldehyde to acetaldehyde ratio have been analyzed to determine the impact of oxyfuels on ambient aldehyde concentrations.

9

OBSERVATIONS FROM A MULTI-YEAR FINE PARTICLE AND VISIBILITY MEASUREMENT STUDY IN THE SOUTHWEST,

Peter K. Mueller, Electric Power Research Institute, Charles E. McDade, ENSR, and Robert C. Nininger, AeroVironment, Inc.

Several industry and government organizations have been joined in a cooperative effort to conduct visibility research in the southwestern United States. Their study, called SCENES, completed a 5-year field measurement phase in the Fall of 1989. The goal of the study is to understand the extent and origin of the visibility impairment that exists in the region under specified meteorological conditions. Toward the achievement of that goal, the chemical composition of the atmospheric particulate matter and the atmospheric extinction prevailing in the region have been measured. Distributions of fine mass, particulate sulfur, particulate organic carbon, elemental carbon and crustal materials are described both spatially and temporally by season using data collected at six observatories that operated over the entire five years of the study. These particle measurements are related to visibility characteristics in the region over the same period. Episodes of impaired visibility are widespread. PM-2.5 particles are composed primarily of carbonaceous material, sulfates and soil dust. The observations characterize the frequency and duration of haze episodes and characterize aerosol composition with reference to climatic conditions.

10

DEVELOPMENT OF THE CHEMILUMINESCENT SELENIUM DETECTOR

Theresa Hosick *and* Donald Stedman, University of Denver, University Park, Denver CO 80208

The development of the chemiluminescent selenium detector introduces a method for selenium detection in the gas phase. Products of a hydrogen flame are drawn through a critical orifice into a low pressure system where they are mixed with ozone. Recent studies indicate that in a hydrogen flame sulfur monoxide is the species which chemiluminesces with the addition of ozone. It is presumed that selenium compounds entering the flame will undergo an analogous reaction to produce selenium monoxide which subsequently reacts with ozone producing selenium dioxide. The selenium dioxide produced la in an excited state which emits light with a peak wavelength near 450 nm. Spectroscopic studies of selenium and ozone will be presented.

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NICKEL CARBONYL CHEMILUMINESCENCE AS A MEANS OF CARBON MONOXIDE DETECTION

Anthony E. Allen, Mona Shahgholi, John A. Lanning and Larry G. Anderson, Department of Chemistry, University of Colorado at Denver, 1200 Larimer Street, Denver, CO 80204.

It is well known that nickel carbonyl, $Ni(CO)_4$, will chemiluminesce when it reacts with ozone. The sensitivity of detection of this chemiluminescence at the parts-per-billion range for nickel carbonyl has provoked our interest in using this phenomenon as a means of measuring trace levels of CO. The chemistry involved in this reaction system is sufficiently complex that we have undertaken some spectroscopic and kinetic studies. In addition, some studies have been conducted to find an efficient means of reacting ambient CO with nickel to form nickel carbonyl. The final goal of this work is to design and implement an instrument for CO detection based on the chemiluminescence of nickel carbonyl with ozone.

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PROGRESS TOWARDS DEVELOPING A NEXT GENERATION CO/CO_2 REMOTE SENSING DEVICE

Paul L. Guenther, Donald H. Stedman University of Denver Department of Chemistry, Denver, Colorado 80208

The Fuel Efficiency Automobile Test (FEAT), developed earlier at the University of Denver, has been demonstrated to be an effective and accurate method of measuring the CO and CO_2 emissions of vehicles as they are being driven. A second generation instrument has been built and shows promise as a slightly more practical version of the original idea. The differences between the old and new instrument as well as the new instrument's calibration and early testing will be discussed.

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SOLAR PHOTOLYSIS OF OZONE TO SINGLET D OXYGEN ATOMS, O(^{1}D).

Solomon T. Bairai. Donald H. Stedman. University of Denver, Chemistry Department, Denver, CO 80208.

Ground level solar photolysis frequencies were measured for photolysis of ozone by sunlight (O_3 + hν ———> O_2 + O(^{1}D)). The O('D) atoms produced react with nitrous oxide (N_2O) to form higher oxides of nitrogen, in particular NO_2. The NO_2 produced is detected by its chemiluminescence reaction with luminol, and thus the signal obtained is a measure of the amount of O(^{1}D) generated. Ground level data are collected at different seasons and the effect of solar zenith angle, total ozone column, cloud cover and temperature on j (O_3) are examined. Continuous data from a j (O_3) photometer with an intereference filter to pass only ozone photolyzing light is also correlated with j (O_3).

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THE NEW CORNUCOPIA: ARRAY DETECTORS AND PULSED DISCHARGES.

Alexander Scheeline, Cheryl A. Bye, Steven W. Rynders and Duane L. Miller, School of Chemical Sciences, University of Illinois, 1209 W. California St., 79 RAL Box 48, Urbana, IL 61801.

A dual grating, cross-dispersion echelle spectrometer has been constructed. It was designed based on constraints appropriate to simultaneous monitoring of a 150 nm range of the ultraviolet or visible spectrum, with a resolution of the order of 0.01 nm. Such range and resolution are required either for diagnostics of analytical discharges or for simultaneous multielement analysis. A charge-coupled array detector (CCD) is employed to provide simultaneous, linear readout of intensity throughout the observation range.

Because cross-dispersion is with a grating, real-time assignment of wavelength is simple. Data reduction is performed through the interaction of firmware sold with the CCD controller, standard spreadsheet programs, custom BASIC or Pascal routines, and commercial graphics software. Limits to spectrometer operation are mainly due to stray light from the echelle grating. Examples of broad-band observation of spark discharge emission, theta pinch discharge emission, and plasma-enhanced *chemical* vapor deposition of amorphous silicon carbide will be shown.

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ANALYSIS OF SOILS & SEDIMENTS BY ICP EMISSION SPECTROMETRY WITH ULTRASONIC NEBULIZATION.

Danton D. Nygaard, Xiaoru Wang, Baird Corporation, 125 Middlesex Turnpike, Bedford, MA 01730.

Ultrasonic nebulization has been shown to be a useful technique for sensitivity enhancement of ICP emission spectrometry when relatively clean water samples are analyzed. This work examines the utility of the technique when applied to more complex soil and sediment samples. Various reference materials are used as representatives of soils and sediments; and the EPA Contract Laboratory Program sample preparation procedure is applied.

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DETERMINATION OF TRACE METALS IN SLURRY SAMPLES USING AUTOMATED ULTRASONIC AGITATION. R.L. Hergenreder, G.R. Carnrick, W. Slavin and D. Bradshaw, Perkin-Elmer Corp., 761 Main Avenue, Norwalk, CT 06859-0219

The introduction of solid particles suspended in a liquid medium into the graphite furnace has a number of advantages over conventional solid sampling techniques. These advantages include: 1) reduced contamination, 2) multiple determinations from a single sample weighing and 3) convenient sample dilution. However, the most important potential advantage of slurry sampling is the ability to fully automate sample introduction. An obstacle to full automation of slurry techniques is the creation and stabilization of homogeneous suspensions. A number of approaches have been used to produce homogeneous suspensions including vortex mixing, and chemical agents such as Viscalex and glycerol. An alternative approach of using ultrasonic agitation was proposed by Miller-Ihli (1). A system will be described that uses ultrasonics as proposed by Miller-Ihli to sonicate solid particles into homogeneous suspensions immediately prior to sampling by a conventional furnace autosampler. All operations are firmware-controlled, making the system fully automated. Results will be presented showing the direct determination of trace metals in a variety of samples including sediment, coal, fly ash and biological materials.

Reference (1) NJ. Miller-Ihli, J. Anal. AL Spectrom. 3, 73 (1988).

17

THE FLEXIBILITY OF FLOW INJECTION AA. Susan Mcintosh. Randy Hergenreder, Perkin-Elmer Corp., 761 Main Avenue, Norwalk, CT 06859-0219.

The Flow Injection technique can extend the capabilities of atomic absorption. Conventional atomic absorption offers the user several advantages - quick analysis, lack of spectral interferences and ease of operation. The disadvantages are the limited detection limit, sample matrices which are restricted to low solids content, limited dynamic range and the high volume of sample used per analysis. Flow Injection automates the sample preparation for flame analysis and addresses the limitations of conventional flame atomic absorption. The use of small sample volumes and the ability to perform sample dilutions automatically, permits the analysis of samples containing high concentrations of analyte. The dynamic range is extended easily without changing instrument parameters. Flexibility is the key with flow injection - to control ionization interference simply add a channel for the addition of cesium chloride, and analysis of elements such as potassium are performed quickly without changing the original sample matrix. The ability to preconcentrate or extract samples automatically permits the analysis of samples containing low concentrations of analyte. Experimental data from the analysis of lead and cadmium in seawater and drinking water using sample preconcentration will be discussed. The flow injection technique can also be used to automate hydride determinations. The analysis of coal fly ash for arsenic, selenium and antimony by flow injection/hydride will be discussed briefly.

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HYDRIDE GENERATION OR GRAPHITE FURNACE ATOMIC ABSORPTION SPECTROPHOTOMETRY: A COMPARISION OF TECHNIQUES FOR ANALYSIS OF HIGHLY MATRIXED SAMPLES. Maria W. Tikkanen, Roger Starek, Robert Peile, Applied Research Laboratories/Fisons Instruments, Inc., 24911 Avenue Stanford, Valencia, CA 91355.

Graphite furnace (GF) and hydride generation (HG) have both been proven effective in providing ultratrace limits of detection for atomic absorption spectrophotometry (AAS). Indeed, the U.S. EPA requires the use of either of these sample introduction technqiues (in conjunction with AAS) to achieve the required analytical sensitivity for methodologies promulgated for such programs as the Safe Drinking Water Act (SDWA), Resource Conservation and Recovery Act (RCRA), National Pollution Discharge and Elimination System (NPDES), and the Contract Laboratory Program (CLP). While highly sensitive, these techniques can be both time consuming and matrix dependent. Automation has greatly aided the AA technique in producing more timely, accurate, as well as cost-effective, results. Results obtained from both hydride generation and graphite furnace sample introduction in the AA can be highly dependent upon the matrix of the sample involved. For example, both arsenic and selenium exhibit a depression in signal response in the presence of high concentrations (greater than 1000 ppm) of transition elements such as Fe, Cu or Ni. Similarly, high concentrations of Fe can cause severe signal depression in the determination of As and Se by graphite furnace AA of high concentrations. Cu and Ni, on the other hand are used as matrix modifiers to enhance signal response for As and Se by graphite furnace AA. Results and mechanisms will be discussed.

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AUTOMATION OF GFAAS ANALYSES FOR EPA CONTRACT LABORATORY SAMPLES

John E. Schmelzel, Gerald Delude, David Pfeil, John Sotera,
Thermo Jarrell Ash Corporation, 175 Jefferson Drive, Menlo Park,
California, 94025

The Contract Laboratory Program (CLP) of the U.S. Environmental Protection Agency (EPA) specifies that only four elements require measurement by graphite furnace atomic absorption spectrometry (GFAAS); As, Se, Pb, and Tl. It has been shown that the analytical efficiency to measure these elements could be increased by 100% by using a dual-channel AAS system resulting in a significant savings in operating cost. This paper describes a way to further reduce operating cost though the juducious automation of the complex CLP analytical protocol. A new automated AA will be described.

20

RECENT DEVELOPMENTS IN AUTOMATED ANALYSIS OF GEOLOGICAL AND ENVIRONMENTAL MATERIALS BY ICP-AES, AND CHEMOMETRIC DATA INTERPRETATION.

Dr. Marc L. Nouri and I.B. Brenner, ISA, Inc., 6 Olsen Avenue, Edison, New Jersey, 08820. M. Borsier, Bureau Recherches Geologiques et Minieres (BRGM), B.P. 6009, 45060, Orleans, Cedex 2, France.

Recent developments in automated computer-assisted multi-element analysis of diverse geochemical and environmental materials (rocks, soils, vegetation and subsurface waters, waste disposal) will be made. Automated robotic sample decomposition and preconcentration devices and techniques will be described.

Interactive system integrated sample preparation cookbooks, calibration, and QC protocols using SRMs will be summarized. Spectral line data bases will be demonstrated, predicting spectral interferences, facilitating optimum analyte line and background selection for a wide range of applications using simultaneous, sequential and combination spectrometers. Simulation of spectral line interferences take into account experimental and theoretical spectroscopic data.

Numerous dissolution and decomposition techniques (acids, sinters, fusions) were studied and the optimum protocols established for various sample types.

Multi-variant chemometric techniques will then be exemplified for geochemical and environmental data interpretation. These include pattern recognition techniques (factor and discriminant analysis) and geochemical and geoenvironmental maps.

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ON-LINE ION EXCHANGE PRECONCENTRATION FOR DETECTION OF IODINE BY FTA ICP-AES.

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Washington DC 20204. Akbar Montaser and Robert H. Clifford. George Washington
University Washington DC 20052.

The detection power of argon inductively coupled plasma atomic emission spectometry (Ar ICP-AES) is not sufficient for the determination of total iodine in most foods. In this presentation, preconcentration of iodide by anion exchange flow injection analysis (FIA) is investigated to improve the detection limit of iodine by ICP-AES.

22

Solvent-Analyte Separator for Atomic Emission and Mass Spectrometry

Siaoming Tan, R. H. Clifford, S. Nam, and A. Montaser. Department of Chemistry, George Washington University, Washington, DC 20052

Solvent loading has been one of most serious problem in achieving high detection powers in plasma spectrometry. A new sample introduction device, based on the use of the membrane separator (1-3), is developed to reduce maximum amount of the solvent introduced into the plasma while retaining majority of the analyte species. Characteristics of the system, including solvent-removal efficiency, analyte-transport efficiency, and droplet size will be reported along with detection limits for both plasma emission and mass spectrometry. These results are compared to those measured with pneumatic and ultrasonic nebulization devices.

1) A. Gustavsson, Spectrochim. Acta, 43B, 917 (1988).
2) A. Gustavsson, Spectrochim. Acta, 42B, 883 (1987).
3) A. Gustavsson, Spectrochim. Acta, 42B, 111 (1987).

23

A NEW COMPACT HYDRIDE GENERATOR FOR AS, SE AND SB DETERMINATIONS IN ENVIRONMENTAL MATERIALS BY ICP-AES. INFLUENCE OF HYDROGEN, SHEATH GAS FLOW AND GENERATOR FREQUENCY ON ANALYTICAL PERFORMANCE.

Dr.Ralph H.Obenauf and I.B. Brenner, ISA Inc., 6 Olsen Ave., Edison, New Jersey, 08820

The favored method for the determination of low concentrations of As, Se, and Sb by ICP-AES utilizes continuous flow hydride generation techniques. The present methodology is problematic due to plasma instability owing to hydrogen entrainment, resulting in degraded limits of detection. In applying this technique the emphasis has been on the chemical conditions; little consideration has been given to transport and plasma effects.

Although the presence of high amounts of hydrogen can cause plasma instability, recent investigations (1,2,3) have shown that it results in an increase in plasma temperature in the preheating zone and in the axial channel. Moreover, the high thermal conductivity of hydrogen results in improved heat transfer in the plasma and enchanced signal-to-background ratios. Data on the behavior of the hydride forming elements were not provided. In this presentation we will discuss the influence of entrained hydrogen, generator frequency, hydride generator size, sheath gas flow, torch geometry (Trassy demountable, low flow) and other ICP operating conditions, particularly the observation zone on the signal-to-background ratios of As, Sb, and Se.

The analytical performance of a new compact hydride generator, installed directly at the base of the torch will be described. The use of a small generator is based on the rationale that the dilution of the metal hydrides and memory effects, will be reduced. Detection capabilities will be compared to those obtained by other hydride generation techniques and generators. Data for a wide range of environmental materials will be provided.

1. Goldwasser, A., and Mermet, J.M., Spectrochim. Acta, 41B, 25, 1986.
2. Murillo, M., and Mermet, J.M., Spectrochim. Acta, 44B, 359, 1989.
3. Schramel, P., Spectrochim. Acta, 33B, 199, 1984.

24

RAPID SCREENING ANALYSIS WITH A SEQUENTIAL ICAP PLASMA SPECTROMETER, John E. Schmelzel, Ann E. Grindle, John Sotera, Thermo Jarrell Ash Corporation, 175 Jefferson Drive, Menlo Park, California, 94025

Traditionally, the quantitative analysis of samples by plasma spectrometry requires initial standardization with a solution or solutions which contain known concentrations of all elements of interest. The preparation and analysis time of the standards required to measure a long list of elements with a sequential ICAP spectrometer can consume a large portion of the analyst's time.

In this work a rapid screening method for semi-quantitative analysis has been developed with a sequential ICP. With this method, thirty lines can be determined in as little as three minutes. All lines are standardized using a simple four element refernce standard in less than one minute. In contrast, conventional analysis of a sample for 30 lines can take as long as 15 minutes or more using a sequential plasma, including standardization. The accuracy of this screening method has been found to be 25 percent or better.

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A NEW ATTEMPT TO IMPROVE DETECTION CAPABILITIES . OF ICP-AES FOR THE DETERMINATION OF Al IN BIOLOGICAL AND ENVIRONMENTAL MATERIALS. Dr. Didier Arniaud and I.B. Brenner, ISA, Inc., 6 Olsen Avenue, Edison, New Jersey, 08820.

The sensitive and accurate determination of aluminum in biomedical materials is of paramount importance due to a variety of deleterious neuro-toxicological effects. This necessity has resulted in extensive evaluations of plasma and graphite furnace techniques by numerous investigators. Currently, if the Al content is below 20-50 ug/l, GFAAS is the accepted technique. However, matrix modification, sample dilution, addition of TRITON X and preconcentration protocols have been applied, not without interference effects and significant contamination. Unfortunately the superior LOD reported by Allain and co-workers using ICP-AES has not always been duplicated. Thus, in the present investigation a re-evaluation of ICP-AES has been made. The following figures of merit using two Al lines (167 and 396.1 nm) were determined: LODs, linear calibration range, the effect of observation height, RF power, sheath gas, generator frequency, nebulization protocols (with or without dilution, nebulizer starvation conditions), memory effects, effects of Na and Ca, buffering effect by high concentrations of Cs, minimum amount of sample required. The long and short term precisions were determined employing a high resolution JY 38 monochromator. Data for synthetic and natural sera will be presented.

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APPLICATIONS OF ION EXCHANGE FOR MATRIX ELIMINATION PRIOR TO INDUCTIVELY COUPLED ARGON PLASMA ATOMIC EMISSION SPECTROSCOPY, (ICAP-AES), Ron M. Manabe, John E. Schmelzel, Thermo Jarrell Ash, 175 Jefferson Dr., Menlo Park, CA 94025, John M. Riviello, Dionex, Sunnyvale, CA, Howard M. Kingston, Archava Sirraks, NIST, Gathersburg, MD

The ICAP analysis of many types of samples is often compromised by matrix interferences. Typical examples include physical interferences such as viscosity, spectral and background interferences from Al, Fe and while these interferences can be minimized spectroscopically by background and interelement corrections, it is preferable to chemically eliminate these interferences.

By using ion exchange resins In conjunction with an ion chromatograph, it is possible to eliminate or reduce common ICAP interferences. In this presentation we will describe the use of various types of ion exchange columns for automated, on-line sample matrix elimination prior to ICAP analysis. The use of high performance anion, cation and chelating columns for matrix elimination will be shown. Applications of this technique for the analysis of brines, concentrated reagents and biological matrices will be given.

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LIQUID CHROMATOGRAPHIC ANALYSIS OF POLYNUCLEAR AROMATIC · HYDROCARBONS WITH DIODE ARRAY DETECTION.

Michael W. Dong and Daniel Clutter. The Perkin-Elmer Corporation, 761 Main Avenue, Norwalk, CT 06859-250

The potential of using a high-sensitivity diode array detector for analysis of polynuclear aromatic hydrocarbons (PAHs) is examined. Separation of 16 priority pollutant PAHs is accomplished in 13 minutes with a 5-um polymeric C18 column. Detection limits of about 1 ng are demonstrated for most PAHs. Wavelength programming enhances the detection specificity while spectral overlay confirms the presence of trace levels of PAHs in complex environmental samples. The sensitivity of this diode array detector is compared to that of a programmable fluorescence detector. The analysis of an urban particulate extract and a contaminated soil sample demonstrates the utility and versatility of this detection approach.

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ANALYSIS OF CARBAMATE PESTICIDES BY LIQUID CHROMATOGRAPHY

Michael W. Dong and Daniel Clutter. The Perkin-Elmer Corporation, 761 Main Avenue, Norwalk, CT 06859-250

This paper provides an overview of carbamate pesticides analysis methods by high performance liquid chromatography (HPLC). Both UV detection (EPA Method 632) and post-column fluorescence derivatization technique (EPA Method 531) are reviewed. The fundamental aspects, instrumental requirements and operating conditions of the post-column technique are described. Estimated detection limits below 100 pq were demonstrated in this study. Method acceptability criteria, operational precautions and troubleshooting procedures are discussed.

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WHOLE COLUMN DETECTION: APPLICATION TO PREPARATIVE-SCALE LIQUID CHROMATOGRAPHY

Kevin L. Kelly. John W. Birks. Department of Chemistry and Biochemistry and Cooperative Institute for Research in Environmental Sciences (CIRES), Campus Box 216, University of Colorado, Boulder, Colorado 80309-0216.

In Whole Column Detection (WCD) chromatography, the column is monitored at multiple sites along its length to obtain the distribution of peaks as a function of column position. This additional dimension results in several advantages over conventional chromatography among which are: 1) real-time optimization of the separation process; 2) quantitation of any adjacent pair of peaks at the earliest moment when sufficient resolution has occurred; 3) complete tracking of highly retained and/or rapidly decaying peaks; 4} reduction in total analysis time; and 5) increased precision and accuracy in the measurement of chromatographic parameters. We have constructed a prototype WCD system based on the use of fiber optics for Preparative-Scale Liquid Chromatography. Analytes are detected in the column by their accompanied change in the refractive index of the mobile phase or by UV/Vis absorption. Preliminary results from this prototype indicate that a full-scale WCD system (≅ 50 on-column detection sites) would be worthwhile to set up.

30 NEW SULFUR-SELECTIVE DETECTOR FOR GAS AND SUPERCRITICAL FLUID CHROMATOGRAPHY: PRINCIPLES OF OPERATION AND APPLICATIONS. Richard S. Hutte, Neil G. Johansen, Marianne F. Legier, Sievers Research, Inc., 1930 Central Avenue, Suite C, Boulder, Colorado 80301.

Sievers Research, Inc. has developed a new sensitive and selective detector for the analysis of sulfur-containing compounds by gas and supercritical fluid chromatography, the Model 350 B Sulfur Chemiluminescence Detector (SCD). Sulfur compounds are combusted in a hydrogen-rich flame using a flame ionization detector to form sulfur monoxide, which is subsequently detected by a chemiluminescent reaction with ozone. Both the FID and the sulfur detector can be operated simultaneously. The detector has a linear and equimolar response to all sulfur-containing analytes. Typical sensitivity of the SCD 350B is -5 pg S/sec and no interference has been observed from saturated hydrocarbons, olefins, water and most common solvents. Applications that will be discussed include the determination of COS in propylene, thiophene in benzene, odorants in natural gas, sulfur compounds in essential oils and the analysis of sulfur-containing pesticides.

31 GAS CHROMATOGRAPHIC CHARACTERIZATION OF OXIDATION PRODUCTS FROM A SURROGATE JET FUEL. William D, Schulz, Department of Chemistry, Eastern Kentucky University, Richmond, Kentucky 40475.

Gum and particulate formation by thermal oxidation of aircraft fuels is of serious concern. Engine malfunctions due to fuel oxidation products have been reported since the early 1960's. In spite of the amount of study generated by a problem as critical as jet engine malfunction, conflicting reports for fuel degradation mechanisms and methods for prevention persist. For this work, a twelve component surrogate JP-8 fuel was formulated to approximate the physical properties of JP-8 and to contain representatives of each hydrocarbon type found in distillate fuel. Surrogate JP-8 was rapidly stressed in bulk and the degree of oxidation determined by GC-MS. This strategy quickly produces large amounts of information on thermal oxidation rates and the effect of variables such as additives, metals, initiators etc., but avoids the extreme complexity of real fuels. Solid phase extraction further simplifies identification of oxidation products. Insoluble products are characterized by pyrolysis-GC-MS. Product identification indicates the surrogate fuel parent compound and allows explanation of the effect of variables on the gum formation mechanism.

32 ADVANCED ION CHROMATOGRAPH DETECTS LOW MEA LEVELS. David B. Palladino, Brinkmann Instruments, Inc., 1 Cantiague Road, Westbury, NY 11590 and Scott Lindsay, Texaco Refining & Marketing, Anacortes, WA 98221

Texaco Refining & Marketing Inc. is using an advanced method of ion chromatography at its Puget Sound refinery in Anacortes, WA, to detect and measure monoethanolamine (MEA) in process effluent water at low ppm levels. The method is electronically suppressed, single-column, ion chromatography (SCIC). The method was selected for use in this service subsequent to successful use to improve titrimetric analysis of wash water, where low-ppm ranges of chlorides needed to be measured. SCIC was also able to detect halides of other constituents, such as bromides and iodides. The advanced method can measure precisely very low levels of both monoethanolamine and ammonia, and it assists in locating the sources that allow the contaminants to escape into the wastewater stream. In these analyses, the SCIC unit operated in less than one third the time of automatic titrimetry and other wet chemistry methods available in the laboratory. It also proved to be more economical than conventional chemically suppressed ion chromatography (CSIC).

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ELECTRODIALYTIC GENERATION OF ELUENTS FOR CHEMICALLY SUPPRESSED ION CHROMATOGRAPHY. J. Stillian, K. Friedman, Dionex Corporation 1228 Titan Way, Sunnyvale, CA 94086 and P. K. Dasgupta, D. Strong Texas Tech Univ., Lubbock TX. 79409

This presentation describes a new device that generates sodium hydroxide electrodialytically on the low pressure side of the analytical pump. The quality of the hydroxide generated is dependent only on the quality of the water supplied to the device thus eliminating carbonate contamination and minimizing background. By programming the applied current it is also possible to electrically generate a gradient of hydroxide thus converting an isocratic analytical pump into a gradient pump for ion chromatography. HCl can also be generated for cation separations in the same way. The paper will discuss the details of the generation of eluents for anion and cation ion chromatography and will describe the details of the electrodialytic cell.

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SOME NEW SOLUTIONS TO SENSITIVITY/SELECTIVITY LIMITATIONS IN ORGANIC ELEMENTAL ANALYSIS BY OXIDATIVE PYROLYSIS/ION CHROMATOGRAPHY. Dutt V. Vinjamoori, Sharon J. Lemp, and Charles H. Condra. Monsanto Company, Physical Sciences Center, Mail Zone S4A, 800 N. Lindbergh Blvd., St. Louis, MO. 63167

Heteroatoms such as halogens and sulfur have important implications in the performance of many industrial process catalysts and in the stability of commercial products. In the elemental analysis of organic species, trace quantitation of heteroatoms continues to be challenging despite significant instrumental advances. The origins of blanks in oxidative pyrolysis-oxygen bomb/ion chromatography and their influence on the limits of sensitivity and selectivity in trace analysis for heteroatoms will be presented. Special sampling techniques and decomposition methods for the trace determination of sulfur and halogens in a variety of organic/biological liquid and solid matrices will be discussed. Strategies for minimization of blanks via pre and post pyrolysis sample treatments and oxidant/carrier gas purification techniques will be outlined.

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A PROCESS FOR THE EXTRACTION OF FLAVOURS FROM MILKFAT WITH SUPERCRITICAL CARBON DIOXIDE. Andre B. de Haan, J. de Graauw, Delft University of Technology, Laboratory for Process Equipment, Leeghwaterstraat 44, 2628 CA Delft, The Netherlands, J.E. Schaap, H.T. Badings, Dutch Institute for Dairy Research, P.O. Box 20, 6710 BA Ede, The Netherlands

Next to triglyceride milkfat contains small amounts (ppm's) of many components (lactones, ketones, aldehydes) that provide milkfat with its characteristic flavour. This paper presents the results of a study to the extraction of these flavours from milkfat with supercritical carbon dioxide in a continuous countercurrent extraction column, equipped with rashig rings. Experiments have shown that concentration factors varying from 20 to 50 could be obtained at carbon dioxide densities of 600 to 700 kg/m^3 and temperatures between 40 and 50 C. The extraction process was modelled with the Kremser equation since only small amounts are extracted from the milkfat. The height equivalent to a theoretical stage in the extraction column, filled with 5 mm steel rashig rings (1000 m^2/m^3), appeared to be approximately 20 cm. If the extraction is carried out in two steps it is possible to extract 95% of the flavour components and concentrate them 500 to 1000 times. The reported experiments were used to scale up to a commercial process with a capacity of 10.000 ton/year milkfat.

From these calculations it appeared that the price of such a commercial extract would lie between 25 and 50 $/kg, depending on the concentration factor.

36 SUPERCRITICAL FLUID SOLID PHASE EXTRACTION/SFC OF PESTICIDES, HERBICIDES
AND RELATED COMPOUNDS IN COMPLEX SAMPLE MATRICES, Balasingam Murugaverl,
and Kent J. Voorhees, Department of Chemistry and Geochemistry, Colorado
School of Mines, Golden, Colorado 80401.

A consolidated supercritical fluid technique to determine pesticide residues in animal tissues has been investigated. Supercritical fluid solid phase extraction (SFSPE) in conjunction with capillary supercritical chromatography (SFC) offers the potential to combine many of the various single residue analytical methods currently employed for the detection of over 500 pesticides, herbicides and related compounds. Direct coupling of SFSPE with SFC allows analysis of solutes in fats and oils for which on-line SFE/SFC is unsuitable. The main features of this technique is that extraction and clean-up are accomplished in one step prior to analysis by capillary SFC, using unmodified CO_2. The extraction/clean-up step is monitored by photo diode array detector which allows selective heartcutting. This technique is relatively simple and inexpensive, and the analysis time is rapid. The detection limits of analytes are in the parts per billion range.

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PACKED MICROBORE SUPERCRITICAL FLUID CHROMATOGRAPHY WITH FLAME
IONIZATION DETECTION OF ABUSED VEGETABLE OILS. John E. France,
Jerry W. King, and Janet M. Snyder. Northern Regional Research
Center, Agricultural Research Service, U.S. Department of
Agriculture, 1815 N. University Street, Peoria, Illinois 61604.

The successful application of packed microbore column supercritical fluid chromatography with flame ionization detection (SFC/FID) for the determination of low levels of free fatty acids in vegetable oils is demonstrated. Previous limitations in packed column SFC are the result of absorptive interactions of polar solutes with uncapped silanols on the surfaces of chromatographic packings. The standard remedy has been to add organic modifiers to the supercritical carbon dioxide mobile phase but this precludes the use of FID. Two different chromatographic methods were examined. One uses a recently developed polymeric resin SFC column while the other method involves high temperature water saturation of the supercritical carbon dioxide. Oils obtained from storage-abused soybeans and commerical frying fats can now be analyzed by this technique.

AUTOMATED SUPERCRITICAL FLUID INSTRUMENTATION:
38 Industrial R&D and Environmental Applications.
Eugene J. Levy, Timothy W. Ryan, Steven M. Lurcott, Sean O'Neill, John Watkins
Computer Chemical Systems, Inc. Rt. 41 & Newark Rd Avondale, PA 19311

ABSTRACT

Supercritical Fluid (SF) Technology has developed rapidly over the past few years for applications in the analytical laboratory and in the processing/QA-QC of foods, pharmaceuticals, and agrochemical industries. SF extraction (SFE) is a proven process in these fields and highly automated analytical instrumentation has been designed and used for improved productivity with new capabilities. An extended pressure range to 10,000 psi is demonstrated for SFE and associated SF uses including SF reaction (SFR), and SF chromatography (SFC) with microbore columns. Method development for the analysis of herbicides, steroids, foods and polymer additives will be shown to include an integral automatic modifier module for the SFE-SFC/GC system. The automated module permits improved extractions/separations using C02 mobile fluid modified with methanol and water. In applications using well established capillary GC methods, the advantages of high pressure SFE sample treatments are combined with on-line high resolution separations of complex mixtures important to the environmental sciences. Applications of the automated SFE-capillary GC system include quantitative analyses of fuel contaminants in soils and demonstrate the diverse problem solving capabilities.

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VOLUMETRIC PROPERTIES OF MOBILE PHASES IN SUPERCRITICAL FLUID CHROMATOGRAPY WITH A PHC EQUATION OF STATE. Maurizio Fermeglia, Jacek Gregorowicz and Ireneo Kikic. Istituto di Chimica Applicata e Industriale, Università di Trieste, 34127 - Trieste, ITALY

The use of an entrainer is a well established method for improving the separation in supercritical fluid chromatography (SFC) and in supercritical fluid extraction (SFE). Small quantities of polar substances are claimed to strongly influence the selectivity and solubility of organic compounds in supercritical fluids. This effect can be ascribed both to specific interactions between the solvents and the solutes and to the different value of the density of the mixed solvents in comparison with the pure supercritical fluid. The evaluation of the volumetric properties of fluid mixtures, and their selectivities towards different solutes, is then of paramount importance for all the practical applications of SFC and SFE. On the other hand, simple equations of state give big errors in the simultaneous description of equilibrium and volumetric properties. In this paper we turned our attention to the PHCT equation of state which gives fairly good results for pure components equilibrium and volumetric properties, and apply it to mixtures interesting for the SFC and SFE. Volumetric properties are calculated for different binary mixtures that are very often employed as mobile phases in SFC. The equation of state is also used to predict the infinite dilution equilibrium properties of different solutes in pure and mixed solvents at conditions relative to supercritical fluid extraction.

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ROBOTIC APPLICATIONS SUGGESTED BY PERSONNEL AT THE U.S. GEOLOGICAL SURVEY NATIONAL WATER QUALITY LABORATORY. G. L. Hoffman, T. J. Bushly, C. J. Patton. U.S. Geological Survey, National Water Quality Laboratory, 5293 Ward Road, Arvada, Colorado 80002.

Implementation of robotic devices in the analytical laboratory requires careful planning to insure minimum disruption of the work place. Robotic devices should be helpful to personnel and not merely novelty items that produce little useful output or, worse yet, require more effort from personnel to produce an equivalent result. If robotic systems are to gain wide acceptance in analytical laboratories, suggestions for applications should also come from the personnel actively engaged in the work of producing chemical results.

A robotic system that will track, partition, and distribute water samples to laboratory personnel for different types of chemical analysis was purchased at the National Water Quality Laboratory of the U.S. Geological Survey. During the programming phase of implementing this robotic system, many laboratory personnel expressed an interest in how the system would function. Input from laboratory personnel was solicited for future uses of robotic systems. This solicitation has provided many new ideas for robotic applications in the laboratory. Several of the applications require little additional programming and tend to build on the present robotic system.

The present robotic system is presented. Several preliminary robotic applications suggested by laboratory personnel also are described as they relate to the present system

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AUTOMATION OF POLYMER PHYSICAL TESTING INSTRUMENTATION, Daniel G. Moldovan, Dow Chemical Company, Texas Operations, Bldg. B-3833, Freeport, TX 77541

Two of the most important physical testing methods for polyolefins have been automated. The two physical tests are melt index and density determination. These two physical tests are very labor intense tasks and constitute the majority of the testing done at our physical testing facility and the production plants.

The automation of the density determination of polyolefins is accomplished using a Zymark PyTechnology robotic system. The system is set-up to duplicate the ASTM density determination method, D-792. The robot method, like the manual method, requires the robot to weigh the polyolefin plaques both dry and submerged in heptane. The robotic density determination method has the same accuracy and better reproducibility than the manual method.

The automated melt index system, the Petromet MI-200 Melt Indexer, is designed by Cypress Design Group. The important concept behind the design is the reusable cartridge which is a 6-inch long steel tube and orifice. The system has run a wide range of melt indices with a standard deviation of 1.4%.

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THE USE OF AUTOMATED GRAVIMETRIC TECHNIQUES FOR ENHANCED ANALYTICAL PRECISION, Brian G. Lightbody and Sally D. Dowling, Zymark Corporation, Zymark Center, Hopkinton, MA 01748

The use of automated equipment for routine sample prep is growing, however it is important to maintain a high level of control to maintain assay precision. Recent developments in automated workstations have resulted in capability to use an on-board 4-place analytical balance to monitor the progress of the sample prep process. This paper will discuss several techniques built into the automated instrumentation which use analytical balance results to help ensure the precision and integrity of the analytical process. Some examples are as follows:

1. The use of concentrate weight to calculate and add a diluent during automated dilutions.
2. The use of sample weight to calculate and add a proportional amount of solvent.
3. The use of sample weight to calculate and add a proportional amount of internal standard.
4. The monitoring of the weight of all reagent additions to ensure adequate system performance.

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AUTOMATED CHEMISTRY WORKSTATIONS - THE FUTURE OF LABORATORY AUTOMATION

by John Petracca, Source For Automation, Inc., 115 Cedar Street, Milford, MA 01757

Automated Chemistry Workstations will discuss an approach to bringing automation into the laboratory. The locus will be on the ability to integrate automated sample preparation with methods selection and sample analysis, through the use of powerful data handling and data base management techniques. Examples from an environmental lab will illustrate how pc controlled sample-prep applications for analytical instruments can replace present autosamplers; an oil laboratory will provide a setting for discussing multiple application modules in a fully integrated workcell. The presentation will conclude with look at the LIMS connection.

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ELECTROCHEMICAL APPLICATIONS OF SOLUBLE POLYELECTROLYTES. S James Schmittle, Ronald B. Sprinkle and C. Michael Elliott, Department of Chemistry, Colorado State University, Fort Collins, CO 80523

Recently we have developed several organic-soluble polymer electrolytes that can be used as supporting electrolytes in voltammetric experiments. Included in our studies are polyelectrolytes of both charge types, for example, polytetraalkylammonium hexafluorophosphate and a tetraalkylammonium polystyrenesulfonate. These polyelectrolytes have a number of unique properties especially when employed in conjunction with redox active polymer films, either in their formation or their subsequent voltammetry. When an electroactive polymer is *formed* in the presence of a polyelectrolyte counter ion the polyelectrolyte may become incorporated into the polymer film such that a stable molecular composite forms (i.e. the polyelectrolyte is trapped and remains in the film irrespective of the redox state and charge of electroactive moieties). Additionally, for reasons of steric bulk, polyelectrolytes are often excluded from entering already formed redox active polymer films. As a consequence it is possible to "shut off" certain redox processes within polymer films by virtue of sterically excluding ion types necessary to maintain charge neutrality.

5 I 1 SPATIALLY RESOLVED ELECTROCHEMICAL DETECTION FOR HIGH PERFORMANCE LIQUID CHROMATOGRAPHY AT SEMICONDUCTING TITANIUM DIOXIDE WIRES.

Garretl N. Brown. John W. Birks, Carl A. Koval. Department of Chemistry and Biochemistry and Cooperative Institute for Research in Environmental Sciences (CIRES), Campus Box 216, University of Colorado. Boulder, Colorado 80309 0216.

Since the discovery by Fujishima and Honda in 1972 that water could be decomposed into hydrogen and oxygen over an illuminated titanium dioxide semiconductor, photoelectrochemistry has expanded into a formidable field encompassing solar energy conversion, photocatalysis, organic synthesis, waste purification and device physics. Due to the unique band energetics of semiconductors, these materials can be utilized in a manner such that they exhibit enhanced redox properties under illumination. Spatial illumination of a semiconductor with a scanning laser Is proposed as a method for determining the spatial distribution of redox species in thin-layer (TLC) and liquid (HPLC) chromatographic systems. Redox properties of several model organic analytes at dark and illuminated TiO_2 has been investigated and suggest problems with the semiconductor preparation method. Excessive anodic dark current is associated with oxidation ot the organic analyte. In theory, anodic current should only occur under illumination and minimization may be required. In this seminar the production, characterization, and optimization of thermally oxidized wire titanium dioxide detection devices for spatial electrochemical detection will be discussed In the context ot whole column liquid chromatography.

46 PULSED ELECTROCHEMICAL DETECTION IN LIQUID CHROMATOGRAPHY.

William R. LaCourse and Dennis C. Johnson, Department of Chemistry, Iowa State University, Ames, Iowa 50011.

Pulsed Electrochemical Detection (PED) has gained prominence as a sensitive detection technique for aliphatic organic compounds. PED waveforms applied at gold and platinum electrodes are applicable for the direct detection of alcohols, amines, glycols, sugar alcohols, carbohydrates, alkanolamines, amino acids, amino sugars, and many sulfur-containing compounds. Detection is accomplished using a multistep potential waveform, which combines amperometric detection with alternating anodic and cathodic polarizations to clean and rejuvenate the electrode surface. The anodic response is based upon the surface catalyzed oxidation of the alcohol, amine, or sulfur-containing functionalities of the molecules. The principles of PED are discussed on the basis of voltammetric response for the compounds detected. A comparison will be made between surface-oxide inhibited and surface-oxide catalyzed oxidations. Chromatographic examples are given to emphasize compatibility and applicability of pulsed electrochemical detection in liquid chromatography.

47 THE ELECTROCHEMICAL DETECTION OF PENICILLIN COMPOUNDS FOLLOWING THEIR SEPARATION BY HPLC.

Lisa M. Koprowski and Lawrence E. Welch, Knox College, Box K-76, Galesburg, Illinois 61401.

A study of penicillin electrochemistry was initiated with hopes of finding a suitable HPLC detection scheme. Current detection methodology for the penicillins involves asborbance detection somewhere between 210 and 230 nm in the ultraviolet region. The lack of selectivity in this region is a hindrance to detection in complex biological matrices. Electrochemical methods can provide better selectivity while maintaining good sensitivity as well. Oxidation of the penicillins took place in the presence of surface oxide on gold and platinum electrodes. Classical amperometric detection of the oxidative current was not acceptable due to fouling of the working electrode. To maintain detector sensitivity, the Pulsed Amperometric Detection (PAD) waveform was applied on gold and platinum electrodes. This allowed sensitive detection without fouling for the penicillins while providing added resistance to fouling from complex sample matrices. PAD was applied following reversed-phase separation of a penicillin mixture on a C-18 column. No derivatization reactions or post-column addition of reagents were necessary.

48 I FUNCTIONAL GROUP SELECTIVITY IN PULSED ELECTROCHEMICAL DETECTION.

William R. LaCourse and Dennis C. Johnson, Department of Chemistry, Iowa State University, Ames, Iowa 50011.

Pulsed Electrochemical Detection (PED), which includes Pulsed Amperometric Detection (PAD) and Integrated Pulsed Amperometric Detection (IPAD), is a simple and sensitive technique for the determination of underivatized aliphatic organic compounds in liquid chromatographic analysis. PED utilizes a multi-step potential waveform to combine amperometric detection with alternating anodic and cathodic polarizations, which maintain reproducible electrode activity. Although PED active functional groups (e.g., alcohols, amines, and sulfur-containing moieties) all respond based upon surface-catalyzed oxidations, the mechanistic pathway by which each functional group proceeds to product formation is uniquely different. This observation allows for selective detection of analyte species in chromatographic effluent streams via exploitation of controllable waveform and other instrumental parameters. The general principles of pulsed electrochemical detection are reviewed on the basis of voltammetric response to various functional groups. Methods of achieving functional group selectivity are discussed and highlighted with chromatographic examples.

49 ENHANCING CONDUCTIVITIES IN ELECTRONICALLY CONDUCTIVE POLYMERS. Charles R. Martin, Department of Chemistry, Colorado State University, Ft Collins CO 80523.

KEYNOTE SPEAKER NO ABSTRACT AVAILABLE.

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INVESTIGATION OF ELECTRON TRANSFER KINETICS AT n-TYPE METAL DICHALCOGENIDE/SOLUTION INTERFACES USING A MICROELECTROCHEMICAL CELL

Jason N. Howard and Carl A. Koval. Department of Chemistry and Biochemistry,
Campus Box 215, University of Colorado, Boulder, Colorado 80309-0215.

Metal dichalcogenide layer compounds, such as WSe_2 and SnS2, have been shown to provide a nearly ideal electrode/solution Interface for investigating fundamental electron transfer processes at this poorly understood junction. Past studies have involved embedding the WSe_2 crystal in epoxy to mask edge sites from the electrolyte. This prohibits cleaving the crystal to provide fresh surfaces. Also, small currents from the edge sites may leak through the epoxy. We have developed a microelectrochemical cell to circumvent these problems. The cell places a *small* drop of *electrolyte* (about 1 mm diameter) on the surface of the working electrode. The electrochemical experiment Is then performed in this drop. This design allows the crystal to be recleaved and also provides better insulation from leakage currents. The microcell will be used to study electron transfer kinetics between n-type WSe_2 and SnS_2 electrodes and metallocene/acetonitrile solutions.

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DETECTION OF HOT ELECTRONS AT A P-TYPE INDIUM PHOSPHIDE PHOTOELECTROCHEMICAL CELL UTILIZING ROTATING RING DISK ELECTRODE VOLTAMMETRY.

Robert Torres, Carl A. Koval. Department of Chemistry, Campus Box 215, University of Colorado, Boulder, CO 80309

The injection of hot electrons from a semiconductor into solution will be investigated utilizing a rotating InP disk electrode and platinum ring electrode (RRDE). This technique will allow us to observe the product of the hot carrier reaction occuring at the disk to be detected at the ring. The detection scheme for quantifying the hot carriers will implement an organotin compound to accept the hot electrons. Upon reduction the organotin compound will dimerize and subsequently be oxidized at the platinum ring. Preliminary research has involved construction, characterization, and testing of the semiconductor RRDE. Employing this type of experimental set-up will permit us to better ascertain values of hot carrier quantum yields and branching ratios and allow us to systematically alter various experimental parameters.

FABRICATION AND ELECTROCHEMISTRY OF MICROHOLE ARRAY ELECTRODES

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Recently introduced microhole array electrodes show steady state currents even in turbulent solutions. This type of electrode is comprised of an array of ultramicroelectrodes that are recessed in high aspect ratio cylindrical pores. These narrow pores minimize the effects of convection in the bulk solution thereby making it easy to attain steady state currents. Because of this special property, microhole array electrodes can be used for such applications as electrochemical detection in flowing streams. We will demonstrate a new method to fabricate such electrodes utilizing microporous membranes. The electrochemical response of these new microhole array electrodes will be compared with theory.

ELECTROCHEMICAL SYNTHESIS OF ULTRATHIN FILM COMPOSITE MEMBRANES

Chao Liu, Mark W. Espenscheid, W-J, Chen and Charles R. Martin
Department of Chemistry, Texas A&M University, College Station, TX 77843

The development of ultra thin film composite membranes was an important breakthrough in the membranes-separation area. Ultrathin film composite membranes consist of a porous support layer, and a dense, ultrathin active layer. The porous support layer provides mechanical strength yet is highly permeable. The separation process occurs primarily in the ultrathin active layer; because this layer is thin, the overall flux of permeate through the membrane is high. Thus, ultrathin film composite membranes can provide good mechanical strength, high selectivity, and high permeability. This combination of attributes usually cannot be obtained with homogeneous membranes.

We have developed a new method for preparing ultrathin film composite membranes. This method involves electrochemically-initiated polymerization at a microporous support-membrane surface and yields an ultrathin polymer film on one face of the suppport-membrane. Composite membranes with separating layers as thin as 50 nm have been prepared using this new electrosynthetic method. We describe the synthesis and characterization of these new membranes in this presentation.

THE USE OF ELECTOPOLYMERIZED METALLOPORPHYRIN FILMS FOR THE SEPARATION OF NITROGEN HETEROCYCLES FROM HYDROCARBON PHASES VIA ELECTROCHEMICALLY MODULATED COMPLEXATION. Douglas E. Wedman and Carl A. Koval. Department of Chemistry and Biochemistry, Campus Box 216, University of Colorado, Boulder, Colorado 80309-0216.

Water soluble metalloporphyrins like iron tetra(N-methyl)pyridial porphyrin are shown to demonstrate preferential binding of nitrogen heterocycles in aqueous solutions. The degree of binding is effectively modulated by an alteration of the oxidation state of the porphyrin's metal center. Past attempts to utilize this differential binding in *a* separation scheme have been hindered by poor solubility and aggregation of these porphyrins in solution. Furthermore, employment of an ion exchange material for immobilization of the carrier complex has added complications concerning the need for electrochemical mediators for modulation of the oxidation state of the carrier. The use of thick electropolymerized porphyrin films as electroactive carriers is currently being studied as a possible alternative to these methods. If successful, this method would offer a high effective concentration of carrier without the need for mediators or immiscible solutions.

EFFECTS OF HYDROXIDE ON THE ELECTROCHEMISTRY OF POLYPYRROLE
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Electronically conductive polymers are a new class of organic materials which are the subject of intense interdisciplinary research. These polymers are interesting from an electrochemical point of view *because* they can be electrochemically switched between electronically insulating and electronically conductive states. One such widely studied electronically conductive polymer is polypyrrole. Polypyrrole is insulating in It's reduced (neutral) state and conductive In it's oxidized (cationic) state. We will show here that OH^- dramatically alters the electrochemical switching process, shifting the redox wave of the polymer ca. -1.0 V, thus extending the potential region where polypyrrole is electronically conductive. This is adventitious in applications of the polymer which require electrical conductivity such as using the polymer to carry out catalytic electrode reactions.

56 INFRARED AND UV-VISIBLE STUDIES OF THE TRAPPED CHARGE WITHIN ELECTROPOLYMERIZED TRIS(VINYLBIPYRIDINE)RUTHENIUM(II). Scott C. Paulson and C. Michael Elliott, Dept. of Chemistry, Colorado State University, Ft. Collins, CO 80523

Polymers of tris(4-methyl-4'-vinyl-2,2'-bipyridine)ruthenium(II)hexafluorophosphate, and related bipyridine complexes, contain trapped charge states when the polymer Is oxidized or reduced and then returned to a potential corresponding to the resting 2+ oxidation state. Currently, the nature and origins of these charge trapped states are poorly understood despite considerable research efforts. We have designed optically transparent thin-layer electrochemical cells, for Infrared and UV-Visible spectroscopy, which are capable of monitoring electropolymerization of this complex, as well as giving insight into the nature of the redox sites responsible for the trapped charge. A unique cell design, coupled with a diode array spectrometer, has allowed "on the fly" analysis of polymers In the UV-Visible spectral region. These studies provide new data on the chemical changes in the complex upon polymer formation, and the spectral differences which occur upon oxidation state change.

OXYGEN REDUCTION AT THE PERFLUOROSULFONATE IONOMER FILM-MICROELECTRODE INTERFACE: TRANSPORT AND KINETICS.

Arvind Parthasarathy and Charles R. Martin
Department of Chemistry, Texas A & M University, College Station, Texas 77843

Perfluorosulfonate ionomers (PFSI's), du Pont's Nafion and Dow PFSI's, have been used in solid polymer electrolyte fuel cells by virtue of their high oxygen solubility, mechanical strength, chemical stability, proton conductivity and permselectivity. The objectives of this work were to determine the mass transport parameters of oxygen in Nafion and the kinetics parameters involved in the reduction of oxygen using a platinum microelectrode. The transient behavior of the current for oxygen reduction is used to simultaneously determine the concentration and diffusion coefficient in the solid state by applying concepts drawn from similar chronoamperometric work done in liguid electrolytes. The cell design that we shall present seeks to reduce contact resistance at the polymer-electrolyte interface and enables electrochemical investigation in the absence of added liquid electrolyte.

58 OXYGEN REDUCTION KINETIC CURRENTS AT PERFLUOROSULFONATE IONOMER FILM-COATED PLATINUM ELECTRODES: RESULTS PERTAINING TO HYDROGEN-OXYGEN PHOSPHORIC ACID FUEL CELLS.

Del R. Lawson and C.R. Martin
Department of Chemistry, Texas A&M University, College Station, TX 77843

The hydrogen-oxygen fuel cell shows potential as an environmentally safe source of electrical energy. Hydrogen-oxygen fuel cells convert the chemical potential difference between hydrogen gas and oxygen gas into electrical energy. This is made possible by reduction of oxygen at the cell cathode and the oxidation of hydrogen at the anode, with H_2O the byproduct.

$$O_2 + 4H^+ + 4e^- \rightarrow 2H_2O \qquad\qquad 2H_2 \rightarrow 4H^+ + 4e^-$$

To prevent the cell from shorting out, the electrodes are separated by an electrolyte which promotes ionic conduction. Phosphoric acid is commonly used as the electrolyte because it is relatively inexpensive and is stable at temperatures (200°C) where the kinetics of the oxygen reduction reaction (rate limiting) are improved. However, the rate of oxygen reduction is still hampered by weak proton activity and low oxygen solubility in phosphoric acid. To overcome the problems associated with the oxygen electrode, we have proposed the use of thin coatings of perfluorosulfonate ionomers (PFSI's) on the oxygen cathode in phosphoric acid fuel cells. PFSI's are ionically conductive materials which in the proton form behave as superacids. In addition, oxygen is very soluble in the teflon-like regions of tetrafluoroethylene ionomer backbone. We report the results of a series of fundamental studies characterizing the kinetics of the oxygen reduction reaction at PFSI film-coated Pt electrodes in phosphoric acid.

59 BATTERY STUDIES IN NEUTRAL ROOM TEMPERATURE CHLOROALUMINATE MOLTEN SALTS.

Jeffrey Boon, John Sanders, Larry Vaughn, and John S. Wilkes. The Frank J. Seiler Research Laboratory, USAF Academy, CO 80840.

Molten salts that are liquid at room temperature and below are attractive candidates for battery electrolytes. Mixtures of aluminum chloride and 1-methyl-3-ethylimidazolium chloride (MEIC) are liquid at low temperatures and stable to relatively high temperatures. The Lewis acid-base properties of these chloroaluminates results in substantially different electrochemical behavior of the electrolyte in $AlCl_3$-rich versus MEIC-rich melts. At the composition where the $AlCl_3$ and MEIC are precisely equal, the electrolyte is Lewis neutral and has an electrochemical window of about 4.5 V. Such a window suggests that very high energy battery electrodes may be attainable, thus providing high energy density battery cells. Sodium chloride acts as a Lewis acid-base buffer to maintain the molten room temperature electrolyte at the neutral composition. At neutrality, cathode materials, such as CuCl and AgCl may be anodically deposited as an insoluble film, which is advantageous for batteries. Sodium metal should be thermodynamically unstable in the $AlCl_3$-MEIC electrolyte, but it is either kinetically unreactive or protected by a passive film such that it may be used as a battery anode. We report some preliminary studies of battery cells employing a sodium anode and transition metal chloride cathodes.

60 HIGH CYCLE LIFE R ALUMINUM BATTERIES. V. R. Koch and C. Nanjundiah, Covalent Associates, Inc., 52 Dragon Court, Woburn, MA 01801 617/938-1140

The National Aeronautical and Space Administration (NASA) has present and future needs for advanced rechargeable batteries to he used in spacecraft and planetary rover missions. These applications require batteries that can safely deliver in excess of 1,000 deep discharge cycles at a 10 mA/cm^2 rate while providing specific energy densities on the order of 100 Wh/kg. To date, rechargeable Li/intercalation cathode systems such as Li/TiS2 and Li/MoS_2 have not met NASA's rate and energy density specifications. We have recently evaluated several new battery couples by combining the highly efficient aluminum anode with a suitable cathode in molten salt electrolytes. Thus, several organic and inorganic cathode materials have been screened in a 60:40 m/o $AlCl_3$:1-methyl-3-ethylimidazolium chloride (ImCl) melt at 25°C, and either in a 50:33:17 m/o $AlCl_3$:NaCl:n-butylpyridinium chloride (BPC), or a 50:33:17 m/o $AlCl_3$:NaCl:ImCl melt at 90°C. Three very promising cathode candidates were discovered, two of which appear to reversibly intercalate and deintercalate Al*3 for over 900 cycles. This work was funded by NASA.

POTENTIOMETRY OF POLAR DISSOLVED ORGANICS USING THE NICKEL ELECTRODE. Ben S. Hui and Calvin O. Huber. Department of Chemistry, University of Wisconsin-Milwaukee, Milwaukee, Wisconsin 532201.

Nickel electrodes in alkaline solution were oxidized to oxidation states above two by electrochemical or by chemical means. The potentiometric response of the resulting higher nickel oxide surface to alcohols, amino acids, and other analytes was examined. The cathodic shift of potentials in the presence of analyte was attributed to analyte reduction of the higher oxide sites. Effects of oxidation mode, ionic strength, alkalinity, competing complexation reactions, etc. were examined. Trends of potentiometric responses among the alcohols or among the amino acids are similar to those reported earlier using amperometry. Lower detection limits are typically 0.1 to 1.0 mM, about an order of magnitude larger than with amperometry, but interferences by alkaline earth cations observed in the amperometric method are absent. The similar reaction mechanisms in potentiometry and the corresponding amperometry allows for comparison of response parameters.

62 A COMPARISON OF HYDROGEN ELECTRODE AND pH GLASS ELECTRODE FOR pH MEASUREMENT. Naila Ashraf and K. L. Cheng. Department of Chemistry, University of Missouri-Kansas City, Kansas City, Missouri 64110.

The membrane electrode immersed in an electrolyte solution yields a double layer at its interface. Its membrane potential is the result of charge separations and forming a leak free capacitor. It functions differently from the hydrogen electrode. Comparisons between the two important electrodes for the pH measurement are made relating to their characteristics and properties such as the construction, mechanism, acid and alkaline errors, potential vs. pH linear relationship, temperature effect, charging, discharging, and recharging, nonaqueous solvent effect, stability, accuracy, advantages and disadvantages, suspension effect, etc. Recent results of the simple solid state pH glass electrode without the Ag/AgCl reference electrode and the internal solution compared with the conventional one will be presented.

63 APPLICATIONS OF ELECTROCHEMISTRY TO THE ANALYSIS OF GEOLOGIC MATERIALS. Larry L. Jackson and Joseph H. Christie. U.S. Geological Survey, Box 25046, MS 973. DFC. Denver, CO 80225.

In the modern geochemical laboratory, multielement automated instrumental techniques dominate the determination of major, minor, and trace elements in geologic materials. However, several elements or species, such as chloride, fluoride, and forms of iron, water, carbon, and sulfur can not be readily determined by multielement techniques. In our laboratory various electrochemical techniques are used to determine these elements and species. Iron (II), chloride, and fluoride are determined potentiometrically. Bound water (H_2O+) and total water are determined after combustion of the geologic sample with a flux by coulometric Karl Fisher titration. Carbonate carbon is also determined by coulometric titration of acid-evolved CO_2. We are using a coulometric titration of H_2S for the direct determination of acid-volatile sulfides and for pyritic sulfur after Cr^{2+} reduction of overburden materials. The procedure compares favorably with conventional ASTM procedures. We have also applied pulse polarography to geological problems. We used differential pulse polarography to determine naturally occurring Cr(VI) in serpentine soils of California.

We will review these applications and show that electroanalytical techniques can be useful tools in geochemistry.

64 **SLOW SCAN CYCLIC VOLTAMMETRIC STUDY OF TRIVALENT GROUP V HINDERED CHLORO-COMPOUNDS. Carlos Arcos. Somchai Saelee, and Richard T, Keys, Department of Chemistry and Biochemistry, California State University, 5151 State University Drive, Los Angeles, CA 90032**

The electrochemistry of trivalent group V compounds having the formula R_2PCl, $RR'PCl$, and R_2AsCl, where R and R' are bulky groups was investigated. Slow scan cyclic voltammmetry was used to determine the reduction and oxidation potentials of these compounds. The results are discussed and compared to those obtained with cholorodiphenylphosphine.

65 ENVIRONMENTAL APPLICATION OF HIGH PERFORMANCE LIQUID CHROMATOGRAPHY/MASS SPECTROMETRY. Robert D. Voyksner. Analytical and Chemical Sciences, Research Triangle Institute, P. O. Box 12194. RTP, NC 27709

Frequently potentially hazardous chemicals are omitted from surveillance because they cannot be identified and/or confirmed by conventional gas chromatography/mass spectrometry (GC/MS). Thermal lability, low volatility and high polarity are the three main reasons for failure in GC/MS identification. With the advent of combined high performance liquid chromatography/mass spectrometry (HPLC/MS) some of these experimental difficulties have been resolved. While research in a number of HPLC/MS interfaces continues, thermospray and particle beam currently appear to be the predominate techniques for environmental monitoring.

This presentation will concentrate on reviewing the most effective HPLC/MS techniques for the analysis of environmental contaminates including pesticides. herbicides, dyes and Appendix VIII/IX compounds. The review will cover operational characteristics and the performance of particle beam and thermospray HPLC/MS techniques. Also, the relative merits and shortcomings for these HPLC/MS interfaces, their applications to environmental analysis and their future role in monitoring our environment will be discussed.

This research was supported in part by the Environmental Protection Agency contracts 68-02-4544 and 68-03-3122 and the Food and Drug Administration Cooperative Agreement No. FD-U-000244.

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DETERMINATION OF LINEAR ALKYLBENZENESULFONATES AND THEIR CARBOXYLATED INTERMEDIATES BY DERIVATIZATION GAS CHROMATOGRAPHY/MASS SPECTROMETRY

Jennifer A. Field and Larry B. Barber, II. U.S. Geological Survey, Box 25046, MS 408, Denver Federal Center, Denver, Colorado 80225

Linear alkylbenzenesulfonates (LAS) and their sulfophenyl carboxylated (SFC) biodegradation intermediates are ionic, water soluble components of waste waters. Process level interpretation of LAS environmental transformation requires analytical methods that can identify specific homologues of LAS and SPCs in contaminated waters. Trifluoroethyl derivatives of LAS and SPCs were prepared by conversion of sodium sulfonate and carboxylated salts to the sulfonyl and acyl chlorides using heated phosphorous pentachloride. Reaction of the sulfonyl and acyl chlorides with 2,2,2- trifluoroethanol produced the trifluoroethyl ester derivatives that were analyzed by gas chromatography/mass spectrometry. Electron-impact mass spectra showed molecular ions for LAS homologues, whereas SPCs of varying chain length showed the loss of m/z 100, corresponding to loss of one trifluoroethyl group. Ion of m/z 253 and 267, common to the trifluoroethyl esters of LAS and surrogate intermediates, are specific to this class of sulfonated contaminants. Concentrations were calculated using trifluoroethyl toluenesulfonic acid as internal standard. Recoveries for standards ranged from 21 to 46% with a mean value of 42%.

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ANALYSIS OF TRIFLUOROETHYL DERIVATIVES OF SULFOPHENYL-CARBOXYLATES BY GAS CHROMATOGRAPHY/NEGATIVE ION CHEMICAL I0NIZAT1ON/MASS SPECTROMETRY.

Colleen E. Rostad and Jennifer A. Field, U.S. Geological Survey, WRD, Box 25046, Mail Stop 408, Lakewood, Colorado 80225.

Sulfophenylcarboxylates (SPC) are biodegradation metabolites of linear alkylbenzenesulfonates (LAS). Standards for SPC, ranging from sulfophenylpropionic acid to sulfophenylundecanoic acid were derivatized to produce di-trifluoroethyl derivatives. The GC/electron impact(EI)/MS spectra of these derivatives were quite complex. The GC/negative ion chemical ionization (NCI)/MS analysis of these derivatives produced primarily three ions. Along with the compound molecular ion, a fragment ion at mass 163, corresponding to the $-SO_3CH_2CF_3$ group was observed. The molecular ion lost a fragment of mass 100 corresponding to the $-OCH_2CF_3$ on the alkyl carboxylic side chain. SPC's isolated from a groundwater well and a sewage treatment plant effluent, were derivatized, and analyzed by GC/NCI/MS. In addition to selected standard derivatives, several isomers of each molecular weight were identified. Interferences present in GC/EI/MS spectra were eliminated because NCI is specific for these halogenated compounds.

AZAARENES IN GROUND WATER FROM AN IN SITU OIL-SHALE RETORT SITE, ROCK SPRINGS, WYOMING.

Larry 3. Barber, II and Jerry A. Leenheer. U.S. Geological Survey, 5293 Ward Road MS 408, Arvada, CO 80002

Ground water samples were collected at an in situ oil-shale retort site 10 years after retorting, and analyzed for nitrogen-heterocyclic compounds (azaarenes). Azaarenes were isolated from the complex groundwater (dissolved organic carbon ranged from 12 to over 4000 mg/L) as the free amine using XAD-8 resin, followed by elution as the hydrochloride with 0.1 N hydrochloric acid. The eluant was rotary evaporated to dryness, and the azaarene hydrochlorides were converted to the free amines by redissolving in distilled water followed by addition of saturated sodium hydroxide. The azaarenes were extracted into methylene chloride, and the extracts were analyzed by gas chromatography/mass spectrometry in full-scan and selected-ion monitoring modes. At the time of sample collection, deuterated pyridine, quinoline and acridine were added as surrogate standards. Recoveries for 18 alkylpyridines, quinolines and acridines spiked into distilled water ranged from 10% to 110% with a mean of 85%. Mean recoveries of the deuterated surrogates from distilled water were 60%, 100%, and 27% for pyridine, quinoline, and acridine respectively, whereas recoveries from the groundwater matrix were 50%, 63% and 34%. Groundwater from the retort chamber contained over 150 alkylpyridine (C1 to C8) and alkylquinoline (C1 to C5) compounds at concentrations ranging from a few ug/L up to 1 mg/L. NO azaarenes were detected in groundwater samples downgradient from the retort chamber.

69 A SIMPLE GC METHOD FOR THE ANALYSIS OF ALKYL PHOSPHONATES IN WATER AND SOIL.

Jesus R. Abril, Elizabeth D. Sexton, and Andrew W. Law.
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A simple and reproducible method for alkyl phosphonate analysis, including diisopropylmethyl phosphonate (DIMP), is presented. While ion chromatography is commonly used for phosphonate determination, that methodology is rather involved when compared to extraction and analysis using gas chromatography with nitrogen-phosphorus detection. Both soil and water samples are extracted with three consecutive ethyl acetate aliquots, followed by concentration of the organic phase and subsequent analysis. DIMP is extracted almost exclusively from soil if the soil is first mixed with water and then partitioned with ethyl acetate. This represents an improvement over older techniques where the extraction of soil produces high background interference which, in turn, causes an elevated detection limit. Minimum detection limits of 0.5 ppb to 1 ppb are achieved using 10 g soil, while a detection limit of 0.1 ppb is observed using 40 ml water. The average recovery of DIMP for both water and soil samples range from 90% and 80%, respectively.

70 MOBILE UNIT FOR FT-IR MEASUREMENTS OF VOC's.

William G. Fateley[*] Marty Spartz, Mark Witkowski,[*] Robert M. Hammaker,[*] Jonathan Fateley,[**] Bill Fairless,[†] Tom Holloway,[†] Jodi Hudson,[†] Don Gurka[#] and Dennis Lane[*]. [*]Chemistry Department, Kansas State University, Manhattan, Kansas 66502; [†]U.S. EPA, Kansas City, Kansas; [#]U.S. EPA, Las Vegas, Nevada; [**]Chemistry Department, University of Kansas, Lawrence, Kansas.

A mobile Fourier transform infrared spectrometer (FT-IR) system has been developed at Kansas State University (KSU) to measure volatile organic compounds (VOCs) in the atmosphere especially on-site measurements and analyses. The ability to do on-site measurements allows the results to be analyzed and reported more quickly.

The mobile laboratory which has been developed consists of many systems to give optimum capabilities in the field. All system components are transported to the site In a van which serves as the mobile laboratory. The instrument is a commercially available Fourier transform infrared spectrometer (FT-IR) equipped with a Cassegrainian telescope. The source is a Nernst glower placed at the focal point of a Newtonian telescope.

71 RAMAN INDICATORS: A POSSIBLE METHOD FOR REMOTE SENSORS?

Dr. Keith T. Carron and Ken I. Mullen. University of Wyoming, Dept. of Chemistry, Laramie, WY , 82071-3838

An important problem in understanding the movement of subsurface contaminates is the ability to monitor groundwater. This problem can be solved with remote sensing of groundwater contaminates with optical fiber probes. Remote sensors afford two advantages to the study of groundwater contamination: (1) they facilitate continuous, direct, and centralized monitoring of contamination plumes, and (2) they allow in situ analysis of the actual contaminates as opposed to tracer surrogates. In situ analysis is critical in remediation studies where chemical analyses of water brought to the surface do not adequately characterize the groundwater under anaerobic conditions in which key chemical and biochemical processes occur. Results of preliminary studies on the feasibility of Raman based optical fiber sensors will be presented. The preliminary results indicate that Raman based sensors possess both the high selectivity and ultrasensitivity necessary to analyze groundwater contamination.

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MONITORING STACK EMISSIONS OF URANIUM FROM AN ENRICHMENT PLANT, Claude R. Beverly, Martin Marietta Energy Systems, P. O. Box 1410, Paducah, Kentucky 42001, U. S. DOE Contract DE-AC05-84OR21400.

Extremely low concentrations of gaseous uranium hexafluoride (UF$_6$) are entrained into a vent stack discharge stream of lower molecular weight gases. Although equipment design and standard operating procedures restrict UF$_6$ emissions to levels which pose no health hazards or environmental insult, continuous monitoring is necessary. An emissions monitoring system is described which incorporates an on-line alpha counting system with off-line thermal ionization mass spectrometer analysis of the contents of a caustic gas scrubber train. The on-line alpha counter provides timely warning of uranium emissions excursions, while the mass spectrometer analysis yields an integrated record of total uranium discharges. Isotopic composition as well as total uranium emissions are determined.

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KINETIC ANALYSIS OF DISSOLUTION OF CROSSLINKED PROPELLANTS BY SOLVOLYSIS, A.S. Tompa. B.R. White, and A.C. Richardson, Naval Surface Warfare Center/Naval Ordnance Station, Indian Head, MD 20640.

The disposal of obsolete propellants by burning contributes to the pollution of the atmosphere and is a waste of the expensive energetic constituents present in propellants. Chemical methods for the safe disposal of propellants by a non-polluting process with the subsequent reclamation of constituents provides an attractive alternate method. It was found that the solvolytic breakdown and dissolution of obsolete crosslinked propellants may be carried out with surprising ease with subsequent recovery of expensive constituents in high yields. An approach was adopted in which degradation was initiated in composites while they were swollen in an appropriate solvent containing additives capable of reacting with chemical bonds located in the polymer chain. A kinetic study of the solvolysis reaction of the urethane linkages in ethanolamine solution was followed by thermogravimetry. First order rate constants for the reaction were found to be higher in the mixed solvent of toluene-isopropanol compared to isopropanol probably because of their differences in swelling behavior. Activation energies for solvolysis were about 5 kcal/mol in toluene-isopropanol and about 8 kcal/mole in isopropanol. The solvolytic degradation of the propellant binder with nitrocellulose was about three times as fast as the binder without nitrocellulose.

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FORMALDEHYDE ANALYSES BY HPLC AS 2,4-DINITROPHENYLHYDRAZONE. Michael J. Diesing and Robert L. Spraggins. Manville Sales Corporation, P.O. Box 5108, Denver, Colorado 80227.

This paper describes analyses of both liquid and solid samples for formaldehyde. Monomeric formaldehyde is gaseous and makes only minor contributions to formaldehyde levels in both solid and liquid matrices. Derivatizations were carried out in strong acid. Under these conditions, formaldehyde can be formed by hydrolysis of larger molecules. Formation of the 2,4-dinitrophenylhydrazone in this reversible reaction is clearly dependent on the concentration of both formaldehyde and 2,4-dinitrophenylhydrazine. Product formation is favored by stresses that result in shifts to reaction equilibra. The method utilized for this work contains an extraction step which prevents aldehyde formation from the hydrazone and provides an added degree of accuracy. Derivatization shows a strong dependence on formaldehyde concentration. Results will be compared to a non-extractive technique as well as to the Chromotropic Acid Method for formaldehyde used by NIOSH. This 2,4-dinitrophenylhydrazone method is both sensitive and specific for formaldehyde determinations.

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FORMALDEHYDE MEASUREMENTS IN AIR, AS ITS OXAZOLIDINE DERIVATIVE.

Timothy J. Wilhelm and Robert L. Spraggins. Manville Sales Corporation, P.O. Box 5108, Denver, Colorado 80227.

Formaldehyde has traditionally been measured in air by a NIOSH approved methodology. This colorimetric procedure is known as the "Chromotropic Acid Method". This method has many known interferences, both positive and negative. The present work involves derivatization of formaldehyde to its nitrogen containing oxazolidine. The derivative is analyzed by gas chromatography using an electrolytic detector operated in the nitrogen mode. This highly specific method of analysis can be used for trace level measurements. Standard formaldehyde samples were generated using permeation devices to provide method standardization. Airborne samples to be discussed include: ambient and source airs, off-gasses from commercial products, and thermal degradation products.

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CHEMICAL CHARACTERIZATION OF HUMIC ACID SUPERNATANT EXTRACTED FROM A PHILIPPINES AGRICULTURAL SOIL.

Ann M. Nefcy and Robert L. Wershaw, U.S.Geological Survey, MS408, 5293 Ward Road, Arvada, CO 80002.

The membrane model of humic substances is one in which the humic substances are composed of the partially degraded molecular components of living organisms, which are held together in ordered,membrane-like or micelle-like,aggregated structures. Humic acid was extracted from a Philippines agricultural soil using methods developed by the International Humic Substances Society. The humic acid was then fractionated into four fractions by gel filtration separation. The first fraction contained substantial amounts of sugars. These sugars were concentrated by precipitating lignins and other compounds at pH 2 and analyzing the supernatant. The sugars in the supernatant were analyzed by a modified Hakomori procedure. The sugars were methylated, hydrolyzed, and then acetylated, and the resulting products were analyzed by gas chromatography/mass spectrometry. For the supernatant, the sample was found to contain 6-linked, 3-6 linked, and terminal linked hexoses, presumably glucose. These data indicate the possibility that these dextrans were formed by bacteria.

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AN ANALYTICAL METHOD FOR DISTINGUISHING FORMS OF CARBON.

Michael J. Diesing. John L. Ouenzer. and Robert L. Spraggins. Manville Sales Corporation, P.O. Box 5108, Denver, Colorado 80227.

Carbon is found in nature as both crystalline (diamond, graphite) and amorphous (lignite, gilsonite) solids. Carbon is found in all organic compounds, while carbon black, activated carbons, and cokes are manufactured by pyrolysis of hydrocarbons and amorphous solid carbon sources. Forms of carbon can be characterized by their degree and type of crystallinity and by their specific gravity. In this work, various forms of carbon were differentiated based on their combustion temperature in a furnace type total organic carbon analyzer. Results for real-world samples including spiking studies will be presented to demonstrate the selectivity of this method for the various forms of carbon. Certain industrial process and waste samples can be easily characterized using these techniques that might require extensive work using more classical methods.

78 PHOTOTRANSFORMATION OF PESTICIDES IN NATURAL WATERS. Donald G. Crosby, Dept. of Environmental Toxicology, University of California, Davis, CA 95616.

Pesticides are found widely in natural waters — rivers, lakes, the sea, rain, fog, and snow — but usually at only µg/L levels (10^{-8} M). Many, such as the herbicide 4-chloro-2-methylphenoxyacetic acid (MCPA), absorb appreciable ultraviolet (UV) energy from sunlight (290-400 nm) and undergo oxidation, reduction, and nucleophilic substitution reactions with natural reagents under laboratory conditions. The same reactions are observed to occur in small suspended droplets (rain drops) and in seawater *in vitro*. Other pesticides, such as thiobencarb, do not absorb solar UV but still undergo indirect photooxidation *via* hydroxyl radicals. Agricultural field water often contains sufficient pesticides (10^{-7} M) to allow verification of the laboratory results, but the importance of phototransformation reactions in most natural waters still remains to be demonstrated.

• COMPARISON OF LARGE SAMPLE LIQUID-LIQUID AND SOLID-PHASE PRECONCENTRATION TECHNIQUES TO LOWER DETECTION LIMITS FOR PESTICIDES IN WATER. G.D. Foster. Department of Chemistry, George Mason University, Fairfax. VA 22030; P.M. Gates and W.T. Foreman, USGS, National Water Quality Laboratory, Arvada, CO 80002.

The application of gas chromatography/mass spectrometry as an analytical tool to study pesticide fate and transport in large river basins can be confined by insufficiently low detection limits. One approach to lowering detection limits in water is concentrating analytes from large water samples, which can be accomplished by using the Goulden large-sample extractor and high-capacity solid-phase sorbent cartridges containing octadecylsilyl-bonded silica. Recoveries of 37 pesticides, including organochlorine and organophosphate insecticides and triazine herbicides, were compared using both large sample preconentration techniques upon fortification of 10-L natural water samples with 10 ng/L of each pesticide. Mean recoveries for each pesticide class using the Goulden large-sample extractor were 85% for the organochlorines, 101% for the organophosphates, and 87% for the triazines; corresponding recoveries using the solid-phase extraction cartridges were 88%, 89%, and 83%, respectively. Both preconentration techniques yielded comparable detection limits; however, differences existed in extraction times and matrix-related effects between the two extraction methods.

80 PESTICIDE OCCURRENCE AND TRANSPORT IN THE YAKIMA RIVER BASIN, WASHINGTON. Paul M. Gates and William T. Foreman. U.S. Geological Survey, National Water Quality Laboratory, 5293 Ward Road, Arvada, Colorado 80002. Gregory D. Foster. George Mason University, Fairfax, Virginia. Stuart W. McKenzie and Frank A. Rinella. U.S. Geological Survey, Portland, Oregon.

The Yakima River Basin in Washington is a heavily irrigated semiarid agricultural area, in which water quality is impacted by pesticides in surface runoff. Water and suspended-sediment samples were collected during June and July 1989, in a synoptic survey of the basin. Sample volumes of 40 to 200 liters were filtered through glass-fiber filters with a nominal pore size of I micrometer. Particulate-bound pesticides collected on the filters were isolated using Soxhlet extraction. Filtrates were extracted using a Goulden large-sample continuous-flow, liquid-liquid extractor to isolate dissolved pesticides. Sample extracts were analyzed for 75 pesticides using gas chromatography-mass spectrometry with selected ion monitoring. Dissolved and suspended pesticide variability within the Yakima River Basin was determined. Thirteen of the 75 target analytes were determined to be contributors to the Columbia River during this survey.

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CHROMATOGRAPHIC DETERMINATION OF ORGANOCHLORINE PESTICIDES IN SERUM.

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The widespread usage of organochlorine pesticides over the years and subsequent bioaccumulation in the food chain has created interest in the analysis of these pesticides in such diverse matrices as plant and animal tissue and blood. A method of determining aldrin, dieldrin, endrin and isodrin in human serum based on EPA methodology published in the "Manual of Analytical Methods for the Analysis of Pesticides in Humans and Environmental Samples" is described. The serum samples are treated with methanol to precipitate the proteins, extracted and analyzed using gas chromatography-electron capture detection with 5% phenyl and 17% cyanophenyl capillary columns. The detection limit for each is 1 ppb using 3 ml serum. The internal standard selected is endosulfan I, while the surrogate is dibutylchlorendate. The response is linear up to 25 ppb and is repeatable and reproducible. A study to evaluate vacutainers, which are evacuated test tubes with plastic or rubber tops used to draw blood, is described. It was feared that the top would introduce phthalate contamination into the sample. It was found that the "dark blue" top vacutainers are the only type which did not introduce phthalate contamination.

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NEW REAGENT AND CADMIUM REACTOR DESIGN FOR REDUCTION OF NITRATE TO NITRITE IN AUTOMATED, COLORIMETRIC DETERMINATION OF NITRATE USING A MINIATURE, AIR-SEGMENTED CONTINUOUS FLOW ANALYZER.

Amy S. Ludtke and Charles J. Patton,
U.S. Geological Survey, 5293 Ward Road, Arvada, Colorado 80002.

Nitrate in surface and ground water is generally determined colorimetrically after being reduced to nitrite with some form of cadmium metal. Variation in sample matrix parameters such as pH, buffer capacity, and the concentrations of chloride and dissolved oxygen can profoundly affect the short- and long-term reduction efficiency and stability of cadmium reactors. Large, packed-bed cadmium reactors (PBCRs) used in batch procedures, and their somewhat smaller counterparts used in second generation (AutoAnalyzer II) air-segmented continuous flow analysis (CFA) procedures may mask these effects by virtue of their excess reduction capacity relative to the amount of nitrate present in samples. For compatibility with high-speed, third generation CFA instruments (RFA, TRAACS), however, PBCRs must be miniaturized to the extent that dispersion within them does not severely limit the rate at which determinations can be performed. As the bed volume of a PBCR is decreased, strict pH control during the reduction step and continuous maintenance of the active surface of the cadmium particles become more and more critical to the precision of analytical results. Details of an imidazole buffer/surface activator reagent and a miniature PBCR are presented, which in conjunction with a third generation CFA instrument, permit nitrate determinations to be performed at rates of 120 samples hr^{-1} with less than 1% carryover. Reduction efficiency is near quantitative, and several hundred surface and ground water samples can be determined before the PBCR needs to be replaced.

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MICROWAVE PREPARATION OF ENVIRONMENTAL SAMPLES FOR TOTAL NITROGEN ANALYSIS.

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The standard Kjedahl technique typically used to prepare plant tissue, soil and water samples for nitrogen analysis is relatively time consuming and hazardous. A closed vessel microwave preparation technique using persulfate is described for these samples. The investigation includes total nitrogen recoveries of reference materials and comparison to TKN values for unknown samples. The advantages of the microwave technique pertaining to speed, recoveries and safety will also be discussed.

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NEW SAMPLE PREPARATION METHODS FOR ENVIRONMENTAL ANALYSIS. H.M. Kingston. F. A. Settle, M. A. Pleva, P. J. Walter, L. B. Jassle, and A. Sirlraks. National Institute of Standards and Technology, Inorganic Analytical Research Division, Chemistry Building, Room A343, Gaithersburg, MD 20899.

Microwave sample preparation methods are gaining a wide degree of acceptance as a standard method for sample preparation. They are being applied in EPA-accepted methods and are required to be transferred between laboratories with a high degree of reproducibility. The control and standardization of these methods *is* a matter that must be addressed as these methods are propagated between organizations and within individual laboratories. Automation is not often thought of as a way to standardize laboratory methods, but rather as a way of controlling equipment. An automated microwave decomposition system has been developed that is computer controlled. It is controlled by a prototype expert system that is being developed to assist the analyst in establishing procedures for microwave dissolution. New chelation separation methods have been developed for environmental analysis that integrate the analyte concentration and separation into instrument detection. This sample preparation can be used in a variety of configurations and can be fully automated.

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A CHELEX RESIN INTEGRATING SAMPLER FOR THE DETERMINATION OF TRACE ELEMENT UPTAKE (CD, CU, PB, ZN) FROM DRINKING WATER SUPPLIES. J.C. Meranger, B. Lo. National Health and Welfare, Environmental Health Directorate, Ottawa, Ontario, Canada, K1A 0L2

The use of integrated monitoring for the analysis of drinking water samples provides a more accurate sampling technique for the estimation of the total daily uptakes of metals leached from the water distribution system. The uptake rate of the sampler remains constant over the entire sampling period with the sampler diverting approximately 1% of the tap water consumed through a chelex resin column. This system has been tested over a wide range of pressures and representing the range of pressures normally encountered in the main water distribution system.

Recovery values for Cd, Cu, Pb and Zn were obtained by standard addition using heated graphite atomic absorption spectrophotometry. Preliminary results will also be presented on the simultaneous determination of Cd, Cu, Pb and Zn using ion chromatography with a cation trap concentrator column. Using this integrated monitoring sampling system, the trace element uptakes of selected high-rise apartment dwellers were estimated at various floor levels to determine the effect of the building water distribution system on the overall quality of tap water.

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APPLICATIONS OF ON-LINE CHELATION CONCENTRATION CHROMATOGRAPHY WITH INDUCTIVELY COUPLED PLASMA - MASS SPECTROMETRY FOR TRACE ELEMENT ANALYSIS OF ENVIRONMENTAL SAMPLES

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Inductively coupled plasma - mass spectrometry (ICP-MS) is a powerful instrumental technique for multielement analysis of trace elements at low (ng/ml) concentrations in many different sample types. However, the matrix constituents of many environmental samples may interfere with the accurate detection of the analytes of interest. Some particularly problematic interferences for ICP-MS are caused by alkali and alkaline earth elements and anions such as chloride or sulfate, common constituents of surface, ground, and saline waters. An on-line chromatographic procedure for chelation concentration and matrix cleanup of samples prior to ICP-MS analysis (CC-ICP-MS) has been developed and evaluated. The application of this procedure to environmental samples is described.

The Use of ICP-MS for the Analysis of Environmental Samples

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The Inductively Coupled Plasma Mass Spectrometry (ICP-MS) techniq provides some major advantages to the analyst. Detection limits generally superior to those provided by Graphite Furnace Atomic Absorption (GFAA) can be obtained on over seventy elements in around two minutes, thus providing extremely cost effective analysis. The power of ICP-MS has encouraged the US Environmental Protection Agency to review it analytical protocol to incorporate the technique. Protocol 6020 utilizes ICP-MS for the Analysis of waters, wastes, soils and sludges under the Superfund Contract Laboratory Program. Method 200.8 is designed for the trace element analysis of water and wastes. Results using these techniques indicate that ICP-HS can provide a superior analysis to existing methods for many elements. Routine ICP-MS performance on typical environmental samples will be reviewed, with reference to the above protocols.

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THE TCLP-CREATING SUPERFUND SITES IN THE FUTURE?

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The TCLP is Creating Superfund Sites in the future. Landfills are being created today of solidified material that passes the Toxicity Contaminant Leachate Procedure (TCLP) but will in the future contaminate the groundwater if leachate is generated. The source of this contamination is amphoteric metals, metals which are solubilized at both low and high pH values. The more common amphoteric metals of environmental concern are lead, tri-valent chromium, zinc and nickel. Methods of removal of these metals from wastewater (and subsequent sludge generation) involve reduction (in the case of chromium) and precipitation of the metal hydroxide at the pH the minimum solubility for that metal (usually pH 7 to pH 10). In order to solidify wastes containing these amphoteric metals so that the resulting material passes the TCLP it is necessary to add sufficient basic material (such as lime, portland cement, cement kiln dust or lime kiln dust) to produce a pH of the TCLP leachate in the range of minimum solubility for that metal. The same material if leached with deionized water will produce a leachate of very high pH value where the amphoteric metal is resolubilized as the negative hydroxy complex. Since most of these amphoteric metal wastes are solidified in place or placed in secure landfills, the concept of leaching by an organic acid (such as is found in a municipal landfill) is not only invalid but potentially deadly.

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SELENIUM INVESTIGATIONS AT THE KENDRICK RECLAMATION PROJECT AREA, CASPER, WYOMING.

J. G. Crock, J. A. Erdman, and R. C. Severson. U.S. Geological Survey, Box 25046, Denver Federal Center, Denver, Colorado 80225.

Selenium in agricultural drainage is an environmental hazard at many irrigation projects in the western U.S. Our study seeks to (1) define the sources of Se and its distribution in agricultural and native plants and soils of the Kendrick Reclamation Project Area (KRPA) near Casper, Wyoming; and (2) evaluate the influence of irrigation on the Se distribution in irrigated lands. Samples of native soil and sagebrush (Artemisia tridentata) were collected from 14 geological units in the study area. Samples of soil and alfalfa (Medicago sativa) were collected from 109 sections in the KRPA where >40 acres per section were under irrigation. Total and water-extractable Se (XW-Se) in soils and total Se in plants were determined. Many samples of sagebrush and alfalfa had high Se contents. About 15% of the alfalfa samples contained >4 ppm Se--a level potentially hazardous to livestock if fed over extended periods of time. About 20% of the sagebrush samples contained >1.1 ppm Se--the maximum reported Se baseline in western U.S. sagebrush. In contrast, native and cultivated soils contained <0.1-3.3 ppm Se, which is not unusual when compared with the baseline values established for soils of the Northern Great Plains. Landscape patterns for total Se in alfalfa and XW-Se in agricultural soils are displaced from total Se in soils, due to ground water flow patterns.

RAPID ESTIMATION OF SATURATION-PASTE SELENIUM AND SODIUM IN WYOMING SOILS BY CONSTANT-RATIO WATER EXTRACTION.

K.C. Stewart. D.L. Fey, and R.R. Tidball. U.S. Geological Survey, DFC, Box 25046, MS 973, Denver, CO 80225 (303) 236-2457.

Saturation-paste (SP) extracts have traditionally been used to evaluate element concentrations available to plants in cultivated soils, but sample preparation is very time consuming. Twenty-two soils from the Kendrick Irrigation Project near Casper, Wyoming, were characterized for available selenium and sodium by the SP extraction and by a more rapid extraction using a constant ratio of soil to water (1:5). Regression analysis shows that 81 percent of the variation in SP selenium ($r^2=0.81$) is accounted for by the equation $\log(\mathrm{Se}_{sp}) - -0.21 + 1.2 \log(\mathrm{Se}_{1:5})$. Ninety-nine percent of the variation in SP sodium ($r^2=0.99$) is accounted for by the equation $\log(\mathrm{Na}_{sp}) = -0.49 + 1.1 \log(\mathrm{Na}_{1:5})$. The high coefficients of determination indicate that the faster 1:5 extraction provides good estimates of SP selenium and sodium, and can therefore be used to evaluate large numbers of samples in a short period of time.

CHEMICAL COMPOSITION OF IRON-RICH BED SEDIMENT FROM A STREAM AFFECTED BY ACID MINE DRAINAGE.

Kathleen S. Smith[1,2]. James F. Ranville[1,2], and Paul H. Briggs[1]. [1]U.S. Geological Survey, Box 25046, Denver Federal Center, M.S. 973, Denver, CO 80225, (303)236-5788. [2]Colorado School of Mines, Golden, CO 80401.

St. Kevin Gulch, CO, a small subalpine stream, receives acidic (pH 2.8) metal-rich water that drains mine dumps and mill tailings from an abandoned silver-mining operation. The metal-rich inflow to St. Kevin Gulch contains about 100 mg/L iron, 1300 mg/L sulfate, and elevated concentrations of zinc, manganese, aluminum, silicon, cadmium, and copper. Iron-rich streambed sediment was collected at several sites along St. Kevin Gulch from May to October, 1988 and 1989. Air-dried sediment contains 10-45 wt. percent iron, 0.5-4 wt. percent sulfur, and 2-13 wt. percent carbon. The pH of St. Kevin Gulch downstream of the acidic inflow ranges between 3.3 and 4.6. Sulfur, lead, arsenic, and copper concentrations in the iron-rich bed sediment vary with the pH of overlying stream water. At lower stream-water pH's, sulfur and arsenic sediment concentrations increase and lead and copper sediment concentrations decrease. We attribute this variation in concentration to pH-dependent sorption of dissolved species by hydrous iron oxides in the streambed sediment. Anions, such as sulfate, sorb onto hydrous iron oxides at low pH; Pb^{2+} and Cu^{2+} are among the few cations that can sorb at the low pH's found in St. Kevin Gulch. Work is in progress to characterize organic carbon in the bed sediment.

92 | EFFECT OF DISSOLVED ORGANIC CARBON ON THE ELECTROPHORETIC MOBILITY OF IRON-RICH SUSPENDED SEDIMENTS IN A STREAM CONTAMINATED BY ACID-MINE DRAINAGE.

James F. Ranville[1,2]. Kathleen S. Smith[1,2] and Diane M. McKnight[1]. [1]U.S. Geological Survey, Box 25046, MS 408, Denver CO. 80225 and [2]Colorado School of Mines, Chemistry/Geochemistry Department, Golden CO., 80401.

Iron hydroxide precipitates are important mineral phases in streams contaminated by acid-mine drainage. Their surface chemistry plays a major role in determining the distribution of metals between water and sediment phases. At low pH, the surface chemistry is modified by adsorption of anions, particularly dissolved organic carbon (DOC). Electrophoretic mobility measurements, utilizing a light-scattering technique, were performed to investigate DOC adsorption. Two years of field data from four sites along St. Kevin Gulch, a low pH (3.5) stream near Leadville, CO., indicate a strong negative correlation between DOC and electrophoretic mobility of iron-rich suspended sediments. During spring runoff, elevated levels of DOC result in negatively charged suspended sediments. During summer and fall, low values of DOC occur and the suspended sediments are positively charged. Electrophoretic mobilities range from -1.4 to 0.6 um/sec/volt/cm while DOC concentrations range from 2.7 to 0.5 mg C/L, respectively. DOC adsorption onto iron-rich sediment was also investigated in laboratory experiments using model components. Adsorption and co-precipitation of Suwannee River fulvic acid on/with ferrihydrite were examined under conditions simulating the stream. Results were in general agreement with field data.

93 U.S. GEOLOGICAL SURVEY'S NATIONAL WATER-QUALITY ASSESSMENT--RESULTS OF THE LOWER KANSAS RIVER PILOT PROJECT. Dwight Q. Tanner, U.S. Geological Survey, 406 Federal Building, Lincoln, Nebraska 68508 and John K. Stamer, U.S. Geological Survey, 4821 Quail Crest Place, Lawrence, Kansas 66049.

The U.S. Geological Survey began the National Water-Quality Assessment (NAWQA) in 1986 to describe the Nation's current water-quality conditions, to define water-quality trends, and to define natural and anthropogenic factors that affect water quality. The lower Kansas River basin in Kansas and Nebraska was chosen as one of seven surface-water pilot projects. Synoptic surveys of the basin have provided descriptions of relatively instantaneous water-quality conditions during low flow at about 60 sites. The upper part of the basin, where land use is predominantly irrigated agriculture, was characterized by relatively large concentrations of sodium in streambed sediments and relatively large concentrations of nitrate and atrazine in streamflow. Densities of Escherichia coli bacteria were larger in the upper part of the basin. The lower part of the basin, which is more densely populated than the upper part, had anomalously large concentrations of lead in streambed sediments. Results from the lower Kansas River NAWQA pilot project are being used to aid in the design of new NAWQA projects across the country.

94 GEOCHEMICAL AND BIOGEOCHEMICAL BASELINES AND TRENDS, KENAI PENINSULA. ALA J. G. Crock, R. C. Severson, and L. P. Gough. U.S. Geological Survey, Box 25046, Denver Federal Center, Denver, Colorado 80225

Investigations on the Kenai Peninsula, including areas within the Kenai National Wildlife Refuge, had two objectives: (1) determine the feasibility of preparing maps showing regional trends for elements in native plants and soils; and (2) define possible element additions to the environment from an industrial complex north of the town of Kenai. The first objective was accomplished using an unbalanced nested analysis-of-variance design. The second was accomplished by establishing three downwind transects for which sample localities were chosen at geometric intervals beginning 0.5 km away from the complex. At each locality, samples of Hylocomium splendens (feather moss, whole plant), Picea glauca (white spruce, twigs and needles), and soil horizons (O2, B2, and C) were collected and analyzed for their major and trace element contents. Our results show that intensive soil or plant sampling would be needed to reliably map the geochemistry of the area, chiefly because of THE large local variability found for the concentrations of most elements. For example, producing reliable element maps of feather moss using a 50-km-cell would require sampling densities of from 4 samples/cell for Al, Co, Fe, La, Li, and V to >15 samples/cell for Cu, Pb, Se, and Zn. Our study of possible industrial contamination revealed no strong trends in soils, but the feather moss collected on the north transect showed a logarithmic decrease for several elements, including Al, Co, Na, S, and V.

DYNAMIC NUCLEAR POLARIZATION AT 140 GHZ. Thomas F. Prisner,[1] Sun Un,[1] Ralph T. Weber,[1] Ken W. Fishbein,[2] Ann E. McDermott,[1] Matthew J. Seaman,[2] Michael Whitmore,[3] David J. Singel[3] and Robert G. Griffin[1,2]. [1]Francis Bitter National Magnet Laboratory, Massachusetts Institute of Technology, [2]Department of Chemistry, Massachusetts Institute of Technology, [3]Department of Chemistry, Harvard University,Cambridge,MA 02139.

Over the past several years, a number of groups have shown that important signal-to-noise enhancements in high resolution solid state NMR spectra can be achieved via DNP (dynamic nuclear polarization). All these experiments were done at low fields (≤ 1.4 T), despite the potential problems with low spectral resolution. We have initiated a program to develop a DNP spectrometer that operates at a field-strength of 5.0 T and we report results of our initial Overhauser-DNP experiments. Our approach to DNP at high fields involves high power microwave pulses instead of cw microwave excitation. Calculations show that this *pulse method* has advantages over the conventional *cw techniques*, especially for inhomogeneous broadened EPR lines and high pulsed field strengths, w_1 satisfying the condition $w_1 > T_{1e}^{-1}$, where T_{1e} is the electronic Zeeman relaxation time.

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CHARACTERIZATION OF THE INTERFACIAL REGION OF POLYSTYRENE-POLYCARBONATE BLENDS BY DYNAMIC NUCLEAR POLARIZATION ^{13}C CPMAS NMR

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Heterogeneous blends of [ring-$^{12}C_6$]polystyrene (or [$^2D_5$]polystyrene) and [3,3'-$^{13}C_2$]polycarbonate have been formed by serial film casting. The polystyrene phase of each blend was doped with 2% by weight of bisdiphenylenephenylallyl free radical. Proton polarization was generated in the polycarbonate phase by direct coupling to electrons in the polystyrene phase under microwave irradiation at 39 GHz. Detection was made selectively by cross-polarization, magic-angle spinning ^{13}C NMR. The detected signal arises from polycarbonate which is within 50 A of the polycarbonate-polystyrene interface. The rings of polycarbonate chains at the interface do not undergo 180° flips, while rings of bulk polycarbonate do undergo flips.

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A NEW ANALYSIS OF SOLITON DYNAMICS IN TRANS-POLY ACETYLENE: MOTIONAL EFFECTS OF DYNAMIC NUCLEAR POLARIZATION SPECTRA.

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We have developed a full, non-perturbative density matrix treatment to simulate Dynamic Nuclear Polarization (DNP) spectra for the interaction of a single electronic defect with a single nucleus, that incorporates motion. The theory is based on the density matrix treatment and includes the full interaction of an electron with a nucleus, including non-secular as well as pseudosecular and secular terms. A motional process is explicitly included in the density matrix, and the effects of two-site hopping are examined. The results of this theory are in complete agreement with standard DNP theory in the slow and fast motion limits, in which the standard theory is meant to apply, and smoothly goes between the two as the motional rate increases. At intermediate motional rates, asymmetric DNP line shapes are simulated. This is in contrast to a previous analysis which concluded that the DNP signal would vanish at intermediate motional rates. It was therefore concluded that asymmetric DNP lineshapes were diagnostic for two species, differing at least in their motional rates. Our results suggest that it is not necessary to adduce more than one defect to explain asymmetric DNP spectra. The application of these results to the DNP spectra of trans-polyacetylene profoundly changes the interpretation of such spectra and the significance of the dynamics of the defect observed by DNP.

EPR PARAMETERS MEASURED VIA NMR.

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The impact of unpaired electrons in carbonaceous materials on parameters that can be measured via NMR and ^{1}H Dynamic Nuclear Polarization (DNP) will be discussed. The following parameters will be considered: (i) The ^{1}H DNP solid-state enhancement; (ii) The ^{1}H Overhauser enhancement: (iii) The ^{1}H Zeeman relaxation; (iv) The ^{1}H rotating-frame relaxation. These ^{1}H parameters, as well as electron parameters measured *via* EPR have been determined in cellulosic chars, pyrolyzed in the temperature range 200-1000°C. It has been found that for pyrolysis temperatures between 250 and 500°C a distribution of electron-electron spin-exchange rates occurs, with spin-exchange frequencies varying from 0 to 10^{12} Hz. For pyrolysis temperatures larger than 500°C only fast spin-exchange rates occur. The ^{1}H parameters can be used to determine small fractions of electrons (1% or less) spin-exchanging with different frequencies. Finally, the ^{1}H rotating-frame relaxation can be used also to determine the electron spin-lattice relaxation

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RADIO FREQUENCIES IN PULSED EPR

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This paper reviews pulsed EPR schemes which use both, microwave and radio frequency fields.

Basic principles, performances and prospects of a number of new pulsed double resonance methods, including

- — optimized population transfer ENDOR schemes
- — hyperfine selective ENDOR
- — rf-driven electron spin echo envelope modulation in solids and liquids
- — EPR-detected transient nutations
- — pulsed ENDOR in liquids
- — coherence transfer ENDOR schemes
- — pulsed population transfer time-domain ENDOR

will be discussed.

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COORDINATION STRUCTURE OF ACTIVE SITES IN METALLOENZYMES AND PROTEINS BY PULSED ELECTRON NUCLEAR MULTIPLE RESONANCE.

H. Thomann and M. Bernardo, EXXON Corporate Research Laboratory, Annandale, NJ 08801.

Metal sites in metalloproteins and enzymes usually serve as active sites for electron transfer or substrate binding. The redox potentials and high activity and selectivity of these active sites are believed to be a function of the protein imposed coordination structure. Pulsed electron nuclear multiple resonance techniques for probing these coordination structures will be described. Applications to mononuclear metal sites and to multinuclear transition metal sulfide sites will be presented.

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DEVELOPMENT OF PULSED ENDOR AND APPLICATION TO ORGANIC RADICALS.

Peter Hofer, Bruker Analytische Messtechnik, 7512 Rheinstetten 4, Federal Republic of Germany

Continuous wave Electron Nuclear Double Resonance has found wide spread use because of the large gain in resolution compared to EPR. The high resolution is obtained, however, at the expense of sensitivity, typically \Z of the EPR signal. Recently developed pulsed ENDOR schemes have shown signals up to twice as large as the ESE amplitude (spinor ENDOR (1)). The elimination of the rf-power broadening without loss of sensitivity has been accomplished with CT-ENDOR (2). With the extension to pulsed TRIPLE resonance positive and negative hfi can be discriminated. The different coherence phenomena involved in these pulsed ENDOR schemes and their application to measure the hfi spectrum and the nuclear relaxation times will be discussed.

(1) M. Mehring, P. Höfer and A. Grupp, Phys. Rev. A 33, 3523, 1986
(2) P. Höfer, A. Grupp and M. Mehring, Phys. Rev. A 33, 3519, 1986

HIGH DYNAMIC NUCLEAR POLARIZATION AT ROOM TEMPERATURE.

102 A. Henstra, T.-S. Lin, J. Schmidt, W. Th. Wenckebach, Kamerlingh Onnes and Huygens Laboratories, P. O. Box 9504, 2300 R. A. Leiden, The Netherlands

The highly polarized photo-excited triplet state of pentacene in a naphthalene crystal is used for pulsed Dynamic Nuclear Polarization at room temperature. Thus far an enhancement of 5500 of the naphthalene proton polarization has been reached. For this purpose, a newly developed technique, the Integrated Solid Effect, performed while obeying the Hartmann-Hahn condition, is used to transfer the triplet polarization efficiently to the nuclear spin system.

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STIMULATED NUCLEAR POLARIZATION STUDY OF SHORT-LIVED RADICAL SPECIES.

103 R. Sagdeev, E. G. Bagryanskaya, Institute of Chemical Kinetics and Combustion, Novosibirsk 90, USSR

Novel results have been obtained in stimulated nuclear polarization (SNP) studies of radical reactions. The effect of solvent polarity on the mechanism of photolysis of anthraquinone with triethylamine has been studied. The spectra of the radical pair (RP) of triethylamine cation radical and aminalkyl radical have been detected. SNP has been used to study the dynamics of RP in micelles, and to estimate the exchange interaction and its influence on singlet-triplet conversion in photolysis of dibenzyl ketone and methyldesoxybenzoin in DDS micelles. Experimental SNP spectra are compared to calculation assuming that the exchange interaction depends on the distance between radicals. Possible mechanisms of SNP spectral line broadening in micelles will be discussed. A new method will be discussed for studying degenerate electron exchange reactions by dynamic nuclear polarization (DNP) effects in detection of NMR signals from diamagnetic products of short-lived ion-radicals. The mechanism of the phenomenon will be considered; calculated and experimental DNP spectra and their dependences on the concentration of reactants, tow field amplitude, and iorrradical parameters will be compared. Electron exchange rate constants for photolytic reactions of anthracene with dimethylaniline, and fumaronitrile with naphthalene in polar media have been obtained. (Related work is described in Chem. Phys. Lett. 114, 138 (1985) and 155, 141 (1989); Chem. Phys. 135, 123 (1989) and (1989), in press.)

TWO-DIMENSIONAL FOURIER TRANSFORM ESR IN THE SLOW MOTIONAL REGIME

Baldev Patyal, Richard H. Crepeau, and Jack H. Freed, Baker Laboratory of Chemistry, Cornell University, Ithaca, NY 14853-1301

Gorcester and Freed have previously performed 2D-FT-ESR experiments on nitroxides in the fast motional regime and have demonstrated their utility for studies of motional dynamics. The extension to the slow motional regime has required increased spectral coverage (ca. 200 MHz), improved methods for removing undesirable artifacts, and powerful data processing methods. 2D-FT-ESR studies on nitroxides in the slow motional regime will be reported. They are of the 2D-SECSY (2 pulse) and 2D-ELDOR (3 pulse) type. They have been made possible by specially designed tunable bridged loop-gap resonators with extremely low Q (~ 40) yet very high microwave magnetic fields in the rotating frame ($B_1 \sim 15G$), the use of new phase cycling sequences that eliminate artifacts, and appropriate time-series analysis. The 2D-SECSY spectra are the FT analogues of the field-swept 2D experiments of Millhauser and Freed, but are achieved an order of magnitude faster. Also, they include echo-modulation Information as a function of (cw) spectral position. 2D-ELDOR spectra provide cross-peaks which map the rate of magnetization transfer from one spectral position to another. The advantages and applications of these methods will be discussed.

105 DYNAMICS AND FOLDING OF VERY HELICAL PEPTIDES REVEALED BY ESR, TIME-DOMAIN ESR AND MOLECULAR DYNAMICS CALCULATIONS.

A. Paul Todd, Siobhan M. Miick, Wayne R. Fiori, Karen M. Casteel, John C. Williams and Glenn L. Millhauser, Department of Chemistry, University of California, Santa Cruz, California 95064.

α-Helices are the most common form of secondary structure in proteins. While the thermodynamics of helix formation appears to be well understood the kinetics of helix formation and the localized dynamics of folded helices remains largely unexplored. The recent and surprising discovery of short peptide segments (approximately 17 residues) of high helical content under physiological conditions provides an excellent opportunity to study these problems. ESR operates on a time scale that matches well with the expected dynamics of short α-helices. We are using spin-labeled versions of these peptides to determine a 'mobility profile' along the helix backbone. Assignment of the dynamics is aided by molecular dynamics calculations of the nitroxide on these labeled helices. Experimentally we find that the nitroxide lineshape parameters do not exhibit the typical Arrhenius behavior observed in freely tumbling spin probes. However, we do find that the lineshape parameters are a function of the extent of peptide helicity. Our results may lead to new models for helix formation.

106 PROBING Cu^{2+} SITES IN ZEOLITES USING ESEEM INDUCED BY FRAMEWORK ^{27}Al.

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We have studied the evolution of the ^{27}Al FT-ESEEM spectra as function of dehydration conditions in zeolites Cu-NaX, Cu-KX and Cu-KA. In fully hydrated zeolites the ^{27}Al ESEEM is characterized by a single modulation frequency at the ^{27}Al Larmor frequency, indicating, as expected, weak interaction with the zeolite framework. Partial dehydration introduces significant changes in the modulation pattern. We identified three distinct Cu^{2+} species which exhibit unique ESR and ^{27}Al FT-ESEEM spectra. In partially dehydrated NaX, the Cu^{2+} cations are located in the center of the hexagonal prism where they are coupled to the Al by weak dipolar interactions as manifested by a single , rather broad peak at the ^{27}Al Larmor frequency. In fully dehydrated NaX and in partially and fully dehydrated KX, the Cu^{2+} cations reside in a more exposed site in the supercage where it is strongly coordinated to framework oxygens such that there a finite spin density on the neighboring Al nuclei. This results in a relatively large isotropic hyperfine coupling which is responsible for the splitting in the ESEEM spectrum. In dehydrated KA Cu^{2+} is located in site II' where the binding of the Cu^{2+} to the framework oxygens is also strong but not as observed in NaX and KX, i.e the isotropic hyperfine constant is smaller.

107 ANALYSIS OF ^{14}N SUPERHYPERFINE INTERACTION TO Cu^{2+} BY MULTIFREQUENCY ESR AND COMPUTER SIMULATIONS.

Janusz **Bednarek** and **Shulamith Schlick**, Department of Chemistry, University of Detroit, Detroit, MI 48221.

The perfluorinated membranes known as Nafion consist of an organic backbone and pendant sulfonic groups SO_3H that can be neutralized by various cations, to give Nafion salts. The local environment of the cations was determined from ESR studies of Nafion neutralized by paramagnetic cations such as Cu^{2+} and Ti^{3+}. The ligation of Cu^{2+} has been studied in detail by swelling the membrane with acetonitrile and analyzing the superhyperfine splittings from ^{14}N nuclei. ESR spectra were taken at L (1.2 GHz), S (2.8 GHz), C (4.7 GHz) and X (9.4 GHz) bands, in the temperature range 77-123 K. Simulations were performed based on axial symmetry of the complexes and Identical principal axes systems for the g-, hyperfine and superhyperfine tensors. The m_I and frequency dependence of the linewidths is due to the strain effect, which leads to a distribution of $g_{\parallel}$ and $A_{\parallel}$ (^{63}Cu) values. Measurements at several microwave frequencies allows determination of the strain parameters and a more accurate and reliable measurement of the ESR parameters. Preferential solvation of cations in Nafion will also be discussed.

Supported by NSF Award DMR-8718947 (Polymer Program).

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COMPUTER SIMULATION OF SPIN RELAXATION IN DILUTED ATTICES. <u>Sushil K. Misra</u> and Ufuk Orhun. Physics Department, Concordia University, 1455 de Maisonneuve West, Montreal, Quebec, Canada H3G 1M8.

Diffusion of spin relaxation from a single site on a square lattice has been simulated on a computer. For a connecting path, it is necessary that a site be occupied, its spin he down, and be chosen by random-walk criterion. In the initial configuration a site is occupied with probability p. with spin-down probability q. Three distinct cases are considered for calculating the diffusion paths: (i) Occupation of sites and spin orientations remain unchanged during simulation. (ii) Occupation of sites remains unchanged, while the spin orientations vary, the total spin-down probability is maintained to be q during simulation, (iii) Both occupation of sites and spin orientations vary, the total probabilities being maintained to be p and q, respectively, during simulation. The variations of both p and q were considered to be over the 0 to 1 range. The percolation threshold, was found to be $t = p \times q \simeq 0.593$, in agreement with the theoretically predicted value $t = 0.59275$ for a square lattice. The connected sites forming clusters, for all three cases, were found to be fractals with the Hausdorff-Besicovitch dimension $D = 1.70 \pm 0.03$. Critical exponents have been calculated. Case (ii) is applicable to diluted magnetic crystals, whose three-dimensional version explains well the observed temperature dependence of Gd^{3+} EPR linewidths in $LiYb_xY_{1-x}F_4$ single crystals as a function of x.

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LINESHAPE SIMULATIONS OF THE LOW FIELD MICROWAVE ABSORPTION O A SUPERCONDUCTING $Bi_2Sr_2CaCu_2O_x$ CRYSTAL. Jerzy T. Masiakowski, Micky Puri, Maurizio Romanelli, Larry Kevan and Robert N. Schwartz. Department of Chemistry and Texas Center for Superconductivity, University of Houston, Texas 77204-5641 and Hughes Research Laboratories, Malibu, California 90265.

Magnetic-field-dependent low-field microwave absorption for a $Bi_2Sr_2CaCu_2O_x$ crystal below the superconducting transition temperature was investigated as a function of temperature, magnetic field modulation amplitude and microwave power. The signal from the crystals stored in vacuum is highly anisotropic and shows a strong temperature dependence. Above 60 K the signal shows a more complex signal shape. The complex signal shape is replaced by a broad, structureless signal when the crystal is stored in air for about one month or when ground into a powder. The signal shapes are well stimulated by a mechanism of microwave loss in Josephson junctions involving boundary and microwave-induced surface currents. The model computer simulation explains the essential aspects of the temperature dependence and microwave power dependence of the signal. The relationship of crystal to powder signals is also investigated by computer simulation.

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FAST ESR-IMAGING. Uwe <u>Ewert</u>, Jack H. Freed, Cornell University, Department of Chemistry, Baker Laboratory, Ithaca, New York, 14853-1301. USA.

A limitation of ESR-imaging is the long measurement time. Short measurement times are, for example, required for diffusion measurements. Current ESR-imaging experiments require several seconds per projection, or several minutes for a 2D- and several hours for a 3D-image. The minimum measurement time depends on the scan time of the magnetic field and the field gradients, the response time of the microwave bridge, and the computational potential. An improvement is possible by combining ESR imaging with Rapid Scan techniques. 2D-images have now been measured in less than 1 minute. A further improvement is obtained by applying an eddy current compensation. Shorter measuring times require optimizing the cavity. A bridged loop gap resonator has now been used for ESR-imaging. The distance between the gradient coils and the coil inductance has been decreased. The assembly is situated in a polymer casing which permits temperature control in a range of -100 to 100 C. The effect of disturbing fields induced by eddy currents has been reduced, and gradient switching times in the sub-microsecond range Favor this resonator for pulsed ESR imaging applications. The minimum time for pulsed ESR-imaging experiments is decreased below one second for 2D-imaging. Minimum measurement times of one millisecond can be expected if rapid transient recorders and computers are available.

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EPR SPECTRA OBTAINED FROM FIELD-CYCLED PEDRI IMAGES

David J. Lurie , Ian Nicholson and John R. Mallard
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In Proton Electron Double-Resonance Imaging (PEDRI) a proton NMR image is collected while the EPR resonance of a dissolved free radical is irradiated. The resulting enhancement of the NMR signal reveals the distribution of the free radical as intense regions in the final image. In Field-Cycled PEDRI the magnetic field strength B_o is lowered during the EPR irradiation and rapidly increased before the NMR excitation and imaging field gradients, giving low RF power deposition and good SNR (D.J. Lurie et al. J.Magn.Reson. 84,431(1989)). The observed enhancement depends on the free radical concentration, the strength of the EPR irradiation and its frequency relative to the EPR line(s). In this work we have used the EPR frequency dependence to derive EPR spectral information. The EPR frequency is kept constant and a series of PEDRI images is collected covering a range of offsets of B_o relative to the EPR line of interest. We have implemented Spectral FC-PEDRI on our proton NMR imager, operating at 0.01T. The EPR irradiation was applied at 288MHz. Three series of twenty 32x32 FC-PEDRI images were collected using a sample containing 0.4mM TEMPOL solution, each series covering one of the TEMPOL resonances centred on 0.0051T, 0.010T and 0.0118T. After collection and processing, region-of-interest software allowed an EPR spectrum to be displayed in real time from any part of the sample. Initial results indicate that superhyperfine structure can be observed, making the method of potential use in EPR oximetry.

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NO ABSTRACT AVAILABLE

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MAGNETIC RESONANCE MEASUREMENTS OF MEDIUM EFFECTS ON HYDROGEN BONDING OF SOLVENTS WITH NITROXIDES.

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Comparison of results obtained by different magnetic resonance techniques on interactions of the nitroxide free radical TWO with solvent nuclei on chloroform, trifluoroethanol and pentafluorophenol is made. Dynamic nuclear polarization at low magnetic fields identifies the dominant coupling between the nuclei and unpaired electron spins. NMR determinations of changes in unpaired electron-induced nuclear relaxation times identify the frequency components of the motional spectrum that drive coupled relaxation transitions. Changes in chemical shift of solvent nuclei in the presence of paramagnetic solutes probe the environment of the interacting nuclear and electron spins and are an important adjunct to relaxation based NMR techniques. However, different interactions within the same system can induce opposing changes in chemical shift; resulting chemical shifts are 'weighted averages' of chemical shift components produced by different interactions. ESR measures directly the shift in unpaired electron density within the TMPO nitrosyl group as a result of interaction with the proton donor. Interpretation of observed hyperfine coupling constants is complicated by changes in medium polarity, but correction of shifts provides improved determinations of formation constants for transient donor:acceptor complexes.

114 ESR IMAGING OF THE DISTRIBUTION OF EXOGENOUS NITROXSIDE RADICALS IN THE RAT HEAD BY AS L-BAND ESS SYSTEM.

N.Tsuchihashi[1], S.Ishida[2], N.Mori[2], H.Kumashiro[2], T.Ogata[3], T.Kitajima[3], H.Kamada[3], and E.Yoshida[4]. RI-Laboratory[1] and Department of Neuro-psychiatry[2], Fukushima Medical College, Fukushima, Japan, Faculty of Engineering, Yamagata University,[3] Yonezawa, and Technical and Engineering Divisin, JEOL Ltd.,[4] Akishima, Japan

ESR imaging of a living rat has been performed by an l,-band ESR system, which is composed of an L-band ESR spectrometer, a field gradient coil and a data processor. The imaging was carried out by Lauterbur's method. A nitroxide, 3-carbamoyl-2,2,5,5-tetramethylpyrrolidine-1-yloxy (CPROXYL), was used as an imaging agent in saline solution at a concentration of 0.2M and administerd intraperitoneally to obtain a constant concentration in the head for about 40 minutes. Both of the 2 dimensional imaging and the cross sectional imaging were made. In the cross sectional image of the ral head the nitroxide rich region was clearly distinguished from the deficient region. The nitroxide deficient areas corresponded well to the brain of the rat. Since the brain holds the blood brain barrier, CPROXYL may be retained here and its concentration in the brain is quite low, which gives weak ESR signals. Us high concentration in the blood gives strong ESR signals. The images obtained here give good information on the distribution of exogenous nitroxide radicals in the rat head.

115 SENSITIVITY AND RESOLUTION ENHANCEMENT FOR SPECTRAL SPATIAL ESR-IMAGING.

Uwe Ewert, Jack H. Freed, Cornell University, Department of Chemistry, Baker Laboratory, Ithaca, New York, 14853-1301, USA.

The projection reconstruction of B -scans for multiple stepped gradients has been proven as the spectral-spătial technique which yields the highest sensitivity. He discuss constraints for optimum sensitivity. The projection reconstruction Is based on filtered back-projection modified by the derivative theorem:

$$\mathrm{Image}(x,y) = \int_0^{\pi} \mathcal{F}^{-1}\left\{-i\mathcal{F}\left[\frac{d}{dr}\mathrm{Pr}(r,\alpha)\right]\right\}d\alpha.$$

The projections (Pr) are filtered by differentiation and noise limitation in the spectrometer. The projection reconstruction requires the same filter function for all projections. To accomplish this one requires that the ratio of scan time to time constant is held constant and the modulation amplitude is changed proportional to $\sin^{-1}\alpha$ with the pseudo projection angle $\alpha = \mathrm{arc\ cot}(\Delta R\cdot \mathrm{grad}\ B/\Delta S)$ where AR is the spatial range and AS is the spectral range. The loss in sensitivity with increasing gradient can be compensated by either increasing the accumulation rate or the scan time per projection in proportion to sin" α. *One* of the disadvantages of the multiple stepped gradient technique is the low spatial resolution in comparison with the modulated gradient technique. A new algorithm for the multiple stepped gradient technique is described. It uses a zoom projection reconstruction with a matched filter function which depends on a.

116 IMAGING FREE RADICALS *IN-VIVO* IN THE AT USING PED

Ian Nicholson, David J. Lurie, Margaret A. Foster and John R. Mallard
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Proton-Electron Double-Resonance Imaging (PEDRI) is a novel method for imaging free radicals in aqueous samples (D.J. Lurie et al. J.Magn.Reson. **76**, 366(1988)). A proton NMR image is collect«1 while tho EPR resonance of a dissolved free radical is irradiated. In regions of the sample where the free radical is causing proton relaxation the NMR signal is enhanced, these regions exhibiting greater intensity in the final image. In this work we *have imaged the distribution of an injected* nitroxide free radical in the rat. 300g adult Sprague-Dawley rats were injected intravenously with 0.5ml of buffered 150mM solution of 3 Carboxy-PROXYL. PEDRI images were obtained using our home-built imager operating at a magnetic field strength of 0.01T. An Alderman-Grant resonator was used to apply the EPR irradiation at. 238MHz with an instantaneous power of 20W. Images were 32x32, 7.5cm field-of-view, obtained using a spin warp pulse sequence with a repetition time of 500ms. Alternate NMR 90° pulses were preceded by 300ms EPR irradiation, so that images obtained with and without *EPR irradiation were collected simultaneously*; after *processing*, a subtracted image was generated showing only regions containing free radical. Each image pair took seconds to collect. The free radical was clearly visible in the kidneys and bladder and could be seen in the ureters. Sequential images showed a reduction in the free radical concentration with time. Experiments are underway to measure the clearance rate from the rat under various conditions.

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EPR IMAGING OF ELECTROCHEMICALLY GENERATED RADICALS, Minoru Sueki, Richard W. Quine, Sandra S. Eaton, and Gareth R. Eaton, Department of Chemistry, University of Denver, Denver, CO 80208, USA

Spectral-spatial EPR imaging reveals the spatial distribution of radicals generated electrochemically in the EPR cavity, and the hyperfine-split EPR spectrum of the radical at each point along the spatial axis. Radicals were generated electrochemically with a three-electrode system in a flat cell oriented with the long axis along the main magnetic field (z axis). The magnetic field gradient was along the z axis. The maximum gradient was 200 to 300 G/cm. The spatial distribution of the radicals around the electrodes was examined for cases in which one radical was generated and cases in which different radicals were generated at two of the electrodes.

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THE USE OF ELECTRONIC COUPLING ADJUSTMENT IN A CAPACITIVELY COUPLED SYSTEM TO REDUCE BOTH COUPLING VARIATION AND MICROPHONIC NOISE IN EPR SPECTROSCOPY OF LIVING ANIMALS Miroslav Peric and Howard J. Halpern, Department of Radiation Oncology and Cellular Biology, Box 442, U. Chicago Med. Ctr., Chicago, IL 60637 Michael K. Bowman, ANL, Argonne, IL 60439

We have described the use of capacitive coupling and its implementation in automatic coupling control (ACC) for use in the context of EPR measurements of a living animal sample (1). We detail this implementation including the amplification circuitry. The assurance of clean separation of absorptive and dispersive components is desirable. The tuning method will be described and spectral fits displayed to indicate that to the level of one to three percent this is achieved in solution samples. The more difficult, but adequate separation with animal samples will also be described. We document a factor of three reduction in the noise-to-signal ratio using the ACC in animal measurements. We also find that the ACC reduces simple solution measurement noise by 40 percent without reduction in the signal, indicating there to be some coupling associated microphonic noise that can be reduced with this system.

1. HJ Halpern, DP Spencer, J van Polen, MK Bowman, AC Nelson, EM Dowey, and BA Teicher, Rev. Sci. Instrum. 60:1040 (1989).

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TIMING AND CONTROL UNIT FOR CONVERSION OF CW EPR SPECTROMETERS TO PULSED OPERATION. Richard W. Quine and Gareth R. Eaton. University of Denver, Departments of Engineering and Chemistry, Denver, CO 80208.

Electronic circuitry to control the microwave pulse sequences for Electron Spin Echo experiments has been constructed. The unit incorporates timing sequences applicable to Saturation - Recovery experiments as well as ESE 2-pulse and 3-pulse experiments. In addition, a two-channel boxcar gated integrator has been incorporated to facilitate data collection. The design is microprocessor-based and incorporates front-panel set-up of all timing parameters. The timing unit is presently used in an S-band EPR spectrometer but the design is generally applicable to the conversion of any cw spectometer to pulsed operation.

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EPR/ENDO 9 GHZ SPECTROMETER SENSITIVITY ENHANCEMENT FOR SMALL SAMPLES USING DIELECTRIC RESONATORS,

R. A. Isaacson and G. Feher, Physics Dept. B-019, Univ. of Calif. San Diego, La Jolla, CA 92093.

Dielectric resonators (DR's) [W. M. Walsh & L. W. Hupp, Jr., RSI 57 Sept. 1986, 2278] have some advantages over loop gap resonators (LGR's) [J. S. Hyde 4 W. Froncisz in Advanced EPR, A. J. Hoff, Ed., Elsevier, 1989) for ENDOR spectroscopy on both lossy and non-lossy samples from room temperature to 80 K. The high dielectric constant materials commercially available (K=30) have background EPR absorptions that are often bothersome for EPR but giving very little ENDOR background. We use a Gordon coupler/waveguide coupling box for coupling to a variety of resonators (LGR's or DR's) with sample tubes ranging from 1 to 3 mm OD and typical sample lengths of 1 to 10 mm. The problems of ENDOR coil alignment and mechanical stability requirements of the sample tube are considerably less for the DR as compared to the 2 loop/2 gap LGR. Our experiments are typically on single crystal reaction center proteins from photosynthetic bacteria and a light pipe is used to irradiate the samples from the top, along the axis of the sample tube hole in the DR material. Typical ENDOR signal enhancements for 3 mm long x 1 mm "wet" crystals are 5 to 20 times compared to a commercial TM_{110} ENDOR cavity. In many cases 5 to 10 times less microwave and 2 to 4 times less RF power is required for signal saturation.

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^{14}N ENDOR OF THE W7 DI-NITROGEN CENTER FOUND IN BROWN DIAMOND.

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The W7 center was first observed by J.H.N. Loubser and A.C.J. Wright (J.Phys. D: Appl.Phys, 6, 1129-1141, (1973)). EPR showed that this is a di-nitrogen center, with a single unpaired electron coupled strongly to one nitrogen and weakly to the second. The W7 center is only found in plastically deformed brown diamonds, and is not isotopically distributed throughout the possible sites in the diamond. This anisotropy is believed to be associated with the plastic deformation. We report here ^{14}N ENDOR measurements that (a) were made by utilizing enhancement of the EPR arising from a rapid repetitive sweep of a radio-frequency source through the ENDOR transitions, while a second source was swept slowly as in a conventional cw-ENDOR experiment (this technique dramatically improved the ENDOR signal to noise ratio, compared to conventional cw-ENDOR), and (b) facilitated accurate determination of the hyperfine and quadrupole couplings of both nitrogens, which were used in combination with other experimental evidence to determine the most probable model for the defect.

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ELECTRON SPIN TRANSIENT NUTATION: A NEW APPROACH TO UNRAVEL COMPLICATED EPR SPECTRA

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In an electron spin transient nutation experiment, the nutation frequency is determined by the microwave field strength and the transition matrix element of the excited EPR line. Since in solid state EPR, the transition matrix elements are dependent on the magnetic parameters of the spin system, the nutation frequency is, in general, different for different EPR transitions. We illustrate by various examples, that the frequency dependence of the electron spin nutations may be used to disentangle overlapping spectra (see Figure), to influence the intensity ratio between allowed and forbidden transitions and to identify electron spin quantum numbers and electron spin transitions.

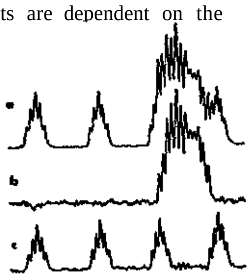

Figure: a) Two overlapping sites, b) site I, c) site II.

123 AN ENDOR AND ESEEM STUDY OF THE LIGAND HYPERFINE AND QUADRUPOLE INTERACTION IN $Fe(CN)_6^{3-}$ DILUTED IN A KCl LATTICE. Deming Wang, and E. de Boer. Department of Molecular Spectroscopy, University of Nijmegen, 6525 ED, Nijmegen, the Netherlands, (080)-612081.

A detailed study by ENDOR and ESEEM of the ligand hyperfine and quadrupole interaction in a transition-metal cyanide complex, $Fe(CN)_6^{3-}$, is presented. The complex was diluted in a KCl lattice. The study was carried out on the predominant center which is perturbed by two cation vacancies at the nearest cation sites. The electronic structure of the low-lying states of this center was obtained through a ligand field analysis of the measured g matrix ($g_x=2.079$, $g_y=3.054$, and $g_z=0.400$). It was found that the splitting of the low-lying states due to the presence of the cation vacancies is comparable with the spin-orbit coupling. A magnificent spin echo modulation due to the nitrogen nuclei has been observed. The combined ENDOR and ESEEM measurements revealed nearly all the coupling constants between the unpaired electron and the ^{13}C and ^{14}N nuclei. The principal values and the tensor orientations were precisely determined by a least-squares fitting. The general features shown in the obtained tensors are: (i) the principal axes of the hyperfine interaction tensor for ^{13}C coincide with that for ^{14}N; (ii) the coupling constants of ^{13}C are an order of magnitude larger than that of ^{14}N, and (iii) the quadrupole interaction of ^{14}N shows an axial symmetry while the hyperfine interaction demonstrates a highly orthorhombic character.

124 STRUCTURE AND CONFORMATION OF SPIN-LABELED METHYL *L*-PHENYLALANATE IN FROZEN SOLUTIONS BY ENDOR SPECTROSCOPY AND MOLECULAR MODELING. Heikki Joela[a], and Marvin W. Makinen. Department of Biochemistry and Molecular Biology, The University of Chicago, 920 East 58th Street, Chicago, Illinois 60637 U.S.A.

A series of deuterated and fluorinated derivatives of *L*-phenylalanine and methyl I-phenylalanate acylated at the amino nitrogen position with the nitroxyl spin-label 2,2,5,5-tetramethylpyrroline-1-oxyl-3-carboxylic acid were studied by ENDOR spectroscopy in frozen solutions of perdeuterated methanol or perdeuterated chloroform/toluene. Proton and fluorine ENDOR spectra were recorded at 20 K with 6-8 kHz modulation depth of the rf field For each class of nuclei, only two pairs of ENDOR features centered about the Larmor frequency were detected indicating axially symmetric hyperfine interactions. Electron-nucleus separations were calculated according to the point-dipole approximation under the constraint $(A_\parallel + 2A_\perp) - 3A_{iso}$. The ENDOR analysis yielded seven distance constraints with less than 5% uncertainties based on line widths. These constraints were used to assign molecular conformations through torsion angle search calculations carried out for a molecular model constructed from X-ray defined molecular fragments. The resulting structure was close to the ideal g^- rotamer (χ_1 *ca.* -75°) in methanol. In toluene/chloroform the value of χ_1 was ca. -100°. With the fluorine substituent in the *ortho* position of the phenyl side chain, two conformations were detected corresponding to values of +92° and -73° for y, due to the rotation around the C^β-C^γ bond. The structure of spin-labeled methyl-*L*-phenylalanate in methanol differed only slightly from that in toluene/chloroform and was closely similar to the structure of spin-labeled *L*-phenylalanine. (Supported by NIH AA06374). [a]Permanent address: Department of Chemistry, University of Jyvaskyla, Jyvaskyla Finland

125 PROTON ENDOR AND EPR SPECTRAL SIMULATIONS OF A NITROXYL RADICAL FORMED FROM N-2,4,6-TETRANITRO-N-METHYLANILINE

M. D. Pace[1] and R. Weber[2], [1]Code 6120, Naval Research Laboratory,
Washington, D. C., 20375-5000; [2]Bruker Instruments, Inc., Manning
Park, Billerica, Mass. 01821

N-2,4,6-tetranitro-N-methylaniline (tetryl), prepared by the nitration of dimethylaniline, has been used as an explosive since 1906. Because tetryl can be handled safely and detonated by a small amount of primer it is employed in blasting caps and detonating gains. The N-nitro group may be split off by 230nm light in either solution phase or solid phase to yield a nitroxyl radical. The solid-state radical is highly stable at room temperature with no evidence of decay even after several months. In addition, we have noticed low level concentrations of the nitroxyl radicals exist with no prior initiation. Understanding this remarkable free radical stability is important to the development of predictive models of sensitivity which include chemistry of the microcrystalline regime. In this study we present ENDOR spectra of the N-methyl proton couplings which show methyl group mobility at 140K and proton ENDOR at which is due either to small ring proton couplings or to matrix ENDOR signals. An EPR analysis of the complicated site-splitting of the crystal spectra will be presented with supporting spectral simulations.

126 SIMULTANEOUS ELECTROCHEMICAL - ELECTRON SPIN RESONANCE STUDIES OF CAROTENOID CATION RADICALS AND DICATIONS: DETECTION OF AN ELECTRON TRANSFER PROCESS by Mazen Khaled, Andreas Hadjipetrou and Lowell Kispert, Chemistry Department, University of Alabama, Tuscaloosa, AL 35487.

Carotenoids are present in the chloroplasts of photosynthetic green plants. They serve as photoprotect devices by preventing the formation of damaging singlet oxygen and act as antenna pigments for the absorption of light energy in the spectral region where chlorophyll is not an efficient absorber. It has also been suggested that carotenoids can play an active role in the photosynthetic electron-transport chain with the carotenoid cation radical as an integral part of the electron-transfer process. The carotenoid cation radicals have been prepared electrochemically and studied using simultaneous electrochemical - electron spin resonance methods. A single unresolved EPR peak was detected for the β-carotene cation radical with an apparent decay half-life of 1.4 minutes in a CH_2Cl_2 solvent. Upon deuteration, and in the presence of excess P-carotene, the apparent half-life increased an order of magnitude. The reason for this large isotope effect is due to the simultaneous formation of the carotenoid dication which reacts preferentially upon deuteration with excess P-carotene via electron transfer to form additional radical cations. Chronocoulometry measurements of a series of carotenoids showed the differences in lifetimes to be due to differences in the diffusion coefficients. Additional cathodic peaks were studied and will be described. This work was supported by the Division of Chemical Sciences, Office of Basic Energy Science, Department of Energy.

EPR DOSIMETRY FOLLOWING A RADIATION ACCIDENT. M. F. Desrosiers. National Institute of Standards and Technology, 245/C214, Gaithersburg, MD 20899

Recently, there was a serious radiological accident in a Central American industrial irradiation facility. Three workers received significant radiation exposures from a cobalt-60 radiation source resulting in the amputation of a leg from two workers. At the request of the Department of Energy sponsored Oak Ridge University medical team (REAC/TS), bone samples from three different sections of the legs were examined to measure directly the absorbed dose and map the exposure. Stable paramagnetic centers are produced in bone tissue exposed to ionizing radiation; electron paramagnetic resonance (EPR) spectrometry can be used to assess the concentration of these centers and thus the absorbed dose. The highest dose was to the extremities and was on the order of 60 gray. These results, which were reported to REAC/TS, demonstrate that bone tissue can be used as a biological indicator of absorbed radiation dose in the absence of a conventional personnel protection dosimeter.

128 NOVEL SPIN TRAPPING STUDIES OF NITROSOAMINE FREE RADICALS. M. F. Desrosiers and D. A. Wink. National Institute of Standards and Technology, 245/C214 Gaithersburg, MD 20899

In vivo and in vitro studies of nitrosamines have demonstrated that they will give metabolites which cause cancer. Chemical intermediates involved in the metabolic steps are difficult to verify due to the complexity of the biological system. We have examined the structure and reactivity of biologically relevant nitrosodimethylamine (NDMA) intermediates by ESR spin-trapping techniques and radiolysis. Radiolysis of NDMA in the presence of the spin trap dibromonitrosobenzenesulphonic acid (DBNBS) did not produce spin adducts of NDMA intermediates but gave unusual redox products of DBNBS. The reactions of hydroxy radical and biologically relevant free radicals with NDMA in the absence of DBNBS resulted in the formation dimethylnitroxide, which decayed by the release of a methyl radical. These results give insight into alternative modes of metabolism of NDMA. These basic measurements will be used to extrapolate to more complex model systems and ultimately to the in vivo chemistry.

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EPR MEASUREMENTS ON SOME MN^{2+} -DOPED TETRA ALKYLAMMONIUM COMPOUNDS * Sushil K. Misra, Concordia University, Montreal, Quebec, H3G 1M8, Michael O. Steinitz and Mojitaba Kahrizi, St. Francis Xavier University, Antigonish, Nova Scotia, Canada, B2G 1C0.

We report on the first X- band EPR measurements on Mn^{2+} -doped single crystals of tetra-alkylammnium compounds from room temperature to liquid nitrogen temperature. The spin Hamiltonian parameters are evaluated using least squares fitting procedures. Special attention is paid to the EPR transition lines in the vicinity of the phase transitions in these compounds. The temperature dependence of the zero field splitting parameters reveals the nature of the phase transitions.

Work supported in part by NSERC.

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EPR STUDIES OF DEMINERALIZED ARGONNE PREMIUM COALS. L. A. Gebhard*, B. G. Silbernagel*, R. A. Flowers+, J. W. Larsen*+ (*Exxon Research and Engineering Company, Route 22 East, Annandale, NJ 08801; +Department of Chemistry, Lehigh University, Bethlehem, PA 18018

Transition metal and carbon radical EPR have been used to study the effects of ion exchange and demineralization in Argonne Premium Coals. These experiments were occasioned by our recent survey of the Argonne Premium Coals, which suggested that mineral matter---and possibly organically complexed transition metal ions---were significantly affecting the EPR properties of the carbon radicals in the coal. Coal samples have been subjected to two procedures: (1) a citric acid wash (CAW), known to remove organically complexed ions, and (2) HCL/HF demineralization. Carbon radical g-values are not affected by these procedures but significant increases in the carbon radical density are observed and the radical linewidth decreases. We attribute these changes to the removal of minerals and transition metal ions from the coal. The only exception occurs in the case of demineralized Illinois #6 coal, where iron species---presumably from reagent attack on the pyrite minerals---remain behind after treatment.

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THE LOW TEMPERATURE OXIDATION OF ARGONNE PREMIUM COALS USING DYNAMIC, IN-SITU 9 GHz CW-EPR ARGONNE, J, Kudynska and H.A. Buckmaster. Dept. of Physics and Astronomy, The University of Calgary, Calgary, AB, Canada, T2N 1N4.

This paper describes the results obtained for the controlled *low* temperature oxidation of the eight Argonne premium coals. The methodology used enables this process to be studied for both dried and moisture saturated samples as they are treated by exposure to 200 ml/min dry air flow inside a 9 GHz TE_{011} cylindrical EPR sample cavity as the temperature is incremented in 5°C steps from 20°C to 150°C and 10°C steps from 150°C to 250°C. The 9 GHz CW-EPR spectra were measured during the last five minutes of the fifteen minute exposure to dry air flow at each temperature. The temperature dependence of the EPR spectral parameters (g-factor, linewidth, relative spin concentration and lineshape) of the different coals enables them to be classified according to rank. It is found that at least two distinct free radical species are present for all ranks and that the reactivity of one species plays a dominant role in characterizing the oxidation process.

132 9 AND 34 GHz CW-EPR STUDIES OF MANGANESE IMPURITY IONS IN AN ALBERTA hv BITUMINOUS COAL. Y-P. Zhang, J. Kudynska and H.A. Buckmaster, Dept. of Physics and Astronomy, The University of Calgary, Calgary, AB, Canada. T2N 1N4.

This poster reports what appears to be the first observation of a resolved hyperfine spectrum due to manganese ions in an Alberta hv bituminous coal. This spectrum has been observed using 9 and 34 GHz CW-EPR. It is very similar to the spectra observed at these frequencies by Bleaney and Rubins[1] for Mn^{2+} ions in clay at 20°C. The effect of dynamic in situ low temperature oxidation of dried and moisture saturated samples on the Mn^{2+} HFS spectrum has been studied in the temperature interval 20°C to 140°C and compared with the changes in the CW-EPR spectral parameters characterizing the free radical species. These measurements provide new insights into the role of minerals in the oxidation process.

[1] B. Bleaney and R.S. Rubins, Proc. Phys. Soc. 77, 103 (1961).

133 EXPERIMENTAL STUDIES OF RADIAL DIFFERENCE a_0d_0-ARGAND DIAGRAMMATIC LINESHAPE ANALYSIS, H.A. Buckmaster, T.H.T. van Kalleveen and S. Esfandabadi. Dept. of Physics and Astronomy, The University of Calgary, Calgary, AB, Canada, T2N 1N4.

This paper describes the results of an experimental study of the modulation broadening of the near Lorentzian lineshape of the EPR resonance for a powdered sample of DPPH and for conduction electrons in Li metal. The objective was to quantify the use of radial difference a_0d_0-Argand diagrammatic lineshape analysis as the first step towards modelling the lineshapes that result from the superposition of the resonances due to two free radicals with similar g-factors but different linewidths and spin concentrations. The observed linewidth distortion due to modulation broadening is correlated with the theoretical broadening in normalized units. The role that various experimental parameters including the phase of the EPR spectrometer microwave synchrodyne power has on the repeatibility of these diagrams is also studied. It is found that the phase must be adjusted and maintained to better than 0.5°C to obtain satisfactory diagrammatic fidelity.

134 EPR-ENDOR SPECTRA OF THE V_K CENTER IN SINGLE CRYSTALS OF KCl.
Y. N. Zhang and S. A. Marshall, Michigan Technological Univ., Houghton, Michigan 49931

The EPR-ENDOR spectra of the (Cl-Cl)$^-$ molecule-ion in single crystals of potassium chloride has been reinvestigated at X-band wave lengths. In particular, the ENDOR spectrum has been observed at 4.2 K and subsequently analysed using a computer code to avoid the possibility of computational errors. In addition to providing a set of somewhat more precise spectral data, a weak set of ENDOR spectral lines has bean observed. Such lines would ordinarilly be considered forbidden. That they are in fact observed is interpreted to be a consequence of a break in the nuclear wave functions' permutation symmetry. Such a break in symmetry suggests that the two nuclei are, in some manner, distinguishable. The purpose of this investigation is to determine the nature of the nuclear distinguishability

* This research performed under the auspices of the U.S. Office of Naval Research.

EPR SPECTRUM UF AG(I) AND AG(III) IN SINGLE CRYSTALS OF KF.*

Cheng Yu and S. A. Marshall, Michigan Technological Univ.,
Houghton, Michigan 49931

The electron paramagnetic resonance absorption spectra of both atomic and divalent silver contained in single crystals of potassium fluoride have been reinvestigated at X-band wavelengths. fit 4.2 K, each spectrum exhibits partially resolved superhyperfine structure due to silver electrons interacting with the six nearest neighbor fluoride ions. The high degree of resolution exhibited by these spectra is due in part to the large nuclear magnetic moment of fluorine and in part to the fact that the spectral lines are narrow compared to those of similar systems in other alkali halides crystals. For the Ag(I) hexafluoride, the cluster is cubic. However, for Ag(III), the cluster is tetragonally distorted with a 4-fold axis along a cube edge with one such set of distorted clusters for each cube edge. Such distortions are predicted the Jahn-Teller theorem.

This research performed under the auspices of the U.S. Office of Naval Research.

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136 ### AN CTRON PARAMAGNETIC RESONANCE STUDY OF POLYCRYSTALLINE TIN (IV) OXIDE DOPED WITH Cr(III) AND Fe(III) IONS.

Jeffrey C. Evans*, C. Ruth Owen and Christopher C. Rowlands. School of Pure and Applied Chemistry, U.W.C.C., PO Box 912, Cardiff, CF1 3TB. * Deceased

200ppm wt/wt transition metal ions have been doped onto polycrystalline tin (IV) oxide (SnO_2) and the effect of calcination temperature studied. It can be seen that the Cr(III) or Fe(III) ions migrate from the surface into the lattice. Cr(III) ions on calcination up to 600°C show an anisotropic signal at $g = 1.97$ corresponding to a surface Cr(V) peak. Above this temperature further signals develop, ranging from $g \simeq 1$ to $g \simeq 6$ and the signal at $g = 1.97$ disappears. These are associated with the migration of Cr(III) ions into the rutile SnO_2 lattice, taking up both interstitial and substitutional sites (S.L.Hou, Phys.Rev, 1967, 154, 2, 258). This is in contrast to Cr(III) doped TiO_2, where only substitutional sites are observed (J.C.Evans, J. of Mat. Sci., 1984, 4, 809). Similar experiments with Fe(III) ions show below 600°C, surface high spin Fe(III) ions are observed at $g = 4.3$ (R.Aasa, J. of Chem. Phys., 1970, 52, 8, 3919). Calcination above this temperature, results in the appearance of many more resonances. These are similar to those observed by Anufrienko,(Sov. Phys. Sol. State, 1971, 13, 8, 1971). Above 1000°C some of the resonances develop to a greater extent. This we explain by preferential doping into an interstitial site.

AN EPR-ENDOR STUDY OF THE PHOTODEGRADATION OF POLY(DIALKILSILANE)S IN SOLUTION.

137 Allan J. McKinley,[a] Takashi Karatsu,[a] Gregory M. Wallraff,[b] Ratnasabapathy Sooriyakumaran,[b] Robert D. Miller,[b] and Josef Michl.[a]
Center for Scructure and Reactivity, Department of Chemistry, The University of Texas at Austin, Austin, TX 78712-1167 and IBM Research Laboratories, Almaden Research Center, San Jose, CA 95120-6099.

The structure of the initial persistent radicals observed upon UV irradiation of poly(dialkylsilane)s, $(RR')Si_n$, in solution has been determined by EPR-ENDOR spectroscopy to be $-SiR_2-SiR-SiR_2-$. A mechanistic pathway is proposed to account for the formation of this radical. The temperature dependence of the EPR spectra has been modelled assuming restricted rotation of the central alkyl group.

[a] The University of Texas at Austin. [b] IBM Research Laboratories.

138 ESR STUDY OF ACTIVE COPPER SITES IN THE CuThO CATALYSTS. Antoine Abou Kais. Rafeh Bechara, Cossi Faustin Aissi, Michel Guelton and Jean-Pierre Bonnelle, Univ. des Sci. et Techn. de Lille I, Laboratoire de Catalyse, URA CNRS N" 402, Bât. C3, 59655 Villeneuve d'Ascq, France.

Copper-thorium oxide catalysts prepared by coprecipitation of the hydroxides and calcination in air up to 1073K have been extensively studied by means of Electron Spin Resonance (ESR) . For atomic ratios $Cu/Th < 0.01$, the CuThO oxides are monophasic systems with the thoria structure, the Cu^{2+} ions occupy substitutional S sites both in the bulk (S_b) and on the surface (S_s) of catalysts ; these species are not affected, even at high temperature (873K), by the hydrogen reduction. For higher copper content ($Cu/Th > 0.01$), the monophasic character of the solids disappears, the Cu^{2+} ions occupy sites only on the surface of CuThO : two monomeric species (M_1, M_2) and one Cu^{2+} ion pairs (D) ; these sites are easily reducible by hydrogen, in particular, these which are less surrounded by oxygen atoms number ; but in the case of copper (II) ion pairs, only one of both Cu^{2+} ions is accessible to the redox treatment whereas the other one which corresponds to Cu^{2+} ion in substitutional surface (S_s) site remains intact. During the cyclic redox treatment of CuThO, the additive formation of CuO crystallites on the surface were evidenced ; this formation is due to the migration of some Cu^{2+} ions from sites which are accessible to the redox treatment.

COBALT-59 NUCLEAR QUADRUPOLE AND LIGAND HYPERFINE COUPLING IN A LOW-SPIN SCHIFF'S BASE COMPLEX. F. S. Jiang, R. B. Clarkson, and R. L. Belford, Department of Chemistry and Illinois EPR Research Center, University of Illinois, 505 S. Mathews. Urbana. IL 61801, USA

Cobalt(II) Schiff's-base complexes are convenient models relevant to catalytic and biological sites. The literature reports few measurements of Co(II) nuclear quadrupole coupling constants. Here we report orientation-dependent single-crystal EPR spectra of a low-spin Co(II) complex with bis(benzoylacetone)ethylenediimine. The Co(II) complex is a substitutional guest in the corresponding Ni(II) diamagnetic host crystal. The crystal is monoclinic with 2 chemically identical but magnetically inequivalent sites. The g. A. and P matrices for the Co-59 sites are reported. In particular, the diagonal elements of the nuclear quadrupole coupling tensor are $P_x = -2.4$ MHz, $P = 2.0$ MHz. $P_z = -0.4$ MHz. Powder EPR spectra are consistent with the single-crystal analyses. Auxiliary proton ENDOR and N-14 ESEEM as well as solution proton NMR spectra were obtained. The Co(II) d^7 configuration $(x^2-y^2)^2(3z^2-r^2)^2(xz)^2(yz)^1$ is indicated.

140 EPR STUDY OF CONFORMATION IN $M(TBSQ)_2L_n$ COMPLEXES IN SOLUTION. Andrzej Ozarowski, Brace R. McGarvey, Clovis Peppe, and Dennis G. Tuck. Department of Chemistry and Biochemistry, University of Windsor, Windsor, Ontario N9B 3P4.

Compounds $M(TBSQ)_2$ (M = Mg, Zn, Cd, Ba) (TBSQ = 2,4-di-t-butyl orthosemiquinone anion) have been prepared. These compounds were dissolved in toluene and various amines added (pyridine, bipyridine, and tetramethyl ethylene diamine). Liquid solutions have EPR spectra typical of TBSQ free radical (S=1/2). Frozen solution spectra show one or more typical biradical (S=1) spectra. Analysis of spectra and theoretical calculations allow us to assign observed resonances to specific conformations of the complex.

141 ELDOR-ENDOR SPECTROSCOPY: PULSED ELECTRON NUCLEAR ELECTRON TRIPLE RESONANCE. M. Bernardo and H. Thomann; EXXON Corporate Research Laboratory, Annandale, NJ 08801.

Two dimensional pulsed electron nuclear electron triple resonance spectroscopy is demonstrated. Two EPR and one NMR transitions are irradiated by pulsed excitation. The advantages of the technique include the ability to resolve overlapping nuclear resonances and a direct assignment of electron nuclear hyperfine and nuclear quadrupole couplings. Applications on simple organic molecules in the solid state and to active sites in metalloenzymes and metalloproteins will be presented.

142 NO ABSTRACT AVAILABLE

143 ESR, NMR AND GC/MS ANALYSIS OF HALOCARBON METABOLISM BY RAT LIVER IN VITRO AND IN VIVO. Rheal A. Towner and Edward G. Janzen, MRI Facility, Ontario Veterinary College, University of Guelph, Guelph, Ontario, Canada. N1G 2W1

The mechanism of hepatotoxicity of CCl_4 and other structurally related halocarbons, such as $BrCCl_3$ or halothane ($CF_3CHClBr$), is thought to be a free radical mediated process leading to peroxidative decomposition of intracellular membrane structures and eventual cell necrosis. Magnetic resonance spectroscopy techniques, including electron spin resonance (ESR) and nuclear magnetic resonance (NMR) were used to study halocarbon-induced hepatic damage in rat liver both ***in** vitro* and *in vivo.* With the use of deuterated spin traps, particularly d_{14}-PBN (α-phenyl-*tert*-butyl nitrone), it is been possible to detect and characterize, by ESR spectroscopy, a number of different free radical intermediates from ***in** vitro* or ***in** vivo* metabolic activation of halocarbons by rat liver. The radicals detected from $^{13}CCl_4$ metabolism include the trichloromethyl radical ($\cdot CCl_3$), carbon-centered ($\cdot CH_2R$) and oxygen-centered ($\cdot \dot{O}R'$) lipid-type radicals, and a carbon dioxide radical anion ($\cdot CO_2^{\cdot}$). From halothane metabolism, a halothanyl radical, as well as lipid type CH_2R and OR' radicals were detected. Further structural characterization of deuterated PBN adducts of the CCl_3 and the $CHClCF^3$ radicals from the metabolism of CCl_4 or halothane, respectively, was obtained by gas chromatography/mass spectrometric (GC/MS) analysis. Acute intoxication of halocarbons in rat liver was also studied *in situ* with the use of ^1H-NMR imaging. Electron microscopy (EM) was used to confirm the halocarbon-induced morphological damage observed by NMR imaging. Pretreatment of rats with PBN, prior to halocarbon exposure, was found to reduce the halocarbon-induced edema.

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SPIN-TRAPPING STUDIES WITH ISOLATED HEPATOCYTES EXPOSED TO TOXIC AGENTS: ETHANOL, ACETALDEHYDE, AND HALOGENATED COMPOUNDS.

J. Lee Poyer, James M. Rau, Lester A. Reinke, and Paul B. McCay.
Oklahoma Medical Research Foundation, Okla. City, OK 73104.

Earlier studies in our laboratory had demonstrated the feasibility of using spin trapping agents to capture and detect free radical intermediates produced in the metabolism of toxic compounds and during radiation both in vivo and in vitro. In this report, we describe investigations using freshly-isolated liver cells in a supporting medium containing alpha-phenyl N-t-butylnitrone (PBN). CCl_4, $CCBr_4$, $CBrCl_3$, $CHBrCl_2$, or $CClBr_2$ (but not $CHCl_3$ and $CHBr_3$) are metabolized in this system yielding the $\cdot CO_2^-$ adduct of PBN. Inclusion of diethyl maleate in the reaction system abolished the production of the $\cdot CO_2^-$ adduct from all of the indicated halogenated hydrocarbons, suggesting that glutathione (GSH) or some other sulfhydryl function is required for this conversion. Studies in R. Mason's laboratory show that a novel intermediate requiring GSH is involved in the conversion of CCl_4 to the $\cdot CO_2^-$ adduct of PBN (Free Rad. Res. Communs. In Press). It is not known whether the role of GSH involves its reaction with the halocarbon radicals first and then with PBN, or if the PBN adduct of these halocarbon radicals reacts with GSH, followed by conversion of either product to $\cdot CO_2^-$ radical adducts. Studies on the metabolism of ethanol indicate that these adducts do not form (or do not survive) in intact rails.

1 5

REACTION OF GLUTATHIONE WITH A FREE RADICAL METABOLITE OF CARBON TETRACHLORIDE.

Henry D. Connor, Lynn B. LaCagnin, Kathryn T. Knecht, and Ronald P. Mason, (Laboratory of Molecular Biophysics, National Institute of Environmental Health Sciences, P.O. Box 12233, Research Triangle Park, N.C. 27709, Ronald G. Thurman, Department of Pharmacology, University of North Carolina, Chapel Hill, N.C. 27514

Carbon tetrachloride and bromotrichloromethane are both metabolized by hepatic enzymes In the presence of phenyl-N-t-butylnitrone (PBN) to the PBN/trichloromethyl (PBN/$\cdot CCl_3$) and the PBN/carbon dioxide anion (PBN/$\cdot CO_2^-$) radical adducts. The formation of the latter species in perfused liver has been found to be dependent on the hepatic glutathione concentration. In microsomal incubations the PBN/$\cdot CO_2^-$ radical adduct was detected only upon the addition of cytosol. In incubations containing PBN, CCl_4 , and GSH but no cytosol, a novel radical adduct has been detected instead. This GSH-dependent (PBN/[GSH-$\cdot CCl_3$]) radical adduct is derived from CCl_4 and may contain GSH. Stoichiometric and time course studies suggest that this adduct is converted to the PBN/$\cdot CO_2$ radical adduct by a cytosolic protein. These studies describe a novel free radical product of CCl_4, a GSH-dependent radical adduct, and thus suggest a role for GSH in the metabolism of CCl_4.

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SPIN TRAPPING OF FREE RADICALS FORMED DURING IN VITRO AND IN VIVO METABOLISM OF 3-METHYLINDOLE.

Tammy M. Bray and Stan Kubow. Dept. of Nutritional Sciences, University of Guelph, Guelph, Ontario, Canada N1G 2W1.

Electron spin-trapping techniques have been used to investigate the in vitro and in vivo formation of free radicals during 3MI metabolism by goat lung. A nitrogen-centered free radical of 3MI has been generated from 3MI in goat lung microsomal incubations. Although a nitrogen-centered free radical can be generated chemically from most of the indolic compounds, only the 3MI free radical can be generated enzymatically. The formation of the nitrogen-centered 3MI free radical was followed by the appearance of a carbon-centered lipid radical in microsomal preparations. The findings that an identical carbon-centered free radical was generated by $FeSO_4$ in the microsomal system in the absence of 3MI and that malonaldehyde formation is stimulated by 3MI in microsomes led to the conclusion that 3M1 metabolism induces lipid peroxidation of microsomal membranes. The formation of 3MI-induced lipid radicals was Inhibited by vitamin E and glutathione. A carbon-centered radical was spin trapped in vivo in the lungs of goats infused with 3MI. This radical had the same splitting constants as the carbon-centered lipid radical trapped in microsomal incubations containing 3MI. This finding indicates that the metabolism of 3MI in goat lung in vivo generates a lipid radical. When lung glutathione levels were depressed by pretreatment with diethylmaleate, tissue concentrations of the carbon-centered lipid radical were increased and 3MI-induced pulmonary toxicity became more severe. These studies support the hypothesis that free radicals are involved in 3MI-induced pneumotoxicity.

147 IN VIVO ESR SPIN-TRAPPING INVESTIGATIONS OF XENOBIOTIC METABOLISM BY RED BLOOD CELLS. Kirk R. Maples. Lovelace Inhalation Toxicology Research Institute, P.O. Box 5890, Albuquerque, New Mexico 87185.

The ESR spin-trapping technique was used to detect the in vivo formation of the 5,5-dimethyl-1-pyrroline-N-oxide/hemoglobin thiyl free radical adduct (DMPO/HbS*) in the blood of rats following the administration of xenobiotics. The first group of xenobiotics studied included phenylhydrazine, phenelzine, hydralazine, isoniazid, and iproniazid. Phenylhydrazine, phenelzine, and iproniazid reacted in vivo to yield DMPO/HbS*, while phenylhydrazine, phenelzine, and hydralazine reacted in vitro with red blood cells to yield this adduct. Isoniazid failed to induce the formation of DMPO/HbS* both in vivo and in vitro. The second group of xenobiotics studied included t-butyl hydroperoxide, cumene hydroperoxide, ethyl hydroperoxide, 2-butanone hydroperoxide, 15(s)-hydroperoxy-5,8,11,13-eicosatetraenoic acid, and hydrogen peroxide. All peroxides examined yielded DMPO/HbS* in vivo, as did those peroxides examined in vitro. The final group of xenobiotics studied included aniline, phenylhydroxylamine, nitrosobenzene, and nitrobenzene. All four compounds were able to induce DMPO/HbS* formation in vivo, but only phenylhydroxylamine and nitrosobenzene were able to induce DMPO/HbS* formation in vitro with red blood cells. Phenylhydroxylamine and nitrosobenzene also induced the formation of the 5,5-dimethyl-1-pyrroline-N-oxide/glutathiyl free radical adduct (DMPO/GS*) in vitro with red blood cells. Finally, in dialyzed hemoglobin solutions, phenylhydroxylamine was able to induce the formation of additional hemoglobin thiyl radical adducts other than that found with rats in vivo.

BILIARY RADICAL ADDUCTS OF CCl_4 AND ETHANOL. Ronald P. Mason and Kathryn T. Knecht. Laboratory of Molecular Biophysics, National Institute of Environmental Health Sciences, NIH, Research Triangle Park, NC 27709.

Our approach to *in vivo* spin trapping has been to examine biological fluids directly for spin adducts using the TM_{110} ESR cavity, which gives the largest possible aqueous sample size in the active region of the cavity (about 100 µl). No background signals other than the ascorbate semidione doublet and Mn^{2+} (only in bile) have been detected. The biological fluids are not extracted, and the difficult question of what happens during extraction other than a physical separation is avoided. This approach has been applied to radical adducts of free radical metabolites in urine, blood and bile. When this new approach was used with rats administered carbon tetrachloride and PBN, a novel radical adduct, $PBN/{}^{\bullet}CO_2^-$, was detected in the urine of rats treated with carbon tetrachloride and PBN. Both $PBN/{}^{\bullet}CO_2^-$ and $PBN/{}^{\bullet}CCl_3$ were detected in bile samples after treatment of rats with PBN intraperitoneally and carbon tetrachloride intragastrically. Free radical metabolism of ethanol has been suggested as a factor in its hepato-toxicity. We have detected the α-hydroxyethyl radical by spin trapping with 4-POBN in bile from alcohol dehydrogenase-deficient deermice administered [^{13}C]-ethanol. In addition, an ethanol-dependent but ^{13}C-invariant radical adduct, presumably lipid-derived, was detected. In principle, ionic, polar, and nonpolar radical adducts can be detected in bile because, in addition to the aqueous phase, the biliary micelles provide a hydrophobic environment.

149 AN EPR AND ODMR STUDY OF INTERCALATED LAYERED SEMICONDUCTOR LATTICES. E. Lifshitz, S. Sibley. A. H. Francis. Department of Chemistry. University of Michigan. Ann Arbor, MI 48109

Transition metal chalcogenides (MX_2, M=transition metal, X=S. Se) and phosphorus chalcogenides (MPS3) crystallize with a layered structure of the CdI_2 type. Because the layers are bonded only by relatively weak van der Waals forces, the lattices may be intercalated with a variety of organic and inorganic species. The intercalate enters the interstitial spaces between layers and may dramatically perturb the physical properties of the host lattice. The MPS_3 lattices also exhibit a unique cation exchange process In which lattice metal cations exchange with intercalate cations.

EPR spectroscopy and ODMR spectroscopy has played an important role in understanding the details of both the mechanism of intercalation and the cation exchange process. The uptake of a variety of paramagnetic transition metal ions by the host lattice can be followed by EPR. Analysis of the EPR results provides a detailed view of the sites occupied by the intercalate species and the dynamics of intercalate motion. ODMR spectroscopy has been of great value in identifying characteristic lattice defects in the MPX_3 materials that play a critical role in the solid-state chemistry of these materials. The applications of both techniques to the study of these materials will be discussed.

150 RADIATION INDUCED DEFECTS IN AMORPHOUS SILICON DIOXIDE: KINETICS OF DEFECT GROWTH. David B. Kerwin and Frank L. Galeener, Colorado State University, Department of Physics, Fort Collins, Colorado 80523.

Recent experiments on the energy dependence of defect formation in x-irradiated amorphous silicon dioxide have indicated that the primary mechanism for defect formation involves the inelastic scattering of energetic secondary electrons in the SiO_2 network. Data on the growth of the E' center and the two oxygen hole centers with x-ray dose will be presented for silicas containing high (1200 ppm) and low concentrations of hydroxyl groups which have been prepared with various fictive temperatures. Kinetic schemes consistent with the above mechanism will be presented, and generalized to ^{60}Co gamma-irradiated silicas.

15 INCLUSION COMPLEX FORMATION OF SURFACE IMMOBILIZED CYCLODEXTRINS USING THE SPIN PROBE METHOD, Angela Hooper, Michael P. Eastman*, and Robert G. Kooser, Knox College, Galesburg, IL 61401

Cyclodextrins bonded to silica (Cyclobond) have been widely used as the stationary phase in liquid chromatographic separations. While inclusion complexes formed by free cyclodextrins in solution have been studied by a wide variety of techniques including spin probes, little is known about complex formation under the conditions found in a chromatographic separation. Various bonded cyclodextrins, differing in the cavity size, have been investigated by Electron Paramagnetic Resonance (EPR) methods under solvent flow conditions using a variety of spin probes (4 piperidine-N-oxyl derivatives and ditertiary butyl nitroxide). In the case of Cyclobond III (alpha-cyclodextrin) there is no evidence for inclusion complex formation, although there is strong EPR evidence for surface association that explains observed chromatographic behavior. On the other hand, in the Cyclobond I case (beta-cyclodextrin), there is good EPR evidence for inclusion complex formation and based on EPR spectral changes with differing solvent compositions, it is possible to assign the geometry of the inclusion complex. For instance, in the TEMPO case, the probe inserts with the nitroxide group pointing out of the cavity, while the other members of the probe family show the opposite type of insertion. Comparisons will be drawn with free solution cyclodextrin complexes as determined by previous investigations.

FIRST OBSERVATION OF PARAMAGNETIC NITROGEN DANGLING BOND CENTERS
IN SILICON NITRIDE

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We report the first observation of nitrogen dangling bonds in silicon nitride. A computer analysis of the ^{14}N hyperfine parameters shows that the unpaired electron is strongly localized on the central nitrogen atom and that the unpaired electron's wavefunction is almost entirely p in character. This is only the second fundamental intrinsic electron paramagentic resonance center to be observed in silicon nitride. The charge state of this point defect shall also be addressed.

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AN ELECTRON NUCLEAR DOUBLE RESONANCE AND ELECTRON SPIN RESONANCE STUDY OF SILICON DANGLIN BOND CENTERS IN SILICON NITRIDE. William L. Warren and Patrick M. Lenahan, The Pennsylvania State University, University Park, PA 16802

We report the first observation of second nearest neighbor hyperfine interactions with an unpaired electron on silicon dangling bond center, K centers, in silicon nitride. We observe this interaction using electron nuclear double resonance (ENDOR) spectroscopy. Our results indicate that the unpaired electron's wave function is one to three percent localized each on nitrogen atom bonded to the central silicon atom. We find that the second neighbor nitrogen hyperfine coupling constant is 4.6G. Combining our ^{14}N ENDOR results with a computer analysis of ^{29}Si hyperfine spectra obtained in standard electron spin resonance measurements, we find that the unpaired electron is approximately 70 percent localized on the central silicon atom. We also find that the g tensor of the K center exhibits very little anisotropy. Our results unambiguously demonstrate that the K center defects are silicons bonded to nitrogen atoms with the unpaired spin density primarily on the silicon. This result is of some importance since these centers appear to be the dominant deep electron and hole trapping center in a rather wide variety of silicon nitride films.

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A ^{29}Si HYPERFINE STUDY OF P_b AND E* CENTERS AT AND NEAR THE Si/SiO$_2$ INTERFACE. Mark A. Jupina and Patrick M. Lenahan, Pennsylvania State University, University Park, PA 16802.

Semiconductor interfaces, particularly the silicon dioxide / silicon interface, play an extremely important role in modern microelectronic technology. This is because the dominant device of modern microelectronics is the metal-oxide-semiconductor field effect transistor (MOSFET). The amorphous silicon dioxide films and their interface with the crystalline silicon substrates are susceptible to several poorly understood instabilities which are quite technologically important. Among the most important instabilities are those caused by exposure to the ionizing radiation of outer space, X-ray and e-beam lithography, hot carrier injection in small geometry devices, and high electric field injection in thin oxide devices. Previous electrical characterization and electron spin resonance studies have determined that two trivalent silicon point defects, P_b centers and E' centers, play important roles in these instabilities. A Si hyperfine study of these centers in MOSFETs by a more sensitive characteriation technique, known as spin dependent recombination, will be presented.

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AN EFFICIENT SEMIANALYTICAL METHOD OF SIMULATION OF EPR POWDER PATTERNS AND SPECTRA. *L.* Gonzālez-Tovany. Instituto Nacional de Investigaciones Nucleares, Mexico, and V. Beltran-Lopez, Instituto de Ciencias Nucleares, Universidad Nacional Autōnoma de Mexico (UNAM), Circuito Exterior, C.U., Mexico, D.F., Mēxico.

Numerical Gaussian quadrature of the single-variable integral arising in an analytical method developed by Beltrān-Lōpez and Castro-Tello is a very efficient semianalytical method for calculating powder patterns, requiring only a few seconds of CPU - time. Direct application of the analytical method to ions in axial and cubic crystal fields yields excellent results, but it meets convergence problems in a general orthorhombic field. The semianalytical method applies equally well to this symmetry yielding precise and reliable powder patterns and simulated spectra. A new type of spectral feature resembling a divergence is clearly shown to exist near the value $\eta = \sqrt{2/3}$ of the asymmetry parameter. The applicability of the semianalytical method to other symmetries is discussed.

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LINESHPES OF EPR SPECTRA OF POLYIMIDE RESINS. Myong K. Ahn, Thomas C. Stringfellow, and Matthew J. Fasano. Indiana State University, Terre Haute, Indiana 47809, and Kenneth J. Bowles, Michael A. Meador, NASA Lewis Research Center, Cleveland, Ohio 44135.

Thermosetting polyimides have been commonly used as matrix resins in fabricating thermally stable carbon fiber composites. After they are produced in chemical reactions in two steps, the polymer is further post-cured at an elevated temperature above 300°C. The resin, thus produced, is amorphous, highly crosslinked and insoluble. Although the chemical structure of the material is expected to be diamagnetic, it is found to produce EPR spectra that depend on the temperature and the the post-curing conditions. The near free electron g-value and the narrow widths of 0.7 mT of these absorption peaks suggest that the paramagnetism is associated with the imide linkages. The EPR lineshapes will be discussed in terms of the Gaussian-Lorentzian convolution.

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AN AUTOMATED METHOD FOR IDENTIFICATION AND QUANTITATION OF FREE RADICALS AND PARAMAGNETIC CENTERS FROM COMPLEX MULTI-COMPONENT EPR SPECTRA. Periannan Kuppusamy and Jay L. Zweier. The EPR Laboratories, Division of Cardiology, Johns Hopkins Medical Institutions, 301 Bayview Blvd, Baltimore, Maryland 21224.

The advent of digital computers has had a tremendous impact on the ability to acquire, analyze and interpret EPR data. Data acquisition with fast real time analog-to-digital conversion enables one to acquire and store the data in digital form which makes the post-processing of the data faster, easier and more precise. The primary part of analysis includes identification of the structure of the spectrum with the determination of the spin Hamiltonian parameters. Though this may be trivial and simple in many cases, it becomes exceedingly difficult and challenging when dealing with multi-line or complex spectra. In addition to identifying the structure of the spectrum it is often important to extract quantitative information regarding the amount of a given paramagnetic center or mixture of centers. We have developed a comprehensive generalized program to analyze and obtain quantitative information from EPR spectral data using desk-top computers. The program consists of several routines including isotropic and anisotropic component simulation, computerized auto-simulation for component optimization, multi-component filling, and quantitation. This type of analysis is shown to be suitable for routine studies of EPR spectra of free radicals and paramagnetic centers, providing reliable and accurate analysis and quantitation in a variety of biological and chemical applications.

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EPRFIT: A COMPUTER MODELING PACKAGE FOR THE SIMULATION OF ISOTROPIC EPR SPECTRA INCLUDING INTRAMOLECULAR EXCHANGE-BROADENING. IBM-AT COMPATIBLE COMPUTER VERSION 1.00. Joseph A. Menapace. Frank J. Seiler Research Laboratory (AFSC), United States Air Force Academy, Colorado 80840-6528.

EPRFIT is a computerized modeling package which simulates isotropic EPR spectra. The package performs both first and second order spectral simulations of both single configuration spin species and exchange-broadened species containing up to seven exchanging configurations. The program simulates spectra composed of up to 2000 individual lines and up to 14 distinct spin species with nuclear spins within the range of 0-9.5 G. Data entry is conducted using a spreadsheet type architecture which provides the user with easy access to data inspection and editing. Simulation data, simulated spectra, and experimental spectrum comparison files can be retrieved and stored from/to hard/floppy disc storage media in either ASCII or packed formats. The simulated and comparison spectra can also be displayed and analyzed graphically within the program. Spectral analysis options include spectrum offsetting, panning, zooming, and peak position and intensity characterization routines. These operations apply to both the simulated and comparison spectra. Hardcopies of the simulation results and spectra can be printed onto an IBM-Proprinter or Epson dot matrix printers for future reference or presentation.

159 On the future of epr SPECTROSCOPY

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The need for recommendations for EPR nomenclature and conventions pertaining to spectra of systems with spin S >1/2 is argued. The existing "Recommendations" 1H. Kon, Chem.Int. 9, 71 (1987)1 pertaining only to systems with S=1/2 are reviewed. Various aspects of EPR spectroscopy of TM and RE ions with spin S>1/2 requiring a unified approach, not considered hitherto, are summarized. This includes EC. Rudowicz, Mag.Res.Rev. 13, 1 (1987)] : (1) definitions of basic notions, (2) confusion of relationships between ZFS Hamiltonian and other Hamiltonians, (3) convention for the axis systems, (4) notations for the operators and parameters used in spin Hamiltonian, and (5) units for the ZFS parameters. The scope of the future comprehensive recommendations is outlined. The present usage of various notations in the literature is critically surveyed. It is argued that one well-defined notation for spin Hamiltonian should be internationally accepted. This is a prerequisite for more efficient application of computers in future EPR studies. Specific proposals in the three areas of application of computers are formulated, namely, (1) package of computer programmes for analysis, simulation and fitting EPR spectra, (2) computerized database of EPR-related information, and (3) communication network. Possible strategy to achieve these goals is discussed.

160 TEMPERATURE DEPENDENCE OF THE BENZYL HYDROGEN HYPERFINE SPLITTING IN EPR SPECTRA OF THE 3,5–DINITROPHENYL BENZYL NITROXIDE RADICAL BETWEEN 195 AND 290 KELVINS.

Joseph A. Menapace, John E. Marlin, and Greg E. Godec. Frank J. Seiler Research Laboratory (AFSC), United States Air Force Academy, Colorado 80840-6528.

ESR spectra of the 3,5–dinitrophenyl benzyl nitroxide radical obtained by photolysis of trinitrobenzene in toluene between 195 and 290 K exhibit a temperature dependence involving the benzyl hydrogens adjacent to the nitroxide functionality. The temperature dependence is attributed to hindered rotation of the benzyl subunit with respect to 3,5–dinitrophenyl nitroxide moiety. Two conformations are present in the radicals which arise from barriers to internal rotation due to the eclipsing of the benzyl group and the nitroxide oxygen and the eclipsing of the benzyl and 3,5-dinitrophenyl groups. The conformations are such that the benzyl subunit is nearly situated 90° from the nitroxide oxygen. At temperatures below 230 K, the benzyl hydrogen contributions to the EPR spectra show that the hydrogens are magnetically inequivalent with the exchange rates between the nonequivalent sites being slow enough that averaging of the hyperfine splitting does not take place. At higher temperatures, the rotation about the C-N bond becomes fast enough that the exchange rates average the hyperfine splittings to a magnetically equivalent value. Semi–empirical computational (MNDO/PM3) of the potential surface governing this motion suggests that the barrier heights involved are about 3 kcal/mol and 6 kcal/mol for the benzyl/nitroxide oxygen and the benzyl/3,5–dinitrophenyl eclipsing, respectively.

161 $[Cr(V)O(EHBA)_2]$ LIGAND EXCHANGE AT CALCIUM SITES ON THE SARCOPLASMIC RETICULUM ATPase.

Carol Coan and Ji-Ying Ji, University of the Pacific, San Francisco, CA 94115.

Bis(2-ethyl-2-hydroxybutanoato(2-))oxo-chromate(V) is moderately stable in aqueous solution and has been shown to exchange organic ligands (Farell, Judd, and Lay, Procd. of the Seventh Australian Electrochemistry Conference, 1988, 233). The similarity of the Cr=O moiety to vanadyl suggested that this complex may be able to exchange ligands at metal binding sites, particularly Ca^{2+} sites, on proteins. We found $[CrO(EHBA)_2]^-$ to be sufficiently stable at neutral pH for ligand exchange at the Ca^{2+} transport sites of the SR ATPase. Slow hydrolysis of the bound Cr(V) ($t_{1/2}$ = 30 min) allowed for most biochemical procedures. The stoichiometry was determined to be 2[Cr(V)] per ATPase, with no evidence of additional binding at higher $[CrO(EHBA)_2]^-$ to ATPase ratios. $[CrO(EHBA)_2]^-$ competed with Ca^{2+} for high affinity sites on the enzyme, prevented Ca^{2+} dependent enzyme activation, but did not compete for Mg^{2+} sites. The EPR spectrum of the CrO·enzyme complex exhibited three major bands at g = 1.9792, which were distinct from the singular band of $[CrO(EHBA_2]^-$ at g = 1.9784. The splitting is probably due to CH_2 groups adjacent to those (i.e. carbonyls) which bind directly to the Cr=O moiety.

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GENERATION OF SUPEROXIDE ANION RADICAL IN CHOLESTEROL OXIDASE RAECTION. Masaru Sonoda, Toshiroh Hanada, Yasushi Nakajima and Yoshikatsu Sakagishi. Dept. of Biochem. Saitama Med. School. 38 Moro-Hongo, Moroyama, Iruma-Gun, Saitama, Japan 350-04.

Many oxidative enzymes such as xanthine oxidase generate immediately superoxide anion radical($O_2^{-}\cdot$), whereas hydrogen peroxide (H_2O_2) is produced in the reactions of cholesterol oxidase and glucose oxidase because any cytochrome c or nitroblue tetrazolium reduction does not occur.

We have pursued on the $O_2^{-}\cdot$ generation mechanism in those enzyme reactions with the DMPO (5,5-dimethyl-1-pyrroline-N-oxide) spin-trapping ESR technique and the reduction method of nitroblue tetrazolium or cytochrome c in the presence of reduced glutathione (GSH) and horseradish peroxidase(POD).

In this paper, we hope to discuss on the mechanism of superoxide and glutathione thiyl radical generation in cholesterol oxidase system, comparing with those obtained from xanthine oxidase-GSH-POD system.

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ESR STUDIES OF ASCORBATE METABOLISM IN THE HUMAN ERYTHROCYTE. Rolf J. Mehlhorn. Lawrence Berkeley Laboratory. Berkeley, CA 94720.

A new assay for ascorbic acid, based on ESR measurements of reduction rates of cationic nitroxides (dimethyl and trimethyl Tempamine) has been developed. It is accurate, relatively free of artifacts, requires only a few minutes, and is suitable for intact cells. The assay was used to demonstrate that dehydroascorbic acid (DHA) is reduced to ascorbic acid more rapidly in the human erythrocyte than by the chemical reaction with glutathione in buffer. Nitroxide reduction in the erythrocyte is entirely due to ascorbate as demonstrated by inhibition of the reduction by ascorbic acid oxidase in hemolysates and lack of reduction in ascorbate-depleted cells. A novel procedure for depleting cells of ascorbate was developed consisting of washing them in the presence of an excess of the membrane-permeable cationic nitroxide. This made it possible to treat cells with low concentrations of DHA, which gave the most dramatic stimulation of reduction rates relative to the chemical process. Nitroxide reduction was transiently inhibited by tert-butyl hydroperoxide, implying that one of the major toxicity mechanisms of hydroperoxides may be loss of free radical scavenging due to glutathione oxidation by the selenium-dependent glutathione peroxidase. Several equivalents of nitroxide were reduced relative to the ascorbate content of cells even after hydroperoxide treatment. Thus ascorbate metabolism provides for sustained free radical scavenging in the erythrocyte.

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METABOLISM OF NITROXIDES BY MOUSE LYMPHOCYTES by Philip D. Morse II. Joann M. Petruszak, and Lauren Reminger. Department of Chemistry, Illinois State University, Normal IL 61761.

Understanding the metabolism of nitroxides is important for their use as contrast agents for magnetic resonance imaging as well as for biophysical studies of structural and functional relationships in complex systems. It is our general aim to study the interaction between nitroxides and cells of the immune system. We have begun this study with lymphocytes. The metabolism of three types of nitroxides were studied; charged nitroxides which cannot enter lymphocytes, uncharged nitroxides which enter the lymphocytes relatively rapidly and ionized nitroxides which enter the lymphocytes slowly. We found that nitroxides which enter lymphocytes were reduced in the order: positively charged > uncharged > negatively charged. Charged nitroxides which could not enter the lymphocytes were reduced most slowly. Piperidine nitroxides were reduced more rapidly than equivalent pyrrolidine nitroxides. Preliminary results show that the reduction of the nitroxide TEMPOL is most sensitive to oxygen concentration in the sample and the age of the mice from which the lymphocytes are derived.

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ATP BINDING TO BOVINE SERUM ALBUMIN (BSA)

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BSA is often employed as an inert additive to enhance the stability of proteins in dilute solutions. In the course of ATP-binding studies with, e.g., F_1ATPase, Ca ATPase and the uncoupling protein employing spin-labeled (SL) derivatives of ATP, we observed highly immobilized spectral components in the presence of BSA typical of protein-bound species. This bound component could be liberated by the addition of ATP or ADP. The spin label itself, e.g., Tempamine, did not bind to BSA. Detailed binding studies using C8-SL-ATP yielded a K_D of about 50 μM. A better fit of the data was obtained by allowing for two different binding sites, however, within a dimer (3 μM and 500 μM). The binding constant was hardly affected by the location of the spin label, i.e., the C8, N or 3' position of adenosine. Binding of SL-AMP was found to be considerably weaker (about one order of magnitude).

This finding may have considerable implication on the interpretation of ATP-binding data from many laboratories whenever BSA was used to stabilize the respective proteins.

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USE OF DOXYL-STEARIC ACID PROBES TO MONITOR CHANGES IN PLASMA MEMBRANE FLUIDITY FOLLOWING INITIATION OF THE FIRST MEIOTIC DIVISION IN RANA OOCYTES.

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We find that stearic acid probes containing the nitroxide (DOXYL) free radical in either the 5, 7, 10, 12 or 16 position are quickly taken up by the intact *Rana* oocyte. More than 95% of the probe is associated with the plasma membrane. After a 15 min exposure to DOXYL-stearic acid in Ringers solution, the plasma-vitelline membrane complex is isolated in isotonic sucrose. Ten-15 membranes are placed in a quartz cavity chamber, and the order parameter is measured using ESR. Hormones that initiate the meiotic divisions (progesterone, insulin) result to a dose-dependent increase in the order parameter (decrease in fluidity) when added either to intact oocytes or to the isolated membranes. Fluidity changes occur within minutes with probes that measure order nearest the membrane surface (5-DOXYL) and increase more slowly with probes (12- or 16-DOXYL) that monitor fluidity deeper within the plasma membrane. Cyclic AMP, which maintains the oocyte in prophase arrest under physiological conditions, produces an increase in membrane fluidity near the membrane surface and blocks and/or reverses the effects of progesterone on membrane order. Cholera toxin, which elevates intracellular cAMP and blocks meiosis, also increases membrane fluidity and inhibits the effect of progesterone. The hormone-induced fluidity changes appear to be essential for initiation of cell division and coincide with an increase in phospholipid N-methylation followed by a release of diacylglycerol from phosphatidylcholine. Supported in part by NIH grants DK 15056, AM 32030 and HD-10463.

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3 mm-HIGH-FIELD EPR ON DONOR AND ACCEPTOR RADICAL IONS RELATED TO PHOTOSYNTHESIS.

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The primary processes of light-induced charge separation in photosynthesis involve several electron transfer steps between pigment molecules in the reaction center (RC):

$$PIQ \xrightarrow{h\nu} P^*IQ \xrightarrow{3ps} P^+I^-Q \xrightarrow{200ps} P^+IQ^-$$

In bacterial photosynthesis P stands for a bacteriochlorophyll dimer, I for a bacteriopheophytin, and Q for a quinone (ubiquinone in Rb. sphaer., menaquinone in Rps. viridis). In frozen RC solutions the radical ions are highly immobilized resulting in broad EPR spectra from which, by conventional X-band EPR experiments, no anisotropic interactions (g and hyperfine tensors) can be resolved. At high magnetic fields, however, efficient magnetoselection via anisotropic Zeeman interactions occurs by which g tensor components (in favorable cases also hf tensor components) become measurable. We have performed high-field EPR experiments (W-band, 95 GHz) on a series of model quinone anions and on P^+ and Q^- in bacterial RC's. The results will be discussed with respect to the structure of the pigment mole-

168 W-BAND EPR OF VARIOUS SYNTHETIC MELANINS: IDENTIFICATION AND DIFFERENTIATION. W. Wang, M. J. Nilges, S. Enochs, P. Gast, R. B. Clarkson, T. Walczak, H. M. Swartz, T. Sarna, and R. L. Belford. Department of Chemistry and Illinois EPR Research Center, University of Illinois, 505 S. Mathews, Urbana, IL 61801, USA

Melanins are heterogeneous biological polymers responsible for pigmentation in animals. They are difficult to study by most spectroscopic approaches, yet they contain stable free radicals detectable by electron paramagnetic resonance. The number of free radicals has been found to increase at high pH or in the presence of non-paramagnetic metal ions. These induced or extrinsic radicals have been identified as chelatable anionic o-semiquinone free radicals, but the nature of the intrinsic radicals which are dominant at neutral and low pH is still unknown. At the usual EPR operating frequency, 9 GHz, the EPR spectra of melanins lack spectral definition. For this reason, we have obtained W band (94 GHz) spectra of synthetic melanins produced from dopa, dopamine, and catechol as well as a pigment produced by oxidation of minocycline. The spectra show dramatic differences as functions not only of pH, but also of the starting monomer. The spectra at pH less than 7 show marked differences, while those at pH greater than 11 show only subtle differences. Thus high-frequency EPR is better able to probe the intrinsic, lower-pH radicals providing ready differentiation between melanins based upon different subunits.

169 ON THE MOTIONAL PROCESSES IN THE ULTRA SLOW MOTIONAL REGIME, STUDIED BY SATURATION RECOVERY EPR AND PULSED ELDOR. D. Haas, R. StDenis, C. Mailer, B.H. Robinson, Department of Chemistry, University of Washington, Seattle, WA 98195

Saturation recovery EPR and Pulsed ELDOR (Electron Nuclear Double Resonance) are two techniques used to obtain direct dynamic information on molecular motional rates slower than 1 MHz. The SR signal for spin labels--randomly oriented in solution-is a multiple exponential decay; the rates of decay of the different components provide information on the molecular dynamics, as well as the nuclear and electronic spin-lattice relaxation rates. We have examined several model systems under a variety of spectrometer conditions, and have used several different methods of data analysis to estimate the multiexponential nature of the recovery curves. We will present data for TEMPOL (in glycerol) as a function of rotational correlation time, and compare experimental and theoretical results. Comparison is made to the linear and ST EPR spectra analyzed by lineshape simulations. We will also compare the results of SR EPR with Pulsed ELDOR in terms of ability to distinguish among different components of the recovery curves and in particular distinguish between secular and pseudosecular effects.

170 AN ESEEM SEQUENCE WITH AN IMPROVED MODULATION DEPTH
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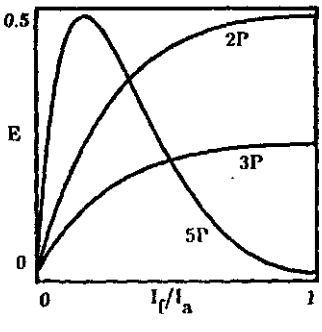
The 5–pulse electron spin echo sequence $(\pi/2)_y-\tau_1-\pi_y-\tau_1-(\pi/2)_x-T-(\pi/2)_x-\tau_2-\pi_x-\tau_2$ is introduced. In most practical cases it generates an ESEEM pattern with larger modulation amplitudes than the one observed in conventional ESEEM schemes. Since nuclear spin coherence evolves during the variable time T, the modulation pattern decays with T_1 and contains only the nuclear transition frequencies. The maximum modulation amplitudes for the 2–pulse, 3-pulse and 5-pulse ESEEM experiment (relative to the amplitude of the unmodulated 2–pulse echo) as a function of the forbidden–to–allowed transition probability ratio are shown in the figure. For a proper choise of τ_1 and τ_2, the 5-pulse echo contains no zero frequency contribution and the maximum modulation depth is already reached at $I_f/I_a = 0.17$. For $I_f/I_a \longrightarrow 0$, the modulation amplitude of the 5-pulse experiment is up to a *factor of eight* larger than in the corresponding 3-pulse experiment.



171 AN ESEEM STUDY OF Cu(II) BINDING TO CHIRAL BIOMIMETIC LIGANDS.

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In an attempt to provide models for copper binding in proteins, symmetric and nonsymmetric chiral ligands (1-3) designed to bind copper in a controlled geometry were synthesized. These ligands are assembled from trifunctional anchors extended by donors containing amino acids such as His and Met.

The copper coordination was studied by orientation selective electron spin echo envelope modulation (ESEEM) experiments. The three-pulse FT-ESEEM spectra of all three complexes consist of peaks at 0.7,1.4,2.1 and 3.0 MHz which positions are practically magnetic field independent, and a peak at about 4 MHz which show significant field dependence. The relative intensities of all lines do vary with with the field. These lines are typical of the remote nitrogen in the imidazole ring. Complexes 1 and 2 have similar ESR and ESEEM spectra indicating that the ancohoring nitrogen in 1 is not coordinated to the copper.

Using computer simulations of the FT-ESEEM spectra recorded at the various field positions along the powder pattern, taking into account the selected excited orientations, some of the ^{14}N hyperfine and quadrupole tensores parameters were determined. From these parameters geometrical information concerning the binding site was obtained.

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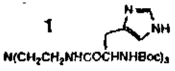

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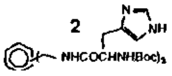

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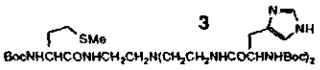

172 FORMATIO OF NE COPPER(II) SPECIES DURING PROPYLENE OXIDATION ON COPPER(II)-EXCHANGED X ZEOLITE.

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University of Houston, Houston, Texas 77204-5641.

The migration of copper(II) species and their coordination complexes in the zeolite framework was investigated during propylene oxidation on CuK-X zeolite in a flow system under conditions of excess oxygen and correlated with the reactivity over the temperature range of 100 to 400 °C. Electron spin resonance (ESR) and electron spin echo modulation (ESEM) are used to monitor the different Cu(II) species generated, their stereochemistry, their site locations, their migration and their coordination during the reaction in K-X zeolite. The development of three new Cu(II) species has been observed by ESR during the reaction depending upon the reaction temperature. One new cupric ion species developed at relatively low reaction temperature is assigned to a copper(II)-CO_2 complex in site SII* in the β-cage. At higher reaction temperature, the development of another new cupric ion species with $g_\perp > g_\parallel$ is assigned to a trigonal bipyramidal cupric ion in site SII between the a and B-cages. This cupric ion coordinates to two hydroxyl groups and three zeolite framework oxygens to give a $Cu(O_2)(OH)_2$ complex. This species is best developed in the reaction temperature range corresponding to 20 to AO % propylene conversion. A third Cu(II) species developed at still higher reaction temperature is suggested to be a copper(II)-C03 complex in site SII* in the α-cage based on CO_2 adsorption experiments and ESEM analysis.

173 INTRAMOLECULAR EFFECT OF CU(II) AND CO(II) ON NITROXYL RELAXATION TIMES,

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A series of spin-labeled pyridines were coordinated to copper(II) bis(hexafluoroacetylacetonate) and to cobalt(II) tetra(p-trifluoromethyl)phenylporphyrin. The exchange and dipolar contributions to the electron-electron spin-spin interaction were determined by computer simulation of resolved splittings In the CW EPR spectra. The metal and nitroxyl T_1 values were determined by saturation recovery measurements and the corresponding T_2 values were determined by spin echo measurements between 6 K and 120 K. The temperature dependence of the effect of the rapidly relaxing metal on the nitroxyl relaxation paralleled the temperature dependence of the metal T_2 except that at lower temperatures the effect of the metal on the nitroxyl relaxation was limited by the metal T_1. The shapes of the saturation recovery curves for the nitroxyl signals were simulated using the known metal g- and A-values and the spin-spin interaction parameters obtained from the CW spectra.

174 NITROXYL T AND T_2 VALUES IN SPIN-LABELED IRON(III) TETRAPHENYLPORPHYRINS.

Margaret H. Rakowsky, Kundalika M. More, Alexander V. Kulikov, Sandra S. Eaton, Gareth R. Eaton. Department of Chemistry, University of Denver, Denver, CO 80208.

A series of iron(III) tetraphenylporphyrins with a nitroxyl spin label attached to the pyrrole ring and their corresponding compounds without metal and/or spin label have been synthesized and studied by EPR and NMR. The effect of the linkage in the side chain, either saturated or unsaturated with *cis* or *trans* geometry, on the nitroxyl-metal spin-spin interaction under varying conditions will be reported. T_1 *and* T_2 from above room temperature to liquid helium temperature were determined by pulsed EPR. The effect of the axial ligand, which causes the iron(III) to be either high spin (S - 5/2) or low spin (S - 1/2), on the nitroxyl-iron(III) spin-spin interaction will also be discussed.

175 PORTABLE ESR SPECTROMETER USING PERMANENT MAGNET CIRCUIT.

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Recently ESR spectrometer is frequently used for the radiation dosimeter and dating etc. We develop the very small size and low cost ESR spectrometer using a permanent magnet circuit. The rare earth permanent magnet "NEOMAX" which our company developed and has produced is enable to obtain the high magnetic field and ppm order homogeneity. The magnet circuit is construted from the NEOMAX magnet, pole piece and adjustable yoke. When the adjustable yoke is moved, the magnetic field of the gap changes about 150C keeping up high level homogeneity. It has the homogeneity of about 100ppm at the gap field Bg=3800G. The microwave circuit consists of the Gunn diode microwave oscillation, coaxial wave guide and rectangular resonant cavity of X-band. Connecting these components, we succeed to develop the portable ESR spectrometer which is quite lighter and more compact than the usual apparatus and so useful for the handy measuring device. Measuring the DPPH standard sample, we obtain the sensitivity of about 10^{12} spins/G. We will report the measuring results of several materials like coals, minerals and fossils and also the dosimetry of radiation damage.

176 A MODULAR LOW FREQUENCY ESR SPECTROMETER

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Biophysics Department, University of Rochester, Rochester, NY 14642

There has been a resurgence of interest in ESR spectroscopy at low frequencies due in part to several biological problems which the technique may help solve. These problems include *in vivo* studies of oximetry, drug metabolism, carcinogens, and naturally occurring free radicals. Since commercial low frequency ESR spectrometers and imagers are not available many researchers might be discouraged from starting research in this field. It is, however, possible to construct such a instrument from commercially available "off the shelf components. We describe a low frequency ESR spectrometer and imager capable of operating at frequencies between 100 and 400 MHz which was constructed primarily from commercially available components. The spectrometer is computer controlled and a has a digital automatic frequency control. At 200 MHz the nitroxide sensitivity on a 10 ml sample volume is 30 μM. Representative spectra and images will be displayed. A block diagram of the spectrometer and a component list will be presented.

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TEACHING MRI AND MRS USING COMPUTER ANIMATION

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Center for Imaging Science, Rochester Institute of Technolog, Rochester, NY 14623

Involving undergraduate students in magnetic resonance research requires a carefully planned educational program in the principles of magnetic resonance. Such a program often compels the student to learn the principles independently as there are usually no appropriate courses at the sophomore and junior level. Several dynamic aspects of magnetic resonance spectroscopy (MRS) and imaging (MRI) are difficult for the student to visualize and understand when textbooks with static diagrams are used. Consequently, significant amounts of time are spent by the research advisor explaining concepts which are better taught by other means. One solution to the problem is to utilize computer animation for teaching magnetic resonance. We have developed computer based teaching packages on the basics of MRS and MRI which present several of the dynamic processes of magnetic resonance with computer animation and text which simultaneously appear on a computer screen. Our studies indicate that topics such as the rotating frame of reference, pulse sequences, the behavior of magnetization during a two dimensional imaging sequence, solid state NMR, and two dimensional Fourier transforms are better taught by computer animation.

ESR STUDIES OF TRIPLET STATE IN DIACETYLENE MONOMER MATERIALS

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Department of Chemical Engineering,National Tsing Hua University,
Hsinchu,Taiwan 30043,R O C

Abstract:

Polydiacetylenes are interesting and exciting materials for all possible applications In electronic and optical devices. At present ,these materials have been used in self-trapping,self-focusing,phase conjugation,optical bistability etc;which are fundamental to all-optical signal processing applications.

Wo have studies two typical diacetylene monomers (2,4-hexadiyne-1,6-diol and 1,6-di-p-toluenesulfonyloxy-2,4-hexadiyne) by various physical and chemical methods. The results will be discussed in terms of one dimensional theoretical electron gas modal.

Our photolysis result on 2,4-hexadiynediol monomer powder indicated the formation of triplet state (diradicals) as the intermediate at 77 k. Because of the axial symmetry of the two triple bonds in the monomer molecule • the triplet state of $R-C=C=C=C-R$ ($R=CH_2OH$) could be characterized as $D = 0.01 \pm 0.001$ cm^{-1}(105 + 5 Gauss),$E \approx 0$, with simple dipolar interaction between these two unpaired electrons in the monomer . the mean distance between the aired electron (r) was calculated about 6.43 ±0.03 Å approximately.

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HIGH FIELD ESR AT 140 GHZ.

Thomas F. Prisner.[1] Sun Un,[1] Ralph T. Weber,[1] Ann E. McDermott[1] and Robert G. Griffin[1,2]. [1]Francis Bitter National Magnet Laboratory, [2]Department of Chemistry, Massachusetts Institute of Technology, Cambridge, MA 02139.

We have assembled a high frequency microwave spectrometer for cw-EPR, pulsed ESR and DNP measurements at a static field of 5.0 T. Our initial cw-EPR measurements demonstrate the increased spectral resolution available: the resolution in g-values is 10^{-7}, with an absolute accuracy of $g < 10^{-6}$. The present sweep-range of the superconducting sweep-coil of our magnet is approximately 1 kG, permitting studies of systems with g-values between 1.98 and 2.02. The investigations we have initiated illustrate the variety of new information accessible at high fields. For example, spectra of spinach plant photosystem I show increased spectral resolution, when compared to measurements at lower fields (X-,K-,Q-band), allowing better separation and identification of signals with only slightly different g-values. The linewidth analysis of oxidized P_{700}^{+} gives a upper limit for the g-anisotropy of $\Delta g < 10^{-4}$, which is considerably smaller than g-anisotropies derived from 35 GHz single crystals studies of bacterial reaction centers [J. P. Allen and G. Feher, Proc. Natl. Acad. Sci. USA 81, 4795 (1984)].

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EPR-ENDOR OF THE COMPOUND I RADICAL IN SITE-DIRECTED MUTANTS OF CYTOCHROME c PEROXIDASE.

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Cytochrome c Peroxidase (CcP) catalyzes ferrocytochrome c oxidation by H_2O_2. In this process there is an intermediate form, Compound I, in which two oxidizing equivalents originating on H_2O_2 are ttansferred to the protein. One equivalent is on ferryl heme, and one is at a radical most likely located at a protein amino acid side group. Perturbations to the Compound I radical center in mutant forms of CcP have been investigated. Previous x-ray, mutagenesis, and spectroscopic studies have pointed to Tryptophan-191 as the radical site. Only mutations that altered Trp-191 or its immediate environment (Aspartate-235, Methionine-230, Methionine-231) produced significant change in the EPR and ENDOR signals of Compound I. The carboxyl of Asp-235 hydrogen bonds to the indole of Trp-191 and the sulfurs of Met-230 and Met-231 are about 4 Å from the indole of Trp-191. The mutations at Met-230 and/or 231 perturbed the EPR lineshape of the Compound I radical but did not eliminate it. ENDOR of these methionine mutants showed alteration to the hyperfine couplings which are characteristic of the Compound I radical electronic structure. In Trp-191 and Asp-235 mutants the characteristic Compound I signal was lost, and narrow radical species with less integrated intensity, different lineshapes, different ENDOR features, and different spin relaxation times from the Compound I signal became obvious.

ULTRA LOW FIELD EPR MEASUREMENTS ON LITHIUM PHTHALOCYANINE RADICAL.

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The lithium phthalocyanine radical exhibits exceptional magnetic properties. The most spectacular one is the oxygen dependence of the EPR linewidth. This effect, instantaneous and reversible, is revealed by extreme narrowing of the EPR line from 1 Gauss to 35 mG when pumping under vacuum. In addition to this property this radical is extremely stable, therefore its use for any oxygen measurements can be envisaged. We describe an ultra low field (0.6 G, 2 MHz) EPR spectrometer providing quantitative parameters. The EPR data of some radicals are presented. They concern especially lithium phthalocyanine and an octasubstituted lithium phthalocyanine for which the linewidth is also linearly oxygen dependent (between 5 Gauss in air and 90 mG when air is removed by pumping). The future development will be the elaboration of a 500 MHz EPR spectrometer which is under construction.

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EPR, ENDOR AND ESEEM SPECTROSCOPY OF NICKEL(III) IN HYDROGENASES.

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Hydrogenases are enzymes that catalyze the production or consumption of hydrogen gas. All of them contain iron-sulfur clusters and some also contain a specialized nickel center which is responsible for the reaction with H_2. The nickel center in hydrogenases such as that from *Desulfovibricgigas* is EPR-detectable, with formal oxidation state Ni(III). The nickel may be interconverted, by suitable oxidation-reduction treatments, between different states of activity, with different EPR characteristics. The active state of the enzymes is characterized by the EPR signal described as Ni-C. It is a photosensitive form and various lines of evidence indicate that it is a dihydrogen complex. Ligands of the nickel site in D. *gigas* hydrogenase have been detected by electron magnetic resonance methods. The presence of a nitrogen, probably imidazole from histidine, was determined by ESEEM. The presence of an oxygen ligand was deduced from ^{17}O broadening of the c.w. spectrum of the enzyme after treatment of the reduced enzyme with Interactions with hydrogen are of particular interest since they represent the substrate for the enzyme. ^1H-^2H exchange at the nickel site with $^2H_2$ or ^2H_2O were observed by ESEEM and ENDOR and were found to be conditional on reduction of the enzyme. The Ni-C spectrum shows a splitting at low temperatures, apparently due to spin-spin interaction with reduced [4Fe-4S) clusters. These results may be assembled to provide a picture of the coordination of the nickel site, its interaction with hydrogen gas, and the pathway of electron transfer to the electron acceptor.

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DETECTION AND CHARACTERIZATION OF EXCHANGEABLE PROTONS BOUND TO THE NICKEL SITE OF DESULFOVIBRIO GIGAS HYDROGENASE: A ^1H AND ^2H Q-BAND ENDOR STUDY,

Chaoliang Fan. Miguel Teixeira, Jose Moura, Isabel Moura, Boi-Hanh Huynh, Jean Le Gall, Harry D. Peck, Jr., Brian M. Hoffman, Department of Chemistry, Northwestern University, Evanston, IL 60208

We present a Q-Band ENDOR study of the nickel site of the as-isolated (Ni-A). H_2-reduced (Ni-C) and reoxidized (Ni-A/Ni-B) states of *Desulfovibrio gigas* hydrogenase. Through proton and deuteron ENDOR measurements we detect and characterize the possible products of heterolytic cleavage of H_2, namely two distinct types of exchangeable protons, bound to the Ni-C site. One proton, H(1), has a hyperfine coupling, $A^H(1)$ - 16.8 MHz; for the other, H(2), $A^H(2) \approx$ 4.4 MHz. We suggest that H(1) exists as a hydride bound in-plane to the nickel ion; H(2) could well be associated with H_xO bound to the nickel. An H(2) signal remains associated with the Ni-B (and possibly Ni-A) center after oxidation of the Ni-C. In addition we confirm that the Ni-A site is inaccessible to solvent protons.

THE COPPER SITE IN CYTOCHROME c OXIDASE AND NITROUS OXIDE REDUCTASE.

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The multicopper enzymes Nitrous Oxide Reductase (N2OR, 8 Cu/M) and Cytochrome c Oxidase (COX, 3 Cu, 2 Fe, 1 Mg, 1 Zn/active unit) were investigated by a variety of different magnetic resonance techniques: (1) CW multifrequency epr at 1.5, 2.5, 3.5, 4.5, 9.5 and 35 GHz in the temperature range 5 - 100 K, (ii) ENDOR at 35 GHz at 4 K, and (iii) LEFE at 1.6 K.

From these experiments, and computer simulations the presence of a mixed-valence S=1/2 (Cu(1.5)...Cu(1.5)) with a strong Cu-Cu interaction is proposed for both enzymes. The existence of similar copper sites in Nitrous Oxide Reductase and Cytochrome c Oxidase is supported by EXAFS, MCD and resonance Raman data. Amino acid sequence results indicate a highly conserved loop in both proteins which, in the case of COX is assumed to bind the so-called Cu_A center.

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EFFECT OF ZERO FIELD SPLITTING ON ESEEM OF MANGANESE

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Manganese (S=5/2, I=5/2) is a surrogate for magnesium in many magnesium containing proteins, thus making these systems suitable for application of EPR techniques. Specifically, Electron Spin Echo Modulation (ESEEM) has been applied to the studies of various manganese-containing proteins with hopes of elucidating active-site structures. Unfortunately, due to the presence of zero field splittings in these systems, the spectra are not well understood. Here, we present a theoretical study on the effect of zero field splitting on manganese ESEEM spectra with applications to experiment.

186 **SUBSTRATE COORDINATION TO THE [2Fe-2S] CLUSTER OF SPINACH DIHYDROXY ACID DEHYDRATASE.** Kouichi Nakagawa, Mark H. Emptage*, Drew Houseman, and Brian M. Hoffman. Department of Chemistry, Northwestern University, Evanston, IL 60208, and *E. I. du. Pont de Nemours and Co., Central Research and Development Department, Wilmington, DE 19898.

The mode of enzyme-substrate interaction for the enzyme, spinach dihydroxy acid dehydratase, was studied by Q-band ENDOR spectroscopy at 2 K. Bound substrates (2,3-dihydroxy-3-methyl butyrate) labeled with ^{17}O at various position were examined. The ENDOR spectra of these protein samples taken with magnetic field settings at extreme edges of the EPR envelope gave single-crystal-like patterns. ^{1}H and ^{17}O ENDOR for labeled and unlabeled substrates yield information concerning enzyme-substrate coordination in the catalytic cycle. They suggest that 3-hydroxyl oxygen in the substrate ligates to iron of the [2Fe-2S] cluster.

187 PROGRESS IN EPR OXIMETRY OF VIABLE BIOLOGICAL SYSTEMS. Harold M. Swartz, James Glockner, Peter Gast, and Robert Clarkson, University of Illinois, 506 South Mathews, Urbana, IL 61801.

The concentration of oxygen [O_2] is a central experimental and clinical issue but most existing methods do not provide the data that are needed. Recently methods based on EPR have been developed which appear to meet many of the requirements for useful measurement of [O_2]. This report covers progress made in the measurement of [O_2] in muscles and the peritoneal cavity of living animals using L-band spectroscopy and in vitro, at concentrations of special biological interest. Liposomes were used to encapsulate perdeuterated "Cat-1," protecting this nitroxide from bioreduction and also helping to keep the nitroxide from washing out of the muscle. The procedures used to obtain the data from living mice had no apparent acute effects on the animals with either type of probe. Changes in [O_2] in vivo were measured readily when the circulation was compromised by either local restriction of blood vessels or removal of oxygen from the breathing gas. These data confirm the expectation that in vivo EPR spectroscopy can be used to measure [O_2] in a living animal under physiologically pertinent conditions, including levels of oxygen that are likely to be encountered *in vivo*. The use of fusinite provides enhanced sensitivity for the measurement of oxygen at physiologically interesting levels (0-20)m); compared to nitroxides it is about 10-fold more sensitive to changes in [O_2]. Preliminary studies with lithium pthalocyanin indicate this may be an even more sensitive probe.

188 TOWARDS A QUANTITATIVE EPR OXYMETRY IN TISSUES OF A LIVING ANIMAL: MEASUREMENT STABILITY AND THE IN VIVO CORRECTION FOR CONFOUNDING EFFECTS. Howard J. Halpern and Miroslav Peric, Dept. Radiation Oncology, U. Chicago Med. Ctr., Chicago, IL 60637, Yuwares J. Lin and Beverly A. Teicher, DFCI, Boston, MA 02115, and Michael K. L-wman, ANL, Argonne, IL 60439

The spectroscopic signal from injected spin label measured with a very low frequency EPR spectrometer (250 MHz) has a signal-to-noise that compares favorably with those from magnetic resonance spectroscopy and provides complementary physiologic information. Oxymetry using a spin label with fully deuterated α,α' methyl groups and a single ring hydrogen has been described. This provides a signature sensitive to the line broadening induced by both oxygen and the spin label itself. It also provides a signature that allows separate estimation of the concentration. We report data from spin label injected into living mice under various levels of anesthesia. This data provides a measure of the stability and extractability of a corrected oxygen signature. The corrected oxygen signature indicates oxygen concentrations consistent with what one would expect in normally perfused tissues. We anticipate the presentation of substantially improved spectral-spatial images allowing the localization of the oxymetry to subregions of the mouse anatomy. The data may substantiate a quantitative oxymetry from animal tissues. This provides an improved measure of a variable crucial to the understanding of the physiology of animal tissue in states of disease and health.

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CHARACTERIZATION OF POLYATOMIC SPECIES IN INDUCTIVELY COUPLED PLASMA-MASS SPECTROMETRY BACKGROUND SPECTRA.

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In spite of the fact that inductively coupled plasma-mass spectrometry is now in routine use in hundreds of laboratories across the world, little attention has been given recently to the characteristics of the polyatomic ions observed in plasma background spectra. The landmark paper by Tan and Horlick(1) that first comprehensively described background spectral species is quoted often, but has seldom been expanded upon. The present paper provides additional information regarding the characteristics of these background ionic species. The ultimate source of the elements comprising the background species is distributed among the sample solvent, the plasma support gas, atmospheric entrainment, and pneumatic and ICP torch hardware components. This defines the relative contribution of each of these sources, and indicates how the species intensities vary with ion source and plasma sampling parameters. This information is useful for optimizing conditions for elements, such as silicon, that are subject to spectral overlap interferences by background species. Data are also provided on comparative background species intensities with alternate sampling devices such as laser sampling and ultrasonic nebulization. In addition, comparisons are made of background spectra generated by pure argon plasmas and by mixed gas plasmas.

1. Tan, S.H. and Horlick, G., *Applied Spectrosc* 40, 445 (1986).

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Recent Advances in ICP-HS Technology

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ICP-HS has reached a stage of maturity, with over 300 instruments in the field, where it can now be viewed as an established technique Most development effort is currently in the area of sample introduction methodology to provide the analyst with more flexibility and problem-solving power.

Instrumentation has also been evolving over the years.

A new plasma/vacuum interface has been designed which offers routinely sub part per trillion (pg/ml) detection limits.

The use of a magnetic sector double focussing mass spectrometer provide! even lower detection limits and allows the resolution of some problemat: molecular interferences.

The performance capabilities of current instrumentation incorporating the recent advances in ICP-MS technology will be reviewed.

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Characterization of the Delsi-Nermag Mass Spectrometer Interfaced to a Versatile ICP System.

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Department of Chemistry, George Washington University, Washington, DC 20052

A DELSI-NERMAG MASS SPECTROMETER IS COUPLED TO A VERSATILE ICP SYSTEM FOR FORMING VARIOUS ICP DISCHARGES ON A SINGLE FACILITY. THE MASS SPECTROMETER IS EQUIPPED WITH A NEW MASS DETECTOR KNOWN AS "CONIPHOT". COMPARED TO THE CONTINUOUS DYNODE ELECTRON MULTIPLIER, CONIPHOT EXHIBITS LONGER LIFE TIME AND HIGHER GAIN. THE EFFECTS OF PLASMA OPERATING CONDITIONS AND ION OPTICS PARAMETERS ON MASS SPECTROMETRIC SIGNALS ARE PRESENTED. ANALYTICAL performance OF THE SYSTEM SUCH AS DETECTION LIMITS, RATIO OF DOUBLY CHARGED TO SINGLY CHARGED ION, OXIDE ION TO ANALYTE ION RATIO, DYNAMIC RANGE, PRECISION, AND matrix EFFECTS ARE ALSO REPORTED. THESE CHARACTERISTICS ARE COMPARED TO THOSE OF OTHER ICP-MS SYSTEMS.

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UTILIZATION OF INDUCTIVELY COUPLED PLASMA-MASS SPECTROMETRY AS AN ELEMENT SPECIFIC DETECTOR FOR SEDIMENTATION FIELD-FLOW FRACTIONATION

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Preliminary experiments have been made to assess the feasibility of using inductively coupled plasma-mass spectrometry (ICP-MS) as an element specific detector for sedimentation field-flow fractionation (Sd-FFF) of suspended sediment of particle diameters <1 micron. Particles in this diameter range are introduced directly into the plasma using a Babington-type nebulizer via an aqueous suspension eluting from the Sd-FFF . Particle separation within the Sd-FFF is primarily based on particle diameter and density. ICP-MS sensitivities of less than 100 picograms permit the determination of trace metals adsorbed to sediment coatings. Therefore, the combination of the two techniques provides the capability of quantitatively determining the distribution of a wide range of analytes associated with specific colloidal-size fractions. The technique was tested using materials of known chemical composition such as lead chromate, alumina, goethite, and a mixture containing all of these. Data from the ICP-MS for Pb, Cr, Al, and Fe are correlated with known size fractions as determined using conventional UV detection. Application to environmental samples was tested using two different riverine suspended sediments. The association of trace metals with particular particle size fractions was verified by the spiked addition of Cd and Pb.

193 NO ABSTRACT AVAILABLE

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DATA QUALITY CONSIDERATIONS IN TH APPLICATION OF ICP/MS LEAD ISOTOPE RATIO DATA TO ENVIRONMENTAL ENFORCEMENT.

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Inductively coupled plasma mass spectrometry (ICP/MS) has been demonstrated to be a versatile technique for measurements of isotopic ratios. Particular emphasis has focused on lead isotopic ratio measurements, which are useful both in geological and environmental applications. Generally speaking, ICP/MS offers much promise in both areas owing to its ability to accomodate high sample throughput with minimal sample preparation requirements.

This paper will discuss a number of topics relating to the use of lead isotope ratios as a tool in environmental enforcement. Of foremost concern are data quality objectives; it will be demonstrated that, for most environmental problems, these objectives are far less stringent than those of geochemical studies. These data quality objectives define tolerable levels of measurement bias and imprecision. Other concerns are as follows: a) the effect of instrumental parameters on precision and bias; b) the "brick wall" of counting statistics; and c) sample matrix effects. Application of the Longerich-Fryer-Strong bias correction method will be discussed. A general operating method and batch quality control practices will be presented. This method is presently being applied to a variety of environmental enforcement problems. It is seen that ICP/MS is probably the ideal means of measuring lead isotopic ratios in this context.

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1

COMPARISON OF INFLUENCE OF OPERATING PARAMETERS UPON PERFORMANCE OF AN ULTRASONIC NEBULIZER AND A PNEUMATIC NEBULIZER IN ICP MASS SPECTROMETRY.

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Considerable effort has been devoted by Horllck and by other investigators to characterize changes in response of a pneumatic nebulizer to variations In Incident power, axial gas flow, and sampling depth. Comparatively little work has been reported concerning the effect of these parameters upon performance of an ultrasonic nebulizer. In this paper, the performance of a Cetac Technologies ultrasonic nebulizer was compared to that of a concentric glass nebulizer for introducing a test solution containing Be, Mg, Co, In, Ce, Pb, and U in 1% nitric acid into a VG Instruments Plasmaquad 2+ICP mass spectrometer. Data were obtained at thirteen masses (9 to 238) and at eighteen combinations of incident power, axial gas flow, and sampling depth. Parameters measured were sensitivity, precision, detection limits, linear range, relative mass response, oxide formation, random background and formation of doubly-charged species. The data obtained demonstrated that the ultrasonic nebulizer possesses considerable advantages for the analysis of solutions containing sub-part-per billion concentrations of analytes in a "clean" matrix. Additional effort will be required to determine the effects of other acids and of concomitant elements upon performance of the ultrasonic nebulizer.

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SPECTROSCOPIC AND SOLUBILITY CHARACTERISTICS OF OZONATED, NITRATED AND SULFONATED SOOTS.

Abdul R. Chughtai, Jabria A. Jassim and Dwight M. Smith, University of Denver, Denver, Colorado 80208

The initial rates for the formation of surface species indicate that the soot $-O_3$ reaction is faster than the rapid soot-NO_2/N_2O_4 reaction which, in turn, is faster than the soot-SO_2 reaction. FT-IR spectroscopy, SEM, X-Ray fluorescence, and surface area measurements of ozonized soot when compared with regular soot indicate that, besides alteration of the soot structure, ozonation creates polar acidic functional groups on the surface which have been identified as carboxylics. Ambient air aerosol samples of less than 10 microns aerodynamic diameter were collected on PM10 filters by the Colorado Department of Health, Air Pollution Division, from four different locations in the Denver Metro area. A significant fraction of the "as sampled" ambient soot was observed to be miscible with water. Of the infrared bands observed for this "soluble" portion of the carbonaceous mass collected on the PM10 filter, those at 3400 cm^{-1}, 1105 cm^{-1} and 1080 cm^{-1}(s. doublet), 1000-900 cm^{-1}(m), 640 and 610 cm^{-1}(doublet), and GOO cm^{-1}(w) infer the presence of sulfate, while bands at 17G7 cm^{-1} (v.w), 1380-1358 cm^{-1}(v.s) and 825 cm^{-1} (m.sp) are indicative of nitrate. However, the ratio of the carboxylic band (1750-1700 cm^{-1}) to the characteristic soot band at 1620 cm^{-1} is indicative of the presence of ozonated soot.

197 THE REACTIVITY OF OXIDANTS WITH SOOT I. A COMPARATIVE STUDY OF O_3 AND NO_2/N_2O_4. Abdul R. Chughtai and Dwight H. Smith, Department of Chemistry, University of Denver, Denver, Colorado 80208

Both ozone and NO_2/N_2O_4 exhibit competitive activated chemisorption78 and redox reactions. Activated chemisorption produces functionalities on the soot while the redox reactions with soot are accompanied by the evolution of CO_2 and CO. At low ozone concentration (50-500 ppm), in addition to the chemisorption reaction, a redox reaction takes place with the unorganized aliphatic and olefinic segments of soot. At moderately high concentrations (1.0 -1.5%), O_3 reActs with soot not only displaying both reactions, hut also revealing variations in oxidation products which are a function of the reactivity of soot segments. At higher O_3 concentrations (more than 2%), soot reacts linearly with ozone. In the case of the soot-NO_2 reaction, however, there is an additional redox reaction which we have termed the minor redox reaction. This reaction occurs under all conditions and produces significantly lower amounts of CO_2 and CO than the major redox reaction in which 82-95% of the soot is converted into CO_2 and CO. This redox process commences near or above 65°C under certain flow condition of NO_2/N_2O_4. Unlike the soot-ozone redox reaction, if activated chemisorption is initiated, it precludes the major redox reaction.

198 GC/TRACER ANALYSIS OF BEERS
Jay R. Powell. Bio-Rad, Digilab Division, 237 Putnam Avenue, Cambridge, Massachusetts 02139.

The analysis of the flavors in foods and beverages is one of the most challenging areas in analytical chemistry. While the components are easily separated by capillary gas chromatography, the identification is more difficult. GC-MS is favored for excellent sensitivity, but often fails to provide unique identification. GC/FT-IR can provide the specificity, however, often falls *to* provide the sensitivity. Recently, a new method for cryogenically trapping the elutant has been developed, which yields tremendously improved infrared sensitivity while maintaining read-time data acquisition. Beer, in one form or another, has been brewed since 6000 BC. Beer is a relatively simple beverage to prepare, consisting of water, carbohydrates, yeast, and hops. Barley is accepted as the standard source of carbohydrates, but other sources, such as wheat, rice, corn, and cane sugar are sometimes used. While natural, air borne yeasts were first employed, cultivation of both top fermenting and bottom fermenting yeasts are now used by most brewers. The hops provide flavoring, and also act as a preservative. However, other flavoring agents have been employed, such as herbs, berries, and even tree bark. Here, we have obtained several different beers from local retail sources, and subjected them to GC/Tracer analysis. Results on various components will be reported, as well as similarities and differences between beers.

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FT-IR CHARACTERIZATION OF CHROMIUM(III) ACETATE IN AQUEOUS SOLUTION. James E. Tackett. Marathon Oil Company, P.O. Box 269, Littleton, CO 80160.

FT-IR in combination with attenuated total reflectance is a convient way to study aqueous solution chemistry. We used this technique to characterize the acetate-chromium interactions in aqueous solutions of chromium(III) triacetate. FT-IR spectra of dried chromium acetate were also used to look at cyclic to linear transitions. We found the addition of base causes the cyclic chromium trimer to hydrolyze and convert to a linear form. Possible structures are discussed.

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STRUCTURAL INTEGRITY ASSESSMENT OF CONCRETE SLABS BY NDE AND FT-IR METHODS. T. V. Rebagay and D. A. Dodd, Analytical Systems Laboratories, Westinghouse Hanford Company, Richland, WA 99352.

Concrete floor and reinforcing bars of a chemical preparation room suspected of being degraded and corroded due to an acid spill were assessed for structural integrity using two methods: nondestructive examination (NDE) and Fourier transform-infrared (FT-IR) spectrometry. The NDE tests revealed that the concrete slabs at several locations in the room were degraded and the top reinforcing bars severely corroded. The FT-IR method indicated that the acid spill was limited to the concrete floor grout and the reinforcing bars were free from corrosion. Based on the FT-IR findings, it was concluded that the concrete slabs were structurally sound requiring only minor repairs which resulted in cost savings to the company.

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ADVANTAGES OF FT-RAMAN SPECTROSCOPY IN THE BIOLOGICAL SCIENCES
Jay R. Powell, David A.C. Compton, and Norman A. Wright. Bio-Rad, Digilab Division, 237 Putnam Avenue, Cambridge, Massachusetts 02139.

For the investigation of molecular conformations and interactions in aqueous biological systems, Raman spectroscopy has long been the choice over classical infrared adsorption. Due to the weak Raman scattering of water, it is far easier to obtain a Raman spectrum without the necessity of precise pathlength control or spectral subtraction of the solvent. However, dispersive Raman does have problems that can interfere with obtaining a good spectrum. Most Raman systems use visible lasers for excitation, operating in the green to blue region. The advantage of using this wavelength range for excitation lies in the fact that the Raman intensity increases as a function of the excitation frequency. However, this range also can yield a strong fluorescence signal, which can swamp the weaker Raman signal by a factor of 1000 or greater. Because many biological systems can generate a strong fluorescence, this is a clear disadvantage. With the introduction of commercial FT-Raman systems, the problems with fluorescence have been solved. Using a Near-Infrared Nd:YAG laser for excitation, sample fluorescence has been eliminated. In addition, the throughput and multiplex advantages of an interferometer yields a spectrum with a higher signal-to-noise ratio In spite of the weaker Raman scattering. Here, we will present some examples of applications of a commercial FT-Raman system.

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DESIGN AND PERFORMANCE OF A NEW INFRARED MICROSCOPE, W. D. Perkins, Perkin-Elmer Corp., 2305 Bering Drive, San Jose, CA 95131, D. W. Schlering and E. F. Young, Perkin-Elmer Corp., Main Avenue, Norwalk, CT 06859.

A new microscope for infrared microspectroscopy incorporates a number of unique features. Viewing is done through a commercial binocular stereomicroscope thus providing stereoscopic viewing of the sample. A special sample preparation stage allows use of the stereo-scope for sample manipulation prior to the taking of Infrared data. Optical coupling to the sample is accomplished with two low-power high numerical aperture Cassegrain optics which are kinematically mounted to eliminate the need for periodic realignment. The low power of the Cassegrain permits an unusually large working distance at the sample position while the higher power of the stereo viewing scope allows detailed examination of the sample and precise positioning of the remote aperture blades to delineate exactly the sample area to be viewed. The microscope functions in both transmission and reflection and accepts a variety of room temperature and cooled detectors. Examples of system performance will be presented for a variety of applications to practical microspectroscopy problems.

203 GAS QUANTITATION MADE EASY.

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1424 North Central Park Avenue, Anaheim, CA 92802.

In the past, infrared measurement of gases has been made quantitative only with a substantial effort. Deviations from the absorption law required plotting of calibration curves for gases under study. Moreover, the calibration would apply only to the instrument being used. The calibrations required much laboratory work and led to much expense in the acquisition of gases. These difficulties have now been surmounted by Infrared Analysis, Inc. through digitized reference spectra on diskette. These digitized spectra can be used on any of the modern FT-IR spectrometers. One diskette replaces a large collection of gas tanks with toxic chemicals in them and a large amount of work. The reference spectra should be used at low absorbance. Small molecules with individual spectral lines require working at absorbance of 0.1 or lower. Large molecules with diffuse bands can be studied at higher absorbance up to 1.0. For small molecules, high resolution improves the quantitation and expands the valid measurement range. A detector cooled to liquid nitrogen temperature should be used. The requirements of low absorbance, high resolution and low-temperature detector are explained in terms of lines widths, spectral details and the transmission-absorbance conversion. The errors in gas quantitation that result from the use of a single digitized reference spectrum are presented as a function of sample absorbance and spectral resolution.

204 FLUORESCENCE MEASUREMENTS OF THE VOLUME, SHAPE, AND FLUOROPHORE COMPOSITION OF FULVIC ACID FROM THE SUWANNEE RIVER.

M. C. Goldberg, U.S G.S., P. O. Box 25046, MS 424, Lakewood, CO, 80225

Information about the molecular conformation, volume, and shape was obtained using steady state and dynamic depolarization measurements where the ratio of temperature to solution viscosity was varied and reciprocal polarization was measured. These measurements indicate that fulvic acid rotates isotropically in water at pH 6.5, which is characteristic of a spherical shape. Measurements of reciprocal polarization as a function of pH show that the shape of fulvic acid in water remains constant throughout the pH range from 3 to 11.5, and indicates that the conformation changes outside this range. The equivalent spherical radius of fulvic acid was measured as 1.167 nanometers in water and 1.043 nanometers in dimethylsulfoxide, corresponding to *hydrodynamic molar volumes* of 3, 950 cubic centimeters and 2, 860 cubic centimeters, respectively. *Phase-resolved emission spectra*, fluorescence-lifetime measurements, and three-dimensional plots of the spectral excitation-emission matrix are reported. The excitation maximum was at 348 nanometers when the excitation was scanned holding the emission constant at 460 nanometers, and the emission maximum was 460 nanometers when the emission was scanned holding the excition constant at 350 nanometers. The phase-resolved emission spectrum was measured at constant excitation of 350 nanometers and contained emission peaks at 410 nanometers and 470 nanometers. All these data indicate that at least two different *fluorophores* are present in fulvic acid. Their fluorescence lifetimes were measured as 1.05±0.12 nanoseconds and 6.54±0.14 nanoseconds in water and 1.31±0.14 nanoseconds and 6.78±0.36 nanoseconds in dimethylsulfoxide at 30 degrees Celsius. With two or more fluorophores, the amount of depolarization depends on the individual lifetimes, making it necessary to use weighted average values for lifetime and limiting polarization values in the calculation of molecular volume.

205 PHOTOINITIATION OF PEROXYOXALATE CHEMILUMINESCENCE: APPLICATION TO FLOW INJECTION ANALYSIS OF CHEMILUMOPHORES

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Cooperative Institute for Research in Environmental Sciences (CIRES), Campus Box 216,
University of Colorado, Boulder, Colorado 80309-0216

Photoinitiation of peroxyoxalate chemiluminescence is reported for the first time and applied to the detection of amino-substituted polycyclic aromatic hydrocarbons in flow injection analysis. This novel detection system is simplified by elimination of the reagent hydrogen peroxide used in most liquid-phase chemiluminescence detection schemes. Like the H_2O_2-initiated reaction, the sensitivity of detection in photoinitiated chemiluminescence (PICL) is enhanced by use of a base catalyst such as imidazole. Limits of detection are in the low to mid picogram range and are comparable to those obtained by fluorescence detection using the same apparatus. It is proposed that the PICL reaction begins with hydrogen abstraction by the triplet-excited state of the oxalate ester, followed by addition of 02. Subsequent steps in the mechanism proceed to form high energy intermediates which transfer energy to the chemilumophore.

206 PHYSICOCHEMICAL INTERACTIONS OF THE AMINOBENZOIC ACID ISOMERS WITH SODIUM ACETATE IN SOLID-MATRIX ROOM-TEMPERATURE LUMINESCENCE SPECTROSCOPY. S.M. Ramasamy and R.J. Hurtubise, Department of Chemistry, University of Wyoming, Laramie, Wyoming 82071.

Among the anions of the aminobenzoic acid isomers adsorbed on sodium acetate, the para isomer has been shown to give a strong room-temperature phosphorescence signal, while the ortho and meta isomers exhibit weak phosphorescence signals. The physicochemical interactions responsible for inducing phosphorescence from these systems were evaluated from a variety of data such as the room-temperature fluoresence and phosphorescence quantum yeilds. The room-temperature fluorescence and phosphorescence spectral data of these isomers showed different kinds of molecular and ionic forms in solution and on the solid-matrix. A diffuse-reflectance infrared spectroscopic technique was also employed to study the interactions of these isomers with the solid-matrix. The luminescence and infrared data, along with crystallographic data from the literature for p-aminobenzoic acid and for sodium acetate, were used to explain the different magnitudes of room-temperature phosphorescence quantum yields of the adsorbed isomers.

207 TRACING THE MOVEMENT OF TRANSPORTED MATERIALS IN THE SOUTH PLATTE RIVER BY EEM LUMINESCENCE SPECTROSCOPY. M. C. Goldberg, U.S. G.S., P. O. Box 25046, MS 424, Lakewood, CO 80225

It is possible to use this effect to characterize colloidal and dissolved materials being transported in a hydrologic system by measuring the Excitation Emission Manifold (EEM) of the fluorescence light. Samples taken at different locations along a watercourse have an EEM spectral pattern characteristic of the transported load. Changes in this pattern at various locations along the watercourse are a direct measure of changes in components of the load. Measurements of EEM spectra were made along a 31 kilometer (km) stretch of the Platte, River, Colorado, between Chatfield Reservoir and 72nd Ave., Denver. At the Belieview sampling point, 6.25 km downstream from the Chatfield Reservoir sampling point, an EEM pattern was established that characterized the transported load. Data from the sampling points at Exposition St., an additional 4.5 km downstream from the Belieview point, showed the load increased; at 8th Ave., 3.3 km downstream from the Exposition St. sampling point, not only did the concentrations continue to increase, but some of the materials changed their proportional amounts, relative to their upstream concentrations; at 70th Ave., 31 km downstream from the Chatfield Reservoir sampling point, the overall load-concentration was about the same as at 8th Ave.; however, particular components of the load were changed in proportion to each other. EEM patterns can be correlated with the movement of specific materials once a given part of the EEM pattern is identified with a given component or components in the system. The transport of these materials can often be monitored by EEM spectroscopy rather than complete chemical analysis, saving time and money.

208 **Measurements of EEM Spectra in Natural Waters by K. K. Francis and M. C. Goldberg, U. S. G. S. P. O. B. 25046 MS 424, Denver Federal Center, Lakewood, CO 80111**

Measurements of EEM fluorescence spectra can be corellated with one another if a non-interfering internal standard is added to the samples. The material which is best suited for this role is Rhodamine-B. which has a strong spectrum in the red, is excited at wavelengths greater than 400 nanometers and emits at wavelengths greater than 400 nanometers. A second parameter which must be regulated is sample absorbance. Samples are adjusted to bring the absorbance below 0.1 taking care to do this on samples where there is enough fluorescence efficiency of the fluorophores to produce a spectrum at this concentration. This step is necessary to avoid the problems of the inner filter effect and to reduce the probability of higher energy fluorescence light stimulating, to any significant degree, the production of lower energy fluorescence light. Once these parameters are adjusted quite good results are obtained for EEM spectral addition and subtraction as well as other spectral processing techniques.

209 **NEAR-IR:** WHERE THE ACTION IS. Donald A Burns, Los Alamos National Laboratory, Los Alamos, NM 87545.

When Sir William Herschel, in 1800, saw a thermometer respond to invisible rays beyond the red end of his spectrum, he most likely couldn't imagine what sophisticated instrumentation would be developed during the two decades beginning 170 years later. But creative scientists and engineers have extracted from that region of the spectrum (about 800 to 2500 nm) a truly amazing package of information. They've used prisms, turrets full of interference filters, gratings, and acousto-optic tunable filters to let us look at single or multiple wavelengths, with slow- or fast-scans, or simultaneously with diode arrays, and with (almost) no moving parts. And when this low-noise hardware is combined with statistical tools such as chemometrics, significant advances accrue in both qualitative and quantitative analyses. Finally, the perceived limitation of "1% and up" is now giving way to parts-per-million sensitivities with surface enhanced Raman spectroscopy in the NIR region. Standing-room-only in a Near-IR session on the last day of a 5-day conference is clear evidence that this is where the action is.

210 THE USE OF MULTIVARIATE STATISTICAL CALIBRATION METHODS IN NIR: IS MORE ALWAYS BETTER? Steven M. Buco. Statistical Resources, Inc., 7332 Highland Road, Baton Rouge, LA. 70808, (504) 766-4921 & Joseph G. Montalvo, Jr, USDA, ARS, Southern Region Research Center, P.O.Box 19687, New Orleans, LA. 70179, (504) 286-4249.

The immense amount of information gathered from near infrared spectra makes multivariate statistical techniques prime candidates for calibration methods. Although computationally complex, the availability of statistical techniques including principal component regression, partial least squares regression, multiple regression and discriminant analysis in user-friendly software packages supplied by instrument manufacturers allows anyone to perform easily these analyses to predict physical and chemical properties using an independent primary method. But optimal results are not always obtained. Using actual NIR spectra from cotton fibers, modified spectra, and simulated spectra, the pitfalls of these multivariate techniques are illustrated. In addition, the relation between the calibration results and the reliability and accuracy of the primary method are presented. Methods to further analyze spectra to develop improved calibration models are demonstrated.

211 EFFECTS OF SCATTERING ON NEAR-INFRARED ANALYSES OF PU AND PAPER. Paul Brimmer, NIRSystems, 2441 Linden Lane, Silver Spring, Maryland 20910.

The characteristics of paper are affected by certain components in paper pulp, such as the relative amount of hardwood and softwood fibers, and the amount of unextracted lignin. Presently, hardwood/softwood ratios are determined by microscopy, which requires a highly skilled microscopist, and is a tedious and time consuming analysis. Hardwood and softwood fibers differ in length and width, which is how these fibers are differentiated by the microscopist. The fiber differences will also affect the reflectance spectrum in an NIR measurement. The differences found in the NIR measurement will be used to demonstrate hardwood/softwood determinations by NIR. The effects of scattering can have deleterious effects on other paper and pulp analyses, such as lignin determinations. Solutions to the problems presented by scattering variations on lignin determinations will also be presented.

218 SEE ABSTRACT #98

219 SEE ABSTRACT #99

220 SEE ABSTRACT #100

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PRECISE DETERMINATION OF INTERPARTICLE DISTANCE THROUGH MAS-NMR SIDEBAND INTENSITY ANALYSIS.

Po-Jen Chu. Dept. Chem., Texas A&M University, College Station, TX 7T843

The approach in determining interparticle distance through MAS spinning sideband intensity analysis is given. A theory is shown to account for the sideband intensities for spectrum governed by both chemical shift anisotropy and the dipolar coupling in either diamagnetic or paramagnetic molecules. Unlike the coupling between two nuclei, the dipolar coupling between unpair electron and nucleus is found to be nonaxially-symmetric and not traceless. To demonstrate the uniqueness of the results and the general applicability of this approach, the following three case studies will be presented. (1) The structure of $AlCl_3 — P(CH_3)_3$ acid-base stablized in zeolite is determined. This information provide the basis for probing Lewis acid site in zeolites. (2) The P-H internuclear distance between the hydroxyal group and the $P(CH_3)_3$ probing molecule is determined. From the temperature variation of the P-H distance, the modulation of the zeolite framework with temperature was for the first time, confirmed. (3) The distance between the carbonyl carbon and unpair electron as well as the orientation of the g-tensor in series of paramagnetic Lanthanum acetates are determined. The results are fully consistent with X-ray and ESR studies. A copy of the computer program is available upon request.

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HYDRODYNAMIC EFFECTS IN A CRITICAL BINARY MIXTURE.

Serge Lacelle, Franco Cau, Luc Tremblay, Stéphane Lavallée. Département de chimie, Université de Sherbrooke, Qc, CANADA, J1K 2R1.

NMR and visualization studies of hydrodynamic effects on the critical binary mixture (aniline/cyclohexane) will be presented. A variety of macroscopic flows were generated with the fluid in the annulus of two concentric and rotating cylinders. A difference in the magnetic susceptibilities of the coexisting phases permitted to investigate by high-resolution NMR the effects of flows on the critical exponents and amplitude of the coexistence curve, on mixing and on diffusivities. Spatio-temporal patterns generated during the spinodal decomposition of the fluid undergoing Taylor vortex flow in a temperature gradient were monitored by photography. In addition, typical domain sizes were measured by NMR In the late stage growth of the phase separation. These results will be discussed in light of existing theories of critical phenomena and fluid mechanics.

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2-D NMR STUDIES OF POWDERED AND ORIENTED MATERIALS WITH SAMPLE REORIENTATION

Craig D. Hughes, Mark H. Sherwood, D. W. Alderman, and David M. Grant
Chemistry Department, University of Utah, Salt Lake City, Utah, 84112

Rapid sample reorientation during the mixing time of a 2-D exchange ^{13}C NMR experiment allows the measurement of multiple ^{13}Cchemical shielding tensor patterns in powdered and oriented materials at two different field orientations. This experiment gives correlated information that relates the frequency in the first field orientation with the frequency in the second field orientation (Henrichs, P.M. *Macromolecules*, **20**, *2099*, 1987). The technique has two distinct applications: the measurement of chemical shielding tensors and their assignment to samples with more than one type of carbon atom, and the characterization of order in macroscopically ordered samples. A powdered sample is randomly distributed relative to the external field, so this experiment gives a spectrum with a symmetric distribution of intensities and frequencies across the diagonal. The 2-D symmetry allows the assignment of all three principle values of a ^{13}Cshielding tensor in cases where several ^{13}C atoms have very similar shielding tensors. An oriented sample has a 2-D spectrum whose intensities are distorted by the preferential distribution of molecules in the field. This spectrum, combined with the assignment of the chemical shielding tensor to the molecular frame, characterizes the orientation distribution function of an ordered sample.

| 224 | COMPUTER AIDED NMR MULTIPLE-PULSE SEQUENCE DESIGN FOR QUADRUPOLAR NUCLEI: AN ARTIFICIAL INTELLIGENT APPROACH.

Po-Jen Chu. Dept. Chem., Texas A&M University, College Station, TX 7T843

Although tremendous success of multiple-pulse techniqeus have been achieved in the studies of spin I=1/2 nucelus, there has not yet available a feasible transient techniques to supress the residual line width of the central transition of spin half quadrupolar nucleus due to the second order broadening. Because of the complexity of the second order quadrupolar Hamiltonian, evaluating the effective Hamiltonina during each M-P time segment becomes a formidable task. Based upon the average Hamiltonian theory devised for the multiple-pulse spin dynamic problems, and by applying the LISP programing in the symbolic calculation, effective NMR M-P sequences to simultaneously supress both the first order chemical shift anisotropy interaction and the second order quadrupolar interaction are obtained. Several studies in narrowing the central transition of quadrupolar nuceli which resulting in resolved quadrupolar resonances are shown. It is clear that the fundamentals of this computer aided design can be generally extended to disign, create and evaluate efficient NMR pulse sequences used in studies of both solid or solution phase.

SOLID-STATE NMR ON THE CMX SPECTROMETER. Victor J. Bartuska, Joseph A. DiVerdi, Allen R. Palmer, Dean W. Sindorf and Robert A. Wind. Chemagnetics, Inc., 208 Commerce Drive, Fort Collins, CO 80524.

A brief review will be given of the possibilities of the CMX Spectrometer. The versatility of this spectrometer will be illustrated with applications in the field of abundant-spin and rare-spin High-Resolution NMR and NMR of quadrupolar nuclei. This applications include ^{1}H variable-temperature CRAMPS on paramethoxybenzoic acid, ^{2}Hpulsed slow-sweep NMR on polymethylmethacrylate, and rare spin (^{13}C, ^{29}Si, ^{129}Xe) variable-temperature CPMAS NMR on various compounds.

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226 CHARACTERIZATION OF HIGH PERFORMANCE SHIM SYSTEM BY FIELD MAPPING.

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Billerica, MA 01821

The performance of individual shim coils in terms of both the strength of primary gradients and impurities is accessible by difference maps obtained by the helical mapping technique. Such knowledge of strength and impurities is valuable in the process of design and production of shim coil assemblies. It provides the necessary information for a directed approach to the shimming process.

In magnet shimming even rudimentary knowledge of the strength of the control gradients allows for iterative shimming. Detailed knowledge of the character of each shim makes this process more efficient because impurities can be anticipated and controlled. The performance of a new matrix shim system presenting a substantial improvement in level of control, gradient purity, and total power deposition will be demonstrated.

227 CROSS POLARIZATION AT HIGH SPINNING SPEEDS. T. M. Barbara, A. Brooke, H. D. W. Hill and E. H. Williams, Varian Associates, 611 Hansen Way, Palo Alto CA 94303

The CP/MAS experiment has served Solid State NMR well, having brought to It the sensitivity and most of the resolution of solution state NMR. The experiment is not without its drawbacks, however. The most notable of these is that, at spinning speeds less than the bandwidth of the CSA, spinning sidebands remain and these tend to obscure interpretation .A number of approaches have been used to remove spinning sidebands, each of which has its own drawbacks. Of these, the simplest, and at low fields, the best, is simply to spin the sample faster than the CSA and so remove the SSBs. However, as higher and higher fields ara used, the spinning speed used must become proportionately higher, leading to complications with the Hartmann-Hahn condition. This paper reviews the dynamics of, and proposes a strategy for maintaining cross polarization efficiency at high spinning speeds.

228 SOLIDS NMR PROBE TECHNOLOGY, F. David Doty, Jonathan B. Spitzmesser, and Michael N. Cllngan. Doty Scientific, Inc., 600 Clemson Road, Columbia, SC 29223.

A review of the state of the art of solids NMR probe technology is presented with emphasis on the interdisciplinary mechanical and electrical engineering principles involved. Nonlinear noise mechanisms in high-power double-tuned probes are discussed.[1] Over-coupling is shown to be an effective method of achieving more than an order-of-magnitude reduction in ring-down with little effect on S/N.[2] Progress and hardware limitations in various applications of high-speed sample rotation are discussed, including Dynamic Angle Spinning (DAS), low temperature (8 K) MAS, and high temperature (600°C) MAS.

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229 NO ABSTRACT AVAILABLE

236 1D AND 2D SOLID STATE NMR OF HOMONUCLEAR SPIN SYSTEMS USING MAGIC ANGLE SPINNING. James C. Duchamp. Xiaoling Wu, and Kurt W. Zilm. Department of Chemistry, Yale University, 225 Prospect St., New Haven, Connecticut 06511.

Homonuclear two dimensional NMR techniques for liquids are one of the most important developments of the last two decades. However many of these useful techniques have not been routinely applied to solids. The majority of homonuclear two dimensional NMR experiments depend on the presence of resolvable scalar couplings. In solids the non-commutativity of the dipolar coupling with the chemical shift for pairs of homonuclear spins has been shown to lead to severe broadening of the NMR lineshape even under MAS. In spite of these problems it can be shown that MAS spectra with resolved J couplings can be observed even when the differences in the anisotropic chemical shifts of coupled pairs of spins are the same order of magnitude as their dipolar coupling. To demonstrate that in many cases it is possible to perform two dimensional NMR experiments in the solid state on strongly coupled homonuclear spin systems, several compounds containing coupled pairs of ^{31}P nuclei have been investigated. In combination with MAS many standard two dimensional NMR experiments give results similar to those obtained in liquids. The lineshapes obtained and their field and spin rate dependence can be explained by extension of previous work by Maricq and Waugh (1979). The possibility of applying additional two dimensional NMR experiments to homonuclear spin systems in the solid state will also be examined.

237 NMR STUDIES OF FLUORINATED POLYCARBONATES. Satoshi Usui*, Brett Cowans†, Young Lee*, Jim Caruthers‡, and John Grutzner*. Departments of Chemistry* and Chemical Engineering ‡, Purdue University, West Lafayette, IN 47907.

A polycarbonate has been prepared from the interfacial condensation of phosgene with hexafluoroisopropylidene bisphenol. The material has M_n - 20,000 ± 3,000 and T_g - 160 ± 5°C. Solution and solid state ^{19}F, ^1H and ^{13}C NMR have been used to characterize the structure and molecular motion. The room temperature solid state fluorine spectrum shows a broadened chemical shift anisotropy pattern which remains essentially unchanged up to Tg. The CSA pattern narrows above T_g. T_1 measurements give values of 1-2 seconds which vary slowly over the 170° range of temperatures studied. The solid state Ml NMR spectrum shows a broadened dipolar coupling pattern. Solid state CP-MAS NMR spectra on the phenolic monomer have been used to estimate the ^{19}F-^{13}C dipole splitting. The CP-MAS spectrum of the polycarbonate shows that dipolar coupling between the carbonate carbons and fluorine is small and indicates that these groups are well separated on adjacent chains. The ring carbon patterns indicate that phenyl rotation is rapid. The internal motions in the polymer will be discussed.

238 SOLID STATE CPMAS-NMR STUDY OF AN A/B BLOCK COPOLYMER OF POLYSTYRENE AND POLY(METHYL METHACRYLATE). E. O. Stejskal, S. S. Sankar, and R. E. Fornes, Departments of Chemistry and Physics, North Carolina State University, Raleigh, NC 27695-8204, (919) 737-2998; and W. W. Fleming, T. P. Russell, and C. G. Wade, IBM Almaden Research Center, San Jose, CA 95120.

We have used ^{13}C-detected $T_{1\rho}(^1H)$ to detect phase separation in A/B block copolymers of polystyrene (PS) and poly(methyl methacrylate) (PMMA). In a homogeneously dispersed system, spin diffusion between protons causes all the protons to relax at about the same rate. However, in a phase separated system, if the domains are large enough, it may be possible to observe different proton relaxation rates in the different regions of the sample. This is most easily done by measuring the proton relaxation via the carbon system, if carbon resonances can be found which may be associated with one block, and not the other. The particular PS/PMMA block copolymers we have studied have sufficiently high molecular weight that they are somewhat phase separated at all times. However, annealing can be seen to cause further phase separation. In addition, annealing also causes changes in the rates of chain motion. This is detected both by changes in $T_{1\rho}(^1H)$ and by changes in $T_{1\rho}(^{13}C)$, which is not subject to averaging by spin diffusion and is thus more directly influenced by molecular motion.

39 DRUG-DNA COMPLEXES - STRUCTURE AND DYNAMICS BY SOLID-STATE NMR

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Using the two-dimensional CP-MAS method of Harbison and Spiess (Chem. Phys. Lett. (1986) 124 128-134) we can obtain structural information about the major forms of native DNA and their complexes with several important drugs and mutagens. The beauty of this method is that allows one, without model building, to determine the orientational distribution function for each residue for which a resolved NMR signal can be obtained. Studies of A and B DNA are in general agreement with the earlier results of fiber diffraction. 2D Spectra of DNA complexed with isotopically-labelled drugs reveal both the orientation of the drug molecule on the DNA, and also the perturbation in DNA structure brought about by the drug. As an example, we have determined important structural features of the intercalation complex of the drug and mutagen proflavine. Using ^{13}C labelled proflavine bound to native Li-DNA fibers, we can show by an analysis of the two-dimensional CP-MAS NMR spectra that the drug is stacked with the aromatic ring plane perpendicular to the fiber axis, and that it is essentially immobile. By monitoring proton cross-relaxation, we can show that the drug is indeed complexed to the DNA. Natural abundance ^{13}C NMR of the DNA itself shows that proflavine binding does not change the puckering of the deoxyribose ring, nor is there a significant change in the orientation of the sugar carbon-oxygen bonds relative to the helix axis. On the other hand, ^{31}P NMR spectra show profound changes in the orientation of the phosphodiester grouping on proflavine binding, with some of the phosphodiesters tilting almost parallel to the helix axis, and a second set almost perpendicular. We assign the first group to phosphodiesters spanning the intercalation sites, and we believe the tilting of the second set to be a compensation for the unwinding of the DNA by the intercalator. Data for the complexes of pentamidine and of cisplatin will also be presented.

240 LOCAL CHAIN MOTION OF POLYMERS WITH BACKBONE AROMATIC RINGS-THE RELATION OF RING FLIPPING TO SUB-TG MECHANICAL RELAXATION* P. Mark Henrichs. Corporate Research Laboratories. Eastman Kodak Company, Rochester NY 14650 and V. A. Nicety and David Fagerburg, Research Laboratories, Eastman Chemical Company, Kingsport, TE 37662.

The sub-Tg motion in bisphenol A polycarbonate (BPAPC) that is most easily detected by NMR spectroscopy is 180° flipping of the aromatic rings. The rate of ring flipping is correlated with the rale of the process responsible for tow-temperature mechanical and dielectric relaxation. However, a continuing puzzle has been that ring flipping alone cannot contribute either to mechanical or dielectric relaxation. Thus there has been interest in other motions of the chain that are mechanically active and occur in conjunction with ring flipping. Schaefer and coworkers have proposed that these other processes involve restructuring of the lattice around the flipping rings. As In BPAPC, ring flipping in poly(phenylene sulfide) (PPS) corresponds to a sub-Tg mechanical process. For PPS, however, deuterium NMR spectroscopy shows that very little reorientation of the polymer chain other than ring flipping takes place at low temperature; the mechanically active process in PPS takes place in the absence of significant chain reorientation. Displacement ot the polymer chains associated, accompanied by changes in the packing structure, provides a mechanism for the mechanically active process that can be coupled to ring flipping and does not require chain reorientation.

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241 SOLID STATE ^{15}N NMR OF NYLONS. Lon J. Mathias, Douglas G. Powell. Allison M. Sikes, and C. Greg Johnson. University of Southern Mississippi, Southern Station Box 10076. Hattiesburg, MS 39406-0076.

Natural abundance and ^{15}N-labeled nylons have been examined by several solid state NMR methods including CP/MAS, CSA, and relaxation measurements coupled with variable temperature analysis. Labeled materials include nylon 6, nylon 11, and nylon 12. Nylons offer a wide range of solid structures which may coexist simultaneously. These include various crystal forms, the amorphous region, and the interfacial domains connecting these various structures. We have used a combination of chemical shift, (traditional CP/MAS), relaxation times and chemical shift anistropy spectra to examine the various domains individually. We have shown that it is possible to examine the a and *y* crystal forms of various nylons at room temperature, and the 8 form of nylon 11 at elevated temperature. These are all thermodynamically stable crystal forms with unique chemical shifts and relaxation time values. The amorphous phase, and especially the more mobile components, are most easily observed using CSA spectroscopy which easily distinguished between rigid and rapidly moving components.

242 ESTIMATING DOMAIN SIZES FOR CHEMICAL AND PHYSICAL HETEROGENEITY IN SOLIDS USING PROTON SPIN DIFFUSION.

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Our use of NMR proton spin diffusion methods for the investigation of domain structures in polymer blends suggests that appropriate experiments may have some general utility in the determination of local structures in solids. The purpose of this presentation is not only to communicate results regarding phase structure in a series of related polymer blends (PEI/PBI with varying thermal histories), but also to point out variations of these experiments for probing physical, rather than chemical, structure. In all cases the establishment of optimum polarization gradients is of primary importance for maximizing structural sensitivity. ^{1}H multiple pulse experiments allow one to create polarization gradients based on chemical shift. Gradients based only on the apparent distribution of isotropic shifts are obtained when the preparation time is an integral number of rotor cycles. If static field inhomogeneity over the sample is small, gradients will be produced localized around regions of magnetic susceptibility anisotropy. Spin diffusion will then give an estimate of the size of the regions of anisotropic susceptibility. Hence it should be possible to investigate distances of orientational correlation in aromatic, glassy polymers. We are also looking into the possibility of investigating the uniformity of mechanical deformation in these materials.

243 SOLID-STATE NMR CHARACTERIZATION OF FUNCTIONALIZED, GRAFTED POLYSTYRENE/POLYPROPYLENE POLYMERS.

Joel R. Garbow, Physical Sciences Center, Monsanto Corporate Research, Monsanto Company, 700 Chesterfield Village Parkway, St. Louis, MO 63198.

Samples of polypropylene (PP) felt having a grafted polystyrene (PS) phase have been studied using cross-polarization magic-angle spinning (CPMAS) ^{13}C and ^{15}N NMR and ^{13}C-^{15}Notational-echo double-resonance (REDOR) NMR. This latter experiment permits the quantitative detection of ^{13}C-^{15}N chemical bonds. The samples were prepared by electron-beam irradiation of PP felt which had been treated with styrene monomer. Following functionalization of the PS rings, this polymer system serves as a substrate for solid-phase peptide synthesis. CPMAS ^{13}C NMR spectra of the felt samples (at natural abundance) show resolved resonances due to the PP and PS and allow the distribution of the PS within the PP to be investigated. The functionalization of the polystyrene rings has been studied using both CPMAS ^{15}N NMR and ^{13}C-^{15}N REDOR. Samples are prepared by alkylating the PS rings with ^{15}N- and/or ^{13}C-enriched hydroxymethylphthalimide (HMP). The incorporation and subsequent reduction of HMP is monitored through a series of CPMAS and REDOR experiments. Unexpected resonances, observed in the spectra of the reduced samples, arise from interaction of HMP moieties on neighboring PS rings. Implications for the performance of these felts as substrates for peptide synthesis are discussed.

244 ^{19}F AND ^{31}P MAS-NMR OF Sb-DOPED FLUOROAPATITE PHOSPHORS: DOPANT SITES AND SPIN-DIFFUSION.

James P. Yesinowski, Liam B. Moran, and Jefferey K. Berkowitz[§], Department of Chemistry, Michigan State University, East Lansing, MI 48824–1322, and [§]GTE Products Corporation, 100 Endicott St., Danvers, MA 01923.

Calcium fluoroapatite ($Ca_5F(PO_4)_3$) doped with Sb^{3+} is a phosphor material used in commercial fluorescent lights; the location in the apatite lattice of the crucial Sb^{3+} "activator" remains controversial. We have obtained high-resolution ^{19}F and ^{31}P MAS-NMR spectra at 9.4T of doped fluoroapatites containing from 0.18% to 3.0% Sb. The ^{31}P spectra consist of a main peak at 2.8ppm with additional weak peaks and shoulders whose relative intensities imply that they most likely arise from a secondary phase such as β–$Ca_3(PO_4)_2$, and not from phosphate groups perturbed by Sb^{3+}. The ^{19}F MAS-NMR spectra exhibit a sharp (HHLW =0.6ppm) main peak at 64ppm from C_6F_6 and in various samples shoulders at 62.9 and 65.4ppm as well as weaker sharp peaks at 68.6 and 72.8ppm. The measured T_1 relaxation times of the weak peaks are long (130–380s) and are equal to the T_1 value of the main peak in the various samples. Spin-diffusion is apparently not quenched by MAS, and results in equal T_1 values for fluorine atoms along the linear chain of apatite. The relaxation data and integrated peak intensifies suggest that the 68.6ppm peak can be assigned to two equivalent fluoride ions in an apatitic lattice which are perturbed by an Sb atom. The data support a model in which $SbO_3{}^{3-}$ replaces a phosphate group in the apatite lattice.

A MULTINUCLEAR (^{19}F, ^{1}H, ^{87}Sr) SOLID-STATE NMR STUDY OF THE FLUORIDATION OF Ca- AND SUBSTITUTED-APATITIC SURFACES, Anthony T. Kreinbrink, Charles D. Sazavsky, John R. Vietfeldt, Dennis G. Nelson, and Robert S. Honkonen. The Procter & Gamble Company, Cincinnati, OH 45239 and Paul S. Marchetti and Gary E. Maciel, Colotado State University, Fort Collins, CO 80523.

Elucidation of the surface chemistry associated with the fluoridation of apatitic surfaces such as dental enamel, dentine, and osteoporotic bone has been hindered by the inability of more traditional spectroscopies to characterize both crystalline and amorphous calcium phosphates and fluoridated calcium phosphate phases in the presence of and/or on the surface of calcium hydroxylapatite (HAP). We are currently using a combination of fast MAS ^{19}F and ^{1}H NMR to study the interaction at sub-monolayer levels of fluoride with mineral and biological apatites. To date, this work has provided spectroscopic evidence for the existence of non-specifically adsorbed fluoride (NSA-F) within the Stern layer, revealed striking differences in the reactivity of mineral and biological apatites, and provided evidence which is inconsistent with OH$^-$/F$^-$ iso-exchange as an important fluoridation mechanism. In addition to these results, our efforts to develop high-field ^{87}Sr NMR as a spectroscopic probe of the surface chemistry associated with/responsible for the incorporation of fluoride by substituted apatites will be discussed.

246 NDE BY NMR IMAGING OF AEROSPACE MATERIALS.* Charles G. Fry and Arthur C. Lind, McDonnell Douglas Research Laboratories, P.O. Box 516, St. Louis, MO 63166

NMR imaging shows potential for becoming an important NDE technique in industry. We discuss the applicability of NMR imaging for the NDE of aerospace materials, where sample conductivity, resolution and sensitivity, slice selection, field-of-view, and chemical sensitivity are issues which need to be resolved. We present an analysis of carbon-fiber composites, and discuss in what cases NMR imaging can be applied to these materials. Efforts to increase field-of-view and improving slice selection will also be presented.

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247 SOLID STATE SILICON-29 MAS NMR STUDY OF NEW HIGH PERFORMANCE CERAMICS. Keith R. Carduner. M. J. Rokosz, S. S. Shinozaki, and Y. Yasutomi . Ford Motor Company, Research Staff, Dearborn, MI, 48121, *Hitachi Research Laboratory, 832-2 Horiguchi, Katsuta-Shi, Ibaraki-Ken, 312 Japan

Application of high performance ceramics have been limited by the unpredictability of net shape changes of complex pieces following sintering. For intricately shaped pieces, machining of the post sintering part is usually required. Recently, a new family of ceramics based on nitriding of Si/SiC green bodies has been developed that shows significantly less shrinkage following sintering. Refinements of this material may literally lead to new near net shape sintered ceramic pieces. Application of NMR to the study of this new ceramic is providing insight into the phase composition of powders prior to sintering as well as the chemistry that accompanies the sintering process. Results from the NMR study of powders prior to sintering and from ceramic bars following sintering will be interpreted in terms of the resulting mechanical properties of the sintered pieces. Some complications related to the sampling of commercial ceramic by NMR will also be presented.

248 DEUTERIUM NMR LINESHAPES AND RELAXATION BEHAVIOR OF INTERCALATION COMPOUNDS. Ta-Hsien Lin, Robert L. Vold and Regitze R. Vold, Department of Chemistry, University of California, San Diego, La Jolla, California 92093, USA.

Deuterium NMR quadrupole echo spectra has been used in a study of the molecular motion of the (deuterated) proton conductor, hydrogen uranyl phosphate ($D(UO_2)PO_4 4D_2O$) and some alkylamine intercalation compounds of this material. We have carried out quadrupole echo lineshape and T_1 anisotropy studies of these compounds at different temperatures. While quadrupole echo lineshapes are very sensitive to motional trajectories and rates in the intermediate regime (10^3 - 10^7 s^{-1}), spin-lattice relaxation measurements are required to obtain motional rates in the fast regime. We have analyzed the anisotropic T_1 inversion recovery behavior of these materials and derived information about the type of motion of the intercalated molecules.

HIGH RESOLUTION NMR OF QUADRUPOLAR NUCLEI IN MOLECULAR SIEVES

249 Yue Wu, Bradley F. Chmelka, Mark E. Davis[1], Pieter J. Grobet[2], Peter A. Jacobs[2].
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Anisotropic broadening from second-order quadrupolar interactions often dominates the NMR spectra of quadrupolar nuclei in polycrystalline solids. This has been a barrier to establishing the local structure of many technologically important inorganic materials, particularly metal oxide systems, such as zeolites and large pore aluminophosphates. Using the new technique of Double Rotation (DOR), this broadening can be eliminated completely to resolve, for example, distinct tetrahedrally coordinated aluminum sites within microporous crystalline lattices. Such microstructural information provides new insight into guest/host ordering in molecular sieves, permitting macroscopic adsorption and reaction properties of these materials to be probed at a molecular level.

250 **DIPOLAR NMR SPECTROSCOPY OF NON-OXIDIC GLASSES. Hellmut Eckert, David Lathrop, Deanna Franke and Robert Maxwell, Department of Chemistry, University of California, Santa Barbara, Goleta CA 93106.**

While most NMR applications to glasses are based on obtaining chemical shift information via magic angle spinning, our studies are aimed at measuring and quantifying multi-spin homo-and heteronuclear dipole-dipole couplings. The latter have the advantage over chemical shifts that they are calculable from first principles and hence can serve as quantitative criteria for examining hypothetical atomic distribution models in glasses. Homonuclear dipole-dipole couplings are conveniently measured by the spin-echo decay method. The heteronuclear dipole-dipole couplings have been measured using spin-echo double resonance, taking advantage of flexible heteronuclear X-Y double resonance capabilities developed in our laboratory. Various applications to non-oxide chalcogenide glasses and glassy and crystalline phosphides and arsenides and comparison to computer generated glass-structure models will be discussed.

1 j PULSED ENDOR SPECTROSCOPY OF ARGONNE PREMIUM COALS. H. Thomann. M. Bernardo, B. G. Silbernagel, and M. T. Melchlor; EXXON Corporate Research Laboratory, Annadale, NJ 08801

Polynuclear aromatic (PNA) molecules in coals are hosts to typically 10^{18}-10^{19} paramagnetic electrons per gram carbon. These PNA radicals serve as convenient probes of coal structure, both by direct detection using EPR and ENDOR techniques and by indirect detection using DNP spectroscopy. Pulsed ENDOR provides the opportunity to utilize the well developed methods of pulsed NMR for obtaining high resolution NMR "sub-level" spectra and for directly probing sub-level spin dynamics for nuclei vhich are strongly coupled to paramagnetic electrons. Recent pulsed ENDOR spectra on coals utilizing sub-level polarization transfer and coherence magnetization transfer schemes as well as sub-level nuclear spin relaxation data will be presented.

252 A BLOCH DECAY AND CPMAS ^{13}C NMR STUDY OF THE ARGONNE PREMIUM COALS: EFFECTS OF HIGH-SPEED SPINNING ON ^{13}C QUANTITATION. James A. Franz and John C. Linehan. Battelle, Pacific Northwest Laboratories, Battelle Boulevard, P.O. Box 999/K2-21, Richland, WA 99352.

The quantitative performance of the CPMAS experiment under conditions of ultra-high-speed magic angle spinning is explored. Bloch Decay and variable contact time ^{13}C CPMAS NMR data at 13 kHz MAS are presented for the Argonne Premium Coals. High field (7.05 T, 75 MHz, 13kHz MAS) aromaticitites are in satisfactory agreement with low field CPMAS (25. MHz, 4 kHz MAS) results, with the exception of the high oxygen-containing Wyodak Coal. Bloch decay aromaticities at 13 kHz MAS agree with CPMAS results at 25 MHz (4kHz MAS) for all of the bituminous coals, but show somewhat higher aromaticities for the lignite (Beulah Zap) and sub-bituminous (Wyodak) coals. A Bloch decay and variable contact time study of the ratios of protonated, non-protonated, and isolated aromatic carbons of acenaphthene revealed satisfactory quantitative results. The results suggest distortions in relative pcak intensities from high speed MAS to be small. Sources pf disagreement between Bloch decay and CPMAS results for Wyodak and Beulah Zap coals are discussed, and the effects of rf power levels during the contact period for low rank coals are discussed. The results of an epr study of the Argonne coals is discussed in connection with NMR quantitation.

253 EPR STUDIES OF DEMINERALIZED ARGONNE PREMIUM COALS. L. A. Gebhard*, B. G. Silbernagel*, R. A. Flowers+, J. W. Larsen*+ (*Exxon Research and Engineering Company, Route 22 East, Annandale, NJ 08801; +Department of Chemistry, Lehigh University, Bethlehem, PA 18018

Transition metal and carbon radical EPR have been used to study the effects of ion exchange and demineralization in Argonne Premium Coals. These experiments were occasioned by our recent survey of the Argonne Premium Coals, which suggested that mineral matter---and possibly organically complexed transition metal ions---were significantly affecting the EPR properties of the carbon radicals in the coal. Coal samples have been subjected to two procedures: (1) a citric acid wash (CAW), known to remove organically complexed ions, and (2) HCL/HF demineralization. Carbon radical g-values are not affected by these procedures but significant increases in the carbon radical density are observed and the radical linewidth decreases. We attribute these changes to the removal of minerals and transition metal ions from the coal. The only exception occurs in the case of demineralized Illinois #6 coal, where iron species---presumably from reagent attack on the pyrite minerals---remain behind after treatment.

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DISTORTION-FREE ^{13}C NMR DM COAL BY MEANS OF ^{1}H ROTATING-FRAME DYNAMIC NUCLEAR POLARIZATION AND ^{1}H-^{13}C CROSS-POLARIZATION.

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In many coals the interplay between the ^{1}H-^{13}C polarization transfer time, T_{CH}, and the ^{1}H rotating-frame relaxation time, $T_{1\rho}$, occurring during a standard Cross-Polarization (CP) experiment, leads to distorted ^{13}C spectra and to erroneous results about, e.g., the detected percentage of carbons. In this paper an alternative CP experiment is described, where the ^{1}H magnetization, utilized in CP, is obtained via Dynamic Nuclear Polarization in the proton Rotating Frame (RF-DNP). This is achieved by a simultaneous irradiation with a strong r.f. field at the ^{1}H Larmor frequency and a microwave field near the Larmor frequency of the unpaired electrons, present in a coal. It is shown that in this so-called RF-DNP-CP experiment interplay effects between T_{CH} and $T_{1\rho}$ are indeed avoided, thus preventing ^{13}C spectral distortions due to these effects. Moreover, multiple-contact RF-DNP-CP experiments are possible, which reduce the measuring time of a spectrum. An application of the RF-DNP-CP technique in a low volatile bituminous coal is given.

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MULTI DIMENSIONAL ELECTRON MAGNETIC RESONANCE OF COAL.

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Disordered systems (e g powders, glasses, frozen liquids) often are difficult to study by magnetic resonance methods because of the large number of effects that simultaneously contribute to spectra. This is especially true for coal samples, where chemical heterogeneity further complicates spectral interpretation. Multi-dimensional approaches applied to electron magnetic resonance (EMR) techniques like EPR. ENDOR. and ESE can sometimes simplify the spectra from such complex systems by emphasizing only a few of the many resonance-sensitive effects at a time, thus improving resolution, specificity (spectral clarity), and at times, even sensitivity Key dimensions for study include magnetic field strength, excitation frequency, and duration (time), together with chemistry. Examples of our current work on coal illustrating the effectiveness of the multidimensional approach will be presented, with emphasis on very high frequency EPR and MRI.

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QUANTITATION OF PROTONS IN THE ARGONNE PREMIUM COALS BY SOLID STATE ^{1}H NMR.

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Quantitation of protons and moisture in the eight coals from the Argonne Premium Coal Sample Program by ^{1}H NMR spectroscopy was performed. The solid echo was utilized to determine the true lineshape of the on-resonance ^{1}H free induction decay (FID). A superposition of Gaussian and Lorentzian decay functions were found to adequately describe the FID of dry coals. The Gaussian fraction corresponds to rigid protons in the macrostructure of coal. The Lorentzian fraction is attributed to fragments in the coal exhibiting hindered molecular mobility. For wet coals, an additional slowly decaying Lorentzian fraction must be added to the description of the FID. Identification of the species responsible for the longest decay was made by liquid state NMR of the condensate obtained by heating the sample at 100°C under static vacuum, and high resolution solid state NMR of the ^{1}H in the coals before, and after removing the matter volatile at 100°C.

257 **THE SOLVATION OF COALS BY PITCHES AND MODEL COMPOUNDS AT HIGH TEMPERATURE.** Richard Sakurovs and Leo J. Lynch, CSIRO Division of Coal Technology, PO Box 136, North Ryde, 2113 Australia.

The fusion of coals, coal tar pitches and model compounds and their mixtures was monitored by Proton Magnetic Resonance Thermal Analysis (PMRTA) between room temperature and 600 C. A linear parameter (M_{2T}) based on the second moment of the truncated frequency spectrum obtained by Fourier transformation of the NMR transverse relaxation signal was used to describe the degree of fusion of the sample. A new approach, based on the difference between the actual M_{2T}'s of a mixture and the M_{2T}'s calculated in the absence of interactive effects was developed to quantify the extent of interaction between coals and additives. Using this approach, it was found that bituminous coals and coal tar pitches interact strongly at temperatures above 300 C, brown coals accelerate the coking of coal tar pitch, and some model compounds can fuse more than three times their weight of certain coals even at concentrations as high as 10% wt/wt.

258 **MAGNETIC RESONANCE STUDIES OF MeAlPO-5.** Z. Levi and D. Goldfarb. Dept. of Isotope Research, The Weizmann Institute of Science, 76 100 Rchovot, Israel

The synthesis of alumino-phosphate molecular sieves with transition elements, such as Mn, Fe, Co and Ti, incorporated into tetrahedral framework sites, as opposed to cation exchanged sites have been recently reported by Flanigen and coworkers[1]. We employed several magnetic resonance techniques to obtain evidence for framework siting of Mn and Co in AlPO-5 and to study in details the local environment of the transition metal as function of activation processes and presence of various adsorbates.

The methods employed were: a) ^{31}P and ^{27}Al magic angle spinning (MAS) NMR where we followed the dipolar paramagnetic shift, which is related to the distance between the Mn^{2+} and its neighboring ^{31}P and ^{27}Al nuclei. b) ESR spectroscopy. c) Electron spin echo modulation envelope (ESEEM) spectroscopy where we look for ^{31}P modulation which is indicative of the transition metal substitution for Al.

The results were compared with those obtained from Mn^{2+} impregnated onto AlPO-5 and exchanged into SAPO-5 which is the corresponding silico-alumino-phosphate molecular sieve. In these materials the Mn^{2+} cannot occupy framework sites. Our results indicate that indeed some Mn^{2+} was incorporated into tetrahedral framework sites, nonetheless, the increase in spin exchange with increasing dehydration temperature, as observed by the ESR spectra, suggests that a *substantial* amount of Mn^{2+} exsists *as* extra-frame work cations as well.

1. Flanigen E.M., Lok B.M., Patton R.L. and Wilson S.T "New Developments in Zeolite Science and Technology", Eds. Murakami A., Lijima A. and Ward J.W., 1986, p.103.

259 **VARIABLE-TEMPERATURE IN-SITU SOLID-STATE NMR INVESTIGATIONS OF REACTIONS ON ZEOLITE CATALYSTS**

Eric J. Munson, Jeffery L. White, MARSHA J. Lambregts, NOEL D. Lazo, AND James T. HAW, Department OF CHEMISTRY, Texas ACM University, College Station, T«XA« 77843

THE in-situ study of REACTIONS occurring ON ZEOLITE CATALYSTS PROVIDES VALUABLE INFORMATION concerning REACTION MECHANISMS AND intermediates FORMED BY these REACTIONS. THE ABILITY TO LOAD samples WITHOUT EXPOSURE TO oxygen OR MOISTURE AND maintain sample integrity AT HIGH temperatures requires modifications of EXPERIMENTAL PROCEDURES IN MAGIC ANGLE spinning spectroscopy. IN THIS PRESENTATION, THESE modifications will BE DISCUSSED AS WELL AS THE APPLICATION OF these TECHNIQUES TO THE study OF SEVERAL reaction IN catalysts OCCURRING AT BOTH HIGH AND LOW temperatures.

260 IN SITU NMR STUDIES OF ZEOLITE CATALYSIS.

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A methodology has been developed to study in situ catalysis occurring in microporous materials using both ^{13}C and ^{1}H MASNMR. The technique involves the manufacture of lap-ground pyrex microreactors which fit tightly inside a zirconia rotor. These reactors are connected to a vacuum line where the sample can be activated at 400 C then charged with reactant. The microreactor can then be sealed and taken to the desired reaction temperature. Then by comparison of the molecular contents of the micropores, assessed by ^{13}C NMR, with the products, assessed by gas chromatography, the time shape-selective nature of the catalyst may be ascertained. ^{13}C MASNMR provides a detailed itinerary of the molecular contents, however, H MASNMR gives information about Bronsted acidity of the catalyst and protonation of reactant species. By variously deuterating the reactant molecules or the acid sites on the catalyst the fate of individual protons may be determined. Assignments of C resonances are made by comparison with literature data, response to cross polarization techniques and more recently by using 2-dimensional J-resolved spectroscopy. Using such methods we have found that the shape-selectivity of, in particular, zeolite catalysts is not only a function of the pore dimensions but is also modified by products that are trapped within the channel system. This makes shape-selective effects very hard to predict

261 Development and Use of the Carr-Purcell Pulse Train for Dipolar Spectroscopy: The Geometry and Reorientational Mobility of Benzene Chemisorbed on Pt/η-Al_2O_3

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Carr-Purcell pulse trains have not been used to make quantitative bond-length measurements, possibly because of a dependence of the experimental results on the rf duty-factor of the sequence. We have found experimentally as well as theoretically that this dependence is linear and have measured C-C bond lengths in both acetic acid and benzene with ~1% accuracy. We also have used this method to measure the C-C bond length in benzene-1,2-$^{13}C_2$ chemisorbed on Pt/η-Al_2O_3 and have found a single Pake doublet, yielding a value of of 1.42A, close to that for bulk benzene (1.39A). This result will be compared with a variety of studies (IR, LEED, STM) of benzene adsorbed on Pt/η-Al_2O_3 as well as on a Pt (111) single crystal surface in which deviation from sixfold symmetry and multiple C-C bond lengths have been postulated. The spectra show clearly that the molecule is rotating rapidly on the NMR time scale (~microseconds) at temperatures as low as 10K, whereas such motion is quenched at 90K in the bulk solid.

262 ^{129}Xe NMR OF METAL-EXCHANGED ZEOLITES.

Cathy Tway and Ton Apple. Dept. of Chemistry, Univ. of Nebraska, Lincoln, NE 68588-0304.

The NMR of xenon atoms in Ru-Y zeolites along with mixed samples containing Na-Y and Ru-Y has been examined. The NMR response is dependent upon the zeolite crystal aggregate size. Mixed zeolites sieved through a fine mesh exhibit exchange effects which indicate that xenon is diffusing over a long range. For fine sieved zeolites a contribution from the interparticle void region is observed. Xenon atoms incorporated into zeolites containing Group VI carbonyls allow easy detection of subcarbonyls.

ↄ3 I **MULTINUCLEAR NMR INVESTIGATIONS OF HETEROGENEOUS CATALYSTS.** Cecil Dybowski,
__J Matthew Smith, Mary Jacintha, Mark Hepp, C. J. Tsiao, and Navin Bansal.
Center for Catalytic Science and Technology and Department of Chemistry and
Biochemistry, University of Delaware 19716.

The use of proton, carbon - 13, deuterium and xenon - 129 NMR spectroscopies in the investigation of supported-metal and zeolite catalysts is discussed. In each case, we describe how a single NMR measurement or a set of measurements combined with other measurements of the material leads to a model for the structure of a catalytic center or a complex formed by the adsorption of a reactive (usually organic) species with the catalytic site. To summarize, we present a brief discussion of the strengths and weaknesses of various NMR strategies for investigating heterogeneous catalysts.

264 **QUADRUPOLAR NUCLIDES IN CATALYTIC ENVIRONMENTS.** Paul D. Ellis, John C.
Edwards, H. Douglass Morris, and Shelton Bank, Departments of Chemistry,
University of South Carolina, Columbia, S.C. 29208 and State *University fa*
New York at Albany, Albany, N. Y. 12222.

First, a brief introduction to the problems of utilizing the nmr parameters of quadrupolar nuclides, e.g. ^{27}Al and ^{95}Mo will be given. Specifically, how to address the broad lines, utility of the resulting parameters, and the feasibility of using these nuclei in cross-polarization experiments. Specific examples will include cross-polarization from ^{1}H to ^{27}Al, where the aluminum is a surface species on γ-alumina, various transition aluminas and clay surfaces. Additionally, examples of cross-polarization from ^{1}H to ^{95}Mo will also be discussed and demonstrated. The particular systems of interest are precursors to HDS catalysts. Finally, progress on adsorption of acetylene and ethylene to supported metal surfaces, e.g. Pt/γ-alumina and Ag/γ-alumina will be summarized.

265 NO ABSTRACT AVAILABLE

266 NO ABSTRACT AVAILABLE

267 l NO ABSTRACT AVAILABLE

268 l CHARACTERIZATION OF COAL MACERALS BY NMR SPECTROSCOPY AND IMAGING.

R. E. Botto, C.-Y. Choi, S. L. Dieckman*, N. Gopalsami*, A. R. Thompson, and C.-J. Tsiao, Chemistry Division and *Material & Components Technology Division, Argonne National Laboratory, Argonne, IL 60439

Liptinite, vitrinite and inertinite macerals isolated from Utah Blind Canyon hv bituminous (APCS #6) coal and West Virginia Lewiston-Stockton hv bituminous (APCS #7) coal were characterized by ^{13}C- and ^{1}H-NMR spectroscopy. Systematic investigations of carbon and proton relaxation times and of free-induction decay (FID) and cross polarization (CP) pulse methods were carried out on the macerals. Although carbon aromaticities showed the expected trends, values obtained in CP experiments were found to be consistently lower. The findings clearly demonstrated the utility of ^{13}C-FID measurements for quantitative analysis. Recent NMR microscopic imaging experiments on a vacuum-dried sample of APCS #6 were carried out by using multipulse ^{1}H-decoupling and back projection reconstruction methods. Reduction in the proton linewidth facilitated imaging of resinite and vitrinite macerals within microlithotypes to a spatial resolution of ca. 200 μm.

*This work was performed under the auspices of the Office of Basic Energy Sciences, Division of Chemical Sciences, U.S. DOE, under contract number W-3I-I09-ENG-38.

B

A STUDY OF THE MORPHOLOGY OF POLYPHOSPHAZENES USING SOLID-STATE NMR

Sharon A. Tavlor. Jeffery L. White, Nicholas C. Elbaum and James F. Haw, Department of Chemistry, Texas ASM University, College Station, Texas 77843

Polyphosphazenes are inorganic polymers which are based on chains of alternating phosphorus and nitrogen atoms. These polymers have complex morphologies which can be investigated in detail by solid-state NMR. In our laboratory, poly[bis(3-methylphenoxy)phospha-zene]-(PB3MPP) has been studied in detail by a variety of NMR techniques. Investigation of PB3MPP by P-31 CP/MAS NMR reveals the presence of two isotropic peaks whose relative intensities are a function of temperature. Based on complimentary Bloch decay experiments, these peaks have been assigned as being due to a relatively rigid crystalline phase and a highly mobile amorphous phase. Spectral evidence suggests that magnetization transfer occurs between the two phases via mass transport (i.e. chemical exchange) or P-31, P-31 spin diffusion. Insight about this process has been gained by studying the relaxation behavior of PB3MPP. The transfer rate has been investigated via a selective inversion experiment. The absence of a temperature dependence is consistent with spin diffusion. The results of a rotating-frame magnetization transfer experiment conclusively demonstrate spin diffusion.

SOLID STATE ^{2}H NMR SPECTROSCOPY OF ORIENTED Li AND Na DNA FIBERS.

G.H.Meresi.[1] R.R.Vold.[1] R.L.Vold.[1] D.R.Kearns.[1] R.Brandes.[2] A.Rupprecht.[3] and W.Köhnlein.[4] [1]Dept. of Chemistry, Univeristy of California, San Diego, La Jolla, California 92093. [2]Magnetic Resonance Unit 11-M, VA Medical Center, San Francisco, California 94121. [3]Arrhenius Laboratory,Division of Physical Chemistry - University of Stockholm, Sweden. [4]Universität Münster, Institut für Strahlenbiologie, D-4400 Münster, West Germany.

As part of an ongoing investigation in our laboratory into the structure and dynamics of DNA (Deoxyribonucleic acid) in the solid state, we have studied oriented DNA fibers with the cytidine bases selectively labeled with deuterium at the 5-position. The results complement earlier studies of solid DNA samples deuterated at the 8-position of the purine bases and allow the determination of the orientation of the base pairs relative to the DNA helix axis. Spectra of two samples with significantly different degrees of order both at 75% relative humidity (~ 8.5 H_2O molecules per nucleotide) will be presented and compared with spectra calculated with the inclusion of both in-plane and out-of-plane librational motion of the base pairs. For an easy understanding of the spectra obtained, two unique directions will be discussed, i.e. with the magnetic field either parallel or perpendicular to the axis of order. The resulting lineshapes from these two unique orientations have been fully analyzed to yield the orientation of the base pairs with respect to the helix axis in terms of both tilt and roll angles.

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SOLID SAMPLE ^{13}C NMR STUDIES OF POLYIMIDES.

Myono K. Ahn, Department of Chemistry, Indiana State University, Terre Haute, Indiana 47809, and Mary Ann Meador, and Kenneth J. Bowles, NASA Lewis Research Center, Cleveland, Ohio 44135.

Thermosetting polyimides have been commonly used as matrix resins in fabricating thermally stable carbon fiber composites. They are manufactured in two steps. The first step is to prepare moderate molecular weight oligomers by a condensation reaction at a relatively low temperature of 120°C. The second step involves in situ polymerization of the oligomers at a temperature above 200°C. The resin, thus produced, is amorphous, highly crosslinked and insoluble. The solid sample MAS ^{13}C NMR of the fully cured sample shows resolved peaks corresponding to the carbons in the phenyl rings, carbonyl group, and N-C=0 of the imide linkages. The effect of proton cross polarization enhancement and HP decoupled T1 measurements of each resolved peak will be discussed also.

272 NUCLEAR ACOUSTIC RESONANCE.

Robert G. Leisure. Department of Physics, Colorado State University, Fort Collins, Colorado 80523.

Nuclear acoustic resonance (NAR) is a phenomenon in which acoustic energy from an external source is resonantly absorbed by the nuclear spins In a sample. NAR is thus the acoustic analog of NMR wherein electromagnetic energy is resonantly absorbed by the nuclei. Although NAR and NMR are similar in many respects, there are important differences. In particular, the coupling of energy to the nuclear spins occurs differently in the two cases. In NAR the coupling arises because the acoustic wave propagating in the material generates internal oscillatory fields, or modulates some internal interaction. The experimental techniques required to observe NAR are, of course, different from those used in NMR. In this talk the phenomenon of NAR will be reviewed and acoustic-wave nuclear-spin coupling mechanisms will be discussed. Experimental methods will be outlined and illustrative experimental results will be presented.

ON THE GROWTH OF MULTIPLE-SPIN COHERENCES IN THE NMR OF SOLIDS.

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Serge Lacelle, Département de chimie, Université de Sherbrooke, Sherbrooke, Qc, CANADA, J1K 2R1.

A novel approach to the understanding of the growth of multiple-quantum coherences in strongly dipolar coupled spin systems will be presented. The discussion will focus on

1) power law dependence for the growth of the number of correlated spins as a function of excitation time and the geometry of the spin network;

2) a localization/delocalization criteria for the propagation of multiple-spin correlations in spin networks;

3) features of the growth process modelled by random graph theory and random multiplicative processes;

4) effects of dissipation and irreversibility in the growth process as modelled by cellular automata.

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DIPOLE MEASUREMENTS WITH COMPENSATED CARR-PURCELL SEQUENCES.

Terry Gullion, Jacob Schaefer, David Baker, Martin Lizak, and Mark Conradi
Departments of Chemistry and Physics, Washington University, St. Louis, MO 63130

Dipole couplings can be measured with Carr-Purcell type sequences in static and rotating samples (REDOR). The performance of these methods can be severely degraded by cumulative pulse errors which arise from off-resonance effects and H_1 inhomogeneity. Recently, new, compensated Carr-Purcell sequences have been demonstrated which greatly minimize cumulative pulse errors from the above sources. These strings are based on x and y phase alternation of the π pulses. Results will be presented that show the ability of the new sequences to compensate cumulative pulse errors for all three components of magnetization using water as a test sample. Homonuclear dipole interactions in static, labeled benzenes have been measured. REDOR results demonstrating the elimination of pulse errors on the measured heteronuclear dipole coupling in a spinning solid will also be presented.

275 ROTATIONAL RESONANCE IN AN RF FIELD FOR NMR OF ROTATING SOLIDS

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In sample spinning NMR experiments, a rotational resonance occurs when the precession frequency of the spin in the rf field matchs the modulation of the chemical shift imposed by sample rotation. At resonance conditions, $\omega_{rf} \approx \omega_r$ or $2\omega_r$, instead of being spin-locked along the rf field, the magnetization nutates in the rotating frame at a frequency which equals the amplitude of the oscillating component of the interaction. The nutation of the magnetization allows the retrieval of the chemical shift anisotropy from MAS spectra in a two-dimensional manner. Average Hamiltonian theory is used to calculate the nutation of the magnetization caused by rotational resonance. The mismatching of the rotational resonance condition due to the rf field inhomogeneity of the coil causes a constant component in the time domain nutation and a central peak in the spectral lineshape in the frequency domain. A good rf field homogeneity is therefore critical to this rotational resonance experiment and its applications.

276 MULTINUCLEAR NMR STUDIES OF SAMPLES BASED ON ALUMINATE AND SILICATE STRUCTURES.

Steven F. Dec. Charles E. Bronnimann, Abdullatef I. Hamza,* John J. Fitzgerald,* and Gary E. Maciel. Department of Chemistry, Colorado State Univ., Fort Collins, CO 80523.

Solid-state multinuclear (^{1}H CRAMPS, ^{27}Al and ^{29}Si) MAS NMR studies of clay minerals, clay-based ceramic precursors and catalytic materials are described. Three major types of solid-state reaction systems, based on kaolinite, montmorillonite and pyroplyllite minerals, have been examined: 1) thermal dehydroxylation reactions between 150 and 850 °C, 2) high-temperature (900-1300 °C) transformation reactions to produce complex Si/Al phase compositions and 3) solid/solution dealumination reactions of clay minerals in aqueous HCl/solutions, used to produce catalytic materials.

^{1}H CRAMPS NMR has been most useful in examining dehydroxylation reactions and the nature of catalytic sites. High-field (14 f) MAS ^{27}Al and CP/MAS or SP/MAS ^{29}Si NMR have been primarily useful for examining structural changes accompanying both dehydroxylation and high-temperature phase transformations, as well as the silicon atom environments in clay-based catalysts. The multinuclear NMR results are discussed in relationship to the mechanisms of dehydroxylation, dealumination and high-temperature phase transformations.

ADVANCES IN HETERONUCLEAR CORRELATION APPROACHES FOR SOLIDS.

Charles E. Bronnimann and Gary E. Maciel. Department of Chemistry, Colorado State University, Fort Collins, Colorado 80523.

We have recently modified our 187 MHz CRAMPS spectrometer to include multiple-pulse double-resonance capabilities. At the time of writing this abstract we have obtained, on model systems, ^{1}H-^{13}C HETCOR results analogous to recent results of Burum and Bielecki, and are exploring a simple method for the separation of CH and CH_2 resonances in solids. Practical aspects of these experiments, such as performance on various chemical systems and the technical demands on one's spectrometer, will be discussed. Prospects for HETCOR on weakly-coupled systems, such as those in inorganic systems and their surfaces, will be discussed.

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STEPPED FREQUENCY NMR SPECTROSCOPY OF QUADRUPOLAR NUCLEI.

Robert L. Vold, Regitze R. Vold, and Michael A. Kennedy, Department of Chemistry, University of California, San Diego, La Jolla, California 92093, USA.

Sindorf and Bartuska recently showed (J. Magn. Reson. 85, 581, (1989)) that it is possible to obtain solid state NMR spectra of very wide quadrupolar powder patterns by using single point by point acquisition after a string of weak pulses whose frequency is stepped digitally across the spectrum. This technique has advantages over conventional, high power quadrupole echo methods — spectral coverage is limited only by probe bandwidth, and large sample coils can be used to increase sensitivity. Especially when the sensitivity of stepped frequency NMR is improved by multipoint acquisition between each frequency step, the method becomes an attractive alternative to strong pulse techniques. Variable under experimental control in a stepped frequency experiment include the pulse amplitude, shape and phase as well as the step rate, filter bandwidth, acquisition delay and number of points acquired per step. Proper selection of experimental conditions is necessary to minimize numerous possibilities for lineshape distortion. Representative spectra will be presented for ^{2}H, ^{27}Al, and ^{14}N.

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CHEMICAL STABILITY OF WET-DEPOSITION SAMPLES SUBSAMPLED DAILY FOR ONE WEEK.

Timothy C. Willoughby, LeRoy J. Schroder, and John D. Gordon, U.S. Geological Survey,
P.O. Box 25046, M. S. 401, Denver, CO 80225

During 1988, the U.S. Geological Survey examined the chemical changes that occur in wet-deposition samples stored in a collector for one week. Samples from ten storms that resulted in 1.3 millimeters or more of precipitation were collected in a wet-only collector using 13-liter polyethylene buckets. About 25 milliliters of the sample was removed daily from the bucket and filtered for each subsampling. After the pH and specific conductance for each daily subsample was determined, the remainder of the sample was preserved for ion chromatography and flame atomic absorption spectrometry or flame atomic emission spectrometry. Chloride, nitrate, and sulfate concentrations were determined by ion chromatography. Calcium concentrations were determined by flame atomic emission spectrometry, and magnesium, sodium, and potassium concentrations were determined by flame atomic absorption spectrometry. The subsamples were chilled at 4 degrees Celsius until all the subsamples for an individual storm were removed. All subsamples from an individual storm were then analyzed.

A Kendall's estimator was used to estimate the change in concentration versus the time the sample remained in the collection buckets for each analyte and a non-parametric regression equation was determined. A Kendall's tau measure of rank correlation was then used to determine if any statistically significant correlations existed between the analyte concentrations and the length of time the sample remained in the collection Ducket. All of the analytes had positive slopes except hydrogen ion and specific conductance indicating increases in concentration. Only calcium and hydrogen ion had statistically significant correlations st a significance level of 0.05.

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APPUCATION OF STATISTICAL QUALITY-CONTROL METHODS TO AN EXTERNAL QUALITY-ASSURANCE PROGRAM OF THE NATIONAL ATMOSPHERIC DEPOSITION PROGRAM/NATIONAL TRENDS NETWORK

John D. Gordon, LeRoy J. Schroder, and Timothy C. Willoughby. U.S. Geological Survey, Denver Federal Center, Box 25046, MS 401, Denver, Colorado B0225

The intersite-comparison program is an external quality-assurance program used to assess the accuracy of onsite pH and specific conductance measurements made by about 200 National Atmospheric Deposition Program/National Trends Network site operators. Site-operator performance is evaluated according to established measurement-accuracy criteria. Because of the large size of the network, no follow-up protocol currently exists for sites that fail to meet measurement-accuracy criteria. A follow-up plan based on statistical quality-control methods has been developed. The follow-up plan is only a model and is not currently an official part of the external quality-assurance program. Implementation will depend upon approval by the Network Operations Subcommittee of the National Atmospheric Deposition Program/National Trends Network Technical Committee. Graphical data-analysis techniques are first used to screen the data. Control charts based on nonparametric data-analysis methods are then used to decide which sites to include for follow-up. The control charts are also used to decide what type of follow-up the sites will receive. Follow-up could consist of sending site operators additional aliquots of test solutions or sending site operators a letter describing common causes of measurement error.

281 **GRAPHICAL METHODS OR EVALUATING ANALYTICAL DATA FROM REFERENCE SAMPLES.** H. Keith Long. U.S. Geological Survey, Water Resources Division, Branch of Quality Assurance, 1526 Cole Blvd., Bldg. 3, Golden, Colorado 80401.

The U.S. Geological Survey conducts a semiannual interlaboratory evaluation. All laboratories that provide water-quality data for use by the U.S. Geological Survey, Water Resources Division, are sent a series of natural matrix water and sediment reference samples for analysis by methods of their choice. Analytical data are evaluated using non-parametric statistics; the results are reported in tables and associated graphs. A large amount of data can be accomodated and quickly evaluated using these techniques.

An alternative approach is to present these data using only graphs. There are three differenct graphical designs. A histogram overlay with a line graph shows the frequency distribution and quartiles of the reported values. A scattergram of reported values, grouped by analytical method, illustrates central tendency, method bias, and the rank of each reported value. The median and hinge spread plotted as a hi-lo graph affords a visual means to evaluate each analytical method.

282 **QUALITY ASSURANCE WITHIN THE ALASKAN LIMNOLOGY PROGRAM THROUGH STATEWIDE STANDARDIZATION OF FIELD AND LABORATORY METHODOLOGIES. Jim A. Edmundson and Jeffrey P. Koenings. Alaska Department of Fish and Game, 34828 Kalifornsky Beach Road, Soldotna, Alaska 99669**

The Alaska Department of Fish and Game Limnology Laboratory conducts both internal and external quality assurance monitoring on water-quality, chlorophyll a (chl a), and zooplankton samples from over 150 lakes statewide. As many study sites are remote, samples are sometimes subjected to unanticipated prolonged storage (2 weeks) prior to analysis of general water-quality parameters. However, we observed negligible differences between insitu and laboratory measurements of conductivity, pH, and alkalinity. Because many lakes are oligotrophic (<2 µg L^{-1} chl a), the laboratory must routinely achieve lower detection limits of <1 L for algal nutrients (nitrogen and phosphorus). In addition, chl a levels derived from samples stored frozen on glass-fiber filters remained stable over a two year period regardless of sample size (volume filtered) or treatment with $MgCO_3$. Moreover, we found no significant differences in macrozooplankton density estimates derived from multiple hauls or between field site and laboratory analyses. Considering all analytical methodologies, levels of precision and accuracy ranged from 5-17% and + 2-7%, respectively.

283 EXTERNAL QUALITY-ASSURANCE PROGRAM FOR U.S. GEOLOGICAL SURVEY ANALYTICAL LABORATORIES by Thomas J. Maloney, U.S. Geological Survey, P.O. Box 25046, MS 401, Lakewood, CO 80225

U.S. Geological Survey analytical laboratories participate in an external quality-assurance program conducted by the Water Resources Division Branch of Quality Assurance. This program monitors and evaluates the quality of major-ion, nutrient, and trace-metal determinations and provides laboratory users information on the precision and accuracy of analytical results. The program is based on the analysis of reference sample mixtures that are submitted to the participating laboratories as regular samples through Survey offices. Reference samples for the quality assurance program make up approximately 5 percent of the laboratory workload for each constituent.

Each week, analytical results are statistically evaluated and control charts prepared based upon most probable concentration and standard-deviation values for each constituent. Least-square regression is used to determine the most probable standard deviation for the individual constituent concentrations. Analytical precision is determined by the relative standard deviation for each reference sample used in the program. The bias (systematic error) for each analytical procedure is evaluated on an annual basis.

During the last 5 years, more than 50,000 determinations have been made on samples submitted by the program. These data have been stored on a national data base that laboratory users can access to evaluate analytical accuracy and precision for selected constituents and user-defined time periods.

QUALITY ASSURANCE REQUIREMENTS FOR SUPERFUND RI/FS ACTIVITIES IN REGION V

284 James H. Adams, Jr., U.S. Environmental Protection Agency, Region V
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The development of an approvable Quality Assurance Plan (QAPjP) is mandatory to conduct a USEPA remedial investigation (RI). An RI QAPjP is prepared to achieve the data quality goals for monitoring activities at a specific Superfund site. A QAPjP describes, in specific, succinct terms, the 1) policy, 2) organization, 3) functional activities (sample collection, chemical analysis, etc.), and 4) data quality goals dictated try intended usage(s) of all data. A QAPjP is prepared and approved prior to initiation of analytical data generation. "Interim Guidelines and Specifications for Preparing Quality Assurance Plans", QAMS-005/80, USEPA, December 1980 is the current EPA guidance document for preparation of QAPjP's. Region V has developed specific guidance documents to supplement the QAMS-005/80 guidance document. The objective of the regional guidance documents when used in conjunction with QAMS-005/80 guidance is to enable the user to prepare an approvable QAPP with site-specific details for a RI.

U.S. ARMY TOXIC AMD HAZARDOUS MATERIALS AGENCY INSTALLATION RESTORATION QUALITY ASSURANCE PROGRAM,

285 Kenneth T. Lanq, U.S. Army Toxic and Hazardous Materials Agency, Aberdeen Proving Ground, Maryland 21010-5401

The Army's Installation Restoration Program (IRP) was established in the mid-1970's to identify, evaluate and clean-up contamination resulting from past waste disposal activities on property under Army control. The U.S. Army Toxic and Hazardous Materials Agency (USATHAMA) was assigned to execute this mission as the IRP central manager. In order to assure that high-quality, verifiable data was produced from chemical analyses of environmental samples, USATHAMA developed and implemented a state-of-the-art Quality Assurance (QA) Program. Since the implementation of the USATHAMA OA Program in the mid-1970's, we have continued with a policy of reevaluation and revision of the program's concepts and methods. Our process of review and analysis includes experts from industry, national laboratories, academia, and other government offices. The main objectives of the USATHAMA QA Program are to: (1) provide a consistent framework for the generation of good analytical data; (2) require contractor laboratories to demonstrate their ability to analyze for all of the compounds of interest in the appropriate sample matrices over a range of concentrations; (3) require the laboratory to analyze daily quality control samples, and to evaluate laboratory performance on a daily basis. Presented here will be a discussion on how USATHAMA accomplished these objectives and some major differences between USATHAMA's QA Program and other programs in common usage.

QUALITY ASSURANCE IN THE SAN JOAQUIN VALLEY DRAINAGE PROGRAM, CALIFORNIA, 1984-89.

286 Marvin L, Yates. U.S. Geological Survey, 2800 Cottage Way, Rm. W-2143, Sacramento, California 93825, William J. Walker and Richard G. Burau, University of California, Davis, California 95616.

The San Joaquin Valley Drainage Program (SJVDP) was established in 1984 aa part of a cooperative effort with the U.S. Department of Interior and the State of California to investigate problems with the drainage of irrigated agricultural lands on the west side of the San Joaquin Valley, California. The analytical and quality assurance/quality control (QA/QC) problems with selenium required an intensive effort to solve these problems in order to establish reliable analytical data. In 1984, the U.S. Department of Interior provided funding to establish a high quality QA/QC program at the U.S. Bureau of Reclamation Water Quality Laboratory in Sacramento, California--a major laboratory in the analysis of selenium in water. Laboratory audits from 1983 to 1989 indicated that the laboratory was consistent in producing reliable analytical data. A 1985 interlaboratory performance evaluation for selenium was carried out. The evaluation showed that the most reliable method for analysis of selenium in waters with high salt concentrations was the hydride generation atomic absorption technique. In 1986, a QA/QC subcommittee of the National Research Council/Water Science and Technology Board began review of the SJVDP QA/QC program. They provided suggestions for improvement in the areas of quality assurance policy and management, including data management. The subcommittee also evaluated QA/QC practices of several participating laboratories. Major QAA3C efforts in the program over the last 3 years include: (I) conducting three multilaboratory reference material exchanges to determine the comparability of laboratory data and the reliability and accuracy of determinations on various media from different laboratories: (2) developing new reference materials of soil, water, and vegetation obtained from the west side of the San Joaquin Valley and establishing most probable values for selenium and other elements including arsenic, boron, and molybdenum in these materials; (3) conducting two QA/QC training courses primarily for project leaders involved in SJVDP supported activities; (4) producing a QA/QC guideline document (1987), and reviewing and evaluating the QA/QC plans required of programs supported by the drainage program. The SJVDP QA/QC officer will provide a compilation of QA/QC data, evaluations, and reports to be included in the SJVDP data-base management program. A library of reference materials will be available for future use.

287 THE SAN JOAQUIN VALLEY DRAINAGE PROGRAM QA/QC PROGRAM: A ISON OF ANALYTICAL METHODS USED FOR THE DETERMINATION OF As, Se, B, Mo, and Cr IN SEVERAL ENVIRONMENTAL MATRICES. William J. Walker and Richard G. Burau, Department of Land, Air and Water Resources, University of California, Davis, CA 95616; Marvin L. Yates, U.S. Geological Survey, 2800 Cottage Way, Sacramento, CA 95825.

As part of the San Joaquin Valley Drainage Program's QA/QC Plan, reference materials and environmental samples of water, vegetation, soil and sediment were distributed at least once per year for three years to program laboratories. The samples were analyzed for As, Se, B, Mo, and Cr and the results returned to U.C. Davis for analysis and for evaluation of the methods used to determine the trace element concentrations. Laboratories determining As and Se commonly used graphite furnace atomic absorption spectrophotometry (GFAAS), hydride generation AAS, and fluorimetry. HGAAS and fluorimetric methods appeared to yield more reliable results compared to GFAAS for all sample types. Boron was determined by either ICP or one of several colorimetric methods all of which produced comparable results for B determination in water. Mo and Cr were determined by either ICP or GFAAS. Results indicated that neither method was entirely satisfactory for most of the samples analyzed. Possible explanations for the failure of some of the methods will be offered.

288 QUALITY ASSURANCE PRACTICES IN A UNIVERSITY SETTING. Robert L. Sutton and Eric R. Allen, Environmental Engineering Sciences Department, University of Florida, Gainesville, FL 32611.

During the past three years, the Air Pollution Analysis Laboratory, Environmental Engineering Sciences Department, University of Florida has participated in two major acid rain monitoring studies. The University of Florida operates three monitoring sites and supports a fourth site located in commercial forests of the southeastern United States as part of the Atmospheric Exposure Cooperative (funded by the US EPA) and the Integrated Forest Study (funded by the USDA) of the national Forest Response Program. In keeping with our philosophy that these projects should provide opportunities for students (undergraduate and graduate) to participate in basic and applied research projects, the laboratory employs five undergraduate students in addition to a full-time laboratory manager. Two graduate students are involved with data analysis and interpretation. This presentation will focus on the methods that are used to fulfill the requirements for stringent quality assurance and quality control as set forth by the granting agencies.

MERCURIC CHLORIDE INTERFERENCE IN LOW LEVEL NUTRIENT ASSAYS. Deborah A. Hunter. Division of Environmental Studies, University of California-Davis, Davis, California 95616

Standard reference water samples issued by the U.S. Geological Survey are routinely preserved with 50mg $HgCl_2$/liter. The effect of mercuric chloride preservation was examined in colorimetric assays for three constituents: ammonia-nitrogen, nitrate-nitrogen, and orthophosphate. The standard curves for both the ammonia-nitrogen and nitrate-nitrogen assays were suppressed compared to their unpreserved counterparts. This suppression was a critical factor when nutrient concentrations were below 20ppb. The mercuric chloride reduced the sensitivity and increased the limit of detection for both of these assays. In addition, standards and samples preserved with mercuric chloride had differential color development when the hydrazine method was used for nitrate-nitrogen analyses. This interference was attributed to precipitate formation that adversely affected the spectrophotometric reading.

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A COLORIMETRIC DETERMINATION OF SELENIUM IN ANIMAL FEED PREMIXES

Jeffrey A. Hurlbut, Roger G. Burkepile, and Carolyn A. Geisler, U.S. Food and Drug Administration, Denver Veterinary Analytical Section, Building 20, Denver Federal Center, Denver, CO 80225-0087

A colorimetric method for the determination of Selenium in feed premixes is described. The premix is extracted in 3 M hydrochloric acid and centrifuged. An aliquot is then subjected to cation exchange chromatography to remove potentially interfering copper, iron, and manganese cations; boiled to reduce any selenate to selenite; pH adjusted; treated with hydroxylamine and ethylenediaminetetraacetic acid; complexed with 3,3′-diaminobenzidine; pH adjusted; extracted into toluene; and absorbance measured at 420 nm. Typical selenium concentrations are between 50 and 400 ug/g, and up to ten samples per day can be run. Recoveries both with and without cation exchange, and both with and without the HC1 boiling step; effectiveness of the ion exchange column in removing cations; operating curve; and a detailed procedure are reported.

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AN UPDATE TO THE EXTERNAL QUALITY ASSURANCE AND ITS IMPACT ON LABORATORY PERFORMANCE IN THE ACID RAIN PROGRAM.

Nabil M. Arafat, Keijo I. Aspila. National Water Research Institute, P.O.BOX 5050, Burlington, Ontario, Canada.

The Quality Assurance Group at the National Water Research Institute provides external quality assurance support to the Federal-Provincial Long Range Transport of Atmospheric pollutants program (LRTAP). The external studies (round robin) now involve over 100 acid rain laboratories in Canada and the United States.

Studies are provided three times per Year. Each study includes 10 soft water samples for analysis of over 20 different constituents. Results are analyzed by non-parametric statistics using Youden techniques to discern bias in the laboratory measurement system. Those results that deviate significantly from interlaboratory medians are flagged high (or low) based on an updated flagging criteria developed from historical LRTAP data. The data output is handled by a computerized database management system which also allows analysis of laboratory performance over time.

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IMPROVED SELENIUM RECOVERY FROM TISSUE WITH MODIFIED DRY ASHING

William G. Brumbaugh and Michael J. Walther. U.S. Fish and Wildlife Service, 4200 New Haven Rd, Columbia, MO 65201.

Recently, we reported on a combined wet chemical and dry ash digestion suitable for determination of arsenic and selenium in tissue by hydride generation atomic absorption (Brumbaugh, W. G., and Walther, M. J. (1989) *J. Assoc. Off. Anal. Chem.* 72, 484-486). This procedure yielded good recoveries for both elements but slight losses (up to 10%) of selenium were noted to occur when selenomethionine was used for spiking. As determined by radiotracer studies, these losses occurred as the digestate mixture initially went to dryness prior to ashing. We have since incorporated a simple modification (addition of a small volume of HCl to the initial digestion mixture) which has yielded higher selenium results for reference tissues and selenomethionine tissue spikes. In contrast, results for inorganic selenium spikes did not improve and actually decreased slightly with this modification. Because the selenium spiked as selenomethionine matched the behavior of the selenium in reference tissues better than the inorganic spikes, we recommend this form for spiking of tissues.

293 CHEMISTRY OF EPISODIC RAINFALL-RUNOFF FROM INERT MICROCATCHMENTS IN THE ADIRONDACK MOUNTAINS, NEW YORK, 1987-88, Paul F. Schuster and Michael M. Reddy, U.S. Geological Survey, 5293 Ward Road, Arvada, Colorado 80002

Interaction of rainfall with basin material affects the chemistry of rainfall-runoff and ultimately affects the chemistry of streams and lakes. If basin rock and soil minerals are nonreactive to the acidic components of rain, the chemistry of streams and lakes within the basin largely may be regulated by the chemistry of the rainfall. An experimental system was designed to identify processes affecting the chemistry of rainfall-runoff. The system monitors fluctuations in the chemistry of rainfall runoff from inert microcatchments (sand-blasted Pyrex glass, 0.1858 square meter). The samples, collected using a volume-based sequential sampler, were analyzed onsite for pH and specific conductance and in the laboratory for major ions Specific examples of dry deposition wash off and atmospheric washout for six summer episodes during 1987-88 will be presented. Dry deposition and washout processes driven by rain intensity appear to regulate the chemical concentrations observed In the rainfall-runoff. During initial stages of rainfall, concentration of pollutant-related species in the rainfall runoff are elevated and reflect either the wash off of accumulated dry deposition on the inert microcatchment or washout from the atmosphere, or both. During rainfall, changes in the concentrations of dissolved species are correlated with changes in rainfall intensity; elevated concentrations of dissolved species in rainfall-runoff occur during initial stages of intense rainfall

A RAPID METHOD FOR DETERMINING METHYLENE BLUE AND ITS METABOLITES IN MILK BY HPLC. Robert K. Munns, David C Holland, Jose E. Roybal, and Jeffrey A. Hurlbut. Food and Drug Administration, Animal Drug Research Center, Denver Federal Center Bldg 20, Denver, Colorado 80225-0087.

A rapid method for the determination of trace levels of methylene blue (MB) and its metabolites in milk has been developed. Milk is first deproteinized with acetonitrile and the liquid fraction diluted with a salt solution. The MB and the metabolites, azure A (AZA) and azure B (AZB), are extracted into chloroform which is then evaporated to dryness under reduced pressure. A final cleanup step using a disposable carboxylic acid column is necessary before the a HPLC/visible determination.
Recovery data presented here uses the maximum absorbance of each compound: MB (660nm), 88.2, 84.1, and 79.0% recovery from milk for 20, 10 and 5 ppb respectively; AZA (620nm), 79.2 and 40.5% recovery at the 20 and 10ppb level respectively; AZB (635nm), 92.2 and 80.5% recovery at 20 and 10ppb respectively.

295 A RAPID METHOD FOR DETERMINING GENTIAN VIOLET IN ANIMAL FEED BY HPLC WITH ELECTROCHEMICAL DETECTION Jose E. Roybal, Robert V. Munns, Jeffrey A. Hurlbut, and Roger G. Burkepile. Food and Drug Administration, Animal Drug Research Center. Denver Federal Center Bldg 20, Denver, Colorado 80225-0087.

A rapid and simple high performance liquid chromatographic (LC) method with electrochemical detection (ED) is presented for the analysis of Gentian violet (GV) in poultry feed (turkey/chicken) at the therapeutic feeding level of 4 ppm - 8 ppm. The procedure consists of extraction of feed with acidified methanol, aliquot and dilution of supernatant with mobile phase, filtering and LC/ED analysis. LC/ED analysis is performed by isocratic elution with a buffered mobile phase using an Alltech CN (cyano) column with amperometric ED detection at +1.00V, Overall recovery from spiked chicken feed at 2.5, 5.0 and 10.0 ppm was 103% (SD - 6.64; %CV - 6.44). Recovery data of GV from chicken and turkey feeds, fortified with 1% GV premix, at 4.0 ppm and 8.0 ppm feeding level is presented and discussed.

296 HANDLING GREAT LAKES DATA; LAKE ERIE, AN EXAMPLE. (A simple approach using mainframe to PC data transfer).

Fernando Rosa. Environment Canada, Lakes Research Branch, NWRI, 867 Lakeshore Road, Burlington, Ontario, CANADA L7R 4A6

Over the past few years a number of programming tools have been assembled to help limnologists develop and understand new scientific principles. Data reduction from large data bases (mainframe) transferred to personal computers (PC), facilitates data interpretation using visual graph display. The VERTICAL-STRUCTURE PROGRAM (VSP), specifically designed for Lake Erie, uses the Great Lakes data bank as its data source. With minor modifications the VSP may be used for any other lake system. Once the output files are created by running a simple mainframe program, the VSP uses this information,(i.e. Location(s)/stations(s)/parameter(s)/depth(s) to handle the data through simple menu-driven commands. Results such as lake contour, showing station locations, data tables, and graphs can be printed in high quality graphics. Combining the VSP output with word processing software allows for a simple and efficient data report in publication quality. This is an easy and efficient way to handle the vast amounts of information gathered through surveillance and monitoring programs.

97 SEQUENTIAL-PARTIAL EXTRACTIONS OF PINAL CREEK AQUIFER MATERIAL NEAR GLOBE, ARIZONA, FOR SULFATE AND PHOSPHATE.

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U.S. Geological Survey, DFC, Box 25046, MS 973, Denver, CO 80225
(303) 236-7357

Sequential-partial extractions are useful for the determination of mode of occurrence of cations in solid materials. Ion chromatography (IC) is adaptable to analyze complex solutions and makes possible the determination of anions in the sequential-partial extractions. Interfering ions must be removed before sulfate and phosphates can be determined. Large quantities of chlorides in some of the solutions can be removed with commercial precolumns.

Environmental-impact concerns have encouraged scientists to develop methods which Identify possible contamination sources and pathways. These procedures have been used on samples collected from solid material located In the Pinal Creek aquifer, an area which receives acid mine waters from mines in the Globe, Arizona, area. The material was subjected to sequential extractions of sodium acetate/acetic acid (carbonate phase), 0.01N HNO_3 + 0.1N $NH_2OH \cdot HCl$ (MnO phase), and 0.25N HCl + 0.25N $NH_2OH \cdot HCl$ (amorphous Iron oxides). Results indicate that sulfate is associated with the carbonate phase and phosphate with the amorphous iron oxide phase. The results will be discussed with regards to analytical reliability and environmental implications.

LC SEPARATION AND UV/FLUORESCENT DETECTION OF CARBOXYLIC ACIDS UTILIZING 1-AROMATIC-2-BROMOETHANONES.

Jeffrey Hurlbut and Linda D. Himmelbauer. Chemistry Department-B52, Metropolitan State College, 1006 11th Street, Denver, CO 80204

A method is presented for the derivatization, separation and determination of carboxylic acids by high performance liquid chromatography with fluorescent and ultraviolet detection. The derivatizing agents used in this study are 1-aromatic-2-bromoethanones where the aromatic portions are anthracene and phenanthrene groups. The synthesis and characterization of the derivatizing agents, the derivatizing conditions, the chromatograms, the detection limits, and the HPLC conditions are reported.

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SUPERCRITICAL FLUID EXTRACTION FROM MEDITERANEEN BROWN ALGA DILOPHUS LIGULATUS. Pascale Subra. Roland Tufeu and Yves Garrabos. L.I.M.H.P. Avenue J.B. Clément, 93430 Villetaneuse. France

The aim of this study is to demonstrate the interest of supercritical fluids as selective extraction agent ol compounds from biological material. A commercial micro-scale equipment (capacity ol 10 ml, maximum pressure of 5000 psi and maximum temperature of 333 K) has been improved by introducing a sapphire extraction cell, and has been coupled to an high pressure vessel in order to collect the extracts. Extractions with this equipment have been conducted with a mediteraneen brovn alga Dilophus ligulatus, which exhibits antifungal properties. By operating a controlled stagewise pressure increase (from 80 to 280 bar) one obtains separate fractions, the colour ol which ranging from yellow to green. Depending on the temperature of the extraction (308-318-328 K) the fractions are coloured at different pressures. The results, in terms ot weight, colour. HPLC and/or HPTLC analysis are discussed.

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SOLUBILITY OF CHLOROPHYLLIAN PIGMENTS IN SUPERCRITICAL CARBON DIOXIDE AND ETHANE. Pascale Subra and Roland Tufeu. L.I.M.H.P. Avenue J.B. Clement. 93430 Villetaneuse, France

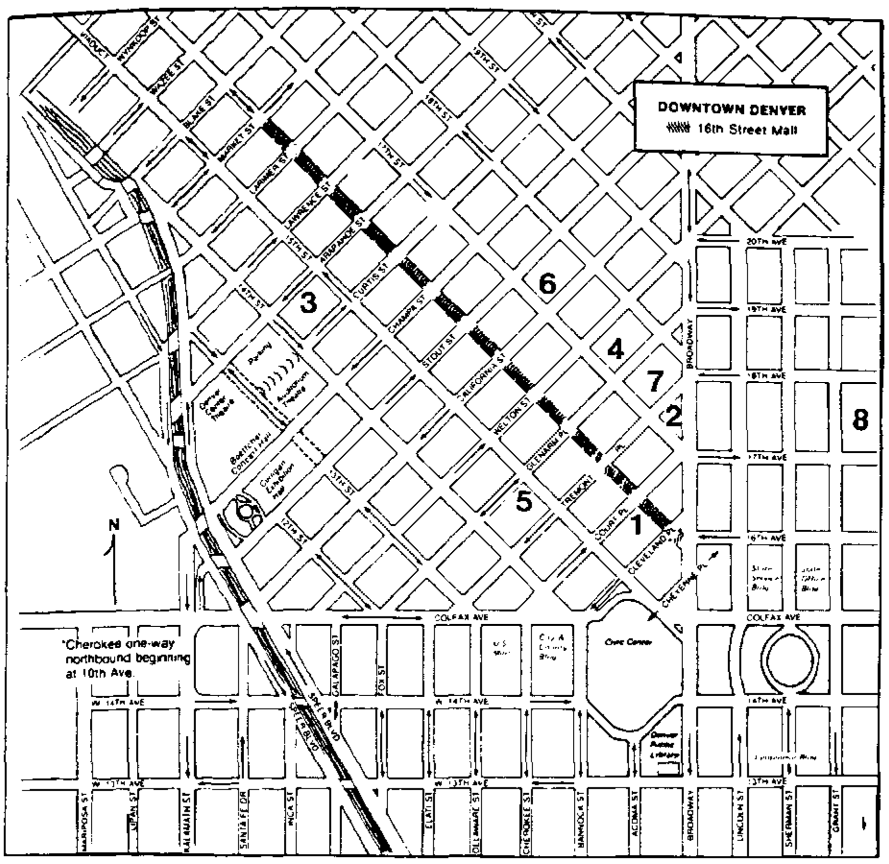
The extraction of pigments from plants by using liquid solvents is a complex procedure involving a sequence of extractions which can lead to denaturization ot the substances. The extraction by supercritical fluids as an alternative method can be considered to overcome the encountered difficulties. In this paper, we present the results ot the measurements of the solubility in supercritical carbone dioxide and in supercritical ethane of pure chlorophyll-a and of chlorophyllian pigments extracted from marine algae, by using spectrofluorimetric measurement. These measurements have been carried on under thermodynamical equilibrium conditions in a variable volume cell made of sapphire. In the investigated pressure range (10 to 20 MPa), the solubilities ot chlorophylls in carbone dioxide and in ethane, which are an increasing function of the pressure or of the density of the fluids, have been estimated.

ADDITION TO LUMINESCENCE SYMPOSIUM

EXTENDING THE SENSITIVITY AND DYNAMIC RANGE OF AN AUTOMATED LIPOSOME IMMUNOASSAY FOR DETECTION OF TRACE ANALYTES.
Laurie Locascio-Brown, Anne L. Plant, William T. Yap, Steven J Choquette, and Richard A. Durst. NIST, Gaithersburg, MD 20899

An automated immunoassay has been developed using liposomes (phospholipid vesicles) with an encapsulated fluorophor to amplify the detection of the interaction between an analyte and its antibody. A flow injection system precisely controls reagent addition and reaction timing. Several parameters which affect the dynamic range and sensitivity of the immunoassay are being modelled and will be discussed. This system is currently being tested with two analytes, theophylline and anti-theophylline antibody, but can be readily modified to measure other large analytes (i.e. proteins or bacteria) or small analytes present in trace amounts. A method of regeneration of the immobilized antibody reactor will be described which maintains 100% of the immobilized antibody activity for greater than 3 months at room temperature. The liposome reagent has been shown to be stable for at least one year when stored at room temperature. Relative standard deviations of less than 5% have been achieved at picomole levels of detection, and complex matrices such as serum have been used in the system with no pre-separation step. potential environmental and clinical applications will be discussed.

DOWNTOWN DENVER



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
7	Comfort Inn
8	Warwick

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