Rocky Mountain Conference on Magnetic Resonance

Volume 35 35th Rocky Mountain Conference on Analytical Chemistry

Article 1

July 1993

35th Rocky Mountain Conference on Analytical Chemistry

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35th Rocky Mountain Conference on Analytical Chemistry

Abstract

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35th Rocky Mountain Conference on Analytical Chemistry

PROGRAM AND ABSTRACTS

JULY 25-29, 1993

HYATT REGENCY DENVER
1750 WELTON STREET
DENVER, COLORADO

SPONSORED BY
ROCKY MOUNTAIN SECTION
SOCIETY FOR APPLIED SPECTROSCOPY
&
COLORADO SECTION
AMERICAN CHEMICAL SOCIETY
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### SYMPOSIA SCHEDULE

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<th>TUESDAY JULY 27, 1993</th>
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WELCOME FROM THE ORGANIZING COMMITTEE

It is our distinct honor and pleasure to welcome all of you to the 35th Rocky Mountain Conference on Analytical Chemistry. The organizing committee of the conference has attempted to broaden the purview of the conference to include not only topics in analytical chemistry, but also selected topics in physical and environmental chemistry and laboratory safety.

The conference is divided into 17 symposia with 355 papers and two panel discussions. Many of these symposia feature keynote speakers of international renown. We encourage you to attend as many of the symposia as you can; we think that you will find many different topics of interest at the conference. All of the symposia are conveniently located in a single compact area of the hotel in order to encourage maximum participation by the conference attendees.

As in previous conferences, we expect that there will be lively discussion of many of the papers. In order to provide additional time for discussion, frequent breaks with complimentary refreshments have been scheduled. These breaks, the two mixers, and the conference banquet will provide you with ample opportunity to meet old friends and colleagues and to make new acquaintances.

In addition to the conference, we urge you to take advantage of the many recreational opportunities available within a short distance of Denver. The Hyatt Hotel has a knowledgeable concierge who can provide you with a wide choice of tours, raft trips, theater and concert tickets, and other diversions.

We trust that you will find your stay in Denver to be professionally rewarding and enjoyable. If you have any problems that we may help you with please do not hesitate to contact one of us.
Organizers of the 35th Rocky Mountain Conference

Conference Chair - Robert Wershaw, U.S. Geological Survey, Denver Federal Center, PO Box 25046, MS408, Denver, CO 80225, (303) 467-8280

Program Chair - Christine White, Coors Brewing Company, CC288, Golden, CO 80401, (303) 277-2275

Exhibits Chair - Vanessa Fishback, 7578 Aberdeen Way, Boulder, CO 80301, (303) 530-5274

Registration Chair - Joel Gray, Coors Brewing Company, CC288, Golden, CO 80401, (303) 277-2275

Publicity Chair - Pat Sulik, Rocky Mountain Instrumental Labs, 456 S. Link Lane, Ft. Collins, CO 80524, (303) 530-1169

Treasurer - Glenda Brown, U.S. Geological Survey, MS407, 5293 Ward Road, Arvada, CO 80002, (303) 467-8122

Mailing List - Carol Gies, EG&G Rocky Flats, General Lab Bldg 881, P.O. Box 464, Golden, CO 80402-0464, (303) 966-7380
SYMPOSIA CHAIRMEN AND CHAIRWOMEN

ATOMIC SPECTROSCOPY

Gary Rayson
New Mexico State University
Chemistry Department
Las Cruces, NM 88003
(505) 646-5839
Fax#: (505) 646-2649

CHROMATOGRAPHY

Denise Kent
11671 Baca Road
Conifer, CO 80433
1-800-632-2708 ext. 2168

COMPOSTING

Cal Kuska
8547 E. Arapahoe Rd.
J221
Greenwood Village, CO 80112
(303) 791-8639
Fax#: (303) 850-0623

ELECTROCHEMISTRY

Dan Buttry
Department of Chemistry
University of Wyoming
Laramie, Wyoming 82071-3838
(307) 766-5677
Fax#: (307) 766-2807

ENVIRONMENTAL CHEMISTRY

Maria Tikkanen
Association of California Water Agencies
910 "K" Street, Suite 250
Sacramento, CA 95814
(916) 441-4545
Fax#: (916) 441-7893

EPR

Gareth Eaton
University of Denver
Chemistry Department
Denver, CO 80208
(303) 871-2980
Fax#: (303) 871-2254

Sandra Eaton
University of Denver
Chemistry Department
Denver, CO 80208
(303) 871-3102
Fax#: (303) 871-2254

FTIR/NIR/RAMAN SPECTROSCOPY

Abdul Chughtai
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GENERAL POSTERS

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QMG National Water Quality Lab
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ICP/MS

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U.S.G.S. MS458
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Federal Center
Denver, CO 80225
(303) 541-3007
Fax#: (303) 447-2505

LABORATORY SAFETY

Marvin Goldberg
U.S. Geological Survey
P.O Box 25046 MS424
Denver, CO 80225
(303) 236-4728
Fax#: (303) 236-4418

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LUMINESCENCE

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Lockheed Environmental Systems
and Technology Company
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Las Vegas, NV 89119
(702) 897-3287
Fax#: (702) 897-6641

Robert Hurubise
University of Wyoming
Department of Chemistry
Box 3838 University Station
Laramie, WY 82071
(307) 766-6241
Fax#: (307) 766-2807

MASS SPECTROMETRY

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Department of Pediatrics
K923
National Jewish Center
Denver, CO 80206
(303) 398-1853
Fax#: (303) 398-1694

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Hellmut Eckert
University of California, Santa Barbara
Department of Chemistry
Santa Barbara, CA 93106
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Fax#: (805) 893-4120

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10236 Marion Park Drive
Kansas City, MO 64137
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Denver, CO 80225
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Fax#: (303) 236-1420

RADIOCHEMISTRY

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5293 Ward Road
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Fax#: (303) 467-8240

ROBOTICS

Jerry Hoffman
U.S.G.S./NWQL
5293 Ward Road
Arvada, CO 80002
(303) 467-8082
Fax#: (303) 467-8240
CONFERENCE LOCATION

Technical sessions and the exhibition for the 35th Rocky Mountain Conference on Analytical Chemistry will be held in the Hyatt Regency Denver, 1750 Welton Street, Denver, Colorado 80202

REGISTRATION

Admission to all technical sessions, vendor sponsored users groups and the exhibition is by the name badge for the 35th Rocky Mountain Conference. Pre-registration, using the form at the back of this program, is encouraged. The deadline for the receipt of the pre-registration form and full remittance of the conference fees is July 10, 1993. Conference fees are payable by check (denominated in $US, only) made payable to the Rocky Mountain Conference.

REGISTRATION FEES - 1993

<table>
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<th>Preregistration (received by 7/10/93)</th>
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<tr>
<td>Registration (entire conference and exhibition)</td>
<td>$65.00</td>
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<tr>
<td>Registration (one specified day)</td>
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<tr>
<td>Student Registration (requires ID)</td>
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<tr>
<td>Additional Vendor Registration</td>
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<td>Unemployed or Retired Registration</td>
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<tr>
<td>Exhibition only (non-vendor)</td>
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<tr>
<td>Banquet</td>
<td>$30.00</td>
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</table>

REFUNDS

Requests for refunds of conference fees must be received by July 10, 1993.
TIMES

On-site registration for the 35th Rocky Mountain Conference will be held in the Imperial Ballroom Foyer of the Hyatt Regency Denver during the following hours:

- Sunday, July 25: 5:00 p.m. - 9:00 p.m.
- Monday, July 26: 7:30 a.m. - 3:30 p.m.
- Tuesday, July 27: 7:30 a.m. - 3:30 p.m.
- Wednesday, July 28: 7:30 a.m. - 3:30 p.m.
- Thursday, July 29: 8:00 a.m. - 2:30 p.m.

EXHIBITION

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

HOURS

- Sunday, July 25: Mixer 7:00 p.m. - 9:00 p.m.
- Monday, July 26: Exhibits 9:30 a.m. - 5:00 p.m.
- Monday, July 26: Posters 2:00 p.m. - 4:00 p.m.
- Monday, July 26: Reception 5:00 p.m. - 7:30 p.m.
- Tuesday, July 27: Exhibits 9:30 a.m. - 5:00 p.m.
- Tuesday, July 27: Banquet 7:00 p.m. - 10:00 p.m.
- Wednesday, July 28: Exhibits 9:30 a.m. - 5:00 p.m.

Posters will be set up in the exhibition area Monday morning through Wednesday afternoon for viewing. For space or information about the exhibition, contact:

Vanessa Fishback
7578 Aberdeen Way
Boulder, CO 80301
(303) 530-5274
The following have reserved space as of June 18, 1993

API
Allen Scientific Glassblowers, Inc
Bruker Instruments, Inc.
Cambridge Isotope
CEM Corp.
FACCS
Finnigan MAT
Fisons Instruments
General Cable Co. - Puregas
High Purity Standards
Huffman Labs
Isotec
JEOL U.S.A., Inc.
Millipore Waters
O.I. Analytical
Ordella Inc.
Otsuka Electronics
Oxford Instruments
Oxford Instruments N.A., Inc.
Perkin Elmer
RESTEK
Rocky Mountain Scientific Glass
Society for Applied Spectroscopy
Tecmag
Thermo Jarrell Ash Corp.
Tremetrics, Inc.
Varian
Wilmad Glass Co.
Zymark

Time and space are also available for exhibitors interested in sponsoring short workshops. Contact Vanessa Fishback at the location on the previous page for more information.

SOCIAL PROGRAM AT THE HYATT REGENCY DENVER

REGISTRATION NIGHT MIXER

A cash bar will be open in the Marquis Room of the Hyatt Regency Denver on Sunday evening, July 25, from 7:00 - 9:00 p.m. Plan to meet other conference attendees and beat the Monday rush to pick up your conference badge and abstract book.

CONFERENCE RECEPTION

On Monday afternoon, July 26, from 5:00 - 7:30 p.m., please join us for a cocktail and hors d'oeuvres at the Hyatt Regency Denver in the Exhibit area.

CONFERENCE BANQUET

The conference banquet will be on Tuesday, July 27th from 7:00 - 10:00 p.m. in the Moulin Rouge Room of the Hyatt Regency Denver. A cash bar
HOTEL ACCOMMODATIONS

Hotel rooms where the conference is being held, at the Hyatt Regency Denver, 1750 Welton Street, Denver, Colorado 80202, (303) 295-1234, are available at the special discounted conference rate of $85 per night (single or double), plus applicable tax. Please identify yourself as a Rocky Mountain Conference attendant when making reservations to receive this discounted rate. Suites are available upon request at the conference discount. The reservation form at the end of the booklet must be returned directly to the hotel. Conference location and all associated social functions for the conference will be held at the Hyatt Regency Denver.

Additional hotels within a reasonable distance from the Hyatt. For rates and reservations, contact the hotel directly.

The Brown Palace Hotel
(303) 297-3111 or (800) 321-2599
(800) 228-2917 in Colorado

Comfort Inn
(303) 296-0400 or (800) 237-8431
(800) 631-2090 in Colorado

Executive Tower Inn
(303) 571-0300 or (800) 525-6651

Hotel Denver - Downtown
(303) 573-1450 or (800) 423-5128
(800) 423-2201 in Colorado

Marriott City Center
(303) 297-1300 or (800) 228-9290

Warwick Hotel
(303) 861-2000 or (800) 525-2888
VISITOR INFORMATION

Contact the Guest Services in the main lobby of the Hyatt Regency Denver for suggestions on the large number of activities that are enjoyable in Denver and the surrounding area. 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 in the Board Room. The telephone number is (303) 295-1234. Indicate the individual is attending the Rocky Mountain Conference so the message can be posted in the proper area.

RESTAURANT SERVICE

The Hyatt Regency Denver Guest Services in the main lobby has sample menus and suggestions for casual to elegant dining experiences throughout the Denver area.

MEMBERSHIP COMMITTEE

Inquiries about membership to the American Chemical Society and Society for Applied Spectroscopy can be addressed to the Colorado Section Membership Committees. Please send inquiries to:

Society for Applied Spectroscopy
Glenda Brown
U.S. Geological Survey
MS407, 5293 Ward Road
Arvada, CO 80002
(303) 467-8122

American Chemical Society
Carl Koval, Chairman
University of Colorado
Campus Box 215
Department of Chemistry
Boulder, CO 80309
(303) 492-5564
EMPLOYMENT CLEARING HOUSE

The Employment Committee of the Colorado Section of the American Chemical Society will conduct an employment clearing house. Resumes will be accepted prior to, and during the meeting, for review by prospective employers. Employers who are interested in using this employment booth should register by contacting one of the employment committee members listed below by July 10, 1993.

Cathy Honda, Chairwoman
Gates Rubber Company
PO Box 5887
Denver, CO 80217
(303) 744-4210

Sonia Atwood
Marathon Oil Company
PO Box 269
Littleton, CO 80160
(303) 347-5452
FAX (303) 794-1720

Douglas B. Manigold
U.S. Geological Survey
5293 Ward Road
Arvada, CO 80002
(303) 467-8000
FAX (303) 467-9598

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

Interested employers and job seekers can receive additional information on available jobs by calling the ACS Employment committee Hotline number which is (303) 933-4375.
VENDOR WORKSHOPS

**Varian NMR Instruments 2nd Conference for Solids System Owners and Users**

Varian Solids Systems' Owners and Users are invited to a half day conference with Varian Application Scientists, R & D Engineers, and Product Managers on Sunday afternoon, July 25, 1993. There will be lectures, including invited presentations, that will focus on emerging applications followed by an open discussion session devoted to specific topics contributed by users. This is an excellent opportunity for long-term Varian customers and newcomers to gather for an afternoon of stimulating scientific interaction which will then adjourn for an evening of dining as guests of Varian. For registration materials, please call Ms. Bee Wallace in Palo Alto, CA at 415-424-4526. Please indicate if you wish to make a presentation.

**BRUKER INSTRUMENTS, INC.**

Bruker Instruments, Inc. will host a one day seminar dedicated to solid state NMR on Sunday, July 25 at the Hyatt Regency Denver hotel. New developments from Bruker will be presented, along with experimental results presented by users of Bruker instrumentation. All NMR spectroscopists are encouraged to attend, regardless of whether they are familiar with Bruker instrumentation or not. If you plan to attend, or for more information, please contact Doug Burum at (508) 667-9580.
VENDOR WORKSHOPS

4th ANNUAL
ADVANCED SOLID STATE NMR SPECTROSCOPY
WORKSHOP

DATES: Friday, July 30th and Saturday, July 31st

LOCATION: Otsuka Electronics
2555 Midpoint Drive
Fort Collins, CO 80525

PROGRAM:

Friday, July 30th: Solid State NMR Techniques and Applications

Emphasis will be laid upon the practical aspects of various Solid State NMR techniques available to date and the developments needed to enhance the reliability and applicability of NMR spectroscopy and imaging in solid material research. The workshop takes the form of a series of informal talks with ample time given for discussion.

Saturday, July 31st: Hands-on "New Techniques" Workshop

New experimental techniques will be discussed and demonstrated on CMX spectrometers. Attendees will be enabled to perform experiments and are encouraged to bring several of their own samples to run.

For further information contact: Dr. Jim Frye (303) 484-0428

To register: Complete the form below and return it to the address shown prior to June 30. There is no fee for the workshop, however local accommodations and meals are at attendees expense.

__________________________________________________________________________

Please register me for this summer’s Advanced Solid State NMR Workshop:

Name: __________________________
Phone: _________________________ FAX: _________________________
Address: ________________________
____________________________________
____________________________________
____________________________________

Mail to: Pat Chester
Otsuka Electronics/Chemagnetics Product Group
2555 Midpoint Drive
Fort Collins, CO 80525
SHORT COURSES
(Sponsored by the Colorado Section of the ACS)
to be held in conjunction with the Rocky Mountain Conference

Basic Principles of Mass Spectrometry and Interpretation of Organic Mass Spectra

July 29-31, 1993 Fee: $400 member; $450 non-member Faculty: Dr. Joseph A. Zirrolli
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 pesticides and pollutants. The course is based upon, and uses as a reference, the text, interpretation of Organic Mass Spectra. Third Edition by F.W. McLafferty, University Books, 1980.

Practical Analytical Atomic Spectroscopy: AAS, ICP/MS, ICP/AES

July 29-30, 1993 Fee: $500 member; $550 non-member Faculty: Dr. Howard E. Taylor and Dr. Theodore Rains
This highly-rated, recently revised course is designed for chemists, biochemists, chemical engineers, analysts, clinicians and quality assurance manager who are interested in research and analytical applications of atomic absorption spectrometry (AAS), inductively coupled plasma/atomic emission spectrometry (ICP/AES), and inductively coupled plasma/mass spectrometry (ICP/MS). Participants are taught the fundamental theory of atomic spectrometry with a minimum of mathematical treatment followed by state-of-the-art instrumentation, data processing/computer, and sample treatment. Practical tips are presented on ways to improve precision and accuracy of analytical measurements. The areas of applications covered include biological/clinical environmental, geological, and metallurgy. New analytical techniques for trace analysis and how to apply them are also discussed.

Spectroscopic Characterization of Polymers

July 29-30, 1993 Fee: $550 member; $600 non-member Faculty: Dr. Jack L. Koenig and Dr. Bruce Chase
This new course is aimed at polymer scientists, laboratory managers, and spectroscopists who have limited experience with polymers. The course will benefit professionals already experienced in spectroscopic analysis of polymers and will help newcomers to the field understand and use state-of-the-art techniques. You will learn about the latest computerized methods of spectral analysis and interpretation, vibrational spectroscopy, methods of high resolution NMR, modern Raman spectroscopic techniques including FT-Raman, Raman microscopy, and wave-guide techniques. You will also receive a copy of the ACS book, Spectroscopy of Polymers, by Jack L. Koenig (1992).

Laboratory Waste Management

July 29-30, 1993 Fee: $550 member; $600 non-member Faculty: Cindy L. Salisbury and Russell W. Phifer
If you are a lab manager, researcher, or technician responsible for management of laboratory waste, you should attend this course. Participants will learn which environmental regulations apply to management of your laboratory’s waste and how to classify laboratory waste in accordance with RCRA regulations. You will also learn how to manage discarded samples, standards, and QA solutions, and the components necessary for an effective laboratory waste management program. You will receive up-to-the-minute regulatory information and citations. You will learn how to implement a comprehensive environmental compliance program at your laboratory.

For registration by July 8, 1993 contact: Tara Barrineau OR Gary Clapp
Marathon Oil Company Hauser Chemical Research
P.O. Box 269 555 Airport Road
Littleton, CO 80160 Boulder, CO 80301
Tel: 303-347-5486 Tel: 303-443-4662
Fax 303-794-1720 Fax 303-441-5803
SYMPOSIUM ON ATOMIC SPECTROSCOPY
Organized by Gary D. Rayson

Monday, July 26, Morning — Vahid Majidi, Presiding

8:50   Introductions

INVITED SPEAKER

9:00   Mass Spectrometric Determination of Analyte Loss Mechanisms During Electrothermal Atomization in Graphite Furnace Atomic Absorption Spectrometry, Garrett N. Brown, Jerry D. Harris and David L. Styris, Pacific Northwest Laboratory, Richland, WA.


10:00  BREAK

10:50  Preparation and Introduction of Standards for Methods Using Direct Solid Analysis by Electrothermal Vaporization, Robert D. Keons, Forensic Science Research and Training Center, FBI Academy, Quantico, VA.

11:10  Combining Cold Vapor Generation with Amalgamation to Improve the Detection Limit of Mercury in Environmental Samples, Susan McIntosh, Perkin-Elmer Corporation, Norwalk, CT, and Randy L. Hergenreder, Perkin-Elmer Corporation, Golden, CO.


Afternoon — Garret Brown, Presiding

KEYNOTE SPEAKER

1:40   Matrix Dependence of Atomization, Ionization, and Excitation Processes in Laser Induced Plasmas, V. Majidi, M. Joseph, N. Xu and M. Owens, University of Kentucky, Lexington, KY.


3:00   BREAK


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Tuesday, July 27, 1993

1:00 Introductory Remarks by Cal Kuska

1:05 The Preparation and Analysis of Soil Compost Material for Inorganic and Explosives Constituents by Stephen Wilson, USGS, Denver, CO 80225.

1:30 Benefits of Composting for Agricultural Producers by Cal Kuska and Fran Kuska, Kuska/Associates, Greenwood Village, CO 80121.


2:45 The Evolution of Land Application and Composting of Biosolids at the Metro Wastewater Reclamation District by William J. Martin, Metro Wastewater Reclamation District, Denver, CO 80229.


4:00 Chemical Structure Comparisons of Dissolved Humic Substances in Various Aquatic Environments

SYMPOSIUM ON ELECTROCHEMISTRY
Organized by Dan Buttry

Monday, July 26, 1993

8:00 Introductory Remarks


8:30 Electrochemistry and LC Applications of Nickel Alloy Electrodes by Ted Kuwana and Frank Luo. Department of Chemistry, University of Kansas, Lawrence, KS 66045.

8:55 Asymmetric Carbonate Ion-Selective Cellulose Acetate Membrane Electrodes with Decreased Salicylate Interference by Geun Sig Cha, Kang Shin Lee, Jae Ho Shin and Min Jong Cha. Department of Chemistry, Kwangwoon University, Seoul, Korea 139-701.


10:10 BREAK


10:40 Fabrication of Random Arrays of Nanometer-Size Ultramicroelectrodes by P. Vinod Menon, C. Anthony Pitrat, and Charles R. Martin. Department of Chemistry, Colorado State University, Fort Collins, CO 80523.


11:20 Surface Measurements and Monte Carlo Simulation of Urea Electroosorption on Pt (100) Electrode by Maria Gamboa, Pawel Mrzecz, Choong K. Rhee, Per A. Rikvold, and Andrzej Wieckowski. Department of Chemistry, University of Illinois at Urbana-Champaign, Urbana, Illinois 61801.

11:50 LUNCH

1:10 Metal Nanoparticle/Aluminum Oxide Preparation and Optical Characterization by G. Louis Hornyak, Phil Martellaro, Jon A. Stockert, Colby A. Foss, Jr., and Charles R. Martin. Colorado State University, Department of Chemistry, Fort Collins, CO 80523.

1:30 Detection of Hot Electrons in a p-InP Photoelectrochemical Cell, by Robert Torres, Carl A. Koval, University of Colorado, Department of Chemistry and Biochemistry, Boulder, CO 80309.

1:55 Etching of SnS2 Photoanodes to Increase the Bye Sensitization Efficiency by Xiumei Dou and Bruce A. Parkinson, Colorado State University, Department of Chemistry, Fort Collins, CO 80523.

2:20 Formation of Dimerized Pi-Complexes in the One-Electron Reduced Form of Viologens In Self-Assembled Monolayers by Xiaoyan Tang, Thomas Schneider, and Daniel A. Buttry, University of Wyoming, Department of Chemistry, Laramie, WY 82071-3838.

2:40 Characterization of Heterodinuclear Complexes Containing Three Bridging Bis-bipyridyl Alkane Ligands by Suzanne Ferrere, Daniel Derr, and C. Michael Elliott, Colorado State University, Department of Chemistry, Fort Collins, CO 80523.

3:05 BREAK

15

3:45 Evaluation of Apparent Formal Potentials of Redox Probes Exchanged in Ionomers on Electrode Surfaces by Jody Redepenning, Harmon M. Tunison, and Jayson Moy, University of Nebraska, Department of Chemistry, Lincoln, NE 68588-0304.

4:10 Differences in Self-Assembly of Thiol and Disulfide Derivatives of Viologens by Thomas Schneider and Daniel A. Buttry, University of Wyoming, Department of Chemistry, Laramie, WY 82071-3838.

4:30 Measurement of Activity Coefficients in Acetonitrile Using the Isopiestic Technique by Eric Mechelke, Sandra Burnham, Benjamin Miller, and Jody Redepenning, University of Nebraska, Department of Chemistry, Lincoln, NE 68688-0304.


SYMPOSIUM ON ENVIRONMENTAL CHEMISTRY

Organized by Maria W. Tikkanen

Sponsorship of this Symposium By Finnigan MAT is gratefully acknowledged.

Monday, July 26, 1993

Edward T. Furlong, Presiding

8:30 Opening Remarks


9:00 Identification of Iodinated Disinfection By-Products, by GC/ECD and GC/MS, by Andrew J. Dunham, Charles N. Hurst, Joann Silverstein, Robert M. Barkle, Robert E. Sievers, Dept. of Chemistry and Biochemist and the Cooperative Institute for Research in Environmental Sciences, University of Colorado, Boulder, CO 80309.


10:15 BREAK

10:40 Invited Speaker in Environmental Mass Spectrometry.

Field Application of Combined Chromatographic/Specrtoscopic Techniques for Environmental Analysis, by Henk L.C. Meuzelaar, Center for Micro Analysis and Reaction Chemistry, University of Utah, Salt Lake City, UT 84112.

11:35 Using Titanium Dioxide Photocatalysis to Treat Aqueous Waste Streams Containing Metal and Organic Contaminants, by Nancy S. Foster, Carl A. Roval, Dept. of Chemistry and Biochemistry Campus Box 215, and Richard D. Noble, Dept. of Chemical Engineering, Campus Box 424, University of Colorado, Boulder, CO 80309.

Noon LUNCH
Maria W. Tikkanen, Presiding


1:55  The Alamosa River: Then and Now, by Theodore A. Mueller, SLV Analytical Services, Inc., P.O. Box 863, 411 Ross Avenue, Alamosa, CO 81101.


2:45 - 3:10  BREAK

3:10  Closed Vessel Microwave Sample Preparation for Mercury Analysis Via Cold Vapor AA and UV Detection Techniques, by W. Gary Engelhart and Sara Littau, CEM Corp, P.O. Box 200, Matthews, NC 28106.

3:35  Alkaloids of Field Bindweed, by Fred G. Todd, Frank R. Stermit, Dept. of Chemistry, Colorado State University, Fort Collins, CO 80523 and Anthony P. Knight, Dept. of Clinical Sciences, Colorado State University, Fort Collins, CO 80523.

4:00  Pumping Metal Ions Against Their Concentration Gradient With Visible Light, by Thanh Thi-Bang To and Carl A. Keval, University of Colorado, Chemistry Dept., Boulder, CO 80309.


Tuesday, July 27, 1993

Maria W. Tikkanen, Presiding

8:30  Opening Remarks


9:00  Sequential Extraction Method to Differentiate Trace Metal Associations in Suspended Sediment and Bed Sediment From National Waters, by Heidi Hayes And Howard Taylor, U.S. Geological Survey, 3215 Marine Street, Boulder, CO 80303.


10:15 - 10:40  BREAK

10:40  Extension of the Capabilities of ICP-MS for the Determination of Trace Metals in Waters, by Diane Beauchemin, Dept of Chemistry, Queen's University, Kingston, Canada K7L3N6.

11:35  The Application of ICP-MS to Elemental Speciation, by Rob Henry and Tom Rettberg, Fisons Instruments, 14513 Spotswood Furnace Road, Fredericksburg, Virginia 22407.
16TH INTERNATIONAL EPR SYMPOSIUM
Organized by Sandra S. Eaton and Gareth R. Eaton

Monday, July 26, 1993, Session I - Bruce Robinson, presiding

8:30 Opening Remarks, S.S. Eaton
8:35 Presentation of International EPR Society Award by Harold M. Swartz, President, to James S. Hyde.
8:45 Award Address: Multiquantum EPR, James S. Hyde, Medical College of Wisconsin.
9:35 Saturation Recovery EPR For The Study Of Protein Structure, W. Francisz, Jagiellonian University, Poland.
10:15 BREAK
11:20 Biophysical Studies of Human Plasma Fibronectin, C.-S. Lai, Medical College of Wisconsin.
12:00 LUNCH

Monday, July 26, 1993, Session II, B.M. Hoffman, presiding

1:30 "Spectroscopic Probes of Molecular Dynamics in Muscle Contraction", D.D. Thomas, University of Minnesota.
2:10 Two Dimensional Fourier Transform ESR Applied To Biophysical Studies, J. Freed, Cornell University.
2:50 BREAK
3:10 Motion Of Molecules In Liquids Studied By Pulsed Etdor, C. Mailer and B. Robinson, University of Washington.
3:50 Microimmiscibility, Protein-rich Regions, and Compartmentalization (Membrane-Skeleton Fence Structure) In The Plasma Membrane As studied By Pulse ESR, Saturation-Transfer ESR and Single Particle Tracking, Akihiro Kusumi, Witold K. Subczynski*, Yasushi Sako, Dept. of Pure Applied Sciences, The University of Tokyo, Meguro-Ku, Tokyo 153, Japan, *Biophysics Dept., Inst. Molecular Biology, Japiellonian University, Krakow, Poland.
4:30 *International EPR Society business meeting.

Tuesday, July 27, 1993, Session III - S. Pfenninger, presiding

8:50 Non-Linear ESR: Applications To Complex Fluids And Microscopic Interpretation, L. Andreozzi, M. Giordano, D. Leporini, Pisa, Italy.
9:10 Site Percolation And Spin-Diffusion Model As Applied To Gd3+ EPR Linewidth Behaviour In Pr5La1-xF3 Single Crystals, S.K. Misra, U. Orhun, Concordia University.


10:10  BREAK


11:00  Proton Hyperfine Anisotropy Of Nitroxides In An Amine Cured Epoxy, M.D. Pace, A.W. Snow, Naval Research Laboratory.


12:00  LUNCH

Tuesday, July 27, 1993, Session IV, W.Trommer, presiding


1:50  Measurement Of Tissue Viscosity And Polarity In The Distribution Compartment Of mHCTPO In Living Tissue With Very Low Frequency EPR, H. Halpern, C. Yu, M. Peric, E. Barth, D. Grdina, B. Teicher, University of Chicago and Harvard Medical School.


2:30  BREAK

Session V - Posters, S.S. Eaton, presiding

3:00 - 4:00  Authors Present For Posters Labeled A

4:00 - 5:00  Authors Present For Posters Labeled B

A  An ESR And Endor Study Of Methylated Anthracene Radical Cations Generated From Arylgermanes And -Stannanes, M. Lehnig, Th. Reiche, S. Reiss, P. Such, Universitat Dortmund and Bruker Instruments

B  Endor Based Structural And Conformational Analysis Of Carboxylic Acid Derivatives Of The Spin-Label 2,2,5,5-Tetramethyl-1-Oxypyrroline, S.J. Kasa, W.E. Boisvert, M.W. Makinen, University of Chicago.


A  Electron Spin Echo Examination Of Structural Changes At The Copper Binding Site Of Azurin Induced By Methionine Mutations In The Coordination Sphere, C. Bender, M. van de Kamp, J. Peisach, G. Canters, Albert Einstein College of Medicine and Leiden University.
Gordon Coupler Design Considerations For Pulsed EPR, C. Bender, J. Peisach,
Albert Einstein College of Medicine.

Solvation Of Co(II)-Substituted Carbonic Anhydrase, P.C. Kang, S.S. Eaton, G.R.
Eaton, University of Denver.

G.R. Eaton, S.S. Eaton, University of Denver.

Analysis Of Cupric Sites With Unusually Fast Relaxation Times, H. Koteiche, W.E.
100 Antholine, C.E. Ruggiero, W.B. Tolman, F. Neese, P.M.H. Kroneck, Medical College
of Wisconsin, University of Minnesota and University of Konstanz.

Evidence In Support Of A Binuclear Site As Cu'a' Site In Cytochrome Oxidase,
A. Jain, G. Palmer, University of Illinois and Rice University.

EPR Spectroscopy Of Cobalt(II) And Copper(II) Encapsulated Complexes, T.M.
Donlevy, G.R. Hanson, L.R. Gahan, University of Queensland.

Security On Bruker EPR/NMR Spectrometers Ethernet Linked To A Network, G.R.
Hanson, University of Queensland.

Magnetic Resonance Investigations Of Copper Zeolites, S.C. Larsen, A. Aylor,
A.T. Bell, J.A. Reimer, Lawrence Berkeley Laboratory and University of California
Berkeley.

Electron Spin Echo Envelope Modulation Studies Of Copper Pterin Complexes,
H.-I. Lee, L. Bharwani, S.J.N. Burgmayer, J.L. McCracken, Michigan State University
and Bryn Mawr College.

Electron Spin Echo Envelope Modulation Of Ammonium Salts Bound To Tri-Aryl-
University.

Sublevel-Echo-Endor Study Of Molecular Dynamics Of Polymer Chain Ends,
G.G. Maresch, M. Hubrich, Max-Planck-Institut für Polymerforschung, Germany.

Eseem Study Of Nitrogen-Containing Vanadyl Complexes, K. Fukui, Y. Mizuta, H. Ohya-Nishiguchi,
H. Kamada, Yamagata Technopolis Foundation and JEOL Ltd.

An EPR And ESEEM Study of X-Ray Irradiated Ag\textsubscript{1}-NaA Zeolite With Methanol Adsorbate,
A. van der Pol, E.J. Reijerse, E. de Boer, J. Michalik, T. Wasowicz, J. Sadlo, University of Nijmegen
and Institute of Nuclear Chemistry and Technology, Warsaw.

1.7 GHz ESEEM Due to \textsuperscript{29}Si In Gamma-Irradiated Fused Quartz, V.V. Kurshev, H.A. Buckmaster,
L. Tykarski, University of Calgary.

Relativistic Effective Hamiltonians - Applications to EPR Spectroscopy, R. Chatterjee, H.A. Buckmaster,
University of Calgary.

Magnetic Resonance Absorption Spectra Of Some Volcanic Ashes, S. Marshall, S. Beske-Diehl, R. Jackson,
R. Cunningham, Michigan Technological University.

Characterization Of Mineral Surfaces By EPR, D.D. Murphy, M.G. Bakker, T.L. Clark, B. Davies,
D.R. Spears, University of Alabama and Bureau of Mines, Tuscaloosa.

The Use Of EPR Techniques To Probe The Structure And Dynamics Of Solvated, Bonded Silicas,
R.G. Keozer, Knox College.

Magnetic Resonance of ZnGeP\textsubscript{2}: Defect Centers In An Optical Parametric Oscillator, M.H. Rakowsky,
W.K. Kuhn, R.A. Manzt, P.J. Drevinsky, M.C. Ohmer, D.F. Bliss, P.G. Schunemann, T.M. Pollack,
Frank J. Seiler Research Laboratory.

Thermal Properties Of Paramagnetic Germanium Centres In Crystalline Silicon Dioxide, M.J. Mom-
bourquette, J.A. Weil, University of Saskatchewan.

20
B Aggregation Of Perfluorinated Ionomers In Solution, From ESR Spectra of Doxyl Stearic Acid Probes, E. Szajdzinska-Pietek, S. Schlick, University of Detroit Mercy.

A Medium Effects On The ESR Spectrum Of The Hydrated Electron, A.V. Veselov, R.W. Fessenden, University of Notre Dame.

B Robust Estimators Of Spectral Parameters, C. Yu, H. Halpern, University of Chicago.

A Computer Package For Conversions, Transformations, And Standardization Of Arbitrary Symmetry Spin Hamiltonian, C. Rudowicz, J. Qin, City Polytechnic of Hong Kong.

B Experimental And Theoretical Investigations Of Spin Hamiltonian Parameters For Mn²⁺ Centers In LiNbO₃, C. Rudowicz, T.H. Yeom, Y.M. Chang, S.H. Choh, City Polytechnic of Hong Kong and Korea University.

A A Full Hamiltonian Treatment Of The Effects Of Zero-Field Splitting On CW-EPR Spectra of Mn(II), A.R. Coffine, J. Peisach, Albert Einstein College of Medicine.


B Oxygen Diffusion Through Polymers As Measured By EPR, With Biological Applications, A.I. Smirnov, S.W. Norby, J.A. Weyhenmeyer, R.B. Clarkson, University of Illinois.

A Anisotropic Motion In Spin-Labelled Lipids Studied By Multifrequency Saturation Recovery EPR, B.H. Robinson, C. Mailer, J.-J. Yin, J.S. Hyde, University of Washington and Medical College of Wisconsin.


A In Vivo Nitroxide Pharmacokinetics By S-Band EPR Spectroscopy, A. Komarov, C.S. Lai, Medical College of Wisconsin.


** See page 39 for addendum.

Wednesday, July 28, 1993, Session VI, James Stathis, presiding

8:30 Introductory remarks, J. Stathis


10:05 BREAK

10:25 Spin-Dependent Recombination And Photo-Electrical EPR In Irradiated Silicon Crystals And Silicon Diodes, L.S. Vlasenko, M.M. Afanasjev, M.P. Vlasenko, Academy of Sciences, St. Petersburg.

10:45 EDEPR Of Deep And Shallow Recombination Centers In A Si Diode And In Bulk Silicon, S. Gruelich-Weber, B. Stich, J.-M. Spaeth, H. Overhof, University of Paderborn.

11:05 Spin-Dependent Recombination At Defects In Si Mosfets, J. H. Stathis, IBM Research Division.

11:25 High Resolution Spin Dependent Recombination Study Of Hot Carrier Damage In Short Channel Metal Oxide Silicon Field Effect Transistors, J. Gabrys, P.M. Lenahan, W. Weber, Pennsylvania State University and Siemens Corporate Research and Development.
11:45  Molecular Hydrogen, $E'$ Centers And $P_y$ Centers In Thin Amorphous Silicon Dioxide Films On Silicon, J.F. Conley, P.M. Lenahan, Pennsylvania State University.

12:05  LUNCH

Wednesday, July 28, 1993, Session VII, S. Cosgrove-Larsen, presiding

1:30  Evidence For 1993 Nitrogen Coordination To The Dinuclear Iron Center In The Hydroxylase Component Of Methane Monoxygenase; An Electron Spin Echo Spectroscopic Study, C. Bender, A. Rosenzweig, J. Peisach, S. Lippard, Albert Einstein College of Medicine and MIT.


2:10  Beating Spectral Diffusion With Coherent Raman Beats, M. Bowman, Pacific Northwest Labs.

2:30  BREAK

Session VIII - Posters, S.S. Eaton, presiding

3:00 - 4:00 Authors Present For Posters Labeled C

4:00 - 5:00 Authors Present For Posters Labeled D

C  ESR Studies Of Interactions Between Gramicidin A' And DPPC, M.-T. Ge, J.H. Freed, Cornell University.

D  Single Crystal EPR Studies Of Radiogenic Pt(III) Complexes Formed In $K_2[Pt(NO_2)_4].H_2O$ And In $K_2[Pt(NO_2)_4].M$. Geoffroy, M. Vermeille, P. Arrizabalaga, G. Gerrardinelli, University of Geneva.

C  Post Irradiation Dark Reactions Of Thyl And Peroxy Radicals Studied By Spin Trapping, B. Mile.


C  Reactive Oxygen Species Produced By Metal-Catalyzed Oxidation Of Bis(Trifluromethyl) Disulfide (TFD) And Protection By ZE, C.M. Arroyo, MRICD, Maryland.

D  Reactivity And Regioselectivity In Free-Radical Substitutions And Additions Using EPR/Spin-Trapping Techniques, D.L. Kolb, R.L. McCarthy, C.M. Arroyo, MRICD, Maryland.

C  A Reexamination Of The Microsomal Transformation Of N-Hydroxynorcocaine To Norcocaine Nitroxide, R.V. Lloyd, L. Shuster, R.P. Mason, Tufts University School of Medicine and NEHS.


C  Effects Of Tempol On Murine T And B Cell Proliferation, J. R. Bobell, P.D. Morse, II, Illinois State University.


C  EPR and ESEEM Characterization Of A "Green" Type 1 Copper Protein Redesigned From The Type 2 Copper Protein, Yeast Cu, Zn Superoxide Dismutase, C. Bender, Y. Lu, J. Selverstone-Valentine, J. Peisach, Albert Einstein College of Medicine and University of California Los Angeles.

D  Electron Spin Echo Spectroscopic Study Of Iron Coordination In Nitrile Hydratase, C. Bender, H. Jin, M. Nelson, J. Peisach, Albert Einstein College of Medicine and Dupont Company.


D  Incorporation Of Cu(II) ions Into SAPO-37: Cu(II) ion Location And Adsorbate Interaction Determined By Electron Spin Resonance and Electron Spin Echo Modulation Studies, M. Zamadies, L. Kevan, University of Houston.


C 160 A Pulsed S-Band ESR Spectrometer, J.H. Hankiewicz, C. Stenland, L. Kevan, University of Houston.

D 161 Noise Reduction Using Balanced RF Power Delivery And An Automatic Coupling Control For Very Low Frequency EPR, H. Halpern, C. Yu, M. Peric, E. Barth, University of Chicago.

C 162 A Low Frequency EPR Spectrometer System For In-Vivo Applications, J. Koscielniak, L.J. Berliner, Ohio State University.

D 163 Probehead With Interchangeable Loop-Gap Resonators And RF Coils For Multifrequency EPR/ENDOR T. Christidis, W. Francisz, T. Oles, J.S. Hyde, Medical College of Wisconsin.


D 165 Method For Adjusting The Q-Value Of An EPR Resonator, S. Pfenninger, W. Francisz, J. Forrer, J. Luglio, J.S. Hyde, Medical College of Wisconsin, Jagiellonian University, and Swiss Federal Institute of Technology.

C 166 Sensitivity Improvement Of Low Power Or Pulsed EPR Spectrometers, S. Pfenninger, W. Francisz, J.S. Hyde, Medical College of Wisconsin and Jagiellonian University.


D 169 The Temperature Dependence Of The Mn2+ HFS Parameter A In Calcite and Coal From 293 K to 673 K, Y.-P. Zhang, J. Kudynska, H.A. Buckmaster, University of Calgary.

C 170 EPR Accidental Radiation Dosimetry Of Human Hair, R. Kudynski, J. Kudynska, H.A. Buckmaster, University of Calgary.

D 171 EPR-Related Database Project - Feasibility Study Report, C. Rudowicz, City Polytechnic of Hong Kong.

C 172 Simulation Of Low Symmetry EPR Transitions By Mathematica Programs, W.K. Siu, C. Rudowicz, City Polytechnic of Hong Kong.


D 177 Characterization Of Paramagnetic Probes For Direct Detection Of Gaseous NO By EPR, S.-W. Norby, A.I. Smirnov, R.B. Clarkson, University of Illinois.

C 178 Hydrocarbon Containing Paramagnetic Centers In Silicon Dioxide Thin Films, M. Hoinkis, B.C. Nguyen, M.L. Galiano, M.S. Crowder, IBM Research and Applied Materials.
Wednesday evening - Open House at the University of Denver, EPR Lab

Thursday, July 29, 1993, Session IX, W. Frncisz, presiding

8:30  
Motional Studies Of Radicals In Polymers By 2D EPR, G.G. Maresch, A.A. Dubinskii, J. Saalmuller,  
181  
H.W. Spiess, Max-Planck-Institut fur Polymerforschung, Germany.

9:00  
Model Dependence In Slow Motional 250 GHz ESR Spectra, K.A. Earle, D.E. Budil, J. Moscicki,  
182  
J.H. Freed, Cornell University.

9:30  
Very High Frequency Step-Tunable ESR Spectroscopy: Low Temperature Investigations Of Biradicals,  
183  
L.C. Brunel, S. Gambarelli, B. Pepin-Donat, A. Rassat, Grenoble High Magnetic Field Laboratory.

9:55  
Nitroaromatic Anions And Copper Sites: 2-4 GHz ESEEM And 95 GHz EPR, W. Shi, W. Wang,  
184  
R.L. Belford, R.B. Clarkson, University of Illinois.

10:20  
BREAK

10:40  
For Infrared ISR Of Some Manganese-Containing Compounds, W.B. Lynch, R.S. Boorse, M.M. Burlitch,  
185  
J.H. Freed, Cornell University.

11:05  
Endor Identification Of Bridging Hydroxide Ligands In The Mixed-Valent Diron Centers Of Methane  
186  
V.J. DeRose, K.E. Liu, D.M. Kurtz, Jr., S.J. Lippard, B.M. Hoffman, Northwestern University, MIT, and University of Georgia.

11:30  
187  
University and Harvard Medical School.

12:00  
LUNCH

Thursday, July 29, 1993, Bruker users 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. Poster display area is approximately 4 ft. x 4 ft.

SYMPOSIUM ON FTIR/NIR/Raman

Organized by A.R. Chuhtai

Monday, July 26, 1993

Keynote Speaker: Professor Dwight M. Smith, Former Chancellor of University of Denver, Presently Professor of Chemistry, Department of Chemistry, University of Denver, Denver, CO 80208.

8:30  
Heterogeneous Photochemical Reactions Involving Carbonaceous Particulate; Shedding Some Light On A  
188  
Dark Subject.

9:10  
A Review Of Sampling Accessories Common To FT-RAMAN And FT-IR, Steve Hill, BIO-RAD, Micro-  
189  
measurements Division, 520 Clyde Avenue, Mountain View, CA 94043-2212.

9:40  
Use Of FTIR To Measure CO2-Induced Crude Oil Asphaltene Deposition Onset. James E. Tackett,  
190  
Marathon Oil Company, 7400 S. Broadway, Littleton, CO 80122.

10:00  
BREAK

10:15  
Electrochemical SERS Detection Of Environmental Cyanide ion. Robert D. Shelton, John M.C. Storey,  
191  
and Eric A. Wachter, Health and Safety Research Division, OakRidge National Laboratory, OakRidge,  
TN 37831-6113.

10:35  
Electrochemical SERS Detection Of Aqueous Chlorinated Hydrocarbons, John M.E. Storye, Robert D.  
192  
Shelton, Tye E. Barber, and Eric A. Wachter, Health and Safety Research Division, OakRidge National  
Laboratory, OakRidge, TN 37831-6113.
11:00 Atomic Force Microscopy Of Thin Ag Film Nanostructure. Shane E. Roark and Kathy L. Rowlen.
193 Department of Chemistry and Biochemistry, University of Colorado, Boulder, CO 80309.

11:20 FTIR Photothermal Beam Deflection Spectroscopy (PBDS) Studies Of Composites And Polymers.
194 T. Mahmood, Y. Tada, and J.R. Schlup, Department of Chemical Engineering, Kansas State University, Manhattan, KS 66506-5102.

11:45 LUNCH


2:40 BREAK

2:55 The Effect Of Changes In PH On The Raman Spectra Of Cellulose Acetate Polymers In Aqueous Solution. Marvin C. Goldberg and Anthony George, U.S. Geological Survey, P.O. Box 25046 MS 424, Lakewood, CO 80225 (20 min).


SYMPOSIUM ON ICP-MS

Organized by Howard E. Taylor

Tuesday, July 27th - Howard E. Taylor, presiding

9:00 Opening remarks, H.E. Taylor

9:10 Keynote lecture Addressing background problems in isotope ratio ICP-MS. S.R. Koirtgohann and Lilian Yu, Department of Chemistry, University of Missouri, Columbia, MO.


10:10 COFFEE BREAK


11:05 Determination Of Magnesium In Estuarine Sediment By Isotope Dilution-Inductively Coupled Plasma Mass Spectrometry, K.E. Murphy and P.J. Paulsen, National Institute of Standards and Technology Gaithersburg, MD.
11:30 High Accuracy Determination Of Selected Transition Metals By ICP-MS Isotope Dilution, E.S. Beary and
204 P.J. Paulsen, National Institute of Standards and Technology, Gaithersburg, MD.

11:55 LUNCH BREAK
F.E. Lichte, presiding

2:00 Multielement Characterization Of Single Fibers By Solid Sampling ETV-ICP-MS, R.D. Koons, Forensic
205 Science Research and Training Center, Federal Bureau of Investigations Academy, Quantico, VA.

2:25 Hydride Trapping On Palladium And Subsequent Determination With Inductively Coupled Plasma Mass
206 Spectrometry (ICP-MS), I. Marawi, J. Wang, L.K. Olson and J.A. Caruso, Dept. of Chemistry, University
of Cincinnati, Cincinnati, OH.

2:50 Analysis Of Semiconductor Materials Using High Resolution Inductively Coupled Plasma Mass Spec-
207 trometry (HR-ICP-MS), R. Henry, N. Reed, P. Sigsworth and R. Hutton, Fisons Instruments, Frederickburg, VA.

3:15 COFFEE BREAK

3:45 Biological Material Analysis Using ICP-MS And FI-ICP-MS, E. Pruszkowski and R. Hergenreder, Perkin
208 Elmer Corp., Irvine, CA.

4:10 The Use Of ICP-MS For The Determination Of Trace Metals In The Rocky Mountain Regional Snow Pack
CO.

SYMPOSIUM ON LABORATORY SAFETY
Organized by Marvin C. Goldberg

Wednesday, July 28th
Time 1:30 - 3:30 P.M.

LABORATORY SAFETY - PANEL DISCUSSION

Because of liability legislation and the current trend to hold each laboratory responsible for safe operating conditions, it is apparent that a greater amount of time and personnel must be devoted to operating and maintaining safe laboratory conditions. The necessity to implement safe laboratory practices and programs to implement these practices has become paramount in laboratory operations. Many facets of this timely subject will be addressed by the members of the panel.

The discussion will deal with common safety problems that one faces on a day to day basis including, establishment of laboratory operating rules, establishing safe operating conditions, special safety equipment, personal protective gear, dealing with crises, and dealing with everyday happenings in the laboratory. Featured in this discussion panel are panel members who are presently working as designated safety officers in their respective organizations. Audience participation will be encouraged.

Panel moderator: Marvin C. Goldberg
U.S. Geological Survey, National Research Program, P.O. Box 25046 MS 424,
Denver, CO

PANEL:
Rick Cameron Vista Laboratory, 325 Interlocken Parkway, Broomfield, CO
Carlos Arozarena U.S. Geological Survey, National Water Laboratory Safety Officer, 52nd and Ward
Road, Denver, CO
Tom Ging U.S. Geological Survey, Geologic Division Safety Officer, Central Region, P.O. Box
25046 MS 973, Denver Federal Center. Lakewood, CO 80225
Diane Shugrue U.S. Public Health Service, Building 41, P.O. Box 25145, Denver Federal Center,
Lakewood, CO 80225 Respirator Fit Test Laboratory
SYMPOSIUM ON LUMINESCENCE

Organized by DeLyle Eastwood and Robert J. Hurtubise

Monday, July 26th

8:55  Introductory Remarks, Robert J. Hurtubise


10:15  BREAK

10:40  Keynote Lecture

10:13  Electrogenerated Chemiluminescence Detection Using Tris (2,2'-bipyridyl)ruthenium(II) by Timothy A. Nieman. Chemistry Department, University of Illinois, 1209 W. California Street, Urbana, Illinois 61801.


12:00  LUNCH

1:55  Remarks, DeLyle Eastwood, Presiding

2:00  Keynote Lecture

2:16  Detection of Metabolites of Polycyclic Aromatic Hydrocarbons in the Urine of Psoriasis Patients Treated With Coal-Tar by Ainsley Weston, Regina M. Santella* and Elise D. Bowman, Laboratory of Human Carcinogenesis, National Cancer Institute, National Institutes of Health, Bethesda, Maryland 20891 and *Columbia University, New York, New York 10032.


3:15  BREAK


27
4:30  Investigation of Binding Environments in Humic Substances Using Fluorescent Probes by Sherry L. Hemmingsen and Linda B. McGown, Duke University, P.M. Gross Chemical Laboratory, P.O. Box 90348, Durham, North Carolina 27709-0348.

4:55  Concluding Remarks, Robert J. Hurtubise

**SYMPOSIUM ON MASS SPECTROMETRY**

*Organized by Joseph A. Zirrolli*

Monday, July 26, 1993

9:00  Metabolism Of Leukotriene B4 In The Primate, Keith L. Clay, Bernard Fruteau de Lacios, and Robert C. Murphy, Department of Pediatrics, National Jewish Center for Immunology and Respiratory Medicine, Denver, CO 80206

9:30  Identification Of Lipid Peroxidation Products Using GC/MS And FAB/MS/MS. Kathleen Kayganich

10:00  Structural Determination Of a Modified Membrane Lipopeptide, Denise K. MacMillian, Robert C. Murphy, Hee-Joo Park and Patrick J. Brennan, Department of Pediatrics, National Jewish Center for Immunology and Respiratory Medicine, Denver, CO 80206 and Department of Microbiology, College of Veterinary Medicine, Colorado State University, Ft. Collins, CO 80523.

10:30  Use Of FAB/SIMS To Measure Iron Absorption IN VIVO, David R. Flory, Leland V. Miller and Paul V. Fennessey, Departments of Pharmacology and Pediatrics, University of Colorado Health Sciences Center, Denver, CO 80262.

11:00  LUNCH & EXHIBITION

1:00  Keynote Speaker: Recent Developments In Electrospray Mass Spectrometry

2:00  Analysis Of Phosphoserine Or Phosphothreonine By Electrospray Mass Spectrometry During Online HPLC Of Chemically Beta Eliminated Peptide Mixtures. Katheryn A. Resing, Richard S. Johnson and Kenneth A. Walsh, Department of Chemistry and Biochemistry, University of Colorado, Boulder, CO 80309-0215 and Department of Biochemistry, University of Washington, Seattle, WA 98195.


3:00  Electrospray Mass Spectrometry of “Small” Biomolecules: Comparision With Fast Atom Bombardment Mass Spectrometry. Joseph A. Zirrolli, Department of Pediatrics, National Jewish Center for Immunology and Respiratory Medicine, Denver, CO 80206.

Tuesday, July 27, 1993


10:30 - 1:00  LUNCH & EXHIBITION
1:00 Flowing Afterglow Studies Of Boron Hydride Anions. Martin Stephan, Michele Krempp, Charles DePuy and Robert Damrauer, Department of Chemistry and Biochemistry, University of Colorado, Boulder, CO 80309-0215 and Department of Chemistry, University of Colorado, Denver, CO.

1:30 Chemistry Of Sillyl Amide Anions. Joseph Hankin, Michele Krempp and Robert Damrauer, Department of Chemistry and Biochemistry, University of Colorado, Boulder, CO 80309-0215 and Department of Chemistry, University of Colorado, Denver, CO.

2:00 Soft-Drift Studies Of Sulfur Anion Reactions. Hack Sung Lee and Veronica Bierbaum, Department of Chemistry and Biochemistry, University of Colorado, Boulder, CO 80309-0215.

2:30 - 2:45 BREAK

2:45 Gas Phase Rearrangement Of The Isocyanomethyl To The Cyanomethyl Anion. Christopher Hadad, Charles DePuy and Veronica Bierbaum, Department of Chemistry and Biochemistry, University of Colorado, Boulder, CO 80309-0215.

3:15 Gas Phase Chemistry Of The Ketenyl And Related Anions. Gustavo Davico and Charles DePuy, Department of Chemistry and Biochemistry, University of Colorado, Boulder, CO 80309-0215.

3:45 - 5:00 EXHIBITION

SYMPOSIUM ON NMR

MONDAY MORNING, July 26, 1993

SPIN DYNAMICS AND NEW TECHNIQUES
A.J. Vega presiding

8:10 WELCOMING REMARKS, H. Eckert
8:15 Dynamic Nuclear Polarization At 740 GHZ (5 TESLA), Lino R. Becerra, Gary Gerfen, Brendan F. Bellew, David J. Singel, and Robert G. Griffin, Massachusetts Institute of Technology, MA and Harvard University, MA.


9:15 Variable Amplitude Crosspolarization MAS NMR, Olve Peersen, Xiaoling Wu, May Han, Gunther Metz, and Steven Smith, Yale University, New Haven, CT.

9:45 BREAK

10:15 CPMAS Spectral Editing By Using Polarization Inversion, Xiaoling Wu and Kurt W. Zilm, Yale University, New Haven, CT.

10:45 $^1H$ And $^{19}F$ Multiple Quantum NMR Dynamics In Quasi One-Dimensional Spin Distributions In Apatites, Gyungoo Cho, Liam B. Moran, and James P. Yesinowski, Naval Research Laboratory, Washington DC.
11:15 \(^{13}\text{C},^{19}\text{F} \text{ Dipolar Dephasing In Monofluorinated Organic Substances, Edward W. Hagaman, Oak Ridge National Laboratory, Oak Ridge, TN.}\)

11:45 \textit{Spin-Spin Coupling Phenomena Involving Phosphorus}, Roderick E. Wasylishen, Klaus Eichele, Mike Lumßen, Kenneth Wright, and Gang Wu, Dalhousie University, Halifax, Canada.

12:15 \textbf{LUNCH}

\textbf{MONDAY AFTERNOON, July 26, 1993}

\textbf{SOLID STATE NMR PARAMETERS AND CALCULATIONS}

H. Eckert presiding

1:30 \textit{The Application Of NMR Shifts To Structural Studies Of Glasses And Minerals. Ray Dupree and S.C. Kohn, University of Warwick, United Kingdom.}

2:00 \textit{Carbon-13 Chemical Shift Tensor Data Compared With Diffraction Structural Parameters Using Quantum Mechanical Calculations}, David M. Grant, Rob Iuliucci, Fang Liu, Julio C. Faccelli, and Don W. Alderman, University of Utah, Salt Lake City.

2:30 \textit{Measurement Of Internuclear Distances In Isolated Pairs Of Spins By NMR: Which Is The Most Appropriate “Hard”’ Experiment? B.C. Gerstein and Marek Pruski, Iowa State University.}

3:00 \textbf{BREAK}

\textbf{SOLID STATE IMAGING}

R. Botto presiding

3:30 \textit{NMR Imaging And Scattering Experiments For Solid State Samples, D.G. Cory, Massachusetts Institute of Technology, Cambridge, MA.}

4:00 \textit{NMR Imaging Of Anomalous Solvent Transport In Glassy And Rubbery Macromolecular Materials}, George D. Cody and Robert Botto, Argonne National Laboratory, Argonne, IL.

4:30 \textit{Short T\textsubscript{2} Magnetic Resonance Imaging Strategies}, David E. Axelson, Ken Green, Jon Goldman, Jim Frosti, and Arno Nauerth, Petroleum Recovery Institute, Alberta, Canada and Bruker Analytische Messtechnik, Germany.

5:00 \textit{Solid State NMR Imaging With Magic Angle Spinning}, Yanhong Sun, Marian Buszko, Herman Lock, and Gary E. Maciel, Colorado State University, Fort Collins, CO.

\textbf{MONDAY EVENING, July 26, 1993}

\textbf{VENDOR SESSION}

B.C. Gerstein presiding

\textbf{TUESDAY MORNING, July 27, 1993}

\textbf{R.W. VAUGHAN PLENARY LECTURE}

H. Eckert presiding

8:30 \textit{High Resolution NMR Of Complicated Solids: Synthetic And Biological Composites And Complexes, Jacob Schaefer, Washington University.}

\textbf{POLYMERS}

H. Thomann presiding

9:25 \textit{Dynamics, Cross-Polarization, R\textsuperscript{2}, And RFDR In MAS Spectra, R.G. Griffin, Massachusetts Institute of Technology, Cambridge MA.}

10:00 \textbf{BREAK}

10:30 \textit{Solid State NMR Studies Of Peptides And Proteins, Stan Opella, University of Pennsylvania.}

11:05 \textit{Spin Relaxation, Molecular Motion, And Morphology In Polymers, Roebert L. Vold and Gina L. Hoatson, College of William and Mary, Williamsburg, VA.}

30
Rocky Mountain Conference on Magnetic Resonance, Vol. 35 [1993], Art. 1

11:40  Progress In Establishing A Link Between The Local Chain Motion Of Aramatic Polymers And Their Bulk Physical Properties, P. Mark Henrichs, Sterling Winthrop, Inc. Malvern, PA.

12:15  LUNCH

TUESDAY AFTERNOON

POLYMERS
H. Thomann presiding

1:30  Solid State NMR Investigation Of Negative Excess Mixing Enthalpy In PVE/PIP Blends, Kenneth McGrath, Joel B. Miller, C. Michael Roland, and Allen N. Garroway, Naval Research Laboratory, Washington, D.C.

2:30  Evidence Of Large Amplitude Motion In The Furanose Ring Of An Oligonucleotide. A Solid State Deuterium NMR Study, Debra L. Mattiello and Gary P. Drobny, University of Washington, Seattle, WA.

3:00  BREAK

3:30  The Detection And Characterization Of Molecular Interactions In Polymer Blends Using Solid State NMR, Jeffery White and Peter A. Mirau, AT&T Bell Laboratories, Murray Hill, NJ.

4:00  NMR Of Polymer Interfaces, M. Afeworki, Exxon Research and Engineering Co., Annandale, NJ.

4:30  Assessing And Developing Pulse Sequences With Interactive Computer Graphics, Jonathan Callahan and Gary Drobny, University of Washington, Seattle, WA.

5:00  Visualization Of Multidimensional NMR Data, Robert Johnson, Dominque Brodbeck, and Richard Richter-Rafey, IBM Almaden, San Jose, CA.

July 28, 1993

WEDNESDAY MORNING, July 28, 1993

INORGANIC MATERIALS
R. Botto, presiding

8:30  Structure And Spin Dynamics Of The Silica Surface, I. Suer Chuang, David R. Kinney, and Gary E. Maciel, Colorado State University, Fort Collins, CO.

9:00  Single Crystal Proton NMR Studies Of Low Concentration Hydrous Species In Minerals, Herman Cho and George Rossman, Pacific Northwest Laboratories, Richland, WA and California Institute of Technology, Pasadena, CA.

9:30  Proton And Deuterium MAS NMR Of Zeolites, Larry W. Beck and James F. Haw, Texas A&M University, College Station TX.

10:00  BREAK

10:30  27Al MAS NMR Studies Of Sodium Aluminate Speciation And The Mechanistics Of Aluminum Hydroxide Precipitation Upon Acid Hydrolysis, John V. Hanna and Susan M. Bradley, CSIRO Division of Coal and Energy Technology, North Ryde, Australia.

11:00  Structure And Disorder In Glassy Ionic Conductors, Kaj. K. Olsen, Sandra L. Tagg, Randall E. Youngman, and Josef W. Zwanziger, Indiana University, Bloomington, IN.

11:30  High-Temperature NMR Of Chalcogenide Glasses And Melts, Robert Maxwell and Hellmut Eckert, University of California, Santa Barbara, CA.

12:00  LUNCH
WEDNESDAY AFTERNOON, July 28, 1993

UNCOMMON MAGNETIC RESONANCE DETECTION METHODS
J. Yesinowski presiding
1:30 Pure \textsuperscript{14}N NQR Of Large Specimens, Michael L. Bueiss, Allen N. Garaway, James P. Yesinowski, and Joel B. Miller, Naval Research Laboratory, Washington, DC.
2:00 SQUID NQR Of Nitrogen -\textsuperscript{14} In Amino Acids And Small Peptides, Ulrike Werner, Bruce Black, Marcia Ziegeweid, and Alexander Pines, University of California, Berkeley, CA.
2:30 Force Detection Of Magnetic Resonance: A New Method Of MR Imaging, Constantino S. Yannoni, Daniel Rugar, Otmar Zuger, and John A. Sidles, IBM Almaden Research Center, San Jose, CA 95120 and University of Washington, Seattle, WA 98195.
3:00 BREAK
3:30 EPR Detection Of Nuclear Dipolar Coherence, Hans Thomann and Marcelino Bernardo, Exxon Research and Engineering, Annandale, NJ.
4:00 Site-Resolved Optical NMR Of Gallium Arsenide, J.Y. Hwang, J.A. Marohn, P.J. Carson, S.K. Buratto, D.N. Shykind, and Daniel P. Wettekamp, California Institute of Technology, Pasadena, CA.
4:30 Dynamics Of Optical Alignment Of Nuclei In High Magnetic Field, Matt Augustine and Kurt W. Zilm, Yale University, New Haven CT.

JULY 29

THURSDAY MORNING, July 29, 1993

CATALYSIS AND CATALYTIC MATERIALS
A.J. Vega presiding
8:30 Dynamics Of Hydrogen On A Catalyst Surface - A Study By Solid State NMR, Frank Engelke, Sandeep Bhatia, Terry S. King, and Marek Pruski, Iowa State University, Ames, IA.
9:00 Recent Developments In In-Situ MAS NMR Of Reactions On Catalysts, James F. Haw, Eric Munson, David Murray, Teng Xu, David Ferguson, and Ali Kheir, Texas A&M University, College Station, TX.
9:30 Solid NMR Investigations Of \textsuperscript{13}C Adsorbates On Powdered Platinum Electrodes, K. Franaszczuk, J. Wu, A. Wieckowski, B. Montez, and E. Oldfield, University of Illinois, Urbana-Champaign, IL.
10:00 BREAK
10:30 Nitrogen Chemistry On Surfaces: Hydrodenitrogenation And NO\textsubscript{x} Decomposition, Jeffrey A. Reimer, Phil Armstrong, Adam Aylor, Alexis Bell, and Sarah Larsen, University of California, Berkeley, CA.
11:00 NMR Studies Of Zeolites At 11.7 T; Cross Polarization And Si/Al Partitioning, J.M. Millar, M.R. Melchior, K. Strohmaier, and D.E.W. Vaughan, Exxon Research and Engineering, Annandale, NJ.
11:30 Sideband Analysis In DOR NMR Spectra, J.P. Amoureux and E. Cochon, Universite de Lille.
12:00 Solid State 207\textsuperscript{Pb} NMR Spectroscopy: Spectroscopic Dilemmas And Chemical Results, Cecil Dybowski, Mark Hepp, Matthew Smith, Guenther Neue, and Dale Perry, University of Delaware, Newark, DE, University of Dortmund, Germany and Lawrence Berkeley Laboratory, Berkeley, CA.

SYMPOSIUM ON PHARMACEUTICAL ANALYSIS
Organized by Mike Cutrera, Robert Lantz, and Patricia Sulik

Tuesday Morning, July 27, 1993 - Robert K. Lantz, presiding
9:00 Welcome And Introduction Of Speaker
9:00 Dissolution: Past, Present & Future. Marvin Delgado, Bill Meneses, Bill Hanson, and Royal Hanson, Hanson Research Corporation, 9810 Varelil Ave., Chatsworth, CA 91311.

2:28 4


2:28 5

10:30 BREAK

2:28 5


2:28 6


2:28 7

11:35 Optical Spectroscopy In The Analysis Of Polypeptide Structure And Stability. James Matsuura, Michael E. Powers, Thomas M. Foster, Heather A. Thomas, Jonathon J. Dormish, John F. Carpenter, Merrick L. Shively and Mark C. Manning, School of Pharmacy, University, University of Colorado Health Sciences Center, Denver, CO 80262.

12:00 LUNCH

Tuesday afternoon - Patricia L. Sulik, presiding

1:20 Thermal Analysis And Dosage Formulations. Walter McCrone, McCrone Research Institute, Chicago, IL.

2:28 8

2:40 A Method For The Pharmacokinetic Evaluation Of Racemic Fenfluramine And Its Major Metabolite Norfenfluramine In Human Plasma Using HPLC Enantiomeric Separation And Quantitation At The Low ng/mL Level Via A Pirkle-Type Chiral Recognition Approach. Jia-ning Aeng, Lin Dou, and Hans H. Stuting, Analytical Chemistry and Clinical Trials Departments, 69 First Avenue, Raritan, NJ 08869.

3:10 BREAK

2:29 0

3:25 Separation And Detection Of Cephalosporins Using HPLC With Pulsed Electrochemical Detection. Lawrence E. Welch, and Elizabeth K. Yun, Chemistry Department, Knox College, Galesburg, IL 61401.

2:29 1


Wednesday morning, July 28, 1993 - Robert K. Lantz, presiding

9:00 INTRODUCTION AND WELCOME

9:05 Applications Of Calorimetry In An Industrial/Pharmaceutical Environment. Tom Hofelich, Thermal Analysis Group, DOW Chemical Company, Midland, MI.

2:29 2

10:15 Pulmonary Drug Delivery Of Fine Aerosol Particles From Supercritical Fluids. Anthony F. Lagalante, Brooks M. Hybertson, John E. Repine, Connic J. Beecher, Kathryn S. Rutledge, Robert E. Sievers, Webb-Waring Institute for Biomedical Research, University of Colorado Health Sciences Center, Denver, CO 80262 and Cooperative Institute for Research in Environmental Sciences and Department of Chemistry and Biochemistry, University of Colorado, Boulder, CO 80309.

2:29 3

10:30 BREAK

2:29 4

10:45 Photostability Of Pharmaceuticals - Instrumental Approach. Lawrence A. Bard, Heraeus DSET Laboratories, Inc. 45601 North 47th Avenue, Phoenix, AZ 85027-7042.

2:29 5

SYMPOSIUM ON QUALITY ASSURANCE
Organized by William J. Shampine

Chairperson: William J. Shampine

Wednesday, July 28, 1993

1:00 Introductory remarks, William J. Shampine.


SYMPOSIUM ON RADIOCHEMISTRY
Organized by Ann Mullin

Sponsorship of this symposium by Rocky Mountain Scientific Glassblowing Co., 4990 E. Ashbury Ave., Denver, CO 80222 is gratefully acknowledged.

Monday, July 26, 1993

8:00 Introduction - Ann Mullin

8:05 Problems With The Lucas Cell As An Analytical Tool by Henry F. Lucas. Lucas Laboratory, Inc., 2860 Hopi Dr. #1A, Sedona, AZ 86336.


9:05 Americium And Plutonium Analysis Of Environmental Samples by Robert Mero. Colorado Department of Health, 4210 East 11th Avenue, Denver, CO 80220.

9:35 BREAK

10:00 New Developments In Alpha Spectrometry Liquid Scintillation Methods by W. Jack McDowell and Betty McDowell. ETRAC Inc., 1009 Alvin Weinberg Drive, Oak Ridge, TN 37830.

10:30 Basis For The Eichrom Column-Cerenkov Counting Radiostrontium Procedure Developed At The Yankee Atomic Environmental Laboratory by David E. McCurdy, Ashok D. Banavali, and Edgar M. Moreno. Yankee Atomic Electric Company, 580 Main Street, Bolton, MA 01740.


11:30 LUNCH

1:00 Calculations Of The Lower Limit Of Detection by T.B. Borak and T.B. Kirchner. Colorado State University, Fort Collins, CO 80523.

1:30 Selection Of Formulas And Techniques For Determining Measurement Detection Limits In Radiometric Analysis, Robert W. Terry. Radiation Control Division, Colorado Department of Health, 4300 E. Cherry Creek S. Drive, Denver, CO 80222-1530.

2:00 Evaluation Of Controls For The Assurance Of Quality Data In Assurance Of Quality Data In A Radiochemistry Laboratory by J.S. Morton. U.S. Department of Energy, Radiological and Environmental Sciences Laboratory, 785 Doe Place, Idaho Falls, ID 83401-1562.
2:30    BREAK

2:45    The Role Of The EPA Radiation Quality Assurance Program In The Measurement Quality Assurance
        Accreditation Program For Radioassay Laboratories by Terence M. Grady, U.S. Environmental Protection
        Agency, P.O. Box 93478, Las Vegas, NV 89193-3478.

3:15    Quality Control For Nuclear Analytical Measurements In Laboratory and Production Environments,
        Richard S. Seymour, Terry Beal, William H.C. Clark, and Geoff Gleason, Oxford Instruments, Oak
        Ridge, TN 37831-2560.

3:45    Analytical Methods Supporting The Radionuclide In Drinking Water Regulations, Paul B. Hahn, and
        Sponsorship of this symposium by Oxford Instruments Inc., Nuclear Measurements Group is gratefully acknowledged.

Tuesday, July 27, 1993

8:30    Panel Discussion
        "Detection limits and uncertainties of radiochemical analysis - their determination and use."
        Moderator - Phil Nyberg, EPA Region 8

        Panel Members -  David McCurdy      Paul Hahn
                         Colin Sanderson    Robert Terry
                         Stan Morton         Daniel Montgomery

11:30   LUNCH

1:00    Using High Resolution Detectors And Low System Background To Improve Sensitivity And Precision
        In Gamma Spectrometric Measurement by Robert W. Terry and L.A. (Tony) Harrison, Radiation Control
        Division, Colorado Department of Health, 4300 E. Cherry Creek S. Drive, Denver, CO 80222-1530.

1:30    Remote Gamma-Ray Spectroscopy With Satellite Data Transmission by Colin G. Sanderson, Environmental
        Measurements Laboratory, U.S. Department of Energy, 376 Hudson Street, New York, New York,
        10014-3621.

2:00    BREAK

2:15    Streamlining And Automation Of Radioanalytical Methods At A Commercial Laboratory by James T.
        Harvey and James W. Dillard, IT Corporation, 9000 Executive Park Drive, Suite A-110, Knoxville,
        TN 37923.

2:45    A Limitation Of Gross-Beta Activity In Environmental Studies Of Ground Water by Alan H. Welch,

3:15    Measuring The Contribution of 222 Rn In Well Water To Indoor Air By Long-Term And Continuous
        Monitoring by Peter F. Folger, Richard B. Wanty, Philip Nyberg, and Eileen Poeter. U.S. Geological
        Survey, MS 916, Denver, CO 80225.

Wednesday, July 28, 1993

8:00    The Fort St. Vrain Independent Spent Fuel Storage Installation Radiation Monitoring Program -
        Results To Date by Ted J. Borst, CHP. Public Service Co. of Colorado, 16805 WCR 19 1/2, Platteville,
        CO, 80651.

8:30    Effects Of Uranium-Mining Releases On Ground-Water Quality In The Puerco River Basin, Arizona And
        New Mexico by Peter C. Van Metre, U.S. Geological Survey, 8011 Cameron Road, Austin, TX 78754-3898.

9:00    Radium-228 And Radium-225 In Sand, Silty Sand, And Ground Water In An Unconfined Aquifer In The
        New Jersey Coastal Plain by Zoltan Szabo. U.S. Geological Survey, 810 Bear Tavern Road, Suite 206,
        W. Trenton, NJ 08628.

9:30    Gamma Ray And Elemental Analyses Of Sediments To Obtain Depositional Histories In The Louisiana
        University of Southwestern Louisiana, Lafayette, LA 70504-4210.
SYMPOSIUM ON ROBOTICS

Chairperson: Gerald L. Hoffman  
Organized by Gerald L. Hoffman

Wednesday, July 28, 1993

8:55 Introductory Remarks, Gerald L. Hoffman


10:00 A Robotic System Optimized For Chemical Analysis, John Rollheiser, Hewlett-Packard, 24 Inverness Place East, Englewood, Colorado 80112.

10:30 BREAK

11:00 Recent Advancements In Laboratory Robotics, John P. Connelly, and R.B. Jamieson, Zymark Corp., Zymark Center, Hopkinton, Massachusetts 01748.

11:45 LUNCH

1:30 Automated Acid Digestion System For The Preparation Of Samples By Approved Procedures. Leatrice A. Kaplan, David C. Yaworsky, Diane S. Layne, Chuck L. Horn, Virginia Power System Laboratory, 11201 Old Stage Road, Chester, Virginia 23831, Rodney A. Stockton, SLR Systems, P.O. Box 1265, 2950 George Washington Way, Richland, Washington 99352.

2:00 Planning Laboratory Automation Using Accurate Computer Simulation. Michael G. Dodson, Jonathan T. Smalley, and Stanley L. Owsley, Jr., Pacific Northwest Laboratory (PNL), P.O. Box 999, Richland, Washington 99352.

2:30 BREAK

3:00 Automation Of EPA Microwave Digestion Methods 3015 And 3051 For Trace Metal Analysis, John Alexander, Jesse Campbell, and Katherine Adams, ICF Technology Inc., 7411 Beach Drive East, Fort Orchard, Washington 98365.

3:30 Evolution Of A Robotics System For Wastewater Analysis. Tracie A. Lango and Robert A. Casselberry, Rohm and Hass Co., P.O. Box 219, Bldg. 40 A. Bristol, Pennsylvania 19007.
SYMPOSIUM ON GENERAL POSTERS
Organized by Mary E. Cast

332 Gas Chromatographic Analysis Of Gentamicin and Neomycin Residues in Raw Milk, by Susan B. Clark, Jeffrey A. Hurlbut, and Carolyn A. Geisler, U.S. Food and Drug Administration, Bldg. 20, Denver Federal Center, P.O. Box 25087, Denver, CO 80225-0087.

333 LC/MS Characterization of Malachite Green and Metabolites, by Sherri B. Turnipseed, Jose E. Roybal, and Austin R. Long, U.S. Food and Drug Administration, Animal Drug Research Center, Bldg. 20, Denver Federal Center, P.O. Box 25087, Denver, CO 80225-0087.

334 Detection of Ketones and Aldehydes by HPLC/UV using 2,4-dinitrophenylhydrazine, by Jeffrey A. Hurlbut, Robert K. Munns, Jose E. Roybal, and Austin R. Long, U.S. Food and Drug Administration, Bldg. 20, Denver Federal Center, P.O. Box 25087, Denver, CO 80225-0087.

335 A Method for the Determination of Thionin, a Metabolite of Methylene Blue, in Milk by VIS/LC, by Jose E. Roybal, Robert K. Munns, David C. Holland, Jeffrey A. Hurlbut, and Austin R. Long, U.S. Food and Drug Administration, Bldg. 20, Denver Federal Center, P.O. Box 25087, Denver, CO 80225-0087.

336 Simultaneous Determination of Nitrofurazone and Furazolidone in Shrimp (Penaeus vannamei) Muscle Tissue by LC with UV Detection, by Heidi S. Rupp, Robert K. Munns, Austin R. Long, U.S. Food and Drug Administration, Bldg. 20, Denver Federal Center, P.O. Box 25087, Denver, CO 80225-0087.

337 Determination of the Anti-coccidial Drug, Halofuginone in Eggs by Liquid Chromatography, by David C. Holland, Robert K. Munns, Jose E. Roybal, Jeffrey A. Hurlbut, Austin R. Long, U.S. Food and Drug Administration, Bldg. 20, Denver Federal Center, P.O. Box 25087, Denver, CO 80225-0087.

338 Radon Sampling in Prince Georges County, Maryland, by Sandra L. Szarzi and G.M. Reimer, U.S. Food and Drug Administration, Bldg. 20, Denver Federal Center, P.O. Box 25087, Denver, CO 80225-0087.

339 EPR Studies of the Glassy Behavior of Proteins, by Heinz J. Steinhoff, Klaus Lieutenant, Christine Karim, Institute of Biophysics, Rhur-University Bochum, 4630 Bochum, F.R.G.


341 Headspace GC Analysis of Residual Organic Solvents in Pharmaceutical Material using Diethylene Glycol as Sample Diluent, by Chen-Hwa Hui, Burroughs Wellcome Co., 3030 Cornwallis Road, Research Triangle Park, NC 27709.

342 Headspace Capillary Gas Chromatographic Determination of Residual Solvents in Phospholipids, by Lynne-Marie Cavallaro, Bristol-Myers Squibb Pharmaceutical Research Institute, P.O. Box 191, One Squibb Dr., New Brunswick, NJ 08903-0191.


344 Determination of Selected Carboxylic Acids and Alcohols in Groundwater by Gas Chromatography/Mass Spectrometry, by Jon Beihoffer and Cindy Ferguson, U.S. Environmental Protection Agency, National Enforcement Center, Bldg. 53, Box 25227, Denver Federal Center, Denver, CO 80225.


346 Mid-Versus Near-Infrared In The Study Of High Moisture Samples: Advantages, Disadvantages, and Complementation. James B. Reeves III, Ruminant Nutrition Lab., LPS1, ARS, USDA, Bldg. 200, Rm. 218, BARC-East, Beltsville, MD 20705.

Distance Measurements in Carbon-13 NMR: Application to DNA, Thomas P. Jarvie, Gershon M. Wolfe, Jonathan Callahan, Gary P. Drobny, Dept. of Chemistry, University of Washington, Seattle, WA.

High-resolution NMR Characterization of Solids, J.P. Amoureux, Universite de Lille 1 Villeneuve d'Ascq - Cedex, F 59655 - FRANCE.

Magic Echo and Spin Warp Microimaging of Polymers Below and Above the Glass Transition Temperature, Winfried Kuhn, Peter Barth, and Siegfried Hafner, Fraunhofer Institute, Ensheimer Str. 48, D-6670 St., Ingbert, Germany.

$^{129}$Xe NMR In Solids: Shielding Tensors and Dynamics, J.A. Ripmeester, C.I. Ratcliffe, I. Moudrakovsky, Steacie Institute for Molecular Sciences, National Research Council of Canada, Ottawa, and H. Tabbara, H. Graves Smith and C. Detellier, Dept. of Chemistry, University of Ottawa

Characterization of Polycrystalline $V_2O_5$ By Solid-State $^{51}$V-NMR, J.P. Amoureux, C. Fernandez, and P. Bodart, Universite de Lille 1, F 59655, Villeneuve D'Ascq, Cedex, FRANCE

Dynamics of Substituted Adamantanes: a NMR Study, J.P. Amoureux, R. Decressain, and E. Cochon, Universite de Lille 1, F 59655, Villeneuve D'Ascq, Cedex, FRANCE
ADDENDUM

16TH INTERNATIONAL EPR SYMPOSIUM

Tuesday, July 27, 1993, Session V - Posters

3:00 - 4:00 Authors Present For Posters Labeled A

A Analytical and Numerical Methods for the Prediction and Interpretation of the Response of 2- and 4-
130 Level Systems To Periodic Stimulation, H.S. Mechaourab, F. Neese, and J.S. Hyde, Medical College
of Wisconsin and University of Konstanz.

Wednesday, July 28, 1993, Session VIII - Posters

3:00 - 4:00 Authors Present For Posters Labeled C

4:00 - 5:00 Authors Present For Posters Labeled D

179 Feix, Medical College of Wisconsin.

C The Aggregation State of Spin Labeled Cecropin Ad In Aqueous Solution, H.S. Mechaourab, J.S. Hyde,
180 and J.B. Feix, Medical College of Wisconsin.
MASS SPECTROMETRIC DETERMINATION OF ANALYTE LOSS MECHANISMS DURING ELECTROTHERMAL ATOMIZATION IN GRAPHITE FURNACE ATOMIC ABSORPTION SPECTROMETRY. Garrett N. Brown, Jerry D. Harris and David L. Styris, Pacific Northwest Laboratory, Richland, WA 99352

The mechanisms that control analyte loss and the electrothermal atomization of tin, indium and gallium were investigated by monitoring real-time mass spectra of gaseous species generated in pyrolytic graphite-coated graphite furnaces. Atmospheric pressure and vacuum vaporization were used to separate homogeneous gas phase and condensed phase interactions. Analyte losses have been observed through the formation of molecular dimers, oxides and carbides emanating from the atomizer surface. Atomic and molecular diffusion is also implicated as a pathway for analyte loss during the vacuum vaporization of group IIIb elements. Bulk diffusion through a 0.3 mm thick graphite barrier is monitored by mass spectrometry during atomization in vacuo. The extent of analyte loss via diffusion is approximately three percent but varies depending upon species and diffusion thickness. This paper presents these data and discusses the overall mechanisms associated with analyte loss during electrothermal atomization.


Sample introduction has frequently been regarded as the "Achilles Heel" of devices such as the inductively coupled plasma. These sources are frequently used with solution nebulization, which necessitates some sort of sample dissolution process prior to analysis. Much research effort has been focused upon mitigating some of the deficiencies of sample introduction. Popular methods of direct introduction of solids include slurry nebulization and electrothermal vaporization. The present paper describes a new technique for electrothermal vaporization using low-temperature heating (900-1100 degrees C) in a quartz tube furnace, which is directly coupled to an ICP for atomic emission or mass spectrometry. The technique is applicable to the direct determination of volatile elements such as Hg, Te, Tl, Sb, As, and Se in solid samples. Determination of less volatile elements may be possible through selective formation of volatile compounds such as metal halides. The technique offers the advantage of accommodating solid samples of up to 0.2 grams, which enhances concentration-based detection limits and allows for a more representative subsample to be introduced.

PREPARATION AND INTRODUCTION OF STANDARDS FOR METHODS USING DIRECT SOLID ANALYSIS BY ELECTROTHERMAL VAPORIZATION. Robert D. Koong, Forensic Science Research and Training Center, FBI Academy, Quantico, VA 22135.

Electrothermal vaporization (ETV) is becoming popular for direct atomization of solid samples because of the advantages gained by avoiding a dissolution step. Forensic applications of solid sampling ETV include elemental determinations in glass, metals, polymers, hair and other tissues, and fibers, where both AAS and ICP-MS have been used for element quantitation. Quantitative analysis requires introduction of appropriate standards into the ETV device. In some instances, it is difficult to produce solution standards with the same matrix as the samples, requiring chemical modifiers to equalize matrices. Most autosamplers designed for solution introduction into ETV devices provide excellent reproducibility, but poor absolute volume delivery. Conversely, it is important when using solid sampling ETV procedures to introduce a precisely known mass of analyte into the furnace. An alternative to solution standards is the use of well characterized solid standards. Solid standards produce special considerations in the precision of element concentrations and heterogeneity effects when mg-sized samples are introduced into the furnace.

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COMBINING COLD VAPOR GENERATION WITH AMALGAMATION TO IMPROVE THE DETECTION LIMIT OF MERCURY IN ENVIRONMENTAL SAMPLES. Susan McIntosh, Perkin-Elmer Corporation, 761 Main Avenue, Norwalk, CT 06859-0215, Randy L. Hergenreder, Perkin-Elmer Corporation, 14818 W. 6th Avenue, Suite 96, Golden, CO 80401.

The determination of mercury in environmental samples has traditionally been performed by cold vapor atomic absorption. The detection limit of this technique is typically 0.2 u/L Hg. Recently, a Flow Injection method was approved by the EPA for the determination of mercury in water and wastewater samples. The flow injection technique increases sample throughput by automating the generation of the mercury vapor and, with the development of new lamp sources, has lowered the method detection limit for drinking waters and wastewater samples to 0.06 u/L Hg. A procedure for the determination of total mercury in environmental samples using a flow injection system coupled with an amalgamation accessory was investigated. The use of amalgamation to preconcentrate mercury is based on the knowledge that mercury readily forms an amalgam with precious metals. The mercury vapor is carried by an argon gas stream from the gas liquid separator of the flow injection system to a quartz tube containing a gold/platinum gauze. The mercury is collected on the gauze and, after a sufficient amount has been collected, the gauze is rapidly heated to drive off the mercury. The results demonstrate that amalgamation can significantly improve the method detection limit of mercury in environmental samples while providing automated sample analysis.

SIMULTANEOUS MULTI-ELEMENT ATOMIC EMISSION WITH A COMBUSTION FLAME. JOHN E. SCHMELZEL, SONYA WALRAVEN, JOHN J. SOTERA, DAVID L. PFEIL, Thermo Jarrell Ash Corporation, 8E Forge Parkway, Franklin, MA 02038

This paper will describe a flame atomic absorption/emission spectrometer which utilizes a rapid scanning galvanometer grating monochromator under computer control to perform multi-element/multi-line determinations. Although the selection of elements is limited to those which are adequately excited with either an air/acetylene or a nitrous oxide flame, the spectrometer has several advantages over an ICP spectrometer. It is less expensive and it can be used in conjunction with atomic absorption. Practical applications of these techniques will be presented. Specifically, the system will be applied to the determination of wear metals in oil by flame emission.

MATRIX DEPENDENCE OF ATOMIZATION, IONIZATION AND EXCITATION PROCESSES IN LASER INDUCED PLASMAS, V. Majidi, M. Joseph, N. Xu and M. Owens, Dept. of Chemistry, University of Kentucky, Lexington, KY 40506, USA.

Virtually all substances are susceptible to breakdown when illuminated by a sufficiently intense laser beam. In the laser induced plasma, molecules completely dissociate to form atoms, ions and electrons. Useful information about the elemental composition of the target material can be obtained either from analysis of the emissions emanating from the plasma volume or by extracting the ions into a mass spectrometer.

The analytical results for mass spectrometric and optical emission detection will be discussed. Non-selective ionization and 100% ionization efficiency are two advantages of laser plasma mass spectrometry. Disadvantages include a severe space-charge effect during the onset of plasma and a dependence of initial kinetic energy of ions on the sample matrix. For best analytical results with optical detection, time-resolved spectroscopy must be employed for observation of excited species. Extensive background emission and line broadening due to high population densities of excited species often hinder emission analysis.
NEW TECHNIQUES FOR IMPROVING ICP-OES SAMPLE THROUGHPUT
K.J. Fredeen, C. Anderau, D.A. Yates, K.W. Barnes, T.J. Gluodenis, Jr., and Z.A. Grosser, The Perkin-Elmer Corporation, 50 Danbury Road, Wilton, CT 06897-0215

This study explores improvements in Inductively Coupled Plasma Optical Emission Spectrometry (ICP-OES) sample throughput that can be realized through the use of recent advances in ICP-OES instrumentation and data collection/processing techniques. ICP-OES is used extensively in environmental trace metal determinations and even small improvements in throughput may impact cost per analysis. Factors that affect overall data collection speed and figures of merit such as detection limits, precision, accuracy, and dynamic range were studied for an ICP-OES system that incorporates an echelle polychromator with a segmented-array charge-coupled detector (SCD). These factors included sampling time, interference correction methods, and sample introduction parameters. By understanding the effects of these factors, it was possible to maximize the sample throughput for several applications, such as RCRA Method 6010A, while meeting the required data quality objectives.

APPROACHES FOR THE DETERMINATION OF INDIUM IN ENVIRONMENTAL AND INDUSTRIAL WASTE SAMPLES USING INDUCTIVELY COUPLED PLASMA ATOMIC EMISSION SPECTROSCOPY.

Indium is a trace element of importance relevant to zinc smelting and refining, and is potentially useful as a definitive indicator of environmental contamination originating from these sources. While many techniques are feasible for determining indium, most are unsuitable for the direct determination of In at native levels (0.1-0.3 mg/kg) or even at elevated environmental levels (0.5-20 mg/kg). The determination of indium using ICP/AES has been studied. A preconcentration scheme involving extraction of In from HBr solution into diethyl ether, followed by back-extraction into dilute aqueous HCl was first investigated. This technique was tedious and did not completely separate In from Fe, which produced a significant spectral interference. Further work involves an on-line implementation of the HBr extraction/HCl back-extraction chemistry with a hydrophobic membrane, and determination of In in the presence of Fe with multivariate calibration. Sample results will be compared to referee values obtained by ICP/MS.

OPTICAL IMAGING FOR MONITORING ETCH UNIFORMITY IN RADIOFREQUENCY PLASMAS*, Willard A. Hareland and Richard J. Buss, Sandia National Laboratories, Albuquerque, NM

Nonuniform etching is a serious problem in plasma processing of semiconductor materials and has important consequences in the quality and yield of microelectronic components. In many of these manufacturing processes, etching occurs at a higher rate near the periphery of a wafer in a plasma etching reactor, resulting in nonuniform removal of specific materials over the wafer surface. This report describes an in situ optical diagnostic technique for monitoring etch uniformity in radiofrequency plasmas. We measured 2-D images from chlorine atomic emission at 726 nm in a chlorine-helium plasma and determined the 3-D distribution of atomic chlorine by Abel inversion. The experimental results showed that the chlorine atomic emission intensity is a maximum near the outer radius of the plasma in a parallel-plane plasma etching reactor and decreases toward the center. Likewise, the actual etch rate, as determined by profilometry on the processed wafer, was approximately 20% greater near the edge of the wafer than at its center. There is a direct correlation between the atomic chlorine emission intensity and the etch rate of polysilicon over the wafer surface. Based on these analyses, 3-D imaging would be a useful diagnostic technique for in situ monitoring of etch uniformity on wafers.

* This work performed at Sandia National Laboratories, supported by the U.S. Department of Energy under Contract Number DE-AC04-76DP00789.
PLASMA OPTICAL EMISSION MASS SPECTROMETRY—A NEW COMBINATION TO ENHANCE ELEMENTAL ANALYSIS. JOHN E. SCHMELZEL, R.W. FOSTER, AND J.J. SOTERA Thermo Jarrell Ash Corporation, 8E Forge Parkway, Franklin, MA 02038

Thermo Jarrell Ash has designed an instrument incorporating both an optical emission detector and a quadrupole mass detector. This instrument, POEMS (Plasma Optical Emission Mass Spectrometer), uses the unique Charge Injection Device (CID) emission detector to pre-screen the sample and then program the spectrometer to divide the work between detectors (diluting the sample if necessary prior to quadrupole introduction). This paper will present the unique design requirements for the dual detector instrument and the analytical benefits.

DESIGN AND PERFORMANCE OF AN ICP ARRAY DETECTOR SPECTROMETER
Danton D. Nygaard, Frank Bulman, and Manny Almeida, Baird Corporation, 125 Middlesex Turnpike, Bedford, MA 01730, (617) 276-6162.

A new ICP emission spectrometer—utilizing a mega-pixel, two dimensional, solid state array detector—is described and its performance is evaluated. With more than one million individual detector elements, the array captures a high resolution electronic photograph of the complete UV-visible emission spectrum. This allows the spectrometer to function like a computer programmable polychromator, providing all the benefits of both simultaneous and sequential spectrometers with none of their limitations. All elements in the periodic table that emit UV-visible light in an ICP discharge can be detected and quantified at any combination of wavelengths.

Among the performance criteria to be reported are: useful wavelength range, resolution across the full wavelength range, representative detection limits for both hard and soft emission lines, calibration linearity range, short term precision, long term stability of both analyte emission intensity and wavelength registration, stray light, spectral interferences, and effect of easily ionizable elements. Analytical performance will be evaluated using both end-on and conventional side-on observation of the plasma discharge. Finally, applicability of the spectrometer to environmental analysis will be evaluated and demonstrated, concentrating on the performance requirements of the EPA’s Contract Laboratory Program.

GPC-VISCOMETRY CHARACTERIZATION OF POLYMERS IN THE ULTRA-HIGH AND ULTRA-LOW MOLECULAR WEIGHT RANGE. Tuan Q. Nguyen, H.H. Kausch, Polymer Laboratory, Swiss Federal Institute of Technology, MX-D, CH-1015 Lausanne

Gel Permeation Chromatography (GPC) with on-line viscometric detection has been described 2 decades ago. Following the recent introduction of reliable commercial instruments, this mode of detection has found widespread acceptance for its ease of use in comparison to the other types of MW-sensitive detectors based on light scattering. Employed in conjunction with a concentration detector (refractive index or UV absorption), on-line viscometry permits to calculate absolute MW averages, intrinsic viscosity distribution and the extent of long chain branching in polymer samples. In spite of the wealth of information available, special cautions should be exercised when using GPC-Viscometry in the extreme MW ranges. For MW larger than a few millions, several factors which are not critical in the normal MW range, like solution viscosity, dependence of elution volume on flow rate, non-newtonian behavior and mechanochemical degradation, can greatly affect the reliability of the results. At the low MW limit, separation of oligomers presents additional difficulties as a result of non-exclusion effects and deviation from the Universal Calibration concept. By adopting a proper methodology specifically tested for each MW range, it is possible to minimize most of these effects and exploit fully the potential of GPC-Viscometry.
PSORALEN PHOTOCHEMISTRY STUDIED BY HPLC. David J. Semin and Kathy L. Rowlen. University of Colorado, Department of Chemistry and Biochemistry, Boulder, CO 80309.

Psoralens are a class of three ring heterocyclic compounds that have been primarily used as biochemical probes for DNA and RNA. Psoralens have two reactive sites which can undergo a [2+2] cycloaddition with olefinic bonds when irradiated with ultraviolet light. Psoralens do not react with aromatics or saturated compounds. Preliminary studies have focused on understanding reactivity rates and photoproducts that occur with olefins and a psoralen derivative (4'-Hydroxymethyl-4,5'-8-Trimethylpsoralen). Differences in reactivity rates between straight chain and cyclic olefins leads to further psoralen selectivity. Thus, this selectivity towards olefins can be taken advantage of to covalently "trap" and then quantify olefins from a complex mixture. By derivatizing psoralen onto a surface (e.g. silica) an olefinic "trap" can be used to separate and quantify olefins from a complex mixture. A further advantage of the "trap" is that it can be regenerated by a photoreversible reaction using shorter wavelength ultraviolet light and therefore the "trap" is regenerated.

ANGLE-RESOLVED PHOTOACOUSTIC SPECTROSCOPY FOR THE STUDY OF MOLECULAR ORIENTATION IN CHROMATOGRAPHIC SYSTEMS. Susan K. Doughty-Moore, Kathy L. Rowlen, Department of Chemistry and Biochemistry, University of Colorado, Boulder, CO 80309

Determining the orientation of molecules at chromatographic surfaces is important in understanding the mechanism of retention in chromatography. Angle-resolved photoacoustic spectroscopy (ARPAS) is being developed as a method to study molecular orientation at these surfaces. ARPAS is based upon the photoacoustic signal generated as the angle between molecular transition dipoles and incident plane polarized light is varied. ARPAS offers the following advantages: the broad applicability of an absorbance technique, sensitivity similar to fluorescence (detection limits of 0.2 monolayer have been achieved), and application to both dielectric and metal surfaces. A simple two-dimensional model to describe the angle-resolved signal has been developed and is currently being tested.

CHROMATOGRAPHIC OPTIMIZATION FOR THE ANALYSIS OF AN EXPANDED LIST OF VOLATILE ORGANIC POLLUTANTS

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Volatile organic analysis (VOA) is one of the most common environmental test procedures for analysis of pollutants in air, water and soil. Current methodology specified in EPA methods involves concentrating the trace volatile organics onto an adsorbent material and then thermally desorbing them onto a chromatographic column. The list of target compounds to be analyzed are similar for air, water and soil matrices and there are indications that additional compounds will be added to the target compound lists in the future. When the target lists of EPA methods TO-14, 524.2, 624, 8240 and 8260 are combined, including various surrogates and internal standards, the list contains over 100 compounds. Resolution of all of these compounds in a single chromatographic analysis can be difficult if not impossible, however, through proper column selection and chromatographic optimization most compounds can be resolved.

This paper will describe a new technique for GC method development using thermodynamic retention indices and computer modeling of the chromatographic process. From the compound retention times using two different chromatographic analyses, it is possible to predict the best oven temperature and flow conditions for the target volatile compounds. This greatly simplifies the task of optimizing the GC method development, especially for complex mixtures. The application of thermodynamic retention indices will be demonstrated for the analysis of an expanded list of volatile organic compounds. Examples will be shown using the 502.2 and 624 stationary phases which are the most commonly used phases for these analyses.
GAS CHROMATOGRAPHIC ANALYSIS OF PETROLEUM HYDROCARBONS (GRO, DRO) FROM LEAKING UNDERGROUND STORAGE TANKS (LUST)

DAVID M. SHELOW AND MICHAEL J. FEENEY
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The analysis of trace petroleum hydrocarbons in soil and water by gas chromatography is commonly used to detect the presence of leaking underground storage tanks (LUST). Each of the states are responsible for specifying an analytical method and detection requirements for total petroleum hydrocarbons (TPH) and the concentrations of benzene, toluene, ethylbenzene and total xylenes (BTEX). Although each of the methods vary, there are general guidelines for selecting the chromatographic conditions, calibrating instrument response and quantifying analysis results.

This paper will describe general procedures for TPH and BTEX analysis for gasoline range organic hydrocarbons (GRO) and diesel range organics (DRO) in soil and water extracts based upon procedures documented by the State of Wisconsin and the American Petroleum Institute. Particular emphasis will be placed upon instrument calibration and evaluating method performance as well as avoiding the most common problems associated with these analyses.

1. Leaking Underground Storage Tank (LUST) Analytical Guidance
Wisconsin Department of Natural Resources
PUBL-SW-130 92 Rev.

2. Method for Determination of Gasoline Range Organics

3. Method for Determination of Diesel Range Organics

APPLICATION OF GAS PHASE CHEMILUMINESCENCE TO THE TRACE ANALYSIS OF NITRITE ION IN WATER. Andrew J. Dunham, John W. Brock, Robert M. Barkley, Robert E. Sievers, Department of Chemistry and Biochemistry and the Cooperative Institute for Research in the Environmental Sciences, University of Colorado, Boulder, Colorado, 80309.

Selective detectors are finding broad application in analytical chemistry due to the inherent sensitivity of these detectors to specific compounds. This paper will describe the use of a nitric oxide (NO) chemiluminescence detector and present the development of a flow injection analysis system for measurement of aqueous nitrite ion that exploits the sensitivity and selectivity of this detector. Trace analysis of nitrite ion is accomplished through the liquid phase conversion of nitrite ion to nitric oxide which is transported to the gas phase through a semi-permeable membrane. The nitrite ion present in a small sample (20 - 40 μL) is selectively converted to NO by aqueous iodide ion in acidic solution. Complex samples can be analyzed with little sample preparation for two reasons. The chemiluminescence based detection is selective for NO and neither sample coloration nor turbidity interfere since detection occurs in the gas phase. This method has a detection limit of 20 ppb nitrite ion with a 40 μL injection size and approximately 120 samples per hour can be analyzed. In addition, observations on the use of a semi-permeable membrane for the removal of NO from an aqueous stream will be presented.

https://digitalcommons.du.edu/rockychem/vol35/iss1/1
A NEW AQUEOUS-PHASE SULFUR-SELECTIVE DETECTOR. Thomas B. Ryerson, Andrew J. Dunham, John W. Brock, Robert M. Barkley, and Robert E. Sievers. Department of Chemistry and Biochemistry and CIRES, University of Colorado, Boulder, CO 80309; (303) 492–1151.

Sensitive and selective detection of sulfur compounds is possible by conversion of these compounds to sulfur monoxide (1), which then can be reacted with ozone in the gas phase (2) to yield a chemiluminescent species (3):

\[
\begin{align*}
\text{(1)} & \quad \text{S-compound} \xrightarrow{\text{Conversion}} \text{SO + products} \\
\text{(2)} & \quad \text{SO}_{(g)} + \text{O}_3 \xrightarrow{\text{Reaction}} \text{SO}_2^* + \text{O}_2 \\
\text{(3)} & \quad \text{SO}_2^* \xrightarrow{\text{Chemiluminescence}} \text{SO}_2 + \text{hv}
\end{align*}
\]

Past application of this process to chromatographic detection has used a flame to effect conversion (Step 1 above), limiting its practical use to volatiles analysis and gas chromatography. We have developed a system in which conversion of S-compounds takes place in liquid aqueous phase, expanding the utility of sulfur chemiluminescence detection to nonvolatile sulfur compound analysis and ion chromatography. This system does not require a flame. The gaseous products of the conversion, including any SO formed, are passed through a semipermeable membrane to separate them from the liquid stream. Subsequent oxidation with ozone produces chemiluminescence according to reactions (2) and (3) above. The process requires no derivatization or labeling, no reagent other than water, and is highly selective for many sulfur-containing compounds. Using this process we have been able to detect S-containing pesticides, proteins, and both organic and inorganic sulfur compounds.


One of the major site remediation programs underway within the Department of Defense involves the treatment of soils contaminated with explosives. Initial investigations using a static pile arrangement indicated that soil composting is capable of reducing trinitrotoluene (TNT) concentrations in soil from 12,000 ppm to <10 ppm in 160 days. In early studies accurate evaluation of the intermediate composting stage was hampered by the poor precision associated with replicate sample analysis. In an attempt to overcome this problem a new homogenization process was developed which macerates the air dried compost mixture using a No. 4 Wiley mill followed by sample splitting using a traditional Jones-type riffle splitter. This new procedure reduces analytical variance associated with replicate analysis from over 200% to 3%. Precision results for inorganic elements and TNT analyses using this new procedure are reported. Examples of TNT degradation using the static pile study are also presented.
BENEFITS OF COMPOSTING FOR AGRICULTURAL PRODUCERS, Cal Kuska, and Fran Kuska, Kuska/Associates, 8547 E. Arapahoe Road, Suite J-221, Greenwood Village, Colorado 80112.

Waste management practices in the agricultural sector have been poorly addressed by the institutions providing technical support to farmers and ranchers. The programs continue to promote storage and disposal rather than reduction, stabilization, and utilization of a valuable organic-based stream which contributes to serious non-point source of pollution and other nuisances. While humus levels decline and erosion becomes more serious, there is still endorsement of antiquated management procedures. There is a failure to encourage and regulate environmentally and economically feasible measures such as composting. Composting, which is practiced by only a few progressive operators, is not actively promoted in curriculums of students or in extension programs. The benefits of composting include: year-around management, odor prevention, elimination of flies, volume reduction, stable storage, leachate generation, weed seed destruction, reduced water use, metals binding, expanded root structure, sustainability and more.

THEORY AND DESIGN CONSIDERATIONS FOR INDUSTRIAL WASTE COMPOSTING
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George S. Nesperke, Environmental Coordinator for Utilities, Coors Brewing Company, Golden, CO 80401.

The use of composting systems to biodegrade organic industrial and hazardous waste is on the rise. The theory and design for composting of municipal waste are well developed, but are not well understood for industrial applications. Composting goals for these two types of waste sources are significantly different. Municipal waste composting focuses on pathogen reduction, biosolids reduction and moisture reduction. In contrast, biodegradation of hydrophobic organics is the goal in composting industrial waste. The phase of the industrial waste is also different (e.g., petroleum residue or organics sorbed to soil). Current design practices for industrial waste composting are based on municipal composting practices due to lack of better information. The fundamental differences between the two types of waste will necessarily affect the design considerations. Thus, a delineation of theory and design considerations for industrial waste composting is important for optimal design.


Soil organic matter (humus) is a major factor in controlling the physical and chemical properties of soils. Properties such as buffering capacity, metal binding capacity, sorption capacity for hydrophobic organic compounds, stability of aggregates of soil particles, and water-holding capacity are a function, to a large extent, of the amount of humus present in a soil. Humus content is also important in maintaining soil fertility. Intensive agricultural methods tend to deplete soils of humus. This depletion leads to increased erosion, loss of macro- and micro-nutrients, and a general decrease in soil fertility, which is normally rectified by application of large amounts of chemical fertilizers. Studies have shown that the addition of compost, sewage sludge, or manure to soils can reduce erosional losses, increase nutrient concentrations, and increase fertility by restoring soil humus. Organic acids leached from compost by water will form coatings on mineral surfaces that are similar to the natural coatings on soil mineral particles. It is proposed that these humus coatings are bilayer membranes. The exterior surfaces of the these membranes are composed mainly of carboxylic acid groups that will interact with ionic species. The interiors of the membranes are composed of nonpolar functional groups into which hydrophobic compounds will partition.
23 THE EVOLUTION OF LAND APPLICATION AND COMPOSTING OF BIOSOLIDS AT THE METRO WASTEWATER RECLAMATION DISTRICT, William J. Martin, Metro Wastewater Reclamation District, 6450 York Street, Denver, Colorado 80229

Since the Metro Wastewater Reclamation District’s facilities went on-line in the fall of 1966, the sludge management program has been driven by social and political issues as well as cost and changes in technology. From 1966-1970, the District’s sludge was processed by dissolved air flotation, vacuum filtration, and flash drying/incineration. Equipment failures severely limited the District’s ability to process the sludge being produced and severe fuel shortages were also experienced. In the late 60s and early 70s the state developed and implemented restrictive new standards for air emissions. In 1969, the "temporary" disposal of sludge on dedicated land began, continuing until June 1986. During that time, the District examined many management alternatives which included Solar Drying/Agricultural Reuse and Dual Utilization consisting of two components: composting dewatered digested sludge and application of dewatered, digested sludge on agricultural land. In the early 80s it was determined that Dual Utilization was the most viable sludge management alternative for the District and Dual Utilization continues today. Currently stringent new federal, state, county, and local regulations combined with environmental and social pressures are forcing the District to begin reexamining sludge management alternatives.


The efficiency of aerated and nonaerated windrow composting to detoxify explosives-contaminated lagoon sediment was determined. Tests included HPLC analysis of explosives and TNT metabolites in the composts and their EPA Synthetic Precipitation Leaching Test leachates, the toxicity of the leachates to Ceriodaphnia dubia, and the bacterial mutagenicity of acetanilide extracts of the composts. Both windrows were highly effective in explosives biotransformation and detoxification, although the nonaerated compost was slightly more efficient. TNT, RDX, and HMX concentrations in the nonaerated compost decreased by 99.9, >99.7, and 98.5% (respectively), and increased by >99.6, 97.7, and 52.5% (respectively) in the leachates, with most of the biotransformation occurring in the first 15 days. Monoamino nitrotoluene and diaminonitrotoluene metabolites of TNT were transient. Also, at least one azoxydimer (2,2',6,6'-tetrans-tetranitro-4,4'-azoxytoluene) was observed at low concentrations (ca. 0.1 - 0.25 mg/L) in the leachates of the days 1 and 5 composts. The toxicity of the nonaerated compost leachates to Ceriodaphnia dubia decreased by 92 and 87% (survival and reproduction endpoints, respectively), and bacterial mutagenicity decreased by 99.6 and 99.3% (strains TA-98 and TA-100, respectively) without S-9 metabolic activation) over the 4-day composting period, although most of the detoxification was complete by day 15. The fate of the biotransformed explosives is the subject of current investigations.

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25 CONDUCTING POLYMER MODIFIED ELECTRODES FOR THE DETECTION OF TRACE ORGANICS IN AQUEOUS SYSTEMS. Susan M. Hendrickson, Michael Krejcik, C. Michael Elliott, Department of Chemistry, Colorado State University, Fort Collins, CO 80523.

The application of conducting polymers for sensing and partitioning in gas systems as well as in liquid systems has been noted by a number of research groups. Our group has focused on the ability of poly(N-methylpyrrole) coated electrodes to sense and partition neutral organics from aqueous systems. Upon exposure to an aqueous solution containing an organic contaminant, the redox potentials of poly(N-methylpyrrole) shift. As a result of this shift, at fixed potential the doping level of the polymer is different in the presence and absence of the organic contaminant. We are developing this phenomenon for use in an amperometric sensor in a flowing system. Preliminary work indicates that this type of sensor will exhibit a large dynamic range in addition to low detection limits for some small organics. Optimization of this system and its detection limits are under current investigation.
ELECTROCHEMISTRY AND LC APPLICATIONS OF NICKEL ALLOY ELECTRODES.
Frank Luo and Ted Kuwana, Department of Chemistry and the Center for Bioanalytical Research, The University of Kansas, Lawrence, Kansas 66045

For several years, our laboratory has been interested in developing a highly sensitive, reproducible and stable electrode for use as a constant-potential amperometric detector for HPLC of carbohydrates and biogenic amines. Although Cu and Ni electrodes exhibit desirable catalytic properties for the oxidation of carbohydrates in alkaline solutions, the sensitivity is time-dependent with these electrodes; the response decreases with time. More recently we found that Ni and Cu based alloys exhibit enhanced stability while retaining the catalytic properties of the base metal. To better understand the mechanistic reasons that determine the sensitivity and longevity of response, a comparative electrochemical study of these alloys was undertaken. Of particular interest was the time dependent oxidative and reductive cyclic voltammetric waves of the surface oxides, which form in the alkaline media. The extent of the catalysis and stability of response in HPLC applications will be discussed in terms of the nature of surface oxides and how they may differ among the alloys.

ASYMMETRIC CARBONATE ION-SELECTIVE CELLULOSE ACETATE MEMBRANE ELECTRODES WITH DECREASED SALICYLATE INTERFERENCE, Geun Sig Cha, Kang Shin Lee, Jae Ho Shin, and Min Jong Cha, Department of Chemistry, Kwangwoon University, 447-1 Wolgye-Dong, Nowon-Ku, Seoul 139-701, Korea, (02) 910-5244

The asymmetric carbonate ion-selective cellulose triacetate membrane electrodes are used to reduce salicylate interference for total CO₂ measurements in physiological samples. These membranes are formed by first casting a thin layer of cellulose triacetate without carrier, hydrolyzing one side of this film with base, and subsequently, casting a second layer of cellulose triacetate containing the membrane active components (i.e., trifluoracetyll-p-butylbenzene as a neutral ionophore). The resulting asymmetric carbonate-selective membranes function equivalently, in terms of the carbonate response, to conventional PVC-based membranes. However, asymmetric membranes exhibited much slower response towards large lipophilic anions such as perchlorate or salicylate compared to PVC-based membranes, while both membranes showed similar response characteristics towards smaller hydrophilic anions such as carbonate. The asymmetric carbonate ion-selective membranes can be used to enhance the selectivity for carbonate ion over other large anions by employing flow-injection arrangements. For preliminary applications, the asymmetric carbonate-ion selective membranes were utilized to determine total CO₂ contents in flowing solutions containing salicylate interferences. It will be shown that the asymmetric membranes are substantially less subject to salicylate interferences compared to the conventional PVC-based membranes. We gratefully acknowledge the Korea Science and Engineering Foundation and E. I. du Pont de Nemours & Company for supporting this work.

ELECTROOSMOSIS DRIVEN FIA: CONDUCTIVITY OF SURFACE AND POTABLE WATER, Calvin O. Huber, Liang Tang, Dept of Chem. and Lab. for Surface Studies, University of Wisconsin-Milwaukee, Milwaukee, WI 53201

An applied field of 100-200 volts per cm is used to inject and to propel solution into a 50-100 micrometer i.d. by 4-10 cm uncoated fused silica capillary tube. A break in the tube provides for measurement of iR voltage drop over one of the two segments. Relative lengths of the two tube segments regulate the trade-off between sample conductivity range and absolute precision of the method. Data on lower limits of conductivity differences, precision, conductivity range, and sampling speed were obtained.
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ELECTROCHEMICAL STUDIES OF DERIVATES OF POLYPYRROLE/POLYSTYRENE-SULFONATE COMPOSITE FILMS. M.Krejcik and C.M.Elliott. Department of Chemistry, Colorado State University, Fort Collins, CO 80523

When pyrrole or its derivatives with free 2- and 5- position are oxidized from solutions containing polyanionic electrolytes such as polystyrenesulfonate or when it is oxidized at an electrode coated with a film of an anionic polymer, molecular composite films are formed which contain both polypyrrole chains and polyelectrolyte. We have studied such films prepared by electrochemical oxidation at constant current. New composite films of N-methylpyrrole, 3,4-diphenylpyrrole, 1-methyl-3,4-diphenylpyrrole, 3,4-dimethylpyrrole and 1,3,4-trimethylpyrrole have been examined. Electrochemical behavior of these films was studied in aprotic solvents and in water. The influence of low concentration of some small organic molecule (e.g., acetone, dichloromethane, acetic acid, benzene) on the electrochemical behavior of these various composite films in water will also be discussed.

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Organic conducting polymers such as poly(pyrrole) have been intensely studied as light-weight alternatives to conventional metals in applications such as batteries and electrochromic displays. In recent years, interest in these materials has broadened to applications involving their chemical and morphological properties. Examples include poly(aniline) and poly(pyrrole) gas separation membranes, and poly(pyrrole) vapor sensors.

We are exploiting conducting polymer films for use as both sensors and separators for trace halocarbons in aqueous systems. We have shown previously that the oxidation state and dopant ion of conducting polymer membranes can have a significant effect on the rates of transport of neutral organic molecules across the membrane. We foresee applications of conducting polymers in economically efficient liquid-liquid separations. The electrochemical quartz crystal microbalance is being used to characterize the sorption processes (equilibrium and kinetic) occurring in these systems. In addition, applications of conducting polymers as amperometric sensors for small halocarbons in water will be discussed.

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FABRICATION OF RANDOM ARRAYS OF NANOMETER SIZE ULTRAMICROELECTRODES. Vinod P. Menon, Anthony C.Pitrat, Charles R. Martin, Department of Chemistry, Colorado State University, Fort Collins CO 80523

We describe a simple and elegant electroless deposition procedure for the fabrication of ultramicroelectrode ensembles (UME) having element radii as small as 15nm. To our knowledge, these are the smallest radii UME's ever reported. UME's offer a large number of advantages over both macroelectrodes as well as single microelectrodes. Our data indicate that we have been able to achieve these advantages. Some preliminary electrochemical data for these UME's will be presented.
NOVEL TEMPLATE METHOD FOR ENZYME MICROENCAPSULATION

Ranjani V. Parthasarathy, Charles R. Martin, Department of Chemistry, Colorado State University, Fort Collins CO 80523

We describe a general method for encapsulating enzymes in conductive polymer microcapsules. To our knowledge, this is the first ever reported use of conductive polymers as encapsulation devices. These capsules are typically less than a micron in diameter and are around 10 μm in length. We have used spectroscopy to show that the encapsulated enzyme retains its activity. Results for a glucose oxidase encapsulated enzymatic system will be presented.

SURFACE MEASUREMENTS AND MONTE CARLO SIMULATION OF UREA ELECTROSORPTION ON Pt(100) ELECTRODE. M. Gamboa, P. Mrozek, C. Rhee, A. Wieckowski Department of Chemistry, University of Illinois at Urbana-Champaign, 1209 West California Street, Urbana, Illinois 61801, P.A. Rüchvold Department of Physics, Center for Material Research and Technology and Supercomputer Computations Research Institute, Florida State University, Tallahassee, Florida 32306.

We report radiochemical, electrochemical and ultra-high vacuum spectroscopy results on urea adsorption on the Pt(100) electrode, and present voltammetric evidence that urea undergoes a first-order (discontinuous) phase-transition with hydrogen adsorbed on the electrode surface. LEED data give evidence for formation of an ordered c(2x4) adsorbed urea phase. The radiochemical and quantitative Auger electron spectroscopy data show packing density corresponding to one urea molecule per four platinum atoms. We also report on Monte Carlo simulations of a new lattice-gas model for urea adsorption and demonstrate that the simulation results agree well with those of our experiments. These include an ordered c(2x4) adsorbed urea phase and sharply peaked voltammograms. We interpret our observations as associated with a phase transition between the urea phase for potentials on the positive side of the peak and a monolayer hydrogen (1x1) phase on the negative end.

METAL NANOPARTICLE /ALUMINUM OXIDE PREPARATION AND OPTICAL CHARACTERIZATION G. Louis Hornykak, Phil Martellaro, Jon A. Stockert, Colby A. Foss, Jr., Charles R. Martin. Department of Chemistry, Colorado State University, Fort Collins, CO 80523.

Electrodeposition of gold and other metals into the pores, less than 20nm in diameter, of an anodically created aluminum oxide matrix results in metal/insulator composite films that optically approach the ideal quasi-static limit of effective medium type theories (EMT). We compare the experimental spectra of these oxide/nanometal composites with those derived from larger particle (60-120nm pore diameter) films discussed earlier. We also discuss the particle shape, particle material and wavelength dependence of Maxwell Garnett-EMT predictions and the spectral effects as the metal particle dielectric properties diverge from bulk values at very small dimensions.
DETECTION OF HOT ELECTRONS IN A p-InP PHOTOCHEMICAL CELL.
Robert Torres, and Carl A. Koval, Department of Chemistry and Biochemistry,
Campus Box 215, University of Colorado, Boulder, CO 80309.

Detection of Products generated from hot electron reactions in a pho
tochemical cell is the focus of this research. Hot Carrier processes were
investigated by utilizing a rotating p-InP disk and a platinum ring electrode. The
detection procedure for quantifying the hot carriers implemented a halogenated
benzene derivative to accept the hot electrons. Upon reduction the organohalide
compound eliminated the halide and the halide anion was subsequently oxidized
quantitatively at the platinum ring. Results involving dependence of band bending
(applied potential), solution redox potential, light intensity, and doping density
upon product distribution will be presented.

ETCHING OF SnS₂ PHOTOANOODES TO INCREASE THE DYE
SENSITIZATION EFFICIENCY. Xiumei Dou, and Bruce A. Parkinson,
Department of Chemistry, Colorado State University, Fort Collins, Colorado
80523.

Dye sensitization of semiconductor electrodes has recently been used as a
potential method for solar energy conversion. The two-dimensional structure
semiconductors have been shown to be superior substrates for studying the fundamentals
of dye sensitization. However, the quantum efficiency of electrons per incident photon is
too low to be used practically even though the quantum yield of electrons per absorbed
photon is near unity. This is probably due to the low light harvesting efficiency by the few
adsorbed dye molecules. In this work, a photoelectrochemically etched two-dimensional
semiconductor electrode, SnS₂, is used to increase the surface area and binding ability to
the dye molecules. The quantum efficiency of electrons per incident photon is enhanced
at least an order of magnitude with respect to unetched electrodes. The sensitization
characteristics of the etched surface are discussed as compared to the smooth surface.

FORMATION OF DIMERIZED PI-COMPLEXES IN THE
ONE-ELECTRON REDUCED FORM OF VIOLGENS IN
SELF-ASSEMBLED MONOLAYERS. Xiaoyan Tang, Thomas Schneider
and Daniel A. Buttry, Department of Chemistry, University of Wyoming,
Laramie, WY 82071-3838.

Thiol derivatives of viologens are shown to self-assemble at Ag and Au electrodes to
give highly organized monolayers. Organization of these systems is revealed by virtue of the
formation of unique pi-complex dimers for the one-electron reduced forms of the viologens
within these monolayers. The presence of these dimers is shown to give extremely sharp
voltammetric waves, and can be unambiguously observed in the surface enhanced Raman
spectra of the self-assembled monolayer.
CHARACTERIZATION OF HETERONUCLEAR COMPLEXES CONTAINING THREE BRIDGING BIS-BIPYRIDYL ALKANE LIGANDS. Suzanne Ferrere, Daniel Derr, and C. Michael Elliott, Department of Chemistry, Colorado State University, Fort Collins, CO 80523

The electrochemistry, structural properties, and electron transfer behavior of several unique heteronuclear complexes will be discussed. Each contains a ruthenium(II) atom bridged, via three bis-bipyridyl alkane (or related) ligands, to an iron(II) atom. The structural rigidity of the complexes due to the triple bridge fixes the ruthenium-iron distance. We have prepared these complexes utilizing several different types of bridging moieties including \(-\text{CH}_2\text{-CH}_2\text{-}\), \(-\text{CH}_2\text{-CH}_2\text{-CH}_2\text{-}\), and \(\text{CH}_2\text{-O-CH}_2\). X-ray crystallography and molecular modelling indicate, however, that for all three of these complexes the metal-metal distance is nearly identical. Thus, we have a system in which the two interacting centers are separated by the same distance, but with three different types of connectivity. Therefore, of particular interest to us is distinguishing "through-space" interactions from "through-bond" interactions in evaluating their electrochemical and electron transfer behavior.

OPERATIONAL ADVANTAGES AND TRADEOFFS OF COMPUTER-CONTROLLED POTENTIOSTATS. Dr. Ted Kuwana, W. Gamini Gunaratna, Dr. Jeffrey Huntington, Dr. Michael Weber, Cypress Systems, Inc., P.O. Box 3931, Lawrence, Kansas, 66046.

Several computer-controlled potentiostats are now being offered commercially. In contrast to the analog instruments, computerization provides the user with the ability to implement one of several techniques readily by selection from a pull-down menu. Thus, it is a matter of quickly switch from cyclic voltammetry to chronoamperometry or square-wave voltammetry. Also, computerization with user-friendly graphics interface allows data to be acquired, displayed, and stored in real-time. Most manufacturers specify the response time based on the potentiostat's rise time. However, the data conversion and transfer rates may limit what can actually be observed in terms of time resolution. Thus, there are always tradeoffs in the design of the hardware and software for such computerized potentiostats. For example, software including Windows may be attractive, but the user should be aware of the program overhead that may restrict speed and real-time operations. The advantages and tradeoffs (and pitfalls) of computerization will be presented in terms of speed, sensitivity, current and power range, noise and user convenience.

EVALUATION OF APPARENT FORMAL POTENTIALS OF REDOX PROBES EXCHANGED IN IONOMERS ON ELECTRODE SURFACES. Harmon M. Tunison, Jayson Moy, Jody Redepenning; Department of Chemistry, University of Nebraska, Lincoln, Nebraska 68588-0304.

Thermodynamic relationships necessary for interpreting the apparent formal potential of redox probes exchanged into ionomers on electrodes surfaces will be discussed. Experimental results will be compared with a model in which the oxidized and reduced forms of the redox couple are free to partition between the solution and polymer phases. Apparent formal potentials will be related to the formal potential of the redox probe in solution, to the equilibrium constants for exchanging the oxidized and reduced forms of the redox probes into the polymer and to the electrolyte activity in solution. Apparent reaction entropies determined by measuring the temperature dependence of the apparent formal potential will also be discussed. The apparent reaction entropy can be described in terms of the reaction entropy of the redox probe in solution, to the entropies of exchange of the redox probe in its oxidized and reduced forms, and to the electrolyte activity in solution.
Differences in Self-Assembly of Thiol and Disulfide Derivatives of Viologens. Thomas Schneider and Daniel A. Buttry, Department of Chemistry, University of Wyoming, Laramie, WY 82071-3838

Several derivatives of viologens bearing either thiol or disulfide groups capable of self-assembly at Au or Ag electrodes are described. Both the synthetic routes to and the electrochemistry of these compounds will be discussed. The behavior of these two types of derivatives is quite different, with the thiol derivatives self-assembling to give higher surface coverages and better organized films. A unique interaction between reduced forms of the viologens in the thiol monolayers is briefly described. These results indicate that monolayers formed from disulfides and thiols are not the same, at least for cases in which the pendent groups are bulky.

Measurement of Activity Coefficients in Acetonitrile Using the Isopiestic Technique. Sandra Burnham, Eric Mechalke, Benjamin Miller, and Jody Redepenning; Department of Chemistry, University of Nebraska, Lincoln, NE 68588-0304

Measurement of standard potentials for electroactive species in nonaqueous solvent is hindered by the fact that very little is known about activity coefficients in these solvents. We have measured activity coefficients for KPF₆ and for NaClO₄ in acetonitrile using the isopiestic technique, a technique which relies on the equilibration of solvent between two different electrolyte solutions. By using the molalities of the electrolyte solutions at a series of concentrations, the activity coefficients can be calculated from the Gibbs-Duhem equation. These activity coefficients will be used to explain shifts in the apparent formal potential of redox probes on electrode surfaces.

Ultramicroelectrode Arrays, Characterization of High and Low Density Ensembles. C. Anthony Pitrat, P. Vinod Menon, Charles R. Martin. Department of Chemistry, Colorado State University, Fort Collins CO 80523.

Ultramicroelectrode ensembles (UME's) are random arrays of microelectrodes. An advantage the UME has over single microelectrodes is that the signal is larger. Recently we have developed a method for quickly and easily making low density UME's by depositing gold into the pores of a microporous polymer membrane. The pore densities are on the order of $1 \times 10^4$ to $6 \times 10^6$ pores per square centimeter. The pore diameters can be varied between 3µm and 150Å. This allows us to compare our random ensembles with theoretical predictions about detection limits and kinetics.
ANALYSIS OF PCBs IN SOIL BY CAPILLARY GAS CHROMATOGRAPHY USING A GC EQUIPPED WITH A DIODE ARRAY ATOMIC EMISSION DETECTOR. Ruben Abru. Colorado Department of Health, 4210 E. 11th Avenue, Denver, CO 80220.

PCBs in water have been of public concern since it was learned of their carcinogenic nature. Gas chromatography coupled with an ECD has been the system of choice to analyze PCBs. Analysis of PCBs in a water matrix presents minimal problems for extraction, and a small amount of interfering substances are essentially recovered. The analysis is complicated when more complex matrices are analyzed such as soil, sludges or oils. In this paper I show the advantages of using a gas chromatograph equipped with an AED (atomic emission detector) to identify and quantify the presence of PCBs in spiked soil. The extraction by itself is a simple technique obtained from an EPA-NIST publication and it proved to give recoveries of 50-80%. The AED, a diode array spectrophotometer, can be set to a particular wavelength of emission for certain atoms, as in this case, chlorine. Interfering substances, devoided of Cl atoms, are not detected, giving a clean chromatographic trace, and a recognizable PCB pattern. The 479.5 nm band of emission for Cl was selected and the soil extracts were chromatographed. All qualitative and quantitative analysis were based on the Cl response. The analysis showed excellent linearity and a minimum instrument detection of 1 mg/Kg which conforms with current EPA guidelines. The method was able to identify and quanitate mixtures composed of PCBs.

IDENTIFICATION OF IODINATED DISINFECTION BY-PRODUCTS BY GC/ECD AND GC/MS. Andrew J. Dunham, Charles N. Hurst, JoAnn Silverstein, Robert M. Barkley, Robert E. Sievers, Department of Chemistry and Biochemistry and the Cooperative Institute for Research in the Environmental Sciences, University of Colorado, Boulder, Colorado, 80309.

Effective disinfection of recycled water on extended manned space missions plays a pivotal role in the success of any such endeavor. Since NASA has chosen iodination as the primary source of recycled water disinfection, the effects of iodination on recycled water quality need to be investigated. This project has focused on the generation and identification of iodinated disinfection by-products (IDPs) via iodination in a water recycling system. Aqueous solutions of organic compounds detected in space shuttle condensate and waste water (such as acetic acid and phenol) were prepared and iodinated. The identities of various IDPs were determined via GC/ECD or GC/MS analysis of extracts of these iodinated organic solutions. The IDP's identified include iodoform and diiodomethane along with several other IDPs where analogous chlorinated compounds were not observed in chlorine disinfected solutions.


Evaluating the quality of water in the United States is crucial to making sound decisions about water use. To assess water quality nationally, it is important that water-quality measurements be consistent. Robust analytical methodologies are required that perform adequately for diverse sample matrices. The U.S. Geological Survey, which is engaged in the congressionally mandated National Water Quality Assessment (NAWQA), has developed an improved method for the analysis of hydrophobic, semivolatile organic, and organochlorine compounds associated with sediment. Substantially more analytes are determined in this method than contained in the U.S. Environmental Protection Agency (USEPA) priority pollutant list; organochlorine insecticides are also determined. The method uses soxhlet extraction, automated high-performance gel-permeation chromatography, and combined alumina-silica chromatography to isolate both semivolatile organic and organochlorine compounds from a single 25-gram (dry-weight) sample. Advantages of this new method include an expanded compound list (90 compounds instead of 60 compounds in the USEPA priority pollutant list), fewer fractions to be analyzed for organochlorine compounds, and lower detection limits than the equivalent USEPA methods for semivolatile and organochlorine compounds. The performance of this new method for the quantitation of polycyclic aromatic hydrocarbons, azarenes, organochlorine insecticides, substituted phenols, and other classes of organic compounds is described.

Suspended matter, as silt and colloidal-size particles, is an important mode of transport for toxic hydrophobic organic compounds. Silt (<63um) was isolated from sixteen sites on the Mississippi River and its major tributaries, from Minneapolis, Minn. to below New Orleans, La., by centrifugation, and colloids were then isolated by ultrafiltration. The colloids comprised about 10% by weight of the suspended matter for most of the river in summer 1991 (low flow). In the fall 1991 (low flow), the proportion of colloids increased to 20% at most sites and 35% at two upper river sites. During spring 1992 (high flow), the colloid portion remained high on the upper river, but decreased to 5% on the lower river. The organic carbon associated with the silt was significantly lower (2 to 5%) than the colloids (7 to 30%). The proportion of organic carbon transport during summer on the colloids averaged 35% of the total suspended matter at most sites and exceeded 50% at two sites. Colloidal transport of pollutants may be as important as silt transport in the Mississippi River.


Advances in miniaturization, automation and ruggedization of chromatographic and spectroscopic instruments are providing for a new generation of hyphenated field portable analytical devices. Recent hyphenated field analytical techniques range from mobile gas chromatography/tandem mass spectrometry (GC/MS²), or man-portable gas chromatography/mass spectrometry (GC/MS) to hand portable gas chromatography/ion mobility spectrometry (GC/IMS). The multidimensional advantage of hyphenated analytical techniques is well recognized in the conventional laboratory environment and, in the opinion of the author, may be even more important in the field. A complex mixture requiring high resolution GC techniques for detection of individual compounds in the laboratory may, in many cases, be analyzed much faster in the field by means of a hyphenated technique combining low to medium resolution GC and MS techniques. Before hyphenated methods can claim their place in the arsenal of field portable analytical methods, however, much work remains to be done on the development of suitable inlet modules for air, water and soil analysis as well as on the development of machine/user interfaces.


Semiconductors have been studied for a variety of processes related to solar energy utilization including organics decomposition and metal deposition in aqueous solutions. Titanium dioxide in a slurry reactor was used to remove and concentrate Cu(II) ions in aqueous solutions through a cyclic process of photodeposition, separation and oxidation. This cyclical process was used to demonstrate a volume reduction process for an aqueous solution containing copper sulfate and excess sodium formate. The Cu(II) in a synthetic waste stream was concentrated to an organic-free solution having 7% of the initial volume. The remaining waste solution contained only 1% of the initial Cu(II). The remaining formate ion was destroyed using conventional TiO₂ photocatalytic oxidation. Extension of this process was used to treat electroless copper plating bath solutions. The overall process demonstrated the ability to separate copper ions from organics using only light and air.
SEDIMENT-WATER INTERACTIONS IN A DESERT STREAM CONTAMINATED BY MINE WASTES, ARIZONA, USA. Donald D. Runnels, Shepherd Miller, Inc., 1600 Specht Point Drive, Ste. F, Ft. Collins, CO 80525; John Rampe, EG & G Rocky Flats, Golden, CO 80401

Boulder Creek comprises one of the major watercourses in an otherwise arid region of western Arizona. Seepage of metal-rich waters from tailings and from a collapsed adit enter the stream at two distinct points. At seasonal low water, heavy precipitates of Fe, As, Al, Cu, and other metals form almost instantaneously below the points at which the contaminated waters mix with creek water. The loss of metals from the water is clearly mirrored by the gain of metals in the stream sediment. Water in the upstream non-polluted portions of Boulder Creek has a pH as high as 8.5, alkalinity up to 282 mg/L as CaCO₃, and is rich in dissolved oxygen. Two distinct seepages from the mine and mill wastes into the stream can be recognized. One seepage has a pH of 2.4 and total concentrations (in mg/L) up to 8550 TDS, 5240 SO₄, 260 Al, 34 As, 100 Cu, 610 Fe, 52 Mn, and 92 Si. As the seepage waters mix with stream water, heavy precipitation occurs. However, at a distance of approximately 1100 meters downstream, the water is clear, the pH has again risen to 8.4, and most of the metals have precipitated. Such a rapid natural recovery would certainly not be the case for less alkaline streams in a more temperate climate.

THE ALAMOSA RIVER: THEN AND NOW. Mary K. Mueller and Theodore A. Mueller. SLV Analytical Services, Inc.; P.O.Box 863; 411 Ross Avenue; Alamosa, Colorado 81101

The Alamosa River extends from its source waters in the south San Juan Mountains of Colorado and enters the southwest portion of the San Luis Valley where it is used primarily for irrigation. It has historically and recently been subjected to repeated onslaughts of wastewaters from mining activities in the area. Data will be presented for water quality that existed before current mining activities. This will be compared to current water quality data.

CONTAMINATION OF A FORESTED AREA NEAR A PRIMARY ZINC SMELTER WITH EXOTIC METALS. Michael E. Ketterer, Nicole Milam, John R. Simon, Jr., and Albert Ossinger, U.S. Environmental Protection Agency, National Enforcement Investigations Center, Box 25227, Building 53, Denver Federal Center, Denver, Colorado 80225.

Primary smelting of nonferrous ores has long been recognized as a significant source of pollutants such as SO₂, and metals such as copper, arsenic, zinc, lead, and cadmium. These metals are released as vapors or fumes during roasting, sintering, and reduction. A study of the former site of a primary zinc smelter in Palmetto, Pennsylvania has been conducted in order to definitively establish that the defunct primary zinc smelter is a source of environmental Zn, Cd, and Pb in neighboring forests. In this work, numerous low-concentration "exotic" metals have been determined in forest litter and mineral soil. This group of elements consists of Ag, In, Sn, Sb, Te, Au, Hg, Tl, and Bi, which were determined using inductively coupled plasma mass spectrometry. The high degree of covariance found between this group of exotic tracer elements and the chief contaminants of concern, along with the geochemistry of the ores processed at Palmetto clearly implicate the primary zinc smelter as the predominant source of Zn, Cd, and Pb in the forest environment.
CLOSED VESSEL MICROWAVE SAMPLE PREPARATION FOR MERCURY ANALYSIS VIA COLD VAPOR AA AND UV DETECTION TECHNIQUES. W. Gary Engelhart and Sara Littau, CEM Corporation, P.O. Box 200, Matthews, NC 28106-0200 (704) 821-7015

Mercury contamination in the environment has become an increasing concern due to the toxic nature of this element. The volatile nature of elemental mercury and organomercury compounds require precautions be taken to avoid possible losses during sample preparation. Acid digestion of environmental samples inside sealed vessels is an EPA approved method of sample preparation for metals analysis by AA and ICP spectroscopy. This study will describe microwave digestion methodology required for the analysis of mercury via cold vapor AA and UV detection techniques. Analytical results obtained following microwave digestion of standard reference materials and real world samples spiked with organomercury standard will be presented. Microwave sample preparation methods for SRM1575 Pine Needles, USEPA Metals in Fish, USEPA Dried Sludge, Raw Swordfish, effluent municipal wastewater, waste motor oil and mixed solvent fuel will be described.

ALKALOIDS OF FIELD BINDWEED (CONVOLVULUS ARvensis). Fred G. Todd and Frank R. Stermitz, Department of Chemistry, Colorado State University, Fort Collins, Colorado 80523. Anthony P. Knight, Department of Clinical Sciences, Colorado State University, Fort Collins, Colorado 80523.

Seven unrelated horses with similar disease symptoms and originating from a localized area east of the Rocky Flats nuclear facility and near Thornton, Colorado, were admitted to the Colorado State University Veterinary Hospital within a 20 month period. All had a history of progressive weight loss and abdominal pain. All needed to be euthanized and necropsy showed marked intestinal fibrosis. The geographic clustering of the animals within a 10 mile radius suggested an environmental causative factor in the disease. Water analysis from the farms showed the heavy metal concentrations to be in the safe range for livestock and it was suggested that pasture examination for toxic plants should be conducted over several seasons. Inspection of one of the affected farms in early spring 1991 revealed that the main horse pasture was overrun by field bindweed, Convolvulus arvensis L. Bindweed was found to contain the tropane alkaloids tropine, pseudotropine, and tropinone and the pyrrolidine alkaloids cuscohygrine and hygrine. Although similar alkaloids have been found in other Convolvulus species and cuscohygrine was previously reported from C. arvensis roots, this is the first report of tropane alkaloids in C. arvensis, a world-wide problem weed. Pseudotropine, the major alkaloid, is known to affect intestinal contractions and might represent the causative agent for the observed equine toxicosis.

PUMPING METAL IONS AGAINST THEIR CONCENTRATION GRADIENT WITH VISIBLE LIGHT. Thanh Thi-Bang To and Carl A. Koval, University of Colorado, Chemistry Department, Boulder, CO 80309-215. (303) 492-0357.

Pumping of metal ions against their concentration gradient was accomplished using a liquid membrane containing a spiropyran dye. In this system, photochromic reactions were coupled to carrier-mediated transport processes to facilitate transport and to concentrate solutes. The dye, 1',3',3'-trimethyl-spiro-8-nitro(2H-1-benzopyran-2', 2'-indoline), isomerized from a colored to a colorless form under visible radiation. Only the colored form complexed with metal ions. When the interface between the membrane and the receiving solution was irradiated with visible light, decomposition became the dominant process at the interface; while complexation was dominant at the nonirradiated interface between the membrane and the reservoir solution. Partial illumination of the membrane provided a means to concentrate metal ions in the receiving solution. Such systems may find application in concentrating trace heavy metals in waste water.
IDENTIFICATION AND QUANTIFICATION OF POLAR ORGANIC COMPOUNDS IN FLAMMABLE HAZARDOUS WASTES BY GC/FT-IR. Jon Beihoffer, John Reschl, and Jimmy L. Seidel, U.S. Environmental Protection Agency, National Enforcement Investigation Center, Building 53, Box 25227, Denver Federal Center, Denver, Colorado 80225

RCRA characteristic wastes which are flammable (D001) are often analyzed to determine the constituents giving rise to the flammable nature of the waste. Common components of these wastes are polar organic compounds having functional groups which strongly absorb infrared radiation. Because of the volatility and infrared activity of these compounds, GC/FT-IR is an ideal technique for their simultaneous quantification and unambiguous identification. A GC/FT-IR method has therefore been developed which is appropriate for the analysis of D001 wastes containing acetate esters, ketones, and alcohols.

ANALYSIS OF NATIONAL INSTITUTE OF STANDARDS AND TECHNOLOGY (NIST) SOIL STANDARD REFERENCE MATERIALS (SRMs) USING THE EPA 3050 ACID EXTRACTION PROCEDURE. Stephen A. Wilson, and Paul H. Briggs, U.S. Geological Survey, PO Box 25046, MS 973, Denver, Co. 80225

Extraction results are presented for 10 major and trace elements in three NIST soil SRMs using the EPA 3050 acid extraction procedure. The three SRMs collected in the western United States are representative of baseline (SRM 2709), moderately contaminated (SRM 2711) and highly contaminated (SRM 2710) soils. Extraction results vary considerably between the three SRMs especially for As (<20-580 ppm), Cd (<4-41 ppm), Cu (30-3000 ppm), Pb (14-5600 ppm) and Zn (97-6600 ppm). Comparison of extractable and total element concentrations reveal that the extent of extractability ranges from 2% to 100% depending on the element and sample matrix, with only Cd, Co, Cu, and P showing extraction values consistently greater than 90%.

SEQUENTIAL EXTRACTION METHOD TO DIFFERENTIATE TRACE METAL ASSOCIATIONS IN SUSPENDED SEDIMENT AND BED SEDIMENT FROM NATURAL WATERS. Heidi C. Hayes and Howard E. Taylor, U.S. Geological Survey, 3215 Marine Street, Boulder, Colorado 80303.

A sequential extraction scheme is developed for studying trace metal interactions with suspended sediments and bed sediments from natural waters. The procedure operationally differentiates among the inorganic, organic and refractory mineral trace metal associations in the sediment. Inorganically bound metals, those which are loosely-held to sediment surfaces and associated with carbonates, manganese oxides, and amorphous iron oxides, are released using the reducing agent 0.25 M hydroxylamine-hydrochloride/0.25 M hydrochloric acid at 50°C for 40 minutes. To solubilize organically bound metals, an oxidizing solution of 0.15 M potassium persulfate/0.2% (v/v) sulfuric acid at 95°C for 1 hour is employed. The remaining residual material, the refractory mineral fraction, is completely digested using a mixture of hydrofluoric acid and aqua regia heated for a total of 6 minutes in a microwave oven at 630 W. Evaluation of the procedure indicates no apparent redistribution of metal ions during the extraction as well as reasonable reagent selectivity for the extracted components. A mass balance evaluation shows that 95-120% of the total digestion concentration of each metal is recovered in the extraction procedure. In addition, a precision of less than 20% relative standard deviation is generally obtainable for each of the extraction steps.
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ARSENIC IN GROUND WATER OF THE WESTERN UNITED STATES1 Alan H. Welch and Michael S. Lico, U.S. Geological Survey, 333 W. Nye Lane, Carson City, Nevada 89706

Natural occurrences of ground water with moderate (10 to 50 micrograms per liter) to high (greater than 50 micrograms per liter) concentrations of arsenic are common throughout much of the Western United States. High concentrations of arsenic are generally associated with one of four geochemical environments: (1) basin-fill deposits of alluvial-lacustrine origin, particularly in semiarid areas, (2) volcanic deposits, (3) geothermal systems, and (4) uranium and gold-mining areas. These findings are based on an extensive literature review, compilation of unpublished reports and data, and the review of data bases containing more than 7,000 analyses of ground-water samples for arsenic. In the first two environments, arsenic appears to be associated with sediments derived, in part, from volcanic rocks of intermediate to acidic composition. Dissolved arsenic concentrations in water from volcanic aquifers in the same regions, however, may be low (less than 10 milligrams per liter). Solid phases (minerals, amorphous solids, and sedimentary organic matter) that supply the dissolved arsenic have not been identified in most areas. Alluvial and lacustrine sedimentary deposits appear to be an important source of arsenic in volcanic areas (such as Lane County, Oregon) and in areas underlain by basin-fill deposits (such as Carson Desert in Nevada and Tulare Lake basin in California). Mobilization of arsenic in sedimentary aquifers may be, in part, a result of changes in the geochemical environment due to agricultural irrigation. In the deeper subsurface, elevated arsenic concentrations are associated with compaction caused by ground-water withdrawals.

1 This abstract was originally published in Ground Water, v. 26, no. 3, p. 333

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In order to evaluate the impact of a more stringent drinking water arsenic regulation, three recent low level arsenic occurrence studies have been conducted. Three analytical methods that could provide low detection limits (DLs) were used. These included the HG-AA and ICP-MS methods (0.5 μg/L DL) and the STGF-AA method (1.0 μg/L DL). A nationwide survey was conducted in January 1993 representing approx. 150 utilities in the continental U.S. and 36% of the U.S. population. Preliminary information indicates approx. 48% of the utilities surveyed had arsenic levels less than 0.5 μg/L, 47% had values between 0.5 and 4.9 μg/L, and 5% had values greater than 5 μg/L. The nationwide survey suggests higher arsenic levels are located in the western U.S. A Southern Californian survey, completed in October 1992, sampled 450 wells, 94% of which had detectable levels of arsenic above 0.5 μg/L and 63% of which had levels greater than 2 μg/L. The California-wide survey, in progress, will detail arsenic levels in over 750 representative ground and surface water sources.

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EXTENSION OF THE CAPABILITIES OF ICP-MS FOR THE DETERMINATION OF TRACE METALS IN WATERS. Diane Beauchemin, Queen’s University, Department of Chemistry, Kingston, Ontario, Canada K7L 3N6.

Inductively coupled plasma mass spectrometry (ICP-MS) is a rapidly expanding technique for elemental analysis, featuring great detection limits, a wide linear dynamic range and the capability for isotopic analysis. The technique is well suited to the analysis of water since it uses solution nebulization for sample introduction, but it is limited to waters with less than 0.2% dissolved solids. During this presentation, coupling to flow injection techniques and liquid chromatography (LC) will be considered to increase the range of application. The separation of the analytes from the bulk of the matrix can be accomplished on-line with ICP-MS by passing the sample through a column of silica-immobilized 8-hydroxyquinoline which selectively retains the analytes but not the alkaloids and, to some extent, the alkaline earths. The analytes can then be eluted into a salt-free matrix, and simultaneously be preconcentrated if the volume of eluent is smaller than that of the sample. The optimization of this on-line separation/preconcentration approach will be described. Finally, ICP-MS can also be used as a powerful and highly selective detector for LC. As an example, the speciation of metals in pore waters will be discussed.
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THE APPLICATION OF ICP-MS TO ELEMENTAL SPECIATION
Rob Henry, Tom Rettinger, Fisons Instruments
14513 Spotswood Furnace Road, Fredericksburg, Virginia 22407

ICP-MS methods for the determination of major, minor and trace elements in environmental and biological samples have already been developed. The toxicity of regulated elements is also known to be dependant on the form in which the element is present in the environment, whether as a particular oxidation state or bound organically. The implementation of ICP-MS as an extremely sensitive on-line chromatography detector for speciation measurements will be discussed in detail.

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MULTIQUANTUM EPR. James S. Hyde, Biophysics Research Institute, Medical College of Wisconsin, Milwaukee, WI 53226.

Multiquantum EPR (MQEPR) is a member of the family of modulation-based advanced EPR techniques that include rapid passage and saturation transfer spectroscopy. MQEPR will be placed in this historical context. Double resonance multiquantum EPR methodologies include MQEPR-ELDOR, and three ENDOR variants: 1) an irradiating microwave pair of frequencies plus one radio frequency, 2) an irradiating pair of radio frequencies plus one microwave frequency, and 3) irradiating pairs of both microwave and radio frequencies. These multiquantum double resonance techniques will be compared with conventional CW double resonance methods.

Recent advances in MQEPR from this laboratory will be described. As of the date of this abstract submission, these include 1) a strategy for phase locking two fundamental Gunn diode oscillators an audio frequency apart, which requires low phase noise oscillators (with J. Luglio); 2) a flexible loop-gap resonator for ENDOR (with T. Christidis); 3) the use of MQEPR to study conformation of the antibiotic cecropin in lipid bilayers (with H. Mchaourab); and 4) the use of MQEPR to study forbidden transitions in square-planar copper complexes (with S. Pfenninger and H. Koteiche).

Future directions for MQEPR development include multifrequency (S- and Q-band) capability, strategies for detection of slow rotational diffusion, and as a readout for saturation recovery.

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APPLICATION OF SATURATION RECOVERY EPR TO STUDY PROTEIN STRUCTURE. Wojciech Frongisz, Institute of Molecular Biology, Jagiellonian University, 31-120 Krakow, Poland.

Spin labeling of proteins with nitroxides has been successfully used for many years as a method to study protein structure. Recent progress in site specific labeling of proteins and improvements in EPR instrumentation make the method more powerful than ever before. As examples of these studies, Saturation Recovery EPR measurements for three spin-labeled proteins: albumin, hemoglobin, and cytochrome c will be presented. In the first case Heisenberg exchange between spin label and spin probes such as oxygen and chromium oxalate have been used to obtain information about the accessibility of nitroxide attached to albumin. For hemoglobin and cytochrome c, the dipole-dipole interaction between specifically and covalently bound nitroxides and heme iron has been used to measure distances during conformational changes of the proteins.

Recombinant DNA technology has made it possible to effectively introduce an amino acid with a nitroxide side chain at any desired position in a protein sequence. Analysis of the EPR spectra of a set of proteins, where each member of the set differs only by the position of a single nitroxide in the sequence, can give detailed information on the structure of the protein. In principle, the structure at the level of backbone folding can be obtained in membrane proteins, and changes in the structure on a millisecond time scale can be observed. Recent advances in this method and its applications will be reviewed, including a new approach to determination of distances of particular side chains from the bilayer surface in membrane proteins, and detection of fast, light-induced structural transitions in the visual pigment protein rhodopsin.

BIOPHYSICAL STUDIES OF HUMAN PLASMA FIBRONECTIN

Ching San Lai, Biophysics Research Institute, Medical College of Wisconsin, 8701 Watertown Plank Road, Milwaukee, Wisconsin 53226

Human plasma fibronectin is a major protein of blood and tissues that plays a central role in cell adhesion. It consists of two nearly identical 230-250-kDa subunits that are joined by two disulfide bonds near their carboxyl termini. Each subunit contains various binding domains composed of three types of homologous repeats. Despite recent progress in determination of the three-dimensional structures of various repeat fragments, little is known about the three-dimensional structure of this multifunctional complex protein. We have employed several biophysical techniques including electron spin resonance, nuclear magnetic resonance, fluorescence energy transfer, and circular dichroism to study the spatial relationships and dynamic interactions of various structural domains of the fibronectin molecule. Our recent studies showed that each chain of fibronectin retains a hydrophobic core structure, consisting of the amino-terminal, the carboxyl-terminal and the central cell-binding regions. The existence of this large structural core may force the chain to assume a compact conformation. On the basis of our results and other published data, the low-resolution beads model for the solution structure of fibronectin has been constructed. Features of this model that shed some light on the biological functions of fibronectin will be discussed.

SPECTROSCOPIC PROBES OF MOLECULAR DYNAMICS IN MUSCLE CONTRACTION,

David D. Thomas, Department of Biochemistry, University of Minnesota, Minneapolis, MN 55455

We have used EPR and phosphorescence spectroscopy to probe the orientation and rotational dynamics of myosin and actin. Site-directed spectroscopic probes (spin labels or phosphorescent dyes) were used to study these proteins both in solution and in muscle fibers, permitting us to test molecular models for the role of rotational dynamics in the mechanism of force generation. The two spectroscopic probe techniques are quite complementary. EPR provides unequalled orientational resolution, essential for resolving the distinct orientations of myosin and actin expected in various physiological states of muscle. Time-resolved phosphorescence anisotropy resolves rotational rates in the microsecond time range. Coordinated spectropic studies of single crystals and oriented muscle fibers permit interpretation of spectra in terms of the absolute orientations of proteins. Muscle fibers or solutions of contractile proteins are activated by laser flash photolysis of caged ATP, permitting us to monitor the rotational dynamics of synchronized populations of proteins during the transient phase of contraction. We can detect not only the global orientations and rotations of myosin heads and actin, but also the internal conformational states of these proteins during the ATPase cycle. Our results are not consistent with the standard model in which the myosin head rotates between two discrete angles to generate force. Rather, we find that myosin heads have a distinct orientation on actin only in the absence of ATP; they undergo rapid microsecond rotational motions during force generation, suggesting a new model in which nearly Brownian rotational diffusion is directed by the ATPase cycle and the asymmetry of the bipolar myosin and actin filament structures.
TWO-DIMENSIONAL FOURIER TRANSFORM ESR APPLIED TO BIOPHYSICAL STUDIES

Jack H. Freed, Chemistry Dept., Cornell University, Ithaca, NY 14853

The nitroxide spin-label technique has permeated many areas of biophysical research, and the principal reliance has been on cw-ESR methods, despite the somewhat limited features of the characteristic hf patterns from $^{14}$N or $^{15}$N. However, new 2D-FT-ESR techniques have been developed for the study of spin relaxation and motional dynamics in membranes and of spin-labeled macromolecules. In particular, SECSY-ESR can provide a display, in a two-dimensional format, of the homogeneous lineshapes across an inhomogeneous ESR spectrum. 2D-ELDOR can provide the cross-relaxation between each pair of points in the spectrum. A particularly difficult problem arises from the study of membrane materials such as vesicles, which exhibit microscopic order but macroscopic disorder (MOMD). Such dispersion samples provide particularly poor resolution. Recent technical advances now permit the study of labelled phospholipids as well as cholestane by 2D-FT-ESR. Despite the considerable inhomogeneous broadening, strong FID-based 2D spectra are obtained, from which the spin echo-like components can be projected. It will be shown how, by careful analysis, these methods provide detailed information on the rotational and translational dynamics of the spin-labelled molecules as well as their microscopic ordering. The implications for sophisticated studies, such as the effect of protein on the lipid structure and dynamics will be addressed. In the case of particularly slow motions, such as the reorientation of spin-labelled proteins, spin-echo based 2D-ESR methods apply and permit the detailed evaluation of the rotational motion and its asymmetry.

MOTION OF MOLECULES IN LIQUIDS STUDIED BY PULSED ELDOR

Colin Mailer and Bruce H. Robinson, Department of Chemistry, University of Washington

We have studied the spin lattice relaxation processes for the electron ($1/T_{1e}$) and the nitrogen nucleus ($1/T_{1n}$) of a nitroxide spin label in a liquid as a function of solvent viscosity and temperature. This study of isotropic motional dynamics covers 8 orders of magnitude - from picoseconds to milliseconds. The relaxation rates over this range are quantitatively explained by a combination of three mechanisms - spin rotation, spin diffusion and electron-nuclear coupling - under the influence of (an)isotropic rotational Brownian dynamics. This completely solves the 20 year old problem of the electron T1e discovered by Hyde in his pioneering experiments with Percival and the 10 year old problem of the T1n mechanism that he found with Mottley and Francisz.

The cellular plasma membrane is a patchwork of various membrane subdomains, including specialized membrane domains such as coated pits and desmosomes, special lipid domains, and protein-rich regions. Our recent observations showed that the membrane receptor molecules are partially confined within the membrane compartments bounded by the membrane-associated cytoskeleton (membrane skeleton), which is termed the "membrane-skeleton fence structure" for receptor diffusion (as observed by single particle tracking using nanovid microscopy). At the lipid level, the fluid-phase immiscibility is prevalent in cis-unsaturated PC-cholesterol membranes, but where cholesterol-rich (or oligomeric) domains are small (several lipids) and/or short lifetime (10^-9 to 10^-7 s; by pulse ESR and simulation of conventional ESR spectra). Band 3 protein from human erythrocytes reconstituted into cis-unsaturated PC-cholesterol membranes tends to form larger aggregates after being excluded from the cholesterol-rich domains (saturation-transfer ESR). Detection and observation of various levels of membrane subdomains and compartments and their relationships with the membrane function will be discussed.


Multifrequency ESEEM and EPR spectroscopy were employed to elucidate the electronic structure of singly reduced tris(1,3-diphenyltriazenido)aluminum. Insight into the electronic structure of the Al complex was obtained through the use of different combinations of ¹⁵N and ¹⁴N isotope labels on the diphenyltriazene rings. Reduction of the Al complex results in localization of the electron onto one of the three diphenyltriazene ligands. Ab initio calculations were performed, using GAUSSIAN90, which give further insight into the electronic structure and aid in the interpretation of the experimental spectra. The experimental ESEEM and EPR results, together with the ab initio calculations, give a coherent, simple picture of the spin density distribution and bonding in the Al(PhNNNPh)₃ molecule obtained upon reduction.
NON-LINEAR ESR: APPLICATIONS TO COMPLEX FLUIDS AND MICROSCOPIC INTERPRETATION

L. Andreozzi, M. Giordano, D. Leporini, Dipartimento di Fisica dell'Universita', P.zza Torricelli 2, 1-56100 Pisa, Italia

"Non-linear ESR" denotes a class of ESR spectroscopies whose signal stems from the non-linear response of the paramagnetic sample to CW microwave fields. In this communication a survey of the experimental and theoretical work carried out by the Pisa ESR group in the last years will be presented. Experimental schemes resorting to second and third-order photon absorption/emission processes will be discussed. It will be shown that proper schemes can be devised to select "slow" states, namely states of the paramagnetic system relaxing on time scales longer than the microscopic correlation time, providing a shortcut to a Redfield-like interpretation. Illustrations will devoted to spectroscopies whose spectral profile coincides with the Laplace transform of the longitudinal magnetization decay. The use of the longitudinal spin relaxation channel to extend the upper bound of the time scale accessible to ESR will be underlined by referring to studies of the microscopic transport properties of spin probes dissolved in polymeric liquid-crystals. Evidence of the strong sensitivity of $T_1$ to the cooperative and local dynamics in the temperature range around the glass transition of the polymer strand will be shown.

SITE PERCOLATION AND A SPIN-DIFFUSION MODEL AS APPLIED TO Gd$^{3+}$EPR LINewidth

82 BEHAVIOUR IN Pr$_x$La$_{1-x}$F$_3$ SINGLE CRYSTALS Sushil K. Misra and Ufuk Orhun, Physics Department, Concordia University, 1455 de Maisonneuve Boulevard West, Montreal, H3G 1M8 Canada

The drastic broadening of the impurity-ion Gd$^{3+}$ EPR linewidth behaviour in Pr$_x$La$_{1-x}$F$_3$ between $x = 0.2$ and $x = 0.3$ as $x$ increases from 0 suggests that the mechanism of EPR line broadening becomes effective somewhere between $x = 0.2$ and $x = 0.3$ due to paramagnetic site percolation. As $x$ is increased further, the sudden reappearance of EPR lines at $x = 0.8$ and further narrowing of lines with increasing values of $x$ suggests that a mechanism of narrowing of lines apparently becomes effective somewhere between $x = 0.7$ and $x = 0.8$ due to spin diffusion. Both of these effects, namely paramagnetic percolation and spin diffusion, are caused by the host ions, Pr$^{3+}$, which exhibit Van Vleck paramagnetism. The calculated paramagnetic percolation threshold, $x_c$, above which the process of spin diffusion is effective, was calculated for the case when the continuity is confined to neighbours located within a distance of $<0.8$ nm. It was found that this value of $x_c$ in conjunction with a simple theory as described by Abragam, predicts quite well the observed Gd$^{3+}$ EPR linewidth behaviour in Pr$_x$La$_{1-x}$F$_3$ host crystals as a function of $x$.

DETERMINATION OF SPECTROSCOPIC PARAMETERS, CORRELATION TIMES AND EXCHANGE RATES FROM THE AUTOMATIC FITTING OF EPR SPECTRA. Edgar J. Soulé and Claude Chachaty, CEA-DSM-DRECAM-SCM, Centre d'Etudes de Saclay, 91191 Gif-sur-Yvette, Cedex, France.

We have simulated the EPR spectra of paramagnetic probes adsorbed in heterogeneous media, e.g., gels and porous inorganic glasses. The A and g tensors are obtained by automatic adjustment of the spectra recorded at low temperatures, in the absence of motion.

Upon warming, the spectra evolve due to reorientational motion. They have been simulated to a good approximation using the Bloch equations modified for Brownian diffusion. The adjustment of the computed spectra to the observed ones yields the reorientation correlation time of the paramagnetic species as well as the intrinsic linewidth.

An extension of the above treatment takes into account the exchange between a site where reorientation is slow and a site where it is fast (F). Extrapolating the correlation times determined in the limiting conditions of very slow and very fast exchange, the exchange rate as well as the fraction of (F) sites in the intermediate regime can be obtained by nonlinear least squares adjustment of the spectra.

The above procedures are illustrated by experiments on vanadyl and copper probes.

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EPR OF RADICALS IN (CONDUCTING) POLYMERS DERIVED FROM MIXED PYRROLE/THIOPHENE/FURAN OLIGOMERS.
Martin G. Bakker, Jason L. Cain, Makarand Joshi, Michael P. Cava, Allan J. McKinley and Robert M. Metzger.
Chemistry Department, The University of Alabama, Tuscaloosa, Al.35487-0336

A series of triheterocycles;

\[
\begin{array}{c}
\text{X} \\
\text{Y} \\
\text{Z}
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\]

for X,Y, Z= OOO, SSS, SOS, SSO, SOO, O(N-Me)O, S(N-Me)O and S(N-Me)S were synthesized, of these O(N-Me)O, SOO and S(N-Me)O are new. The triheterocycles were chemically polymerized and oxidized with NOPF₆. Only the polymers derived from SSS, SOS and SSO show appreciable conductivities. EPR studies indicate the presence of polarons in SSS, SOS, SSO and, at lower concentrations, in OOO. All the samples appear to show an easily saturable EPR signal assigned to localized radicals. In SOO, O(N-Me)O, S(N-Me)O and S(N-Me)S this signal displays considerable asymmetry, and g-values significantly above the free electron value. S(N-Me)S shows a higher g-value consistent with a loss of planarity caused by steric interactions of the methyl group with the thiophene rings.

The likely causes of the low conductivities observed are (1) Short conjugation lengths resulting from β-branching and off chain coupling (2) localization of the polarons and bipolarons.

DOPED ORGANIC CRYSTALS ESR INVESTIGATION OF MECHANISMS OF PHOTOCHEMICAL REACTIONS AND ASYMMETRIC RELAXATION PROCESSES. Georgii G. Lazarev, Institute of Chemical Physics, Russian Academy of Science, Moscow, Russia. Present address: Inst. of Chemistry, National University of Mexico, Mexico City, Coyoacán 04510, MEXICO

Investigation of intermediate paramagnetic products of photochemical reactions help to understand the mechanisms of such reactions. Typical spectra of radical pairs arise if the distance between two radicals is not more than 7Å to 10Å. In this case the dipole-dipole magnetic interaction of the electron spins is large enough to cause a detectable splitting in the ESR spectrum. In crystal matrix it is possible to see hyperfine splitting more distinctly so giving more information about the nature of the radicals in the pair. Two types of asymmetric relaxation processes have been identified in the ESR spectra of radical pairs. The ratio of intensities of high-field and low-field components depends on the level of microwave power, angle of rotation and another parameters. The explanation was done on the basis of intersection of singlet and triplet levels.

PROTON HYPERFINE ANISOTROPY OF NITROXIDES IN AN AMINE CURED DGEBA (DIGLYCIDYL ETHER BISPHENOL A) EPoxy AND SPIN LABELED DGEBA COPOLYMER BY ENDOR SPECTROSCOPY. M. D. Page and A. W. Snow, Code 6120, Naval Research Laboratory, 4555 Overlook Ave, S. W., Washington, D. C. 20375-5342

In this study, we show that ENDOR (electron-nuclear double resonance) is superior to EPR (electron paramagnetic resonance) spectroscopy for measuring anisotropy and conformation changes of spin probes in an epoxy matrix or of a nitrooxide spin labeled polymer. Nitrooxide spin labeled synthetic polymers or nitrooxide spin probes in an epoxy matrix are commonly studied using EPR to detect polymer chain ordering or dynamics near the glass transition temperature (Tg). Line shape changes of the nitrooxide EPR spin label or spin probe spectra give information about polymer chain mobility. At temperatures well below Tg of the polymer, EPR nitrooxide spectra approach a rigid limit line shape making measurement of probe or label anisotropy effects difficult. TANOLD spin probes (4-hydroxy-2,2,6,6-piperidinyl-1-oxy-d₃) in amine cured diglycidyl ether of bisphenol A and a spin labeled copolymer of DGEBA reacted with TAMINE (4-amino-2,2,6,6-tetramethyl-piperidin-1-yl-oxy) and cyclohexyl amine were studied using ENDOR from temperatures near 77 K to room temperature. Proton hyperfine coupling anisotropy of a few kHz were easily detected using ENDOR whereas the rigid limit EPR spectrum showed no detectable line shape changes.
AN ENDOR STUDY OF THE CANTHAXANTHIN CATION RADICAL IN SOLUTION AND ON AN ACTIVATED SILICA-ALUMINA SOLID SUPPORT. A. S. Jeeravarajan, L. D. Kispert and L. Piekara-Sady, Department of Chemistry, The University of Alabama, Tuscaloosa, AL 35487.

Carotenoids play an important role in photosynthesis as antenna pigments and as photoprotect devices against the destructive properties of singlet oxygen. Other useful properties include its electron donor ability which results in the formation of carotenoid cation radicals. The structure of the carotenoid cation radical in solution has previously not been established. We report here for the first time the ENDOR spectrum of the cation radical of the carotenoid canthaxanthin generated electrochemically. The ENDOR derived isotropic hyperfine couplings for the methyl (C(5)-CH_3, C(13)-CH_3 and C(9)-CH_3) protons agree with those observed for the canthaxanthin cation radical generated on an activated silica-alumina solid support. The isotropic proton hyperfine coupling constants are in reasonable agreement with those calculated by RHF-INDO/SP molecular orbital methods for a planar all trans polyene configuration. Proton couplings less than 1 MHz were not detected in solution due to incomplete hyperfine separation and chemical exchange processes. The bulk electrolysis techniques used to generate sufficient carotenoid cation radical for ENDOR detection will be described. This work was supported by the Division of Chemical Sciences, Office of Basic Energy Sciences of the U. S. Department of Energy.

ON EPR STUDIES OF HIGH $T_c$ SUPERCONDUCTOR YBCO DOPED WITH Fe IONS. C. Rudowicz, H.Y. Chan, Dept. of Applied Science, City Polytechnic of Hong Kong, Hong Kong, W.L. Yu, M.L. Du, Sichuan Normal University, Chengdu, PR China, and Y.Y. Yeung, Dept. of Applied Physics, Hong Kong Polytechnic, Hong Kong

Crystal field (CF) study within 5D term (Rudowicz et al., Supercond. Sci. & Techn. 4, 535 (1991)) of Fe$^{2+}$ and Fe$^{3+}$ ions at Cu(1)-plannar, pyramidal and octahedral sites, and Cu(2) site in YBa$_2$(Cu$_{1-x}$Fe$_x$)$_3$O$_{7-d}$ indicates an orbital singlet ground state with spin S=2 and mostly well separated from the excited states. Using the microscopic spin Hamiltonian, the zero-field splitting (ZFS) parameters $b_k$ and $g_1$ are determined for each ion/site case using the values of $\lambda$ (spin-orbit), $\rho$ (spin-spin) and $\Delta_1$ (CF energies). The Fe$^{2+}$(1)-plannar site exhibits very large ZFS ($b_2^2$). The variation of $b_k$ and $g_1$ with x is also studied. For Fe$^{2+}$(1) and Fe$^{4+}$(1) octahedral sites $b_k^2$ (k=2, 4) become zero at x>0.04, where YBCO undergoes orthorhombic to tetragonal phase transition. Simulation of EPR transitions suggests feasibility of high-frequency and high-field EPR studies of Fe$^{2+}$ and Fe$^{4+}$ (S=2) ions in YBa$_2$(Cu$_{1-x}$Fe$_x$)$_3$O$_{7-d}$. The extended CF and ZFS calculations within the whole d^4 and d^6 configuration are also outlined.

CLINICAL (In Vivo) EPR: THE TIME HAS COME??!!? Harold M. Swartz, Fuminori Goda, Ke J. Liu, and Ted Walczak, Dartmouth Medical School, HB 7252, 308 Strasenburgh Hall, Hanover, NH 03755-3863

The ability to perform in vivo EPR studies continues to progress at a rapid rate. The most likely applications appear to be for the measurement of the concentration of oxygen (actually pO$_2$) in tissues, especially in tumors. The development of instrumentation is proceeding in several laboratories including explorations of the use of different frequencies, different types of detectors, different kinds of data (i.e. imaging and spectroscopy) and different paramagnetic substances. Results now have been obtained in experimental animals under physiologically and pathologically pertinent conditions in tumors, brain, muscle, skin, and heart. The principal obstacle to the adaptation of these techniques to patients has been the time required to demonstrate the safety of the paramagnetic substances used to obtain pO$_2$. Very recently, we have found a substance which already is used commonly in humans which also has a very strong response to pO$_2$ over the range of most interest. The results of these first measurements of pO$_2$ in people will be presented.
MEASUREMENT TISSUE VISCOSITY AND POLARITY IN THE DISTRIBUTION COMPARTMENT OF mHCTPO IN LIVING TISSUE WITH VERY LOW FREQUENCY EPR

The linewidth asymmetries are, from elementary linewidth and liquid models, measures of the solvent rotational diffusion constants, viscosities, and, thereby, translational diffusion constants. Solvent polarity modulates nitrogen and, with 5% of its effect on nitrogen, hydrogen splittings. We measure the nitrogen splitting to be much less subject to spin exchange shifts than hydrogen. Thus the nitrogen splitting can be used to measure environment polarity. At very low magnetic fields (90 G), field stability and linearity to within 1 mG allows precise measurement of these parameters. Low frequency allows these measurements in living tissue. We have measured the linewidth asymmetry and the nitrogen splitting with both $^{15}$N and $^{14}$N-4-hydro-2, 2, 5, 5-tetrameruteromethyl-3-pyrrolin-1-oxyl (mHCTPO) injected IP in C3H mice with FSA and NFSA fibrosarcomas grown in their thighs. Measurements were made localized to the tumor and nearby thigh tissue. Measurements indicate that the polarity of the compartment in which the mHCTPO distributes has the same polarity as water. The viscosity of this compartment diminishes as tumor size increases. This appears to be the case even in the absence of histologically evident liquefactive necrosis. The linewidth asymmetry measurements recapitulate the results of $T_2$ measurements with NMR; but they may be more specific.

A PROPOSED MECHANISM EXPLAINING DIFFERENCES IN NITROXIDE METABOLISM

Last year we proposed that differences in TEMPO metabolism between adenovirus-transformed (983.2) and untransformed (BHK) Baby Hamster Kidney cells were the result of changes in the ability of the transformed cells to metabolize superoxide. New evidence has allowed us to postulate a model for nitroxide metabolism which includes superoxide. We have begun to test some of its predictions.

Krishna et al (Proc. Natl. Acad. Sci. USA (1992),89:5537-5541) showed that nitroxides act as superoxide dismutate (SOD) mimetics but are oxidized to the oxaommonium instead of reduced to the hydroxylamine (as they previously stated, Samuni et al, J. Biol. Chem. (1988),263:17921-17924). Our data supports their more recent conclusions. In our mechanism, TEMPO is reduced by two mechanisms, 1) by one electron reduction via the electron transport system and 2) by two electron reduction from the oxoamnonium ion produced by SOD-like activity of the nitroxide. Peroxide re-oxidizes the hydroxylamine to the nitroxide and plays a major role in determining overall nitoxide reduction rates. Catalase activity in the 983.2 cells is only 5% of that in the BHK cells which may allow excess peroxide to recycle the hydroxylamine back to the nitroxide. This would explain the lower overall TEMPO reduction rates seen in 983.2 cells compared to BHK cells. Our model and the evidence in support of it will be presented in detail.

Supported by NIH Grants R15 GM44365-01 to PDM and R15 CA52091-01A1 to LAL.

92 AN ESR AND ENDOR STUDY OF METHYLATED ANTHRACENE RADICAL CATIONS GENERATED FROM ARYLGERMANES AND -STANNANES. M.Lehnig, Th.Reiche, and S.Reiss, FB Chemie, Universität Dortmund, Germany, P.Such, BRUKER Anal.Meßtechnik, D-7512 Rheinstetten

The radical cation of anthracene (I) is observed during the reaction of tetraphenylgermane and -stannane or hexaphenyldigermane or -stannane with AlCl$_3$ in CH$_2$Cl$_2$. Radical cations of 2,6-dimethylantracene (II), 1,2,3,4,5,6,7,8-octamethylantracene (III), 1,3,5,7-tetramethylantracene (IV), and 1,2,3,5,7,8,9,10-octamethylantracene (V) are formed during the reaction of various methylated arylermanes and -stannanes with AlCl$_3$ in CH$_2$Cl$_2$ or CBCl$_2$-CH$_3$. ESR data of the radical cations are given. The first radical formation step is an electrophilic ipso substitution leading to α-chlorotoluences which is followed by a Scholl condensation to the anthracenes which are oxidised in the following. (III) is the only stable radical cation from higher methylated radical cations.
ENDOR BASED STRUCTURAL AND CONFORMATIONAL ANALYSIS OF CARBOXYLIC ACID DERIVATIVES OF THE SPIN-LABEL 2,2,5,5-TETRAMETHYL-1-OXYPYRROLINE.
Seppo J. Kasa, William E. Boisvert, and Marvin W. Makinen, Department of Biochemistry and Molecular Biology, The University of Chicago, Chicago, Illinois 60637

Multiple conformers of carboxylic acid derivatives of the spin-label 2,2,5,5-tetramethyl-1-oxypyrroline in frozen solutions have been identified and structurally characterized by ENDOR spectroscopy and molecular modeling. From ENDOR spectra of (2,2,5,5-tetramethyl-1-oxypyrroliny1)-acetic acid and 3-(2,2,5,5-tetramethyl-1-oxypyrroliny1)-2-propenamide, the resonance absorption features have been assigned for each side chain proton. From the maximum and minimum ENDOR shifts that correspond to the principal hyperfine coupling (hfc) components, the dipolar hfc components were calculated to estimate the electron-proton distances (r). Based on ENDOR linewidths, uncertainties in the values of r were estimated to be less than 5%. While the spin-labeled propenamide exhibited only one essentially planar trans s-cis conformation, spin-labeled acetic acid exhibited two main conformers. The molecular structure of each conformer for each spin-labeled derivative was assigned on the basis of torsion angle search calculations constrained by both van der Waals hard sphere limits and the ENDOR determined values of r. (Supported by NIH AA06374).

ORIENTATION SELECTED ENDOR ...A NEW LOOK. Peter E. Doan, Brian M. Hoffman, Department of Chemistry, Northwestern University, Evanston, IL, 60208-3113

In the presence of g-anisotropy, an ENDOR (or ESEEM) spectrum taken on a powder sample at a single field includes contributions from a limited subset of molecular orientations. We present both a modification of our existing method as well as a new parameterization of the orientation-selection process. These newer methods provide for more facile analysis as well as computational efficiency. The extension of the newer methods to spherical averaging is also discussed. These methods are demonstrated for the ENDOR spectra of a series of metalloenzymes.

ELECTRON SPIN RESONANCE (ESR) STUDIES OF THE Ti-CATALYST USED IN THE SYNDIOTACTIC POLYMERIZATION OF STYRENE PART I: CATALYST MIXTURE IN TOluENE SOLUTIONS.
A. S. Ellaboudy and R. E. Campbell, Jr. The Dow Chemical Company, Midland, Michigan 48667

The addition of methylaluminoxane (MAO), triisobutylaluminum (TIBA) or a mixture of both to a solution of (R5Cp)TiX3, where R is either H or CH3, X is Cl, OCH3, OPr, OPh, OPh3 and Cp is the cyclopentadienyl anion, results in a 75 to 100% reduction of Ti(IV) to Ti(III) as well as the formation of a hydride or alkylated Ti derivative.

Solutions of Ti4+ compounds with MAO or MAO/TIBA mixtures show ESR spectra that depend on R but not X. For CpTiX3-MAO solutions a doublet ESR signal was observed at g-value of 1.987 and hyperfine coupling constant, \( a_t \), of 13 Gauss. When Cp is replaced by the Cp* ligand a sextet ESR signal was observed with an intensity ratio of 1:5:10:10:5:1 and centered at a g-value of 1.998 and \( a_t = 9.5 \) Gauss. In the presence of MAO/TIBA mixture the ESR spectra are different. Solutions of CpTiX3 complexes yielded a quartet ESR signal at \( g = 1.989 \) and \( a_t = 4.7 \) Gauss while Cp*TiX3 solutions yielded a 12 line spectra having a g-value of 1.989 and \( a_t \) of 2 to 3 Gauss.

Although the results suggest that Ti4+ complexes are the active species in SPS polymerizations, the presence of a minor amount of Ti4+ in these solutions is evident and its role as an active site cannot be ruled out.
Site directed mutants of azurin from *Pseudomonas aeruginosa* were used to probe the structural and electrostatic influence of methionines 44 and 121 at the copper binding site. Mutation M44K, which does not involve a directly coordinating ligand, changes the midpoint potential of the protein by 60mV, although ESEEM and LEFE indicate no change in the histidine ligand interactions no copper site symmetry. At pH > 10, the lysine substituted for methionine at position 44 deprotonates, with a change in the superhyperfine interactions of the histidine ligand imino nitrogens that can be correlated to structural and electrostatic changes by spectral simulation. We have also examined the changes in the same histidine superhyperfine interactions as the copper coordinating methionine is changed to a glutamine. The FT spectrum of the echo modulation from the latter is characterized by a lifting of the equivalence of the two histidines' imino nitrogens. We tentatively attribute this to differences in the isotropic hyperfine component.
MAGNETIC FIELD DEPENDENCE OF ELECTRON SPIN-LATTICE RELAXATION TIMES, Jing-Long Du, Gareth R. Eaton, and Sandra S. Eaton, Department of Chemistry, University of Denver, Denver, Colorado 80208

The orientation dependence of $T_1$ was measured by X-band saturation recovery for the nitroxyl radical tempone, copper bis(diethylidithiocarbamate), Cu(dtc)$_2$, and vanadyl tetratolyiporphyrin, VOTTTP. At 50 and 100 K the longest values of $T_1$ were observed along the molecular $z$ axis and shorter values were observed in the $x$, $y$ plane. The orientation dependence of $T_1$ was greater in doped solids than in frozen solution. Longer values of $T_m$ were observed for Cu(dtc)$_2$ and VOTTTP at orientations for which small changes in molecular orientation caused little change in resonant field, and shorter values of $T_m$ were observed at orientations for which small changes in orientation caused larger changes in resonant field. The orientation dependence of $T_m$ was greater in frozen solution than in doped solids, which is the opposite of the pattern for $T_1$. Thus, the mechanism that accounts for the orientation dependence of $T_1$ is different from that for $T_m$.


The multiquantum method developed by Hyde and coworkers has been used to measure the spin lattice relaxation time, $T_1$, for the EPR-detectable site in nitrous oxide reductase, N$_2$OR. The $T_1$'s for N$_2$OR are unusually fast for the cupric site and are very similar to $T_1$'s for the EPR-detectable site in cytochrome c oxidase, COX. In this study, the method of continuous saturation has been used to quantitate the electron spin relaxation in terms of $P_{1/2}$, the power at which the signal amplitude is half that without saturation. Cupric sites, for which no saturation could be observed at 77 K, were selected. Two of the cupric complexes were the NO$_2$ and Cl$^-$ adducts of [HB($t$-butylpyrazolyl)$_3$]Cu. These two compounds saturate with a $P_{1/2}$ of about 13 dB at 15 K (X-band). A third cupric complex, the NO adduct of [HB($t$-butylpyrazolyl)$_3$]Cu does not show a signal at 77 K and is found not to saturate at 20 K (C-band). These examples demonstrate that it is not always necessary to invoke a mixed valence binuclear structure to account for fast relaxation. Thus, the fast relaxation for the mixed valence [Cu(1.5)...Cu(1.5)], $S = 1/2$ site of N$_2$OR ($P_{1/2} = 15$ dB at 15 K) and, presumably, COX ($P_{1/2} = 14$ dB at 15 K) may not be as unusual as previously thought. Supported by NSF DMD-9105519, NIH GM47365, and Deutsche Forschungsgemeinschaft.
EVIDENCE IN SUPPORT OF A BINUCLEAR CENTER AS THE Cu'A' SITE IN CYTOCHROME OXIDASE. Ambar Jain and Graham Palmer, IERC, College of Medicine, 506 S. Mathews, University of Illinois Urbana, IL 61801 and Department of Biochemistry and Cell Biology, Rice University, P.O.Box 1892, Houston, TX 77251

When cytochrome c oxidase is incubated with the thiol reagent p-chloro mercuri sulphonic acid for 12-24 h. at 17 C, a proportion of Cu'A' site is converted into a type II copper as judged by changes in the 830 nm absorption and changes in the EPR spectrum of the enzyme. Comparison with the control shows that the heme chromophores are not significantly perturbed. The binuclear active site does not get affected by the modification as observed by reacting different ligands such as formate, cyanide, and carbon monoxide with modified enzyme and recording uv-vis, m.c.d. and EPR spectra. However it does show 40% loss of catalytic activity. Residual enzyme was obtained by removing type II copper from the modified enzyme. The quantitative analysis of EPR spectra of control, modified, and residual enzyme shows the total integral due to combined copper increased significantly. The ratio of the modified Cu'A' and native Cu'A' lost is 1.8, close to 2. This is consistent with the presence of two different types of copper, presumably mixed-valence copper, as Cu'A' as has been suggested earlier by Kroneck et al. (FEBS letters 214, 1988, 70). This work was supported by grants from NIH (GM21337; resources provided by P41RR01811) and Welch Foundation (C636)(GP).

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EPR SPECTROSCOPY OF COBALT(II) AND COPPER(II) ENCAPSULATED COMPLEXES. T.M. Donlevy*, G.R. Hanson*, L.R. Gahan*, Department of Chemistry and the Centre for Magnetic Resonance, The University of Queensland, Queensland, Australia, 4072.

A series of structurally well defined cobalt(II) and copper(II) complexes have been prepared from the ligands 1,8-Diamine-3,6,10,13,16,19-hexaaazabicyclo[6.6.6]icosane (AMN₄S₄sar), 1-Amine-8-methyl-3,13-dithia-6,10,16,19-tetraazabicyclo[6.6.6]-icosane (AMN₄S₃sar) and 8-Amine-1-methyl-3,13,16-trithia-6,10,19-triazabicyclo[6.6.6]icosane (AMN₃S₄sar). EPR spectroscopy has been employed to monitor the changes in the electronic environment around the cobalt(II) and copper(II) ions present in these encapsulated complexes. While the cobalt(II) complexes with AMN₄S₄sar and AMN₃S₄sar are high and low spin respectively, the [Co (AMN₃S₄sarH)]³⁺ complex exhibits a spin equilibrium. Increased tetragonal distortion around the cobalt(II) and copper(II) ions are observed as the number of sulfur atoms is increased.

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SECURITY ON BRUKER EPR/NMR SPECTROMETERS ETHERNET LINKED TO A NETWORK. G.R. Hanson, Centre for Magnetic Resonance, The University of Queensland, Queensland, Australia, 4072. (Email: G.Hanson@cmr.uq.oz.au)

The Centre has a number of Bruker EPR and NMR spectrometers ethernet linked to SUN workstations, personal computers and the world through the Universities Prentice Computer Centre. As a consequence of hackers, we have been forced to introduce a number of measures to preclude this activity. These will be outlined in this poster. Copies of this poster can be obtained by email.
MAGNETIC RESONANCE INVESTIGATIONS OF COPPER ZEOLITES. Sarah C. Larsen, Adam Aylor, Alexis T. Bell and Jeffrey A. Reimer, Materials Science Division, Lawrence Berkeley Laboratory, 1 Cyclotron Road, Berkeley, CA, 94720 and Department of Chemical Engineering, University of California, Berkeley, CA, 94720.

Excessively exchanged copper ZSM-5 possesses high catalytic activity for the direct decomposition of NO to N₂ and O₂. Although the copper exchange level can be correlated with catalytic activity, little is known about the environment of copper in the zeolite structure. We have utilized CW and pulsed EPR spectroscopies to probe the local structure of the Cu²⁺ sites for a series of copper zeolites with different levels of copper substitution. As a function of copper concentration and dehydration temperature, the measured g and A values and the observed ESEEM spectra provide information about the structure of the paramagnetic copper complexes formed. The copper catalysts have also been studied with EPR under more realistic conditions such as high temperature and in the presence of NO adsorbates. Additionally, ²⁹Si MAS (magic angle spinning) NMR experiments were undertaken to correlate ²⁹Si relaxation times with the Cu²⁺ concentration.

ELECTRON SPIN ECHO ENVELOPE MODULATION STUDIES OF COPPER PTERIN COMPLEXES. Hong-In Lee¹, Lavina Bharwani², Sharon J. Nieter Burgmayer², and John McCracken¹, Departments of Chemistry, Michigan State University¹, East Lansing, MI 48823, and Bryn Mawr College², Bryn Mawr, PA 19010

ESEEM methods have been used to characterize the ligation of pteridine ligands to Cu(II) in a variety of complexes prepared in aqueous and non-aqueous solvents. These studies were aimed at understanding the structural relationship between the Cu and pterin cofactors in Phenylalanine Hydroxylase (PAH) from C. Violaceum where previous cw-EPR results have provided evidence for equatorial binding of 6,7-dimethyltetrahydroppterin to the metal through N-5. Previous ESEEM studies of the protein identified two histidyl imidazole groups equatorially bound to Cu(II), but provided no evidence for coordinated pterin. For the model compounds in which pterin groups are equatorially bound to Cu(II) through O-4 and N-5, deep ¹⁴N modulations were observed. ESEEM of compounds where mixed equatorial-axial ligation of the pterin moiety has been found by X-ray analysis, show little or no ¹⁴N contributions in their spectra. Because the ¹⁴N ESEEM response from equatorially coordinated pterin is intense and the peaks occur in a spectral region where there would be little interference from the protein, our results are most consistent with a mixed equatorial-axial ligation of this cofactor at the Cu(II) site of PAH.

ELECTRON SPIN ECHO ENVELOPE MODULATION OF AMMONIUM SALTS BOUND TO TRI-ARYLMETHYL RADICALS. Hong-In Lee, Sei-Hum Jang, James E. Jackson, and John McCracken, Department of Chemistry, Michigan State University, East Lansing, MI 48824.

The electron spin echo envelope modulation (ESEEM) technique of pulsed EPR spectroscopy has been used to study the binding of ammonium salts to tri-arylmethyl radicals. Our goal in these studies is to characterize the structure of compounds that might serve as precursors to molecular magnets. For monomeric models where stoichiometric ratios of the salt to tri-3,5-hexachloraryl methyl radicals were 1:1 or 1:2, the ESEEM spectra consist of only a single peak at 1.9 MHz. Analysis of these data indicates that such spectra are common when the anisotropic hyperfine interaction energy is about half of the isotropic coupling. ¹⁵N-ESEEM studies were done to refine our analysis of ¹⁴N couplings. The "coupling ranges" for which ¹⁴N spectra of the type presented here are predicted will be discussed.
SUBLEVEL-ECHO-ENDOR STUDY OF MOLECULAR DYNAMICS OF POLYMER CHAIN ENDS. Günter G. Maresch and Michael Hubrich, Max-Planck-Institut für Polymerforschung, PO Box 3148, W-6500 Mainz, Germany

ENDOR techniques are well established since many years. Sensitivity and applicability to broad temperature ranges are greatly enhanced by pulsed ENDOR methods which are less dependent on favourable relaxation conditions. Up to now the main results from these experiments are molecular structural informations. However, spin relaxation in general allows also to study molecular motions especially in solids in which these motions are slow and don't affect the spectral line shape. With a modified Bruker pulsed EPR spectrometer the proton phase memory times of chain end radicals of liquid crystalline polymers are measured by sublevel-echo ENDOR. These radicals are generated during production and processing of high-strength polymers. Two-dimensional EPR images show that the organic radicals are localized mainly at the sample surfaces. The conventional EPR spectrum is a structureless Gaussian line with unresolved proton hyperfine interaction. By pulsed ENDOR in the temperature region from 250 K to 350 K molecular motions of the polymer chain ends on a microsecond timescale are observed in the solid state far below the melting point of the polymer.

ESEEM STUDY ON NITROGEN-CONTAINING VANADYL COMPLEXES.
Kouichi Fukui, Yukio Mizuta*, Hiroaki Ohya-Nishiguchi, and Hitoshi Kamada.
Division of Life Support Technology, Yamagata Technopolis Foundation, Kurumanomae 683, Numagi, Yamagata 990, and JEOL Ltd., Musashino 3-1-2, Akishima, Tokyo 196, Japan.

Electron spin echo envelope modulation (ESEEM) spectroscopy was applied to some nitrogen containing vanadyl complexes; \( V^{4+}O(oep)(1) \), \( V^{4+}O(salen)(2) \), and \( V^{4+}O(salphen)(3) \), possible models mimicking the structure of bromoperoxidases. Two- and three-pulse measurements were performed at the fields corresponding to \( B/Iz \), \( I_2 = -7/2 \), and \( B/Iz \), \( I_2 = -3/2 \). The ESEEM spectra obtained using maximum enthoropy method (MEM) exhibited superhyperfine peaks due to the coordinated nitrogen nuclear spins. Computer simulation of the spectra afforded the principal values and the principal axis directions of the nitrogen superhyperfine \( A \) and quadrupole \( Q \) tensors. The features of the simulation results are as follows: (1) The \( A \) tensors are rather isotropic with \( A_{iso} \approx 7.2 \text{ MHz} \) for 1, and 6.0 MHz for 2 and 3, slightly larger than the corresponding values for iron(III) porphyrin. (2) \( eQq \approx 1.9 - 2.2 \text{ MHz} \) and \( \eta = 0.5 \). (3) The tensor axes are well coincident with the electron \( g \) axes in 1, while the \( z \) axes in 2 and 3 were found to lean by ca. 30° from the \( g_\tau \) axes. These data demonstrate an effective extension of the pulsed EPR to bioinorganic chemistry.

AN EPR AND ESEEM STUDY OF X-RAY IRRADIATED Ag⁺-NaA ZEOLITE WITH METHANOL ADSORBATE. A. van der Pol, E.J. Reijerse, E. de Boer. Department of Molecular Spectroscopy, University of Nijmegen, Toernooiveld, 6525 ED, Nijmegen, The Netherlands and J. Michalik, T. Wadowsicz, J. Sadło. Department of Radiation Chemistry and Technology, Institute of Nuclear Chemistry and Technology, Dorodna 16, 03-195, Warsaw, Poland.

X-ray irradiated NaA zeolite loaded with one Ag⁺ cation per unit cell and adsorbed with methanol produces \( \text{AgCH}_3\text{OH}^+ \), in which silver is covalently bonded to carbon. The formation of this radical can be followed by EPR spectroscopy. From the experiments it can be concluded that the organosilver radical is formed in the \( \alpha \)-cage by reaction of the \( \text{Ag}^+ \) cation with the methanol radical \( \cdot\text{CH}_3\text{OH} \). To make the reaction possible the \( \text{Ag}^+ \) cation has to migrate from the \( \beta \)-cage to the larger \( \alpha \)-cage. The identity of the \( \text{AgCH}_3\text{OH}^+ \) radical is further substantiated by ESEEM experiments on deuterium labeled methanol compounds. Besides \( ^{27}\text{Al} \) modulations the echo envelope exhibits modulations due to \( ^2\text{D} \). From this the distance from the unpaired electron to the deuterium from the OD group can be deduced.
110 1.7 GHz ESEEM DUE TO $^{28}$Si IN $\gamma$-IRRADIATED FUSED QUARTZ. V.V. Kurchev, H.A. Buckmaster, L. Tykarski, Dept. of Physics and Astronomy, The University of Calgary, Calgary, AB, Canada, T2N 1N4.

This poster describes the results obtained using $\gamma$-irradiated fused quartz to evaluate the sensitivity of a newly developed, computer controlled 1.7 GHz electron spin echo (ESE) spectrometer. It is shown that a ESE envelope modulation (ESEEM) waveform is observable at this frequency using a three pulse sequence which can be ascribed to the interaction of $E_1$' -centre with the silicon isotope $^{28}$Si (natural abundance 4.7%) for which $I = 1/2$ and $\mu = -0.5553 \mu_n$. This modulation, which was not observable at 9 GHz, was modelled successfully by assuming that the $E_1$' -centre is located at a silicon vacancy in tetrahedral lattice and that it interacts with only those nuclei that are located outside a 0.5 nm radius sphere.

111 RELATIVISTIC EFFECTIVE HAMILTONIANS - APPLICATION TO EPR SPECTROSCOPY. R. Chatterjee, H.A. Buckmaster, Department of Physics and Astronomy, The University of Calgary, Calgary, AB, Canada, T2N 1N4

This poster discusses the derivation of relativistic effective Hamiltonians. These Hamiltonians are an extension of phenomenological spin Hamiltonians which were introduced to parameterize EPR spectral data. They are required to describe the EPR spectra of S-state ions such as Mn$^{2+}$, Fe$^{3+}$ and Gd$^{3+}$ because of the relativistic origin of the observed zero field splittings of the ground states for these ions. The most important consequence of this relativistic crystalline electric field formalism is that the decomposition of the effective double tensor operators in terms of L and S into products of single tensor operators leads to odd rank tensor operators which were not allowed in the phenomenological spin Hamiltonian formalism because they violated Kramers' theorem so a relativistic version of this theorem must be formulated. It is shown that the use of tesseral angular momentum operators eliminates problems associated with the hermitian adjoint and time reversal invariance of tensor angular momentum operators and enables the microscopic local crystalline electric field symmetry at a quasi S-state impurity ion site to be determined from the angular variation of the EPR spectrum.

112 MAGNETIC RESONANCE ABSORPTION SPECTRA OF SOME VOLCANIC ASHES. S. Marshall, Suzanne Beske-Diehl, R. Jackson, and R. Cunningham, Michigan Technological University, Houghton, Michigan 49931

Magnetic resonance absorption spectra have been observed in ash specimens taken from the ejecta of nine volcanoes. The purpose of this investigation is to determine whether volcanic ash display magnetic resonance spectra having signatures or identifiable characteristics and to estimate the amount of ash required from each volcano to provide a minimum detectable signal. The magnetic spectra of ash from these volcanos were studied at both room temperature and 77 K. Each ash was found to exhibit unique spectral characteristics. At 77 K, the spectra of some of the ash were found to differ in a qualitative manner from their room temperature spectra. Finally, of the nine volcanic ash studied, it was found that blind tests succeeded in identifying the spectrum of each ash with its parent volcano.
113 CHARACTERIZATION OF MINERAL SURFACES BY EPR
Dexter D. Murphy, Martin G. Bakker, Terry L. Clark, Brandon Davis and D. Ross Spears
The Chemistry Department, The University of Alabama, Tuscaloosa, AL 35487-0336 and the U.S.
Bureau of Mines, Tuscaloosa Station, Tuscaloosa, AL 35487

Separation processes in mineral recovery based on the chemical properties of minerals, require
that there exist a significant difference in the chemical properties of the minerals. Such differences
could be in the types of binding sites, the energies of the binding sites and the number and distribution of such
sites. Characterization of surfaces is therefore crucial in the choice of polymers, surfactants, suppressors
and other reagents required to achieve a satisfactory separation. Functionalized EPR spin labels have
much to offer in surface characterization.

Studies of the adsorption of 4-amino-TEMPO and 4-hydroxy-TEMPO from cyclohexane on the
surface of forsterite and chromite minerals from the Stillwater complex in Montana were carried out.
Adsorption isotherms were determined by EPR and checked by GC. TEMPO does not significantly adsorb on
either mineral. It was found that significantly more 4-amino-TEMPO was adsorbed on forsterite than on chromite. Preliminary results suggested that 4-hydroxy-TEMPO adsorbed more strongly on forsterite than on chromite. This latter result successfully predicted that a long chain alcohol would adsorb preferentially on forsterite as judged by flotation tests.

114 THE USE OF EPR TECHNIQUES TO PROBE THE STRUCTURE AND DYNAMICS OF
SOLVATED, BONDED SILICAS, Robert G. Kooser Chemistry, Knox College,
Galesburg, Illinois 61401-4999

Modified silicas are of interest because of their wide use as stationary phases in
High Performance Liquid Chromatography (HPLC). Three EPR techniques have been used in
characterizing these systems. In the label-probe studies, a 6-carbon spin labeled silica,
using a DOXYL group at the beta position from the free terminus, is allowed to interact
with methanol solutions of small spin probes of the TEMPO family. Depending on the
intercalation site of the probe relative to the label, spin exchange effects can be used to
determine probe-label separations. This gives us a site map of probe intercalation.
Spin probes of the TEMPO family have been studied as they insert into C18 silicas that
have been solvated with methanol-water solvents. The character of the functional group
at the 4 position of the TEMPO ring determines the motional characteristics of the probe
and this information will be drawn about the surface. Early investigations for a
HPLC-EPR detector have been done. Using a spin labeled column in the EPR cavity, we
have shown that the passage of solutes through the column causes changes in the motional
behavior of the label, thus turning the EPR into an HPLC detector.

115 MAGNETIC RESONANCE OF ZnGeP2: DEFECT CENTERS IN AN OPTICAL
PARAMETRIC OSCILLATOR. M.H. Rakowsky, W. K. Kuhn, R.A. Mantz, P.J. Drevinsky, M.C.
Ohmer, D.F. Bliss, P.G. Schunemann, T.M. Pollak. The Frank J. Seiler Research Laboratory, USAF
ACADEMY, CO 80840-6272; Phillips Laboratory, Edwards AFB, CA 93524-7068 and Hanscom AFB, MA
01731-3010; Wright Laboratory, Wright Patterson AFB, OH 45433-7707; Rome Laboratory, Hanscom
AFB, MA 01731-3010; Lockheed Sanders, Inc., Nashua, NH 03061-2035.

Magnetic resonance was used to examine defect centers in ZnGeP2. The ZnGeP2 is used as an OPO
material in tunable solid-state lasers. The objective is to improve the optical quality of the material. Its
performance is improved by reducing absorption at wavelengths below 2 microns. EPR and 31P MAS
NMR were used to structurally characterize the ZnGeP2 and its defect centers. The materials examined
included polycrystalline zinc germanium phosphide and as-grown and annealed single crystals both before
and after irradiation with 1 MeV electrons. The annealed single crystals were processed by annealing at
500°C for over 300 hours. The orientationally dependent EPR spectra were collected at 77K. 31P MAS
nuclear magnetic resonance as a function of temperature and EPR were used for structural characterization
of polycrystalline zinc germanium phosphide. The relationship of the improvement in optical properties,
processing procedures, and the EPR characterization is presented.
THERMAL PROPERTIES OF PARAMAGNETIC GERMANIUM CENTRES IN CRYSTALLINE SILICON DIOXIDE.

Michael J. Mombourquette and John A. Weil. Department of Chemistry, University of Saskatchewan, Saskatoon, SK, S7N 0W0 Canada.

The defects [GeO₄/Li]⁰₋₋ in α-quartz exhibit very appreciable thermal effects, as observed by EPR. Accurate measurements of the relevant spin-hamiltonian parameters [matrices g, A^7 Li and A^73 Ge] have now been measured in the range 20-300 K. These will be discussed in terms of spin relaxation, phonon densities and local dynamics.

AGGREGATION OF PERFLUORINATED IONOMERS IN SOLUTION, FROM ESR SPECTRA OF DOXYL STEARIC ACID PROBES Ewa Szajdzinska-Pietek and Shulamith Schlick, Department of Chemistry, University of Detroit Mercy, Detroit, Michigan 48219-0900.

ESR spectra of doxyl stearic spin probes in solutions of perfluorinated ionomers with long pendant chains (Nafion, made by DuPont) were measured as a function of temperature and ionomer concentration. Solvents in a range of polarities were chosen: ethanol (ε=25), water (ε=79), formamide (ε=109) and N-methyl formamide (NMF, ε=180). At 300 K two spectral components were detected for ionomer solutions in water and in formamide, with a relative intensity ratio that depends on the polymer concentration. The more rigid component is assigned to aggregation of polymer chains into micellar structures, with an order parameter of ≈0.6 in water at 300 K. The spectra for the solutions are compared with those obtained for membranes swollen by the same solvent and with ¹⁹F NMR spectra. The results will be discussed taking into account the structural models proposed for the solutions and the membranes, the distribution of the spin probe between the solvent-rich and the polymeric pseudophases and the probe orientation and location in solution and membranes.

Supported by the National Science Foundation and AAUW

MEDIUM EFFECTS ON THE ESR SPECTRUM OF THE HYDRATED ELECTRON.
Andrei V. Veselov and Richard W. Fessenden, Radiation Laboratory and Department of Chemistry and Biochemistry, University of Notre Dame, IN 46556.

The ESR spectrum of e⁻ₐq⁻ produced by continuous photolysis of p-cresol anion in water has been studied in the presence of various inorganic salts. The g factor decreases approximately linearly with concentration of the salt. The effectiveness of the various ions in shifting the g factor (the negative of the slope of a plot of g factor against molar concentration) increased with atomic number from approximately 0 x 10⁻⁵ M⁻¹ for Li⁺ to 160 x 10⁻⁵ M⁻¹ for Cs⁺. Somewhat surprisingly, Cl⁻ (with the same charge as e⁻ₐq⁻) was more effective (8 x 10⁻⁵) than K⁺ (5 x 10⁻⁵), with a comparable atomic number. No effect (Δg < 1 x 10⁻⁵) could be seen for OH⁻, SO₄²⁻ or PO₄³⁻. In contrast, the radicals SO₃⁻ and the anion radical of benzoate, were studied with added salt and no (<1 x 10⁻⁵) change in g factor was found for 0.5 and 0.9 M KBr, respectively. The g factor shift can be explained by overlap of the electron wave function with the orbitals on the ions as has been used to explain similar effects for F centers in alkali halide crystals.
ROBUST ESTIMATORS OF SPECTRAL PARAMETERS
C. Yu, H. Halpern, U. Chicago, Chicago IL 60637

The most popular criterion for the estimate of goodness-of-fit of data to an analytic shape hypothesis is the chisquare. Minimization of the chisquare provides optimal fit with this criterion. It assumes that the deviates from the hypothesis are normally distributed (Gaussian distribution). A common criticism of this is its heavy weighting of deviant points. Thus, large variations of the parameters of the hypothesis may result from a small contamination of the data with samples whose deviation is distributed with a much larger variance. Use of a strict least absolute magnitude optimum criterion on the other hand produces instability to small deviations traceable to the discontinuity in the minimization criterion. Other criteria have been proposed that both reduce instability in the face of both small and large deviations, robust estimators. Using a popular robust estimator we compare results with those from the chisquare in extracting parameters from noisy spectra. The differences appear to be negligible for our data, verifying an effective normal distribution of our deviates.

COMPUTER PACKAGE FOR CONVERSIONS, TRANSFORMATIONS AND STANDARDIZATION OF ARBITRARY SYMMETRY SPIN HAMILTONIAN. Czesław Rudowicz and Jian Qin, Dept. Applied Science, City Polytechnic of Hong Kong, Kowloon, Hong Kong

The abundance of spin Hamiltonian (SH) notations and the axis systems used in EPR studies of transition-metal and rare-earth ions at low symmetry sites prevents direct comparison of EPR data and often leads to misinterpretations (see, e.g. Yeom et al. Acta Phys. Polon. 82A, 503 (1992)). To elevate this problem a user-friendly computer package is worked out for arbitrary symmetry spin Hamiltonian including: (1) conversions of the zero-field splitting [ZFS] parameters expressed in several major notations as well as conversions of units, (2) arbitrary (α, β, γ) transformations of SH yielding relationships between ZFS parameters expressed in different axis systems, and (3) standardization (Rudowicz CR, Mol. Phys. 74, 1159 (1991)) of orthorhombic or lower symmetry SH, i.e. confining the ratio b^2^0_0/b^2 to the standard range (0, 1). Our earlier results (CR, Mag. Res. Rev. 13, 1 (1987) and references therein) derived by ALTRAN are here utilized. The package will incorporate also superposition model formulas for arbitrary symmetry. Since the mathematical form of the spin Hamiltonian is identical with the crystal field (CF) Hamiltonian all the functions included in the package will be also applicable to CF Hamiltonian. Thus the package provides a handy kit for direct application by EPR experimentalists, especially, those working on low symmetry systems.


X-band EPR spectra of Mn^{2+} ions in ferroelectric LiNbO_3 single crystal at room temperature are analyzed using spin Hamiltonian of C3 symmetry. Superposition model for the spin Hamiltonian (A) as well as for the crystal field Hamiltonian (B) is worked out. This enables correlation of optical absorption and EPR data. The zero-field splitting [ZFS] energy levels predicted by the model B for Mn^{2+} centre at either the Li and Nb site are compared with those obtained from EPR experiment. The experimental fourth-order ZFS parameters B^0, B^2, and B^4 are compared with those predicted by the model A, i.e. the spin Hamiltonian superposition model. The calculated ZFS energy levels as well as the fourth-order ZFS parameters for Mn^{2+} center at the Nb site agree better than those for Mn^{2+} center at the Li site with the respective experimental values. This confirms that the spectra of Mn^{2+} in LiNbO_3 can be attributed to Mn^{2+} ions at the Nb sites.
A FULL HAMILTONIAN TREATMENT OF THE EFFECTS OF ZERO-FIELD SPLITTING ON CW-EPR SPECTRA OF Mn(II) Alan R. Coffino and Jack Peisach, Department of Molecular Pharmacology, Albert Einstein College of Medicine, Bronx, NY 10461.

Continuous Wave Electron Paramagnetic Resonance (CW-EPR) techniques are commonly used to study metalloproteins containing high-spin ions such as Mn(II) (S=5/2, I=5/2). A complication of the EPR properties of Mn(II) arises from the zero-field splitting. Previous theoretical approaches have been limited to treating the ZFS with perturbation-type methods. These have met with moderate success when simulating the -1/2 -> +1/2 electron transition at or above 35 GHz for small values of the ZFS. When either the ZFS term becomes too large or the frequency small, these methods have not been successful. Also, they have not been useful when treating the higher-order electron transitions for Mn(II), which have been demonstrated to be of particular importance for the wealth of ZFS that they contain (A.R. Coffino and J. Peisach, J. Chem. Phys., 97, 3072-3091, 1992). We have developed an algorithm for the simulation of CW-EPR spectra of Mn(II) which includes ZFS and involves diagonalization of the full Hamiltonian. This program is capable of examining the contributions from all terms in the Hamiltonian and distinguishing between the CW contributions from the 5 individual electron transitions for Mn(II).


The VHF (95 GHz) EPR technique has been applied to study the structure-spectral relationship of a homologous series of thiophenic compounds. Two successful methods to generate the cation radicals of thiophenes have been found. The g matrices of the thiophenic radicals have been obtained for the first time. The small differences between anisotropic components of a g matrix can be unambiguously resolved. Correlations of the experimentally measured g matrices with the molecular and electronic structures are reported. The g-shifts are observed to linearly correlate with the HMO λ; the largest components of the g matrices are proportional to the σ spin densities on sulfur for the homologous series. In addition, the small proton hyperfine interactions of dibenzothiophene (DBT) have been observed by CW VHF EPR. A multifrequency approach (including an auxiliary measurement of S-band ESEEM) has shown that a single set of spin Hamiltonian parameters can be used to describe the spin system of DBT over a microwave frequency span of 3 to 95 GHz. These newly available, detailed, and accurate data provide a valuable opportunity to test, and perhaps to improve, the existing theoretical models for predictions on the g matrices of organic radicals. Work supported by the U.S. DOE, the Illinois Department of Energy and Natural Resources (through ICCI), and NIH (through resource grant RR01811).

Molecular dynamics play a key role in determining and predicting the efficacy of transition metal magnetic resonance imaging (MRI) contrast agents. We have used EPR and nuclear magnetic relaxation dispaersion (NMRD) data on dendrimer-bound and free metal chelate complexes with \( \text{VO}^{2+} \) and TEMPOL to obtain precise dynamical information, as well as provide an expanded data base of paramagnetic center/proton relaxation. Both the NMRD and EPR data are consistent with a significant increase in the rotational correlation time on binding chelate to dendrimeric polymer. The NMRD profiles show a peak in the high-field region (6-60 MHz proton Larmor frequency), consistent with increasing \( \tau_{r} \). Correlation times of \( 0.7 < \tau_{r} < 2.7 \) ns are measured by EPR over physiological temperatures, which are much larger than 0.1 ns as predicted by other authors. These results confirm qualitatively the predictions of the Solomon-Bloembergen-Morgan (SBM) theory, and provide an excellent platform from which to expand our understanding of motional effects on contrast agent-proton relaxation. Research supported by NIH (GM42208 and 5T32-CA-09067 with resources provided by RR01811).


Polymer materials are often used for food packing and for experimental and sampling equipment. Oxygen and other gases could diffuse through the polymers and this would affect the application of the polymer. We suggest a simple and accurate method of measuring oxygen diffusion based on new oxygen-sensitive EPR probes (lithium phthalocyanine, fusinite and carbohydrate chars). The method was applied in temperature studies of oxygen diffusion through teflon and polyethylene tubings. The kinetics of oxygen permeability of teflon tubing in the temperature range 260-350 K was fitted to an Arrhenius expression. The activation energy for oxygen diffusion was 12 kJ/mol. In another application the characterized teflon tubing was used to study the temperature dependence of cellular respiration of neuroblastoma cells. The work was supported by NIH grants RR01811 and GM 42208.

ANISOTROPIC MOTION IN SPIN-LABELLED LIPIDS STUDIED BY MULTIFREQUENCY SATURATION RECOVERY EPR, Bruce H. Robinson, Colin Mailer, Jun-Jie Yin and James S. Hyde, Department of Chemistry, University of Washington and Medical College of Wisconsin.

The multifrequency saturation recovery spin-lattice relaxation time data in spin labelled lipids reported at the 1992 Rocky Mountain Conference (Poster #124) have been completely and quantitatively explained by a combination of three mechanisms—spin rotation, spin diffusion and electron-nuclear coupling—under the influence of anisotropic rotational Brownian dynamics. The stearic acid spin label T1e results are best fit by motion about the lipid axis 50 times faster than perpendicular to it.
A BIOMODEL COPPER SYSTEM IN DIFFERENT MOTIONAL STATES: A MULTIFREQUENCY EPR STUDY. Riccardo Basosi, Rebecca Pogni, Giovanni Della Lunga, Department of Chemistry, University of Siena, 53100 Siena, Italy.

In the analysis of copper in bioinorganic systems, high quality information can be extracted from multifrequency EPR according to Hyde's pioneer work of the last decade. Studies on frequency effects on relaxation times and linewidths and critical testing of theoretical simulations are reported in this paper for a model system in solution. The aim is determination of effective Spin Hamiltonian parameters for copper complexes under a broad range of motional conditions. The Cu-GlyHis model was found suitable for analysing the slow motion conditions obtained by adding highly viscous glycerol to water solutions. Slow motion computer programs originally created by J. Freed for spin labels were modified to extend their application to copper complexes of biological interest. Nonsecular terms, which are not negligible for metal ions at low frequency, and spin–rotational contributions were taken into account. Attention was focused on hyperfine interaction for copper-nitrogen in solution under fast and slow motion limit conditions. The Convolution Theorem was used under the reasonable assumption of purely isotropic hyperfine interaction for nitrogens, to simulate EPR spectra of the model systems with a wide range of correlation times. A simple method for baseline correction was made necessary for massive use of "best fit" programs.

IN VIVO NITROXIDE PHARMACOKINETICS BY S-BAND EPR SPECTROSCOPY
Andrei Komarov and Ching San Lai, Biophysics Research Institute, Medical College of Wisconsin, 8701 Watertown Plank Road, Milwaukee, Wisconsin 53226

A non-invasive S-band EPR method has been used to study the in vivo distribution and metabolism of more than twenty different nitroxide radical compounds by monitoring continuously the nitroxide EPR signal in the blood circulation of the mouse tail. After intravenous injection of the nitroxide agent through the base of the tail vein, the animal was housed in a restrainer to reduce its mobility; no anesthetic agent was needed. Other important features of this study include the use of S-band (3.5 GHz) loop-gap resonator, which increases the sensitivity by at least three folds, compared to that of the L-band methods (1.4 GHz) used previously by other investigators in similar studies. Comparison of the in vivo decay kinetics of six pairs of the five-member and the six-member rings of the nitroxide compounds with same functional groups showed that the $t_{1/2}$ values of the former are 2 to 20 times longer than those of the latter. This S-band method should be useful for studying in vivo pharmacokinetics of free or encapsulated nitroxide drugs in the blood circulation of small animals under conscious conditions.

IN VIVO DETECTION OF NITRIC OXIDE BY S-BAND EPR SPECTROSCOPY
Andrei Komarov, David Mattson, and Ching San Lai, Biophysics Research Institute, and Department of Physiology, Medical College of Wisconsin, Milwaukee, Wisconsin 53226.

Sodium nitroprusside, Na$_2$[Fe(CN)$_5$NO], has been used clinically in the treatment of severe hypertension and myocardial infarction. Its vasodilating effect is attributed to releasing nitric oxide (NO•) which activates the cytosolic enzyme of guanylate cyclase (EC 4.6.1.2). We have used a non-invasive S-band EPR method with Fe(II)-dithiocarbamate (DTC) complexes as trapping agents to detect the in vivo release of NO• from sodium nitroprusside by monitoring continuously the EPR signal of the [DTC-Fe-NO•] complex formed in the blood circulation of the mouse tail. After simultaneously intravenous injection of sodium nitroprusside and the trapping agent, the three-line spectrum of the [DTC-Fe-NO•] complex ($a^0=12.2$ G and $g_{iso}=2.04$) appeared immediately and reached a maximum at 15 to 20 minutes. Hemodynamic effects, including heart rate and mean arterial blood pressure, of sodium nitroprusside with and without the trapping agents were also measured. This represents the first time that nitric oxide is detected in vivo by EPR spectroscopy.
ANALYTICAL AND NUMERICAL METHODS FOR THE PREDICTION AND INTERPRETATION OF THE RESPONSE OF 2- AND 4-LEVEL SYSTEMS TO PERIODIC STIMULATION.
H. S. Mchaourab†, F. Neese‡, and J. S. Hyde† †Biophysics Research Institute, Medical College of Wisconsin, Milwaukee, 53226 and ‡Facultät für Biologie, Universität Konstanz, Konstanz, Germany 7750.

A general theoretical framework has been developed for the interpretation and simulation of multiple quantum (MQ) EPR experiments. This framework is based on the dressed-atom formalism, which permits the prediction of the frequency response of the spin system by application of the principle of conservation of total angular momentum (C. C. Tannoudji et al. Atom Photon Interactions: Basic Processes and Applications, Wiley, 1992). The semi-classical Floquet theory can then be used to solve the equation of motion of the density matrix and to determine the functional dependence of its elements on spectral parameters. This general approach can be used for the physical understanding of the response of a spin system to any periodic perturbation regardless of how complex the interaction Hamiltonian may be. Application of this approach for the simulation of the signals observed in MQ-EPR, MQ-ENDOR, and MQ-ELDOR will be presented. The response of the spin system can also be predicted by numerical integration of the equation of motion of the density matrix. An algorithm based on the stiff Euler method was developed and used to obtain the two-dimensional field-frequency spectrum of a two-level system under a variety of steady-state periodic excitation schemes. The result is shown to be consistent with the response predicted based on the dressed-atom formalism.

SPIN DEPENDENT TRANSPORT IN A TWO-DIMENSIONAL ELECTRON GAS USING A STRIP-LINE RESONATOR, Ruby N. Ghosh, National Institute of Standards & Technology, Electricity Division, Gaithersburg, MD 20899 and Robert H. Silsbee, Laboratory of Atomic & Solid State Physics, Cornell University, Ithaca NY 14853

A novel magnetic resonance technique, spin-dependent transport (SDT), that can can detect $\leq 10^8$ spins has been developed. SDT was utilized to measure the scattering of conduction electrons by neutral impurities in a Si two-dimensional electron gas (2DEG). A specially designed field-effect transistor that operates at 4K was fabricated and a strip-line resonator was incorporated into the transistor gate to couple microwave power to the sample. SDT was observed by monitoring the conductivity of the device while modulating the electron spin populations via microwave saturation of the spin resonance. By utilizing the differences in the singlet and triplet state neutral impurity scattering cross sections, the technique provides the first direct measure of neutral impurity scattering. The SDT spectrum was characterized as a function of temperature, microwave power, Fermi energy of the 2DEG, and magnetic-field orientation. A lower bound for the difference in singlet and triplet scattering cross sections was also obtained. The present sample contains $10^8$ spins, which demonstrates the enhanced sensitivity of SDT over conventional electron spin resonance methods. In smaller devices we expect to be sensitive to $10^4$ or even fewer spins and use SDT to probe spin resonance effects in two or lower dimensional structures.
SPIN DEPENDENT ELECTRON-HOLE PAIR RECOMBINATION AND GENERATION PROCESSES VIA A SINGLE DEEP LEVEL IN SEMICONDUCTORS. F. Christopher Rong and Edward H. Poindexter, Army Research Laboratory, EPSD, AMSRL-EP-EC-D, Fort Monmouth, NJ 07703

In semiconductors, an excited electron and a hole may form a pair and recombine according to the spin selection rule of spin angular momentum conservation; therefore, the spin dependent recombination rate may be changed by electron paramagnetic resonance (EPR) transitions between spin allowed and forbidden states of the excited pair. These microwave transitions may be observed by using ordinary EPR techniques if there are enough pairs; however, they can also be observed by electrically detected magnetic resonance (EDMR), in which EPR-induced changes of the recombination rate are detected by electrical measurements such as electrical conductivity and photoconductivity. Recently EDMR has received considerable attention mainly because of its ultra-high sensitivity and its ability to directly probe microscopic electronic structure of electrically-active defects in semiconductor device structures such as p-n junctions. Even though EDMR has been around for more than 20 years, it is still poorly understood. The objective of this talk is to review our current understanding of EDMR in several important spin dependent recombination processes. In particular, we will review Kaplan-Solomon-Mott spin dependent recombination model which is a phenomenological model that highlights the concept of pair but does not consider any particular recombination mechanism; therefore, it is not completely adequate for EDMR application on defects in semiconductors. We have developed a model to explain not only the relative intensity of EDMR signals, but also spectral features that have been observed in most EDMR studies, based on a modified Shockley-Read model in which spin dependent recombination and generation processes can occur directly at a single paramagnetic deep defect without the need for other defects nearby. Specific aspects of this model will be related to recent EDMR studies.


The scanning tunneling microscope is a new revolutionary technique which is capable of atomic resolution. The principle of operation together with results which will illustrate the possibilities of the technique will be given. Then, several ESR-STM experiments will be described. In this technique, the tip of an STM (scanning tunneling microscope) scans a surface which contains isolated paramagnetic spin centers. The individual spin centers are applying a time dependent perturbation on the tunneling electrons, giving rise to a time dependent component of the tunneling current - at the Larmor frequency ($J(\omega_L)$). This occurs only when the tunneling region is close to the spin center. Therefore $J(\omega_L)$ is spatially localized. Reproducibility of the spatial localization together with a reproducible tip dependent frequency shift were observed. In higher magnetic fields the average linewidths together with the fluctuations in the frequency of the signal (probably due to the electric fields near the spin center) are larger. The proposed mechanism is that electric dipole moment oscillations which are modulated by the Larmor frequency (the Zeeman effect) will give a significant $J(\omega_L)$ component close to the tunneling region by modulating both the barrier height and width.

SPIN-DEPENDENT RECOMBINATION AND PHOTO-ELECTRICAL EPR IN IRRADIATED SILICON CRYSTALS AND SILICON DIODES. Leonid S. Vlasenko, Michail M. Afanas'ev, and Marina F. Vlasenko, A.Fl'loffe Physico-Technical Institute, Academy of Sciences of Russia, 194021, St.-Petersburg, Russia.

New effects of the spin-dependent recombination have been studied in irradiated silicon crystals. The model of spin-dependent recombination through excited triplet states of radiation defects have been supposed. On the basis of these investigations new more sensitive EPR methods were developed for study the defects in irradiated silicon. The contribution of different spin-dependent recombination channels was studied in this material. Also, some new EPR spectra of the excited spin-1 states of radiation defects were found. New EPR methods were applied also for study the defects in irradiated silicon p-n junctions and in the commercial diodes. Spin-dependent recombination effects through excited spin-1 states of defects were found in diodes under injection of nonequilibrium carriers without optical excitation.
EDEPR OF DEEP AND SHALLOW RECOMBINATION CENTERS IN A SI DIODE AND IN BULK SILICON. S. Greulich-Weber, B. Stich, J.-M. Spaeth and H. Overhof
University of Paderborn, FB 6, Warburger Str. 100 A, D-4790 Paderborn, Germany

Commercial Si diodes were investigated with electrical detection of the electron paramagnetic resonance (EDEPR) between 3.5 and 300 K. At 300 K a single EDEPR line was observed in 1N4007 diodes which is generally believed to be due to surface defects. At temperatures between 3.5K and 100K we found a new anisotropic hyperfine split EDEPR spectrum that is tentatively interpreted as a P1-C6S pair defect. The dependences of the EDEPR spectrum upon temperature, microwave power and illumination were investigated. The spectrum was also observed with photovoltaic detection. With Photo Conductive Resonance (PCR) and EDEPR we investigated electron-irradiated Czochralski bulk silicon doped with phosphorus. With EDEPR we observed the shallow phosphorus donor, the thermal donors NL8 [1] with defect concentrations of about $10^{14}$ cm$^{-3}$ and $10^{17}$ cm$^{-3}$, respectively, and the SL1 centre [2] with a concentration below $10^{13}$ cm$^{-3}$. In bulk silicon we demonstrate that EDEPR is measured in a thin surface layer of the crystal. The spin dependent recombination processes are discussed which can explain the observations.


SPIN-DEPENDENT RECOMBINATION AT DEFECTS IN Si MOSFETs.
James H. Statthis, IBM Research Division, Thomas J. Watson Research Center, Yorktown Heights, NY 10598

Spin-dependent recombination (SDR) is able to detect as few as $10^7$ spins in a 500 μm$^2$ metal-oxide-silicon field-effect transistor (MOSFET). It is thus a powerful tool for studying defects in semiconductor devices. When electrons are injected into the gate insulator (SiO2) of the MOSFET and accelerated at high fields (>3MV/cm), various reactions occur which result in the generation of new electron traps at the Si/SiO2 interface. These generated traps adversely affect the device performance, and are the primary factor limiting the reliability of advanced semiconductor technology. It is therefore crucial to understand the microscopic mechanisms of interface defect creation in electrically-stressed devices. Using SDR we have revealed, for the first time, that different species of defects are generated in different ranges of field, oxide thickness, and electron fluence. Characterization of the behavior of the SDR signal as a function of temperature, microwave power, and MOSFET bias is beginning to reveal a complete picture of the SDR mechanism, although significant quantitative puzzles remain.
HIGH RESOLUTION SPIN DEPENDENT RECOMBINATION STUDY OF HOT CARRIER DAMAGE IN SHORT CHANNEL METAL OXIDE SILICON FIELD EFFECT TRANSISTORS.

We use extremely high sensitivity Spin Dependent Recombination (SDR) measurements to study hot carrier damage in the near drain region of short channel Metal Oxide Silicon Field Effect Transistors (MOSFETs). The short channel MOSFETs have been damaged via hot hole injection in the near drain region. This damage produces silicon dangling bond defects at the Si/SiO$_2$ interface in a region only 400µm by 0.10µm. The SDR signal to noise ratio is high enough to allow observation of the $^{29}$Si hyperfine spectra of P$_{b0}$ centers. Our results help to clear up several controversies regarding hot carrier damage in MOSFETs and considerably extend the first SDR results on hot carrier damage (J.T. Krick, P.M. Lenahan, G.J. Dunn, Appl. Phys. Lett., 59, 3439 (1991)). In addition, the study reveals the remarkable sensitivity of SDR in dealing with real technological problems in individual transistors in integrated circuits. To the best of our knowledge, the sensitivity in these measurements — $10^2$ to $10^3$ Spins/Gauss represents the most sensitive spin resonance work ever done in solids.

MOLECULAR HYDROGEN, E' CENTERS AND P$_b$ CENTERS IN THIN AMORPHOUS SILICON DIOXIDE FILMS ON SILICON. John F. Conley and P.M. Lenahan, The Pennsylvania State University, University Park, Pa 16802.

By exposing thin films of SiO$_2$ on silicon to vacuum ultraviolet (VUV) illumination (hc/$\lambda \leq 10.2$eV) and subsequently exposing the films to molecular hydrogen at room temperature, we generate two hydrogen complexed E' center defects. One hydrogen complex spectra consists of two lines separated by 74 Gauss; the other consists of two lines separated by 10.4 G. In "thermally grown" SiO$_2$ films on silicon we also observe the creation of P$_b$ center defects at the Si/SiO$_2$ boundary. The P$_b$ centers appear only if E' centers are initially present. In "control" experiments, no P$_b$ signal is generated without paramagnetic E' centers within the oxide. The P$_b$ center generation takes place in approximately the same time period required for the E'/hydrogen reactions. Our observations may help to explain several poorly understood, but technologically important instabilities in metal oxide silicon field effect transistors.
EVIDENCE FOR NITROGEN COORDINATION TO THE DINUCLEAR IRON CENTER IN THE HYDROXYLASE COMPONENT OF METHANE MONOOXYGENASE: AN ELECTRON SPIN ECHO SPECTROSCOPIC STUDY. Chris Bender, Amy Rosenzweig, Jack Peisach, and Stephen Lippard. Biotechnology Resource for Pulsed EPR, Albert Einstein College of Medicine, 1300 Morris Park Avenue, Bronx, NY 10461. Department of Chemistry, Massachusetts Institute of Technology, Cambridge, MA 02139.

Pulsed electron spin resonance was used to examine the coordination sphere of the mixed valence Fe(II)/Fe(III) diiron center in the hydroxylase component of methane monooxygenase from Methylococcus capsulatus (Bath). The electron spin echo modulation obtained is characteristically shallow, like semimethemerythrin and purple acid phosphatases. Linear Electric Field Effect data suggest that the spin is localized. The cosine Fourier transform spectra of modulation data resolve several sets of distinguishable features attributable to $^{14}\text{N}$. Simulations of these data suggest that two types of nitrogens are in the coordination sphere: tentatively assigned as an amino peptide nitrogen hydrogen bonded to the metal complex, and imino nitrogen of a coordinated histidine.


Methylamine dehydrogenase catalyzes the oxidative deamination of methylamine to formaldehyde, ammonia and two reducing equivalents. The active site cofactor, tryptophan tryptophylquinone (TTQ), is formed from two crosslinked tryptophan indole side chains, in which one of the 6-member rings incorporates an ortho-carbonyl structure. Addition of substrate methylamine to MADH leads to rapid two-electron reduction of TTQ and release of product formaldehyde. Release of ammonia requires long distance, single-electron transfer from reduced TTQ to the copper protein amicyanin. To address the fate of the substrate nitrogen atom during the catalytic cycle, we have used electron spin echo envelope modulation (ESEEM) spectroscopy to examine electron-nuclear hyperfine interactions in the TTQ semiquinone intermediate generated by controlled, one-electron oxidation of identical samples of MADH that had been reduced with $^{14}\text{N}$- or $^{15}\text{N}$-methylamine. Comparison of ESEEM spectra of divided envelope modulation, obtained using the stimulated echo pulse sequence at microwave frequencies of 8.8-13.7 GHz, reveals features characteristic of $^{14}\text{N}$ near exact cancellation (at 0.32 T) ($A_{\text{iso}}=2.4$ MHz; $A_{\text{dip}}\leq0.3$ MHz). These results indicate that the substrate nitrogen atom is linked covalently to the semiquinone intermediate. Therefore, the substrate nitrogen is incorporated into TTQ during catalysis, and return of the cofactor to the fully-oxidized state is required for elimination of ammonia. Envelope modulation is also observed from the two indole $^{14}\text{N}$ nuclei, demonstrating that unpaired spin density is delocalized onto both indole rings. Comparison of the indole $^{14}\text{N}$ hyperfine coupling in substrate-generated and dithionite-reduced TTQ semiquinone reveals that the spin density distribution is influenced by chemical transformations at the active carbonyl center. The influence of these changes on the electron transfer reaction will be assessed. Supported by: NIH GM-37300 (G.T.B.), GM-41574 (V.L.D.) and GM-45795 (J.L.M.).

ABSTRACT NOT AVAILABLE
The MD model (microscopically ordered and macroscopically disordered) was used to simulate ESR spectra of 16-PC, 10-PC, 5-PC in multilamellar vesicles of DPPC granicidin A with lipid/peptide ratio ranging from 50 to 1 at temperatures above the gel to liquid crystal transition of DPPC. Simulation results show that:

1. Incorporation of granicidin A (GA) into DPPC greatly induces heterogeneity in ordering of lipid bilayers and only affects the mobility of the lipid slightly. No immobilized boundary lipid was found in GA/DPPC mixtures.

2. As GA is added into DPPC, the average order parameters $<d^2>$ of 16-PC, 10-PC, and 5-PC increase from 0.06, 0.26 and 0.40 respectively (pure DPPC, without GA) to 0.67, 0.86 and 0.80 respectively (DPPC/GA 1:1). The model simulations are consistent with the population of gauche conformer in the lipid chain measured by 5-PC decreasing with increasing GA concentration until a molar ratio of DPPC/GA 3:1 is reached. Upon further increasing the GA concentration, the population of gauche conformer increases. This indicates that low concentrations of GA increase the chain order of DPPC bilayers, however high concentration of GA reduces the chain order in the region near the headgroup.

3. GA increases the $A_{zz}$ component of the $A$-tensor for all three spin probes, indicating that water has deeply penetrated into DPPC bilayers containing GA.

Single crystals of K$_2$[Pt(NO$_2$)$_4$] and K$_2$[Pt(NO$_2$)$_4$] have been grown, X-irradiated at 77K and studied by EPR. The angular variations of the spectra as well as their temperature dependence have been obtained. They indicate that Pt(III) complexes are trapped in the crystal and that the nature of these species is dependant upon the presence of water molecules in the crystal lattice. The crystal structure of K$_2$[Pt(NO$_2$)$_4$], 2H$_2$O is described (that of K$_2$[Pt(NO$_2$)$_4$] is already known). The crystallographic bond directions are compared with the eigenvectors of the $g$ and $195$Pt tensors determined for the radiogenic Pt(III) species. These results give information about the oxidation mechanism of the Pt(II) precursor and about the stabilization of the Pt(III) complex. It is also shown that the EPR signals previously assigned to a Pt(III) species trapped in an X-irradiated powder of K$_2$[Pt(NO$_2$)$_4$], 2H$_2$O were not correctly identified.

Post irradiation dark reactions of thiy1 and peroxy radicals studied by spin trapping. Brymner Mile, Philip Sillman, Christopher C.Rowlands, School of Chemistry and Applied Chemistry, University of Wales College of Cardiff, P.O.Box 912, Cardiff, CF1 3TB, U.K. and A.J.Holmes, Shell Research Ltd., Thornton Research Centre, P.O.Box 1, Chester CH1 3SH, U.K.

Photolysis of trans-2,2'azoisobutane and dialkyl and diaryl disulfides in oxygenated 2-methylbutane at temperatures below 230K results in a very low photosationary state of peroxy radical, because of the high efficiency of the mixed termination reaction to form a thioperoxide.

$$^{1}\text{RO}_{2}^{+} + {\text{R}}S_{\text{-}} 

^{1}\text{RO}_{2}S_{\text{R}} \quad \ldots \quad (1)$$

Surprisingly, after photolysis is stopped there is an immediate threefold rise in the peroxy radical concentration over about a three minute period, which is then followed by a slow decay. This fast illumination dark reaction is not due to the trans/cis 2,2'azoisobutane photoisomerization/thermolysis but is interpreted and accurately modelled using an in-house Shell algorithm, by assuming an irreversible decomposition of the thioperoxide into alkoxy and sulphinyl radicals.

$$^{1}\text{RO}_{2}S_{\text{R}} 

^{1}\text{RO}_{\text{-}} + {\text{R}}S_{\text{O}_{\text{-}}} \quad \ldots \quad (2)$$

followed by regeneration of peroxyls from alkoxy by the reaction sequence.

Values of the rate parameters for a number of these reactions have been measured and Arrhenius parameters $E_2 = 34$ kJmol$^{-1}$, $A_2 = 10^8$ s$^{-1}$, $E_2 = 14$ kJmol$^{-1}$, $A_2 = 10^2$ s$^{-1}$ determined for the decomposition of phenyl and tert-butyl thioperoxides respectively.

Edemagenic gases have been studied to determine physicochemical properties and basic mechanism(s) of response. The reaction of phosgene with nitrene spin traps was investigated using EPR/Spin Trapping techniques. A carbamoyl monochloride intermediate was obtained. Isotopic substitution of $^{13}$C-phosgene was employed to verify the hyperfine coupling constant assignments. Furthermore, applying EPR/Spin Trapping techniques several intermediate species were identified in the reaction of perfluorosobutylene (PFIB) with nitrene and nitroso spin trap agents: a carbon dioxide radical ion ($\text{CO}_2^-$), a carbamoyl monofluoride intermediate ($^*\text{COF}$), and vinyl carbanions of PFIB. Nitrene compounds formed 1,3-cycloaddition products with PFIB under anaerobic and aprotic conditions. Nitroso compounds reacted with carbanions derived from PFIB, which raises the possibility that electron transfer reactions of this type might account for the observed nitroxides. From these studies it appears that the toxicity of PFIB may be correlated with its susceptibility to nucleophilic attack. In the case of phosgene, a propagated electron transfer catalysis may be partially responsible for the pathogenesis of acute lung injury from inhalation of phosgene.

REACTIVE OXYGEN SPECIES PRODUCED IN METAL-CATALYZED OXIDATION OF BIS(TRIFLUOROMETHYL)DISULFIDE (TFD) AND PROTECTION BY ZE$^\text{TM}$. Carmen M. Arroyo, Commander, U.S.A. MRICD, ATTN: SGRD-UV-YY/Carmen M. Arroyo, APG-EA, MD 21010-5425.

Bis(trifluoromethyl)disulfide (TFD), used as an industrial fumigant, was found to generate a thyl free radical as seen by EPR/Spin Trapping. Oxygen appears to be an absolute requirement for thyl radical production. The results obtained in this investigation clearly implicate the production of thyl and reactive oxygen species (ROS), superoxide radical anion and hydroxyl radicals, during TFD autoxidation. The rate of production of these free radical intermediates was found to increase in the presence of iron(III) and copper(II). In addition, the metal ion chelator, DETAPAC, and ROS scavengers, ethanol, mannitol, and PEG-SOD/catalase, were found to inhibit free radical production. Reactive oxygen species were not formed when a high potency zinc plus antioxidant ZE CAPSTM was present. These results provide support for the pro-oxidation of TFD and a protective role for zinc.


The reaction between a chlorine gas and ethane gas in the presence of N-t-butyl-α-phenylnitrone (PBN), α-(4-pyridyl-1-oxide)-N-t-butylnitrotrone (POBN) and 5,5-dimethyl-1-pyrroline-N-oxide (DMPO) were studied:

\[
\begin{align*}
\text{CH}_3\text{CH}_3 \ (\text{g}) + \text{Cl}_2 \ (\text{g}) & \quad \rightarrow \quad \text{CH}_3\text{CH}_2\text{Cl} + \text{H}^+ \\
\text{HCl} + \text{CH}_3\text{CH}_2^* & \quad \Delta H = -5 \text{ Kcal/mol} \\
\Delta H = 17 \text{ Kcal/mol} & \quad \text{An ethyl radical adduct for the three different nitrotrone spin trap agents was obtained. The hydrogen radical adduct was not detected. It appears that the principal reason for these observation is steric, since the abstraction of a univalent atom is energetically more favored.}
\end{align*}
\]

Cocaine is known to be associated with hepatotoxicity in laboratory animals, and there is recent evidence that it also induces liver damage in humans. Cocaine is first N-demethylated to norcocaine, followed by oxidation to N-hydroxynorcocaine (NCNO) and norcocaine nitroxide (NCNO'). On the basis of ESR studies of NCNO with rat liver microsomes, it has been proposed that NCNO' induces hepatotoxicity by futile redox cycling between NCNO' and NCNO at the expense of NADPH. The reaction is reported to be accompanied by formation of superoxide and lipid peroxyl radicals. It has also been reported that the same toxic sequence occurs with rat brain microsomes, leading to the formation of reactive free radicals in the brain. We have reexamined the microsomal metabolism of NCNOH in order to investigate the mechanism more thoroughly. Spin traps (DMPO and 4-POBN) were used to investigate the formation of reactive free radicals, including superoxide, in liver and brain microsomal incubations. Our results showed that brain microsomes are completely inactive, contrary to the literature. In addition, we did not find any NCNO'- or NCNOH-dependent formation of superoxide with either brain or liver microsomes.

ATP-BINDING TO DnaK PROTEIN FROM E. COLI (hsp 70) AS STUDIED BY MEANS OF SPIN-LABELED ANALOGS

Holger Theysen (a), Bernd Bukau (b), Jochen Reinstein (c), Pia D. Vogel (a) and Wolfgang E. Trommer(a), a) Universität Kaiserslautern, b) ZMBH and c) MPI für Medizinische Forschung, Heidelberg, Germany

The binding of ATP derivatives spin-labeled (SL) at N^6 or C8 of the adenine ring or at the ribose moiety (C2',C3') to nucleotide-free DnaK protein from E. coli was studied by ESR spectroscopy. Whereas binding of the N^6 and C2',C3' analogs is very weak, K_d for C8-SL-ATP is about 70 μM with half an equivalent binding per monomer (70 KDa). The ESR spectrum of protein-bound C8-SL-ATP is typical for a highly immobilized species (2 A_{zz} = 55 Gauss). ATP itself prevents binding of C8-SL-ATP.

DnaK modified at a single cystein residue with N-ethyl maleimide is still capable of binding C8-SL-ATP. We are presently investigating DnaK spin-labeled at this position with TEMPO-maleimide and possible interactions with C8-SL-ATP.
EFFECTS OF TEMPOL ON MURINE T AND B CELL PROLIFERATION  *John R. Bobell and Philip D. Morse II., Departments of Chemistry & *Biology, Illinois State University, Normal IL 61761.

In previous unpublished work, we showed that 72 hour exposure of 5 and 1mM concentrations of the nitroxide Tempol inhibited proliferation of Murine T-cells. This may have been a result of increased cell death. We now have data showing inhibition of both T and B cell proliferation by exposure to Tempol for only 8 hours. This inhibition does not appear to be simply a function of increased cell death.

Mixed lymphocyte and macrophage cultures stimulated with either the T cell mitogen ConA (4μg/ml) or the B cell mitogen lipopolysaccharide (25μg/ml) were incubated with 5, 1, 0.5 or 0.1mM Tempol during the first 8 hours of proliferation. The cells were then washed free of Tempol. Uptake of 3H thymidine and cell viability were determined at subsequent times of 24, 48 and 72 hours.

Unstimulated cells show decreased viability over 72 hours compared to proliferating cells. In the presence of 5 mM Tempol, cell viability is similar to that of unstimulated cells. 5mM Tempol inhibits proliferation of T and B lymphocytes. 1mM Tempol showed slight inhibition of proliferation with no decrease in cell viability compared to stimulated controls free of Tempol. Lower concentrations of Tempol had no effect on proliferation or cell viability.

We conclude that Tempol or its hydroxylamine interferes with the mitogenically induced proliferation process itself. The effect of Tempol on the immune system should be considered when contemplating introduction of Tempol into the blood stream for medical purposes.

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EFFECT OF ENVIRONMENTAL CONDITIONS ON THE PARTITION OF ANTHRACYCLINE SEMIQUINONES INTO PC BILAYERS. Antonio E. Alegria, Luis Zayas, and Marilyn Hernández. UPR-Humacao Univ. College, Dept. Chemistry, CUH Station, Humacao, PR 00791-9730 (Supported by Grant NIH-GM08216)

The semiquinones of daunomycin (Dauno) and N,N-dimethyl Daunomycin (DDauno) were generated by the hypoxanthine/xanthine oxidase system in argon-saturated phosphate buffer (pH 7.4) in the presence of egg-yolk phosphatidylycholine multilamellar vesicles (MLVs) containing 1 mol% of a doxylstearic acid (DSA)isomer. The initial rates of DSA destruction were taken as an indirect measure of the preferential location of the generated semiquinone. Larger rates of destruction are obtained for the 12- and 16-DSA isomers which indicates that these semiquinones can localize preferentially about the depth of the 12th and 16th positions of stearic acid in membranes. DSA destruction is due to a reversible reduction of DSA to the hydroxylamine species. No difference in membrane localization depth was detected between Dauno and DDauno which suggests that it is the aglycone semiquinone which partitions into the hydrophobic bilayer. No significant change in preferential depth was detected if buffer ionic strength, pH, membrane charge (33 mol% of phosphatidic acid or stearylamine added to PC) or membrane rigidity (33 mol% cholesterol) were changed, which is evidence for a neutral semiquinone diffusing through the bilayer. However, a dramatic decrease in the rate of DSA destruction is detected if MLVs are enriched with 33% mol cardiolipin. This work shows that anthracycline semiquinones can partition into phosphatidylycholine bilayers under anoxic conditions.
EPR AND ESEEM CHARACTERIZATION OF A "GREEN" TYPE 1 COPPER PROTEIN REDESIGNED FROM THE TYPE 2 COPPER PROTEIN, YEAST Cu,Zn SUPEROXIDE DISMUTASE Chris Bender, Yi Lu, Joan Selverstone-Valentine, Jack Peisach. Biotechnology Resource in Pulsed EPR, Albert Einstein College of Medicine, 1300 Morris Park Avenue, Bronx, NY 10461. Department of Chemistry and Biochemistry, University of California, Los Angeles, CA

Superoxide dismutase normally contains copper and zinc binding sites in which the metals are bridged by an imidazole. Site directed mutagenesis of the histidine residues associated with the metal binding sites have been examined for their effect on the enzyme's spectral properties. One mutation, which replaces His80 with a cysteine, results in a "Green" Type I copper site following copper reconstitution in what was formerly the Zn binding site. The cw-EPR spectrum of the reconstituted site resembles that of stellacyanin, and the FT-spectrum of the electron spin echo envelope modulation indicates that the two metal sites are no longer bridged by a histidine. We shall present cw- and pulsed EPR data of the H80C and other site-directed mutants that illustrate the unique properties of these engineered proteins.

ELECTRON SPIN ECHO SPECTROSCOPIC STUDY OF IRON COORDINATION IN NITRILE HYDRATASE Chris Bender, Haiyong Jin, Mark Nelson, Jack Peisach. Biotechnology Resource in Pulsed EPR, Albert Einstein College of Medicine, 1300 Morris Park Avenue, Bronx, NY 10461. Dupont Company, Wilmington, DE 19880.

We have used electron spin echo spectroscopy to examine the coordination sphere of the non-heme iron of nitrile hydratase, which catalyzes the hydration of nitriles to amines. The FT-spectrum of echo modulation from $^{15}$N-enriched enzyme indicates that there are three nitrogens associated with the iron. As expected, the echo modulation of the enzyme with native $^{14}$N is complicated, however, with the $^{15}$N data as a guide, we are able to extract quadrupole parameters for three nitrogens by spectral simulation. The parametric values fall in the range $\epsilon^2\eta Q < 2.5$ MHz and $0.4 < \eta$, which are consistent with values obtained for imino nitrogen atoms of coordinated histidines.


Odom and Rink (Geology, v. 17, p. 55-58, 1989) and Rink (Dissertation, Florida State University, 1990) investigated the EPR signals from the $E'$ center and oxygen hole-related center (OHRC) in a variety of natural quartz samples. They concluded that the initial concentration of these point defects increased over geologic time due to alpha recoil of atoms in the natural decay chains. This study extends their work to include increases which might be caused by cosmic ray bombardment. A pegmatite vein at elevation 3795 meters on Mt. Evans and a quartz vein at elevation 2377 meters were sampled at depths up to 3.7 and 6 meters respectively and purified quartz separates prepared from each sample. The $E'$ and OHRC EPR signals for the 2377-meter separates were small and changed randomly with depth. These same signals for the 3795-meter separates were several times larger and first increased and then decreased with depth. The rate of decrease is consistent with a mean free path for the bombarding particles of 500 to 600 g/cm$^2$. 
INCORPORATION OF Cu(II) IONS INTO SAPO-37: Cu(II) ION LOCATION AND ADSORBATE INTERACTION DETERMINED BY ELECTRON SPIN RESONANCE AND ELECTRON SPIN ECHO MODULATION STUDIES. Maggie Zamades and Larry Kevan, Department of Chemistry, University of Houston, Houston, Texas 77204-5641.

The Cu(II) species formed in the silicoaluminophosphate type 37 molecular sieve after equilibration with various adsorbates are studied by electron spin resonance and electron spin echo modulation techniques. These results are interpreted in terms of Cu(II) ion coordination and are compared with similar results determined for zeolite type X and Y. In hydrated SAPO-37 a Cu(II)(O)(3H(2)O)2 complex (where O refers to a framework oxygen) is generated. The adsorption of ammonia and pyridine generates a Cu(II) species which is coordinated to three adsorbate ligands. In contrast, the Cu(II) species in zeolite X is coordinated with four adsorbates in a square planar geometry. The Cu(II) species generated in SAPO-37 after the adsorption of ethanol and propanol is tetrahedrally coordinated to three framework oxygen atoms and one ethanol molecule while the Cu(II) species in zeolite X is coordinated to three ethanol molecules. In both SAPO-37 and zeolite X the Cu(II) ion coordinates to three methanol ligands. In SAPO-37 as well as zeolite X the Cu(II) ion is coordinated with two dimethylsulfoxide ligands, however the electron spin resonance parameters are significantly different suggesting that the stereochemistry of these two Cu(II) complexes is not identical.

ELECTRON SPIN RESONANCE ELECTRON SPIN ECHO MODULATION AND ELECTRON NUCLEAR DOUBLE RESONANCE STUDIES OF THE PHOTIOIZATION OF N-ALKYL,N,N',N'-TRIMETHYLENEDIAMINE IN ANIONIC AND CATIONIC MICELLES. Chris Stenland and Larry Kevan, Department of Chemistry, University of Houston, Houston, Texas 77204-5641.

N-Alkyl, N,N',N'-trimethyleneamidens (C-TMB, n = 1,2,3,4,5,6,8) were synthesized and photolized in rapidly frozen anionic and cationic micelles. The photoyields of the cation radicals were investigated by electron spin resonance spectroscopy. Electron spin echo modulation spectroscopy and proton matrix electron nuclear double resonance were used to determine the relative location of the photoproduced cation radical with respect to the deuterated aqueous interface. No dependence on the photoyield as a function of the electron donor alkyl chain length is observed, although increasing the alkyl chain length on the benzidine moiety moves its location towards the aqueous interface. The lack of a photoyield trend is interpreted in terms of the solubilization geometry which determines the paths of electron escape to form charge separated products. An electron escape cone defined as the solid angle formed from the center of the electron donor moiety through the width of the spin distribution that intersects the interface changes only slowly as a function of radial location over a limited range, hence the photoyield is little changed.


To obtain ENDOR signals from the primary electron acceptor, which in the native bacteria is a ubiquinone (Q(ox)) magnetically coupled to an Fe, it is necessary to replace the Fe atom in the reaction center (RC) by a diamagnetic atom, e.g. Zn. The replacement was accomplished in 2 ways: By (1) biosynthetic growth or by (2) site specific mutation, histidine to cysteine at 266M in the region of the Fe. Method (1) produces 20 to 30% Zn replacement compared to >90% for method (2). The reduction of Q was accomplished by the addition of diithionite to the crystal. The proton ENDOR spectra reveal small differences between the two preparations but the mutant is a good approximation of the native Qz ENDOR spectra. The ENDOR spectra provide hydrogen bond information that cannot be directly obtained from the present X-ray structure of the RC. In Qz three types of protons have been identified: the methyl, the methine and the exchangeables. The latter are interesting for understanding electron transfer interactions. The complete methyl proton hyperfine tensor has been obtained for the mutant and progress has been made toward obtaining the methine hyperfine tensor.

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MAGNETIC SUSCEPTIBILITY EFFECTS ON EPR SPECTRA. Minory Sueki, Sandra S. Eaton, and Gareth R. Eaton, Department of Chemistry, University of Denver, Denver, Colorado 80208

The first-derivative CW EPR spectrum of polypyrrole deposited on gold wire, tungsten wire, platinum-coated tungsten wire or platinum foil is a singlet with a peak-to-peak linewidth of 0.2 to 0.4 G. However, when a film of polypyrrole is deposited on platinum or palladium wire (1.0 mm diameter), the X-band signal is an apparent doublet with a splitting of 0.6 G (Pt) or 2.2 G (Pd), which is attributed to the perturbation of the magnetic field by the relatively high magnetic susceptibility of the wire. The splitting of the polypyrrole signal on 0.25 mm diameter Pd or Pt wire increased as the external field was increased with S-band (1260 G) < X-band (3270 G) < Q-band (12550 G). The variation in magnetic field around the Pt and Pd wires was confirmed by spectral-spatial EPR imaging at X-band. The splitting of the EPR signals and the spatial variation of the magnetic field in the images are in good agreement with calculations of the effect of an infinitely long cylinder of magnetic material on a static magnetic field.


Loop-gap resonators have been constructed using copper-coated Teflon, solid copper sheet, and other materials. Depending on the application, resonators can be attached directly to the EPR sample tube to yield high filling factors. Impedance-matching circuits have been produced on high-dielectric substrates. Experience with inductive and capacitive coupling, and with varactor-tuning of the coupling, will be described. The relation of resonator design and coupling to signal and noise in the EPR spectrum will be presented.

A PULSED S-BAND ESR SPECTROMETER. Janusz H. Hankiewicz, Christopher Stenland, and Larry Kevan, Department of Chemistry, University of Houston, Houston, Texas 77204-5641.

A computer-controlled pulsed ESR spectrometer operating at S-band (2 - 4 GHz) was designed for the study of weak interactions between paramagnetic centers and surrounding magnetic nuclei by electron spin-echo modulation (ESEM) techniques. The incorporation of loop-gap resonators gives good sensitivity and allows use over the full octave bandwidth range. Free induction decay and electron spin-echo signals at room temperature and at liquid helium temperature are shown in selected sample types. The expected increase of the electron spin-echo modulation depths relative to X-band (∼ 9 GHz) frequencies is demonstrated. Evidence of proton modulation in nominally pure C₆₀ is shown.
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NOISE REDUCTION USING BALANCED RF POWER DELIVERY AND AN AUTOMATIC COUPLING CONTROL FOR VERY LOW FREQUENCY EPR
H. Halpern, C. Yu, M. Peric and E. Barth, U. Chicago IL 60637

RF power is usually delivered to low frequency EPR spectrometers via coaxial conductors due to the prohibitive size of waveguide at longer wavelengths. Others have noted the reduction of ground loop noise by transforming the voltages from this unbalanced system to a balanced system (a balun). In the context of a capacitive coupling system we have applied balanced power delivery to our EPR resonators. We present spectra indicating a factor of three noise reduction under conditions of low modulation fields and power. This may be due either to the theoretical reduction of the ground loop voltages and currents by a factor of two or the elimination of the need for a ground connection altogether (the resonator floats). We are implementing balanced automatic coupling control to the balanced capacitive coupling of a 250 MHz spectrometer. This strategy can be applied as easily to inductive coupling as to capacitive coupling. The benefits of this system with high modulation fields and powers is currently under investigation.

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A LOW FREQUENCY EPR SPECTROMETER SYSTEM FOR IN-VIVO APPLICATIONS.
Janusz Koscielniak, Lawrence J. Berliner, Department of Chemistry, The Ohio State University, 120 W. 18-th Ave., Columbus OH 43210.

The next generation of CW ESR spectrometer for in-vivo applications developed in LIVERS laboratory operates at frequencies 100-1000MHz. This wide frequency range will allow us to explore in greater details the frequencies below L-band in order to optimize object size versus frequency for variety of resonators and biological sample sizes. Microwave bridge uses HP 8657A Synthesized Signal Generator as a microwave source and the design is based on L-band bridge design presented last year1. The system uses no standard spectrometer console. Instead the DSP Lock-In amplifier (model SR850 from Stanford Research) performs all functions usually associated with consoles including computer data acquisition. Several performance aspects have been already tested with loop-gap and re-entrant type resonators and spectra are presented.

1 Koscielniak J., Berliner L.J. 34rd Rocky Mountain Conference, Poster 154, Denver, Aug 2-6, 1992

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A PROBEHEAD WITH INTERCHANGEABLE LOOP-GAP RESONATORS AND RF COILS FOR MULTIFREQUENCY EPR/ENDOR. T. Christidis, W. Francisz, T. Oles, and James S. Hyde.

It is extremely desirable to have a single probehead for multifrequency magnetic resonance. In this work, we describe a probehead that can be used for EPR/ENDOR spectroscopy from 1-10 GHz. The probehead employs loop-gap resonators. A precision coupling mechanism allows accurate magnetic coupling of the microwaves to the resonator. The Rexolite support of the loop-gap resonator acts as a spool for the ENDOR rf coil. The coil and resonator can be easily changed to cover the range of 1-10 GHz. Preliminary ENDOR measurements have been made on liquid samples at X and S bands. Due to the rf enhancement, the nitrogen ENDOR enhancement of tempone dissolved in n-heptane at 2.3 GHz is 15 times larger than that at 9.3 GHz.
VERSATILE SATURATION RECOVERY SPECTROMETER. Susanne Pfenninger, Joseph Ratke, Theodore Camenisch, Jun-Jie Yin, Christopher C. Felix, and James S. Hyde. Biophysics Research Institute, Medical College of Wisconsin, Milwaukee, WI 53226

A new, more versatile saturation recovery spectrometer is being constructed utilizing commercially available fast digital signal processors (DSP Technology, Inc). The timing of the spectrometer is controlled by a 200 MHz oscillator that is also used as the external clock of the transient recorder. Two 10 MHz outputs trigger the pulse generators (Stanford Research System, Inc). The averager supports an addition and subtraction mode for suppression of switching transients and baseline corrections using field modulation. With our design, it is possible to measure both very short (100 ns) and very long (10 ms) decays, which gives a better insight into relaxation mechanisms. The use of a commercially available signal processor facilitates transfer of the spectrometer design to other laboratories. The instrument is configured to permit switching between our X-band and multifrequency (S- and K-band) saturation recovery spectrometers. Because the saturation recovery signal is d.c., the detection is very sensitive to microwave reflections or baseline drifts. Switching transients of the microwave switches and the biphase modulator as well as reflections from the resonator have been studied. The reduction of the deadtime is very important for short or multi-exponential saturation-recovery signals. Preliminary results are shown for reduction of the deadtime by switching the Q-value of a loop-gap resonator between the excitation and detection periods.

METHOD FOR ADJUSTING THE Q-VALUE OF AN EPR RESONATOR. Susanne Pfenninger, Wojciech Frąncisz, Jörg Forrer, Juan Luglio and James S. Hyde. Biophysics Research Institute, Medical College of Wisconsin, Milwaukee, WI 53226, Institute for Molecular Biology, Jagiellonian University, 31-120 Krakow, Poland, Laboratory of Physical Chemistry, Swiss Federal Institute of Technology, CH-8092 Zürich, Switzerland.

It is customary to adjust the loaded Q-value of EPR resonators by over- or under-coupling, which results in large reflected power. We present a method in which the unloaded Q-value can be switched during the experiment over a range of temperatures from 300 to 4 K. A PIN diode is coupled inductively or capacitively to the microwave structure. The change of the Q-value is determined by the amount of the forward resistance and the coupling. The setup is shown for the five-loop four-gap resonator (Medical Advances, Milwaukee, WI) and the bridged loop-gap resonator. The maximum decrease of the Q-value for a critically coupled resonator is about a factor of 9. The coupling range is the limiting factor for the adjustable Q-value range assuming critical coupling. A resistor rather than a PIN diode can be used at low temperature for multiple frequency experiments including ELDOR and multiquantum EPR. The applicability of the PIN diode for Q-value control is limited by the maximum rating of the power dissipation and reverse voltage. It is very promising for reduction of the deadtime in time-domain EPR spectroscopy. By combination of this structure with a varactor, switching of the Q-value while maintaining critical coupling is possible.
SENSITIVITY IMPROVEMENT OF LOW POWER OR PULSED EPR SPECTROMETERS
Susanne Pfenninger\textsuperscript{a}, Wojciech Francisz\textsuperscript{b}, and James S. Hyde\textsuperscript{a}. \textsuperscript{a}Biophysics Research Institute, Medical College of Wisconsin, Milwaukee, WI 53226, \textsuperscript{b}Institute for Molecular Biology, Jagiellonian University, 31-12 Krakow, Poland.

Sources of noise in spectrometers can arise from the microwave source, the microwave amplifier environmental microphonics, electrical grounds, or thermal noise of the resonator. We present a sensitivity improvement for pulsed or low power EPR spectrometers, where the source noise is low, using a X-band cryogenic preamplifier from Berkshire with a noise figure of 0.5 dB and a gain of 30 dB. Calculations and measurements are in good agreement and show that the limiting noise source is the thermal noise of the resonator and not the preamplifier when it is cooled. An increase of the signal-to-noise ratio by a factor of 1.8 has been measured by cooling the resonator from 294 K to 28 K if we neglect the difference in the Boltzmann factor. If the noise figure of the preamplifier increases or the losses of the resonator to the preamplifier are high, the improvement in the signal-to-noise ratio by cooling the resonator decreases quickly. The cryogenic preamplifier shows almost a constant noise figure as a function of the demodulation frequency of the signal down to 5 kHz. It is also advantageous to use the preamplifier for ENDOR spectroscopy or for samples where the demodulation frequency must be lowered because of rapid passage effects.

STOPPED-FLOW EPR BASED ON A DIELECTRIC RESONATOR: ELIMINATION OF TRANSIENT ARTIFACTS - A SENSITIVE, ROBUST AND LOW COST DESIGN. Andrzej Sienkiewicz, Jinjie Jiang, Kunbin Qu, and Charles P. Scholes, Department of Physics, State University of New York at Albany, Albany, NY 12222.

Dielectric resonators (DRs) have proved useful for enhancing EPR sensitivity, especially for small, high dielectric loss, aqueous samples. We have combined the DR with the stopped-flow apparatus (Update Instrument, Inc.) in order to improve the EPR signal detection in stopped-flow kinetic studies. The DR was designed around a pair of stacked ceramic cylinders (X-Band Murata Erie resonators). This structure was coupled to the microwave line using a loop, located close to the side of the stacked ceramic resonators. For small, low loss samples the sensitivity was approximately 30 X that of the TE\textsubscript{102} and for aqueous samples the signal enhancement factor was close to 15 (for the same number of spins). Signal enhancement (up to 50\%) was also observed when the DR-based structure was compared to our stopped-flow EPR, designed around a loop gap resonator (Medical Advances, Inc.). For stopped-flow EPR, the DR-based design gave much improved elimination of transient, stopping-induced artifacts because it better separated microwave electric field E, from the sample position. The DR is easily assembled or disassembled and is mechanically robust. The entire structure was made with readily available plastics and commercially available ceramic resonators.
DEVELOPMENT OF HIGH SENSITIVE PORTABLE ESR SPECTROMETER

Akio Nakanishi, Nahoko Sugahara and Hitoshi Yamamoto
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We have developed the portable ESR spectrometer useful for practical measurements using a small magnet circuit with the strongest permanent magnet (NEOMAX). The magnet circuit produces a strong magnetic field with the homogeneity of 93 ppm in a 5×20' volume and two coils wound around pole pieces sweep linearly the magnetic field of 300 Oe. Temperature stability of the magnetic field is about 40 ppm/°C. The microwave circuit is assembled compactly with semi-rigid coaxial microwaveguide and no need to adjust. The electric circuits are composed of digital devices. So a personal computer is available for the control of system and the analysis of experimental results. The spectrometer is very small compared with the commercial ones. The sensitivity is 3×10^10 spins/Oe. As hyperfine structure of Perylene cation radical in concentrated H_2SO_4 is split clearly, the resolving power is below 0.5 Oe. Alanine samples irradiated 10 Gy to 30 Kgy were measured by this spectrometer. The signals with enough high S/N ratio were obtained. Each signal disperses less than about 2% and shows a good linear correlation with the irradiated dose. The characteristic of the spectrometer and the measured results of some materials are reported.


This poster reports the results of a 9 GHz CW-EPR study of the temperature dependence of the S_3 symmetry spin Hamiltonian parameters describing the Mn^{2+} central transition HFS spectrum observed in calcite and coal. The objective was to obtain further quantitative evidence to support the conclusion that the Mn^{2+} spectrum observed in coal arises from Mn^{2+} impurity ions in the calcite mineral impurity component. These measurements confirm this conclusion since the temperature dependence of the spin Hamiltonian parameters agree to within ~5%.


This poster describes the results of a γ-irradiated human hair study using a 9 GHz CW-EPR. This study was motivated by the potential of using the time dependence of the EPR spectral intensity to estimate the dose received when humans are exposed accidentally to ionizing radiation. It is shown that the radiation centre in hair is characterized by a single decay constant with k = 0.0205 (11) s^{-1} for initial doses between 50 and 600 Gy. This enables human hair to be used as a dosimetric sample for accidental irradiation with an accuracy of ~5% provided that the EPR measurements are initiated within ~30 hr.
EPR-RELATED DATABASE PROJECT - FEASIBILITY STUDY REPORT. Czeslaw Rudowicz, Dept. Applied Science, City Polytechnic of Hong Kong, Kowloon, Hong Kong

EPR studies provide a wealth of information, which can be best utilized if available in a computer-searchable form. The proposed EPR-database is perceived as a service to the EPR community under the auspices of the International EPR Society. As the first stage of development an EPR-database questionnaire has been worked out and dispatched, starting in late 1991, to about 900 researchers active in the EPR area within the last decade. The questionnaire comprises, among others, questions on the preferred spin Hamiltonian notation, the axis systems, zero-field splitting parameter notations and units, most useful data types, important compounds/materials, ions/species as well as technical questions on the database structure and organisation. The potential users' requirements could thus be investigated. However, the response rate has been rather low so far. In this Report we present the analysis of about 70 valid responses received to date. At the second stage we plan to produce and test a small-scale prototype. To this end a detailed study of the data structure and possible query system has recently been carried out. The results are also presented to encourage wide consultation. For successful development of a full-scale EPR-database the feedback and strong support from EPR community as well as from the IEPRS is vital.

SIMULATION OF LOW SYMMETRY EPR TRANSITIONS BY MATHEMATICA PROGRAMS. W.K. Siu and Czeslaw Rudowicz, Dept. Applied Science, City Polytechnic of Hong Kong, Hong Kong

Solutions to several problems in EPR of the transition-metal ions can be easily visualized using MATHEMATICA. A set of MATHEMATICA programs is worked out for systems with spin $S = 1, 3/2, 2, 5/2$ at tetragonal, trigonal (including in both cases the "imaginary" zero-field splitting [ZFS] terms), orthorhombic, monoclinic and triclinic symmetry. For $S \geq 2$ the fourth-order ZFS terms are included. The package consists of three simulation programs: (1) ELEVELS - for energy levels versus the magnetic field for $B \parallel x, y$ or $z$-axis and arbitrary orientation, (2) MAGSUSC - for magnetic susceptibility versus temperature both for single crystal and powder and (3) RESFIELD for resonance fields, i.e., the predicted EPR transitions as a function of the ZF parameter $B^0_2$ (with other $B^q_k$ fixed) versus $B$. All the simulated data may be either plotted on screen or stored in a file. The programs can be run on a PC in MATHEMATICA environment. All three programs can visualize the significance of the fourth-order and low-symmetry ZFS terms. ELEVELS can visualize also the energy level crossings, whereas RESFIELD enables also initial estimates of ZFS parameters for least squares fitting of EPR spectra. The usefulness of the package is twofold - it may help: a) experimentalists in interpretation of EPR spectra and b) teaching students basic ideas about EPR and magnetic susceptibility.

Recently, EPR studies of carbonaceous materials have become more interesting because of successful application of such materials as paramagnetic gas probes (e.g. oxygen sensors) in biology and experimental medicine. Carbonaceous materials usually exhibit single-line EPR spectra because of substantial spin delocalization and strong exchange interaction. Here we report a weak EPR resonance (satellite or "half-field" line) at exactly half of the main resonance field in some synthetic carbohydrate chars. The satellite line has a lineshape similar to the main resonance and was observed in experiments with longitudinal as well as with transverse microwave excitation. The observed satellite line may originate from a strong coupling between a few spins within isolated aromatic clusters or from a low-dimensional spin-exchange network within the solid. The EPR results are compared with temperature- and field-dependent SQUID data on static magnetic susceptibility. Work supported by grants from US DOE and NIH (GM42208; resources provided by RR01811).


The W-band (95 GHz) EPR spectrometer at Illinois EPR Research Center was designed as a multi-purpose scientific instrument. The capabilities of the spectrometer have been extended by adding a fast magnetic field sweep system (maximum 1000 G sweep in a minimum of 1 sec.) and a specially designed cryostat for variable temperature studies (2-300 K) with a vacuum-tight microwave window. The fast sweep system employs a room-temperature water-cooled solenoid and a modified Techron (Techron, IN) power supply. The modified Ultrastab 864U Current Transducer System (GMW, CA) was used for stabilization of the current through the coil (with 15 ppm stability). The sweep system features a digital scan with 14 bit resolution. Some applications are described. The W-band system is a part of a NIH Biomedical Technology Research Resource (supported by grant P41-RR01811) and is accessible to others for collaborative or service use.

DIRECT OBSERVATION BY ESR OF ELECTRON SELF-TRAPPING IN PURE PbCl₂ CRYSTALS. Dirk Schoemaker, Sergiu Nistor, Etienne Goovaerts, Physics Department, University of Antwerp (UIA), B-2610 Antwerp, Belgium.

Direct experimental evidence is reported for the self-trapping of mobile electrons produced at 80 K either by x-ray irradiation or by UV-illumination across the bandgap, in single crystals of pure PbCl₂ which possess orthorhombic (D₁₉₃) symmetry. The analysis of the ESR spectra demonstrates that the electron is trapped at a pair of nearest neighbor substitutional Pb²⁺ ions, along the crystallographic direction, resulting in a paramagnetic Pb²⁺ molecular ion. Its electronic configuration is complementary to that of the self-trapped hole (V₉) center in the alkali halides, i.e., a singly occupied σ₂ ground orbital composed of a ⁶p-6s hybrid. The analysis of the Pb²⁺ hyperfine structure originating from interaction with one or two naturally abundant ²⁰⁷Pb isotope nuclei, with spin I = 1/2, shows that the molecular bond is bent in the a-c plane by about 33 degrees from the a direction. The main reason for electron self-trapping on two Pb²⁺ ions derives from the substantial ⁶p character of the PbCl₂ conduction band.

With a very-high-frequency (W-band, 95 GHz) cw spectrometer and a low-frequency (S-band, 2-4 GHz) pulsed spectrometer, we have studied surface-bound nitroaromatic radicals which are produced on activated metal oxide surfaces by catalytic action of molecular oxygen. Here, nitrobenzene and meta-dinitrobenzene (mDNB) on activated alumina and magnesia are reported. The W-band spectra show g-resolution and sufficient hyperfine resolution of one N in each case to provide good spin-Hamiltonian matrices. The S-band ESEEM patterns report modulations from the other N-14 or N-15 nucleus in mDNB and from Al, Mg, and O-17. Analysis of these modulations provides (1) details of weak nitrogen coupling including nuclear quadrupole coupling information, (2) demonstrations of the "exact cancellation" effect previously described by Singel et al., (3) a clue to the fate of the molecular oxygen catalyst, and (4) structural information about the surface binding sites and bound radicals. The work used resources of the NIH Biomedical Research Technologies Program (P41-RR01811) and was supported by grants from the US Department of Energy and National Institute of General Medical Sciences (GM42208).

CHARACTERIZATION OF PARAMAGNETIC PROBES FOR DIRECT DETECTION OF GASEOUS NO BY EPR. Shong-Wan Norby, Alex I. Smirnov, and R. B. Clarkson, Illinois EPR Research Center, University of Illinois, 190 MSB, 506 S. Mathews, Urbana, IL 61801.

The demonstration of NO formation (1989) by an enzyme in vascular endothelial cells has led to new extensive biological research. The existing methods of NO detection are usually indirect, complicated, and/or insensitive to low level of NO. The need for a simple, direct method for NO measurement prompted this study. That NO can reversibly change the width of EPR signal of some carbonaceous material was described 30 years ago by Singer. We have explored 3 classes of paramagnetic probes for measuring NO: They are (1) nitroxide N\textsuperscript{15}PDT (pre-deuterated tempone), (2) LiPc (lithium phthalocyanine) and (3) fusinite (a type of coal) and synthetic carbohydrate chars. The NO effect on EPR linewidth of these probes is very similar to that of O\textsubscript{2} reported in our previous oximetry studies. In essence, the linewidth change is the result of modulation of spin exchange at the surface sites and/or spin-spin exchange interaction. Measurements of NO have to be made in an oxygen-free environment due to the effect of O\textsubscript{2} on the linewidth. This study is supported by grants from NIH (GM42208; resources provided by RR01811) and DOE.

HYDROCARBON CONTAINING PARAMAGNETIC CENTERS IN SILICON DIOXIDE THIN FILMS, Mark Hoinik, B. C. Nguyen\textsuperscript{*}, Maria L. Galiano\textsuperscript{*}, and Mark S. Crowder, IBM Research, 650 Harry Road, San Jose, CA 95120 and \textsuperscript{*}Applied Materials, 3100 Bowers Avenue, Santa Clara, CA 95054.

Silicon dioxide thin films, deposited by the plasma-enhanced chemical vapor deposition (PE-CVD) of tetraethyloxythosilicate (TEOS) and oxygen were investigated by electron paramagnetic resonance (EPR) spectroscopy. Thin film oxide deposition results from the decomposition of TEOS to form silicon dioxide on a substrate surface. If the ethyl groups of TEOS or fragments of these groups are incorporated into the film during deposition, there will be hydrocarbon groups incorporated in the film. A paramagnetic center associated with a methyl group was detected in films deposited at 360 C. The methyl-associated center was found to anneal at temperatures greater than 500 C. Thin films annealed between 700 C and 950 C displayed a paramagnetic signal which is identified as a dimethyl-associated center. S-band and X-band EPR spectra indicate that the dimethyl-associated center contains axial hyperfine coupling constants and g-values. These findings clearly indicate that hydrocarbon components are incorporated in silicon dioxide thin films prepared by PE-CVD of TEOS.
INTERACTION OF CECROPIN AD WITH MEMBRANES: A SPIN-LABEL STUDY. H. S. Mchaourab, J. S. Hyde, and J. B. Feix, Biophysics Research Institute, Milwaukee, Wisconsin, 53226.

The cecropins are a class of antibacterial peptides first isolated from the North American silk moth, Hyalophora cecropia, and later found to be widely distributed across the animal kingdom. These peptides are unordered in aqueous solution, but form a structure rich in helices in 15% hexafluoropropanol. The mechanism of bacterial killing is unknown, but has been proposed to occur via voltage-dependent ion conformation of bound species. We have synthesized a cecropin analogue, cysteine-33 cecropin AD (cys33-CAD) and spin labeled the introduced cysteine residue. The peptide was purified by reverse-phase HPLC and characterized by amino acid analyses, mass spectrometry, and SDS-PAGE. CW-EPR shows that binding of the spin-labeled peptide to the membrane is mainly electrostatic and can be modulated by varying the percentage of negatively charged lipids or by changing the salt concentration. The binding was also affected by the inclusion of cholesterol, which changed both the membrane fluidity as well as the dipole potential. Localization of the spin-labeled site was determined using multiquantum EPR. The cys33-CAD-bound spin label was more affected by molecular O₂ when the peptide was membrane bound than in the aqueous phase, indicating that the spin-labeled site is buried in the membrane. These results support the critical role of the lysine-rich N-terminus in mediating the binding to the membrane and suggest that, in the absence of transmembrane potential, the C-terminus helical region is inserted into the membrane bilayer.

THE AGGREGATION STATE OF SPIN LABELED CECROPIN AD IN AQUEOUS SOLUTION. H. S. Mchaourab, J. S. Hyde, and J. B. Feix, Biophysics Research Institute, Medical College of Wisconsin, Milwaukee, WI 53226.

A spin-labeled derivative of the ion channel peptide Cecropin AD was synthesized and used to investigate its aggregate state in water and in the presence of helix promoting solvent. A cysteine was introduced at position 33 and spin labeled using the methanethiosulfonate spin label. In aqueous solution, the peptide was monomeric, and the EPR spectrum indicates a high degree of segmental flexibility. The correlation time was 0.3 ns, which is consistent with a predominantly random coil conformation. Upon the addition of 5-10% hexafluoro-propanol (HFP), the motion of the spin label becomes more restricted with 3 ns correlation time and displayed spin-spin line broadening. At higher percentages of HFP, no spin-spin interaction was detected. This data suggest that the peptide switches between two ordered conformations by passing from a self-associated form to a helix monomer, both stabilized by intramolecular interaction. The temperature dependence of the aggregation process indicates that it is entropy driven. Furthermore, aggregation is promoted by salt and destabilized in the presence of urea, which is consistent with a hydrophobic interaction bringing the spin-labeled C termini into close proximity. The monomer aggregate equilibrium represents a balance between folding of the peptide stabilized by hydrophobic interaction with folding stabilized by intramolecular hydrogen bonding.
MOTIONAL STUDIES OF RADICALS IN POLYMERS BY 2D EPR. Günter G. Maresch, Alexander A. Dubinskii, Jürgen Saalmüller and Hans W. Spiess, Max-Planck-Institut für Polymerforschung, PO Box 3148, W-6500 Mainz, Germany

Two-dimensional electron spin-echo (2D ESE) spectroscopy is a highly sensitive tool for studies of slow motions in solids. 2D ESE spectra are obtained from nitroxyl spin probes and labels in liquid-crystalline (LC) side-group polymers. Temperature dependent measurements of 2D ESE spectra allow to identify three different mechanisms which are effective for anisotropic electronic phase relaxation in temperatures well below the glass transition of the polymer. Two-dimensional field-step electron double resonance (2D-FS-ELDOR) spectroscopy on spin labels in these LC polymers give additional information about the different possible relaxation effects. Anisotropic nuclear, electron phase and electron spin-lattice relaxations lead to characteristic patterns in the 2D plane. A motional model with small angular fluctuations allows to simulate theoretical spectra. As a result a whole range of correlation times is obtained which is the special feature of 2D ELDOR spectroscopy because of its selective sensitivity to the different spin relaxation processes.

MODEL DEPENDENCE IN SLOW MOTIONAL 250GHz ESR SPECTRA. Keith A. Earle, David E. Budil, Josef Moscicki, and Jack H. Freed, Baker Laboratory of Chemistry, Cornell University, Ithaca, NY 14850.

We present a careful 250GHz ESR study of the rotational diffusion of perdeuterated 2,2',6,6'-tetramethyl-4-piperidine (PDT) and cholestan (CSL) in toluene. The spin probe PDT is a nearly spherical spin probe; CSL, however, is cigar shaped, which allows us to exploit the effects of rotational anisotropy on the spectra. We present data in the slow-motional and near-rigid limit regions, which correspond to rotational correlation times $10^{-9} > \tau_R > 10^{-6}$ sec. An important feature of this analysis is the high resolution of spectral features that we obtain at a Larmor field of 9T. In order to explore our enhanced spectral resolution, we have determined the magnetic tensor parameters of the spin probes we have used from rigid limit spectra at 250GHz and compared them to the parameters determined from rigid limit spectra at X-band. We analyze our diffusion data in terms of the three canonical models of diffusion: Brownian, approximate free diffusion, and jump diffusion. We also discuss a quantitative theory to explain anomalous microwave phase effects in our spectrometer.


There are two main interests in high frequency step-tunable E.S.R. spectroscopy. first one is the possibility to overcome an energy barrier and measure the spectra of large zero field splitting compounds. The second one is to increase the resolution and make possible a precise identification and determination of the components of a system. We describe the spectrometer which operates at frequencies from 100 GHz to 500 GHz, at temperatures in the 4K to 300K range. We illustrate the potential of the instrument applications in Physics, Chemistry and Biology. We then present a detailed study of biradicals for which the measurements at high frequency and low temperature allows a precise analysis of the g-tensor and of the D-tensor components.

With a wide range of microwave frequencies (spectroscopic quanta) and magnetic field strengths one can tune the effective (spin) Hamiltonian to emphasize or deemphasize the Zeeman interactions relative to the couplings (fine structure, hyperfine interactions, quadrupole couplings) intrinsic to the material under study. Such a capability provides a powerful tool in disentangling these interactions from each other and achieving the best resolution. Here we describe some applications of a very-high-frequency (W-band, 95 GHz) cw spectrometer and a low-frequency (S-band, 2-4 GHz) pulsed spectrometer. We have studied surface-bound nitroaromatic radical anions, on activated alumina and magnesia, catalytically produced by action of molecular oxygen. Thiophenic radical cations and solvated copper complexes in frozen aqueous solution are also reported. The W-band spectra show remarkable g-resolution. The S-band ESEEM patterns report modulations from several nuclei and provide (1) details of weak nitrogen couplings including quadrupole coupling information, (2) exact cancellation demonstrations, and (3) structural information about the paramagnetic centers. The work used resources of the NIH Biomedical Research Technologies Program (P41-RR01811) and was supported by grants from the US Department of Energy and National Institute of General Medical Sciences (GM42208).


We will present ESR spectra at 250 GHz for the compounds Mn(γ-picoline)₄X₂, where X = Cl, Br, and I. The compounds were studied as powders at room temperature and all five electron spin transitions for the d⁵ manganese ion were observed. Hyperfine splitting was not seen due to spin exchange in the neat sample. Acceptable fits of the spectra were made using field-swept, third-order perturbation theory of all five electron spin transitions in the high-field limit. We find that the compounds are mainly axially symmetric with a zero-field splitting parameter, D, ranging from 0.19 cm⁻¹ for the chloride compound, to over 0.93 cm⁻¹ for the iodine compound. We have also observed many of the electron spin transitions in Mn (II) protoporphyrin IX dissolved in aqueous phosphate buffer or aqueous NaOH. The spectrum is similar to that of the Mn(γ-picoline)₄X₂ complexes except for features characteristic of a small amount of rhombic distortion. Preliminary analysis indicates that D is about 0.80 cm⁻¹ and E/D is about 0.05.

ENDOR IDENTIFICATION OF BRIDGING HYDROXIDE LIGANDS IN THE MIXED-VALENT DIRON CENTERS OF METHANE MONOOXYGENASE AND HEMERYTHRIN. Victoria J. DeRose, a Katherine E. Liu, b Donald M. Kurtz, Jr., c Stephen J. Lippard b and Brian M. Hoffman, a Departments of Chemistry, aNorthwestern University, Evanston, IL 60208; bMassachusetts Institute of Technology, Cambridge, MA 02139; cUniversity of Georgia, Athens, GA 30602.

Electron nuclear double resonance (ENDOR) spectroscopic studies have been carried out at 35 GHz on the mixed valent, Fe(II)Fe(III) forms of the hydroxylase protein of methane monooxygenase (MMO) and azidohemerythrin (HrN₃). In both cases there is a distinctive, highly anisotropic hyperfine coupling to a solvent-exchangeable proton, with a hyperfine interaction increasing from 14 MHz at g₁ to a maximum of 30 MHz at g₂. For both proteins this signal is assigned to the proton of a hydroxide ligand bridging the dinuclear iron center. An additional class of proton resonances is observed in MMO. This class of protons is exchangeable and has a roughly isotropic hyperfine coupling of 8 MHz, and is assigned as the proton(s) from a terminal ligand H₃O. The analysis of both classes of protons is discussed for these exchange-coupled binuclear Fe centers.
187 **NO BIOCHEMISTRY AND EPR SPECTROSCOPY.** Mark E. Mullins, Christian T. Farrar, Jonathan S. Stamler, David J. Singel. Department of Chemistry, Harvard University, 12 Oxford Street, Cambridge, MA 02138, and Department of Medicine, Respiratory Division, Brigham and Women's Hospital, Harvard Medical School Boston, MA

Nitrogen monoxide (NO) has recently been implicated in numerous, diverse physiological processes - including smooth muscle relaxation, platelet inhibition, neurotransmission, and immune regulation. EPR spectroscopy is playing a significant and growing role in illuminating many aspects of NO biochemistry. For example, the EPR detection of metal-nitrosyl compounds accompanying the cytotoxic action of macrophage, or upon stimulated emission of endogenous vasodilators from endothelial cells, has provided primary evidence for the production of NO in these cells. Recent advances in methods for the isolation of enzymes responsible for NO synthesis have made possible the initiation of detailed EPR studies of this heme- and flavin-containing protein; metal-nitrosyl compound, of interest both as intermediaries in NO biochemistry and in the activation of guanylyl cyclase, have long been targets of EPR investigation. A overview, of the links between NO biochemistry and EPR spectroscopy will be presented, with results from recent EPR and ESEEM studies of biologically significant NO compounds.

188 Recent experiments on the influence of simulated solar radiation on reactions between carbonaceous particulate (soot, black carbon) and tropospheric pollutant species, including SO₂, NOx and O₃, have revealed significant photochemical effects. In the case of the NO₂/N₂O₅-soot reaction system, changes in the rate can be attributed to the photolytic dissociation of NO₂. The formation of identifiable S(VI)-oxygen species at the carbon surface results from the interaction of radiation with the soot/SO₂/O₃/H₂O reaction system. These results and other are discussed with respect to their implications for tropospheric chemistry.

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189 **A REVIEW OF SAMPLING ACCESSORIES COMMON TO FT-RAMAN AND FT-IR.**
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FT-Raman Spectroscopy is well-known as a complementary technique with FT-IR spectroscopy for the study of molecular bonding of both organic and Inorganics species. Each approach has been most effectively applied to the comparison of samples: Good vs. bad, New vs. Used, Unknown vs. Standard. The ulterior goal of such analyses is to develop a procedure for sample discrimination. A sampling methodology should address the demands of analysis repeatability, both in terms of sensitivity to preparation and the reproducability of spectral response.

The measurements of high resolution data on an FT-IR instrument becomes progressively more challenging as the wavelengths of light become shorter. For example, a 1 cm⁻¹ spectrum in the near infrared region requires an instrumental aperture which has a diameter 2.5x smaller than that for mid infrared region. In additional, the demands placed upon instrument alignment are more severe for the measurements of progressively shorter wavelengths. The Bio-Rad FT-Raman system has piezo-scan dynamic alignment, computerized collimation control, and a variety of sampling accessories to address the most demanding applications. The advantages of step-can operation as related to thermal effects and laser kinetics will be discussed.
USE OF FTIR TO MEASURE CO₂-INDUCED CRUDE OIL ASPHALTENE DEPOSITION ON-SET. James E. Tackett, Marathon Oil Company, 7400 S. Broadway, Littleton, CO 80122.

Carbon dioxide flooding is a popular enhanced oil recovery technique. However, when sufficient CO₂ is added to a crude oil, asphaltene deposition can cause formation damage and production problems. It is important to avoid reservoir conditions that favor this behavior. Computer modeling can be used to predict these conditions, but information about asphaltene deposition on-set is necessary to tune these models.

Our efforts to use FTIR to detect CO₂-induced asphaltene deposition will be discussed. It is not difficult to use this technique to measure the amount of CO₂ dissolved in crude oil under a variety of pressure/temperature conditions, but detection of asphaltene precipitation requires some interpretative courage.

ELECTROCHEMICAL SERS DETECTION OF ENVIRONMENTAL CYANIDE ION, Robert D. Shelton, John M.E. Storey, and Eric A. Wachter, Health and Safety Research Division, Oak Ridge National Laboratory, Oak Ridge, Tennessee 37831-6113.

Cyanide ion (CN⁻) has been the subject of numerous studies probing the mechanisms underlying the surface-enhanced Raman scattering (SERS) phenomenon. This work examines various aspects critical to application of SERS for direct detection of trace cyanide in wastewater streams and groundwater. Possible applications include environmental characterization, discharge tracking, and process control. A new method for direct quantitation of cyanide in aqueous electrolyte has been developed, and the effects of two common background ions, nitrate (NO₃⁻) and sulfate (SO₄²⁻), have been characterized. By using an ex-situ oxidation-reduction cycle to precondition a planar silver electrode, cyanide ion could be detected in 0.1 M KCl with a linear response between 100 ppm and 10 ppb; the estimated limit of detection was approximately 5 ppb. Increases in the electrolyte concentration can be used to improve the LOD to approximately 1 ppb. The response of the electrode was found to be sensitive to pH, with optimal performance observed at neutral pH. The addition of 10 ppm sulfate ion decreases response approximately 40%, while the presence of nitrate ion at concentrations up to 100 ppm has a negligible effect on SERS response. These results suggest that cyanide ion can be detected directly in high ionic strength aqueous solutions, such as groundwater.

ELECTROCHEMICAL SERS DETECTION OF AQUEOUS CHLORINATED HYDROCARBONS, John M.E. Storey, Robert D. Shelton, Tye E. Barber, and Eric A. Wachter, Health and Safety Research Division, Oak Ridge National Laboratory, Oak Ridge, Tennessee 37831-6113.

Surface-enhanced Raman scattering (SERS) is a powerful technique for the study of trace analytes because of the large enhancement in Raman-scattering intensities. The coupling of SERS with selective electrochemistry makes electrochemical SERS (ESERS) a natural choice for the detection of environmental contaminants in aqueous systems, both in the laboratory and in natural waters. In this study, ESERS has been used to investigate the detection of chlorinated hydrocarbons (CHCs) in water. These include trichloroethylene (TCE), 1,2-dichloroethylene (DCE), carbon tetrachloride (CCl₄), chloroform (CHCl₃), chlorobenzene (Ph-Cl), and 1,1,2-trichloroethane (TCA). Experiments have focused on the electrochemical and excitation conditions necessary to optimize the ESERS technique for CHCs. Copper- and silver-foil electrodes and various electrolytes (such as KCl, KBr, KIO₃, and K₂SO₄) have been examined. Under suitable conditions, the CHCs appear to react at the surface of the electrode, allowing detection of reaction products by SERS. Two-color experiments using visible excitation to induce photochemistry and near-IR excitation to probe the SERS effect have also been done. Results indicate that there is much SERS activity on the electrodes due to both the species of interest and the electrolyte. Calibration data for the detection of CHCs in waters will be presented along with early efforts to develop a prototype sensor for in situ, remote ESERS measurements of CHCs directly in groundwater.
ATOMIC FORCE MICROSCOPY OF THIN Ag FILM NANOSTRUCTURE.

Surface-enhanced Raman scattering (SERS) substrates prepared by vapor-deposition of thin silver films are commonly used because they offer the advantages of simplicity and reproducibility of surface morphology. Although the surface structure of thin silver films is qualitatively well characterized, a more quantitative understanding is necessary to produce optimum SERS substrates and relate the exact surface structure to the optical properties. Atomic force microscopy (AFM) allows direct three-dimensional measurements of critical surface features such as mean particle height, radius, aspect ratio and the distribution in these parameters. In addition, AFM can be used for non-conducting samples and requires no special sample preparation. The effect of the solid support material on the surface structure of thin silver films has been quantitatively investigated by AFM for silver deposited simultaneously onto glass and poly(vinyl formal). The results of this study will be compared to the optical properties of thin silver films on glass and poly(vinyl formal). The effect of the morphological differences on the Raman enhancement capabilities will also be demonstrated.

FT-IR PHOTOTHERMAL BEAM DEFLECTION SPECTROSCOPY (PBDS): STUDIES OF COMPOSITES AND POLYMERS. T. Mahmood, Y. Tada, and J.R. Schlup, Department of Chemical Engineering, Kansas State University, Manhattan, KS 66506-5102.

FT-IR/photothermal beam deflection spectra (PBDS) of thin polymers have been recorded. In the past, carbon tetrachloride has been widely used as a deflecting medium to enhance the photothermal signal. The results presented were obtained using a reverse mirage technique and six different solvents as alternatives to carbon tetrachloride. The application of photothermal beam deflection spectroscopy with FT-IR to obtain spectra of thin polymer films will be discussed.

IDENTIFICATION OF CARBON FILLED ELASTOMERS USING FT-IR SPECTROSCOPY.
W.D. Perkins, The Perkin-Elmer Corporation, 2305 Bering Drive, San Jose, California 95131.

The routine identification of carbon filled elastomers by infrared spectroscopy involves both the selection of a sampling technique for obtaining their spectra and a procedure for comparing sample spectra with a reference collection and then making the identification. This paper will address both issues. Various techniques for obtaining the spectra will be compared and contrasted. A PC based computer program will then be described in which the sample spectrum is compared with spectra in a user generated library. Positive identification requires both that a user selected correlation coefficient be met or exceeded and that there be a significant difference between the correlation coefficients of the best and next best matches between the unknown and the spectra in the library.
THE ENHANCEMENT OF IR MICROSCOPY THROUGH THE USE OF SPECIAL IR OBJECTIVES (GAO & ATR)

The grazing angle objective (GAO) extends the capabilities of infrared microscopy to the analysis of thin films, stains, and coatings on surfaces to the monolayer level. The ATR objective for the microscope lets you analyze soft materials, filled polymers, paper, biological samples and liquids. In many cases, tedious sample preparation is eliminated which greatly improves the ease and speed of analysis.

ROOM TEMPERATURE MEASUREMENT OF PHOTOLUMINESCENCE SPECTRA OF SEMICONDUCTORS USING AN FT-RAMAN SPECTROMETER.
S. M. Vernon, Spire Corporation, Bedford, MA 01730

This paper demonstrates the utility of an FT-Raman accessory for an FTIR spectrometer in obtaining the room-temperature photoluminescence (PL) spectra of semiconductors used in photovoltaic and electro-optical devices. Sample types analysed by FTIR-PL spectroscopy included bulk silicon and films of gallium indium arsenide phosphide (GaInAsP), copper indium diselenide (CuInSe2), and gallium arsenide-germanium alloy in various substrates. The FTIR-PL technique exhibits advantages in speed, sensitivity, and freedom from stray light over conventional dispersive methods, and can be used in some cases to characterize complete semiconductor devices as well as component materials at room temperature. Some suggestions for improving the spectral range of the technique and removing instrumental spectral artifacts are presented.

THE EFFECT OF HYDROGEN ION CONCENTRATION ON CELLULOSE ACETATE POLYMERS IN AQUEOUS SUSPENSION by Marvin C. Goldberg and Anthony George, U.S. Geological Survey, P. O. Box 25046 MS 424, Denver, CO 80225

Raman spectra were taken of cellulose acetate membranes at varying conditions of pH. Some of the effects noted are reduction in band intensities as the materials were exposed over long periods of time to high and low pH solutions. The 2290 and 3020 wavenumber (cm\(^{-1}\)) peaks lose 80% intensity because of loss of methine protons. Similarly the 2965 CH\(_2\) acetate stretch diminishes. The rate of acetate loss is 2.1 x 10\(^{-4}\) percent per hour and at 2148 hours about 70 percent of the acetate is gone. The 1434 cm\(^{-1}\) band due to COO\(^-\) ions and HCH bending at acetate locations are similarly reduced. The 1381 Band denoting bending and stretching of COH also shows this loss. The 1340 cm\(^{-1}\) peak due to the C-O ester vibration gives the same loss rates. Glycosidal loss shown by the HCC and HCO bending and stretching at 1296 cm\(^{-1}\) indicate some polymer degradation. The 1170 and 1123 peak due to C-C and C-O stretch in the skeleton are also much lower in intensity than the same peak in the original membrane. The 980 wavenumber peak has disappeared. This peak is due to the perpendicular orientation of the side chains. The 919 cm\(^{-1}\) peak which is partly due to the aliphatic ether COC has been reduced by 40 percent over the original material at the end of 2158 hours. The polymer seems to have lost some of the polymeric COC linkages. The 569 cm\(^{-1}\) peak which includes the skeletal COC, OCC and OCO and OCH polymeric bands is intact. In general cellulose acetate polymers are vigorously attacked by acid and base pH solutions. A 3% concentration of pH 10 solution will almost entirely eliminate the structural integrity of the polymer in less than 40 hours, at pH 4 this same degradation takes 2 orders of magnitude more time.
RAMAN SPECTROSCOPIC DETERMINATION OF INTERMOLECULAR INTERACTIONS IN UREA–PEPTIDE MODEL SYSTEMS. Joel A. Drewes, Kathy L. Rowlen, University of Colorado, Boulder, CO 80309.

Raman spectroscopic methods have been used to examine the solution phase dynamics and interactions of small molecules. Specifically, interactions between peptide-like molecules and urea can be used to develop a basis set for relating vibrational changes to specific intermolecular interacitons. The use of small molecules as models for peptides allows the type and number of intermolecular interactions to be controlled. The basis set developed from these interactions may then be used to model interactions between globular proteins and urea. Time-resolved measurements provide additional information about the type and extent of various intermolecular interactions.

Addressing Background Problems in Isotope Ratio ICP-MS
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It is well known that molecular ions and isobaric interferences result in high background at a number of masses of interest in ICP-MS. The need for high precision in isotope ratio measurements enhances the importance of controlling and stabilizing background levels, though statistical considerations differ in the way background impacts the isotope ratio measurements relative to elemental analysis. In our laboratory, the primary focus is on ratios measurements for elements of biological significance which include a number (sulfur, potassium, calcium, and iron) with severe background interference problems. For sulfur and iron, the background ions at most masses include oxygen and are significantly reduced by thorough aerosol desolvation. Cryogenic and membrane desolvation have been used to reduce O2 interference on S-32 and ArO on Fe-56 by factors of 10 and 10 respectively. A further ~10 fold reduction at each mass can be obtained by adding a small amount of nitrogen to the plasma argon but at the price of a dramatic increase in background at Fe-54 due to ArN. Solvent related background problems can be avoided completely by laser ablation sampling but the precision obtained with the laser to date is not acceptable for isotope ratio work. Other approaches to background reduction have included flame ionization for K-39 and 41 to avoid interference due to Ar-40 and flame plus laser enhanced ionization for calcium isotopes.
The Analysis of Small Mineral Grains by Laser Ablation Inductively Coupled Plasma Mass Spectrometry

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Information about the trace and minor elemental concentrations in minerals is used to study the geochemical and physical genesis of the host rock. Laser ablation inductively coupled plasma mass spectrometry is rapidly becoming the method of choice for many analytical programs. The analysis of mineral grains utilizes both the technique's high sensitivity and its spatial resolution. Depending on the optical absorptivity of the mineral at 1064 nm, the Nd/YAG laser is operated either in the Q-switched or free running mode. For the analysis of minerals, large grains (>5mm) can be analyzed in-situ on a polished section, smaller grains need to be separated from the host material and mounted on thin-section slides or glued to white teflon. Separately mounted minerals can be smaller than the diameter of the crater created by the laser (50um) with some loss in sensitivity. Limits of detection approach 1 ug/g for most elements, and the technique is useful for approximately 70 elements on each mineral grain. Examples of the techniques unique capabilities will be discussed.


The Mississippi River is an important natural resource providing water for drinking and irrigation to numerous communities. The Mississippi River system can be divided into two distinct reaches. The reach from Minneapolis, MN, to St. Louis, MO, which has 29 lock and dam structures that restrict natural flow and impound suspended sediment and the reach from St. Louis, MO, to New Orleans, LA, that flows unimpeded to the Gulf of Mexico transporting vast amounts of sediment. The water quality of this resource, from the perspective of the heavy metals, is affected by several sources, the major ones being wastewater treatment, agricultural fertilization and cultivation practices, industrial manufacturing, and mining activities. A study of the Mississippi River system was undertaken to measure heavy metal concentrations associated with both the dissolved and solid phases. Together with the discharge measured at the time of sample collection, mass transport of heavy metals were calculated. Influences from seasonal variations were investigated by sampling during the summer of 1991, fall of 1991, and the spring of 1992. Duplicate depth-integrated, equal-width increment, composited raw water samples were collected from twelve sites on the Mississippi River. Dissolved heavy metal concentrations were well below EPA Drinking Water Standards and therefore only a small percentage of heavy metals were being transported in the water phase. Suspended sediment was separated from water and fractionated using continuous-flow centrifugation and tangential-flow ultrafiltration. The chemical form of the heavy metals in the suspended sediment was determined using sequential chemical extractions. Results indicated that the highest percentage of heavy metal concentrations were associated with the inorganic phase of the suspended sediment, especially in the colloid fraction. Correspondingly, the highest percentage of heavy metals were transported by the suspended sediment.
DETERMINATION OF MAGNESIUM IN ESTUARINE SEDIMENT BY ISOTOPE DILUTION - INDUCTIVELY COUPLED PLASMA MASS SPECTROMETRY. Karen E. Murphy, and Paul J. Paulsen, NIST, Gaithersburg, MD 20899

The National Institute of Standards and Technology (NIST) is in the process of certifying the elemental concentrations of the renewal SRM 1646a, Estuarine Sediment. The magnesium concentration in this material was quantified by ID - ICP-MS at 0.388 Wt % Mg. The samples were dissolved and aliquoted before spiking with $^{25}$Mg. The accuracy of the concentrations determined in this manner were verified by spiking several samples directly. Good agreement was obtained both between the aliquoted and directly spiked samples and between two different dissolution procedures. The advantage of analyzing these samples by ICP-MS is that they are run directly after dissolution and proper dilution without the need for the chemical separations that would traditionally be required for analysis by TIMS. The lack of molecular interferences in the Mg mass spectrum was proven by comparing the isotopic composition of pure Mg metal with the isotopic composition of the estuarine sediment. The precision of the ID - ICP-MS procedure was on the order of 0.2% rsd which allowed us to determine the Mg sample homogeneity.

HIGH ACCURACY DETERMINATION OF SELECTED TRANSITION METALS BY ICP-MS ISOTOPE DILUTION; Ellyn S. Beary and Paul J. Paulsen, National Institute of Standards and Technology, Gaithersburg, Maryland, 20899.

High accuracy determinations of mid-mass elements such as Ni, Cu, Mo and Cd in complex matrices is often not possible by direct ICP-MS analysis. Significant amounts of (low probability) molecular ions are formed in the plasma due to high concentration of argon, water and major matrix elements. When these molecular ions involve low mass matrix elements (often alkaline earth elements in combination with oxygen), interferences with trace analytes in the mid-mass range can occur. Interferences are implied when the measured isotopic ratios of an element in a complex matrix do not exactly match the measured ratios of the pure natural element. ICP-MS has been used to detect sources of interferences and to assess appropriate chemical separations. Rapid and broad-based assessment capabilities of the ICP-MS permit the customization of traditional separations for specific analytes in specific matrices. In addition, quantitation of the analyte by isotope dilution offers considerable flexibility in separations design since high accuracy does not depend upon quantitative recovery. Analyte quantitation is obtained using the ICP-MS in the peak jump mode. This approach was used in the certification of ppb-ppm levels of Ni, Cu, Mo and Cd in a variety of new SRMs including leaves and sediments. Estimated precision and accuracy was better than 1% rsd.

MULTIELEMENT CHARACTERIZATION OF SINGLE FIBERS BY SOLID SAMPLING ETV-ICP-MS. Robert D. Koong, Forensic Science Research and Training Center, FBI Academy, Quantico, VA 22135.

Forensic investigations frequently entail comparison and characterization of individual fibers recovered from the scene of a crime and those from a suspect's environment. Optical microscopy, and infrared and x-ray fluorescence spectroscopies are often used to compare fibers in a nondestructive manner. As an additional point of comparison, element concentrations resulting from inorganic pigments, metallized dyes, and similar additives can be semiquantitatively determined in millimeter length single fibers by direct insertion into ETV and multiple ion monitoring using ICP-MS. Discussion will include characterization of some common fiber types and examples where added discrimination occurs when ETV-ICP-MS is used in conjunction with nondestructive techniques. Elements detected include those added to affect particular end uses, manufacturer specific markers, and post manufacturing environmental additions. The importance of sample heterogeneity effects in fiber comparisons will be discussed.
HYDRIDE TRAPPING ON PALLADIUM AND SUBSEQUENT DETERMINATION WITH INDUCTIVELY COUPLED PLASMA MASS SPECTROMETRY (ICP-MS). I. Marawi, J. Wang, L.K. Olson, and J.A. Caruso, Dept. of Chemistry, University of Cincinnati, M.L. 172, Cincinnati, Oh 45221-0172

Hydride generation has become a popular method for sample introduction in atomic spectrochemical analysis. This technique is most effective for elements which form volatile hydrides. Among those elements are As, Sn, Bi, Se, and Pb. One of the advantages this method can offer is the ability to concentrate the analytes before they are analyzed. Trapping in a graphite furnace has proven to be an effective method for preconcentrating those hydrides. Previous work have shown that trapping after the deposition of 20 μg palladium on the L'vov platform inside the furnace was nearly 100% efficient. The limit of detection obtained for arsenic using this method was 3 ppt. To maintain the high trapping efficiency, deposition of the palladium solution had to be made before every run. The deposition step is not just cumbersome and time consuming, it also causes faster graphite tube degradation. One of the problems associated with the tube degradation is the formation and discharge of refractory carbides during the atomization step, which are transported to the plasma causing random interferences on the mass analyzer. In this work, an attempt to eliminate this problem was made by bonding the palladium to a metallic substrate platform.

ANALYSIS OF SEMICONDUCTOR MATERIALS USING HIGH RESOLUTION INDUCTIVELY COUPLED PLASMA MASS SPECTROMETRY (HR-ICP-MS).

Rob Henry, Nicola Reed, Paul Sigsworth, Robert Hutton, Fisons Instruments, 14513 Spotswood Furnace Road, Fredericksburg, Virginia 22407.

HR-ICP-MS has been used to analyze materials to Semiconductor Equipment & Materials International (SEMI) Grade 3 specifications. During method development molecular species in the plasma were identified which limit the use of quadrupole-based ICP-MS instruments for this type of analysis. The HR-ICP-MS provides resolution of up to 10,000 plus the high sensitivity needed to analyze semiconductor materials to the levels required by the industry.

BIOLOGICAL MATERIAL ANALYSIS USING ICP-MS AND FI-ICP-MS. Ewa Pruszkowski, and Randy Hergenreder, Perkin Elmer Corp., 10 Faraday, Irvine, California 92718.

ICP-MASS Spectrometry is developing the reputation of being able to solve a variety of analytical problems that have been troublesome to other techniques. However, some specific analyte-matrix combinations can be difficult even for this technique. Among the applications that still present significant challenges is the analysis of biological fluids. In clinical, toxicological and forensic areas, a considerable need exists for an analytical method allowing multielement determination of very low concentrations in urine, blood and serum.

This paper will describe analysis of biological materials using and ICP-MS instrument with a standard sample introduction and will show the possibilities which are opened for the flow injection-ICP-MS determinations.

Depth-integrated snowpack samples from various selected sites of the Rocky Mountain region were collected in March-April 1993. Inductively Coupled Plasma-Mass Spectroscopy was used for the determination of trace metals. Ultraclean processing procedures were used to insure the integrity of the samples with trace level concentrations. The processing procedure as well as the analytical procedure used for this study will be discussed. Data will be presented showing the spacial distribution of trace elements.

THE RELATIONSHIP BETWEEN MODULUS AND SOLID-MATRIX PHOSPHORESCENCE UNDER DIFFERENT HUMIDITY CONDITIONS. Jie Chen and R.J.Hurtubise, Chemistry Department, University of Wyoming, Laramie, Wyoming 82071-3838.

Solid-matrix room-temperature phosphorescence (RTP) is quenched by moisture. The quenching effects of moisture on the RTP of adsorbed phosphors using filter paper as the solid matrix is believed to be related to the modulus of the filter paper. Modulus, in turn, is related to the characteristics and density of the hydrogen-bonds within and between cellulose fibers. The modulus of filter paper samples with different adsorbed salts at various relative humidities and the adsorption isotherms of the filter paper were obtained. The relationships between properties of the hydrogen-bonds within and between cellulose fibers and the modulus data of the filter paper at room temperature were considered. Also, the solid-matrix phosphorescence intensities and phosphorescence lifetimes of various phosphors at different humidity were acquired. The luminescence data were compared with the modulus data from the filter paper. The comparisons revealed some of the important physicochemical interactions responsible for moisture quenching of RTP.

CHEMILUMINESCENCE IN THE QUANTITATION OF CELL FUNCTION. ROSS U. ROBINSON, CARDINAL ASSOCIATES, INC., PO BOX 5220, SANTA FE, NEW MEXICO 87502

Chemiluminescent techniques are proving useful in development of tests for bacterial growth, for measurement of free radical production in blood cells, for chemosensitivity testing, for evaluation of environmental factors and in monitoring of oxidative stress.

These measurements prove valuable as molecular biologists, using an array of technologies to modify cells at the molecular level, research and create advances now being commercialized by the biotechnology industry. It is critical to know how the molecular modifications being made influence the functioning of the total cell.
SYNCHRONOUS LUMINESCENCE AS A PROMISING FIELD SCREENING TECHNIQUE. DeLyle Eastwood, Russell L. Lidberg, Lockheed Environmental Systems and Technologies Company, 980 Kelly Johnson Drive, Las Vegas, Nevada 89119, and Tuan Vo-Dinh, J.P. Alarie, Oak Ridge National Laboratory, P.O. Box 2008, Oak Ridge, Tennessee, 37831

Earlier work by the authors and others have shown that synchronous luminescence is a potentially valuable technique for polycyclic aromatic hydrocarbons (PAHs), petroleums, oils and lubricants (POLs), for polychlorinated biphenyls (PCBs) and for phenols and chlorinated phenols. Recently, a battery-powered portable scanning spectrofluorometer developed by T. Vo-Dinh’s group at ORNL and evaluated by the authors has increased the field capability for synchronous luminescence as a field screening technique. This paper explores the potential of synchronous luminescence for field screening and includes examples of spectra of real world samples for a variety of pollutants with a discussion of appropriate field methodologies and QA/QC.

ELECTROGENERATED CHEMILUMINESCENCE DETECTION USING TRIS(2,2'-BIPYRIDYL)RUTHENIUM(II). Timothy A. Nieman, Chemistry Department, University of Illinois, 1209 W. California Street, Urbana, IL 61801

Tris(2,2'-bipyridyl)ruthenium(II) (Ru(bpy)_3^{2+}) can be oxidized to Ru(bpy)_3^{3+}, which undergoes chemiluminescence (CL) reaction with oxalate and aliphatic amines to produce emission at about 605 nm plus Ru(bpy)_3^{2+}. Because the Ru(bpy)_3^{2+} species is regenerated during the CL reaction, and because of the facile electrochemical interconversion of the key oxidation states it can be advantageous to immobilize Ru(bpy)_3^{2+} on the surface of an electrode. Several different methods of immobilizing Ru(bpy)_3^{2+} have been investigated and the characteristics of these forms for CL detection in flow injection and HPLC applications will be presented. NADH is one of the species that can be sensitively detected; results will be presented for biosensors created by coupling immobilized Ru(bpy)_3^{2+} with immobilized dehydrogenase enzymes. Finally, a comparison will be made of the use of constant and modulated electrode potential with Ru(bpy)_3^{2+} electrogenerated chemiluminescence.

DETECTION OF ORGANIC SUBSTRATES IN POTASSIUM HALIDE MATRICES USING ROOM TEMPERATURE PHOSPHORESCENCE METHOD. Wendy Schurt and Yuzhuo Li, Department of Chemistry, Clarkson University, Potsdam, New York 13699-5810.

Although filter paper is the most prominent supporting material for the detection of organic substrates using solid state room temperature phosphorescence (SSRTP), special drying processes and solvents are needed to avoid the quenching of RTP signals. Furthermore, filter paper often yields a broad emission peak which raises the detection limit of the analyte. Heavy atoms are often necessary to achieve acceptable detection limits. Potassium halide matrices are employed as the media in our SSRTP studies. The solid sample provides a rigid, impermeable medium that dramatically reduces non-radiational deactivation processes without the use of special solvents or drying techniques. The detection limits for organic compounds are lower than in other supporting media such as filter paper. The potassium halide matrices also enhance the RTP signal through the heavy atom effect. This technique is the only known method of obtaining a phosphorescence signal from trans-stilbene at room temperature besides in a Zeolite medium (V. Ramamurthy, D.F. Eaton, and J.V. Caspar, Acc. Chem. Res., 1992, 25(7), 299-307).
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FLUORESCENCE SPECTRAL CHARACTERISTICS OF THE TETROLS OF BENZO(a)PYRENE-DNA ADDUCTS IN SOLID MATRICES AT ROOM TEMPERATURE AND LOW TEMPERATURE. Luchuan Shu and Robert J. Hurtubise, Department of Chemistry, University of Wyoming, Laramie, WY 82071-3838.

A laser-based fluorescence measurement system was constructed which can be utilized to obtain room-temperature fluorescence spectra (RTF) and low-temperature fluorescence spectra (LTF) for fluorescent compounds adsorbed on solid matrices. The laser-based system shows unique advantages in characterizing the fine structure of fluorescence spectra compared with those spectra obtained from non-laser based, commercial spectrophotometers. In this work, RTF and LTF spectra of tetrals adsorbed on solid matrices were obtained with the laser-based system and the spectral characteristics of the RTF and LTF were considered. Tetrals are important in cancer research because they are obtained from benzo(a)pyrene-DNA adducts. With the laser-based system, a new gate-width dependence method was developed which can be used to identify and characterize the four stereoisomers of tetrals adsorbed on 10% α-cyclodextrin/NaCl at both room and low temperature. At low temperature, the gate-width dependence method has a higher analytical potential for tetrals and for the general analytical identification and characterization of the fluorescent stereoisomers, compared to room temperature conditions.

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DETECTION OF METABOLITES OF POLYCYCLIC AROMATIC HYDROCARBONS IN THE URINE OF PSORIASIS PATIENTS TREATED WITH COAL-TAR. Ainsley Weston, Regina M. Santella† and Elise D. Bowman. Laboratory of Human Carcinogenesis, National Cancer Institute, National Institutes of Health, Bethesda, MD 20892 and †Columbia University, New York, NY 10032.

Immunofluorescence microscopy, high performance liquid chromatography and synchronous fluorescence spectroscopy have been used in combination to isolate and determine levels of PAH-metabolites in urine samples from coal-tar treated psoriasis patients (N=26) and untreated control subjects (N=24). A tritium tagged standard was used to establish a recovery of 34% with an assay detection limit of 10 fmol/ml urine. Levels of r-7, t-8, t-9, c-10-tetrahydroxy-7,8,9,10-tetrahydrobenzo[a]pyrene were found to be elevated in coal-tar treated patients (<10-330 fmol/ml) compared to controls (<10-40 fmol/ml) (p=0.001). A more polar, β-glucuronidase labile, metabolite containing a pyrene fluorophore was also found to be elevated in coal-tar treated patients (60-16900 fmol/ml) compared to controls (12-220 fmol/ml) (p=0.0001). Preliminary analyses indicated that urinary PAH-metabolite levels were not associated with tobacco smoking. This assay method may be useful for human monitoring of PAH exposure.

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LUMINESCEENCE PARAMETERS AND RATE CONSTANTS OF THE GUANOSINE ADDUCT OF BENZO(A)PYRENE ADSORBED ON 1% α-CYCLODEXTRIN/NaCl AND 25% Trehalose/NaCl SOLID MATRICES. Yu Chu and Robert J. Hurtubise, Department of Chemistry, University of Wyoming, Laramie, WY 82071.

The guanosine adduct of benzo(a)pyrene (B(a)P-guanosine) is one of the degradation products of B(a)P-DNA adducts. It is important to study B(a)P-guanosine because its luminescence spectral properties, luminescence quantum yields and lifetimes, and rate constants can be compared to the luminescence properties of the B(a)P-DNA adducts. Fluorescence and phosphorescence lifetimes of the B(a)P-guanosine adsorbed on 1% α-cyclodextrin/NaCl and 25% trehalose/NaCl solid matrices were obtained both at room temperature and 93 K. No changes in fluorescence lifetimes were observed on either solid matrix as a function of temperature. However, a moderate increase in phosphorescence lifetimes was observed as the temperature was lowered. This indicated that the phosphorescence of the B(a)P-guanosine from the solid matrices was more dependent on the environment than the fluorescence. In addition, fluorescence and phosphorescence quantum yields of the B(a)P-guanosine adsorbed on 1% α-cyclodextrin/NaCl and 25% trehalose/NaCl solid matrices were obtained at several temperatures. A number of photophysical rate constants for various photophysical processes were calculated. Also, comparisons were made between room-temperature and low-temperature photophysical parameters obtained from both solid matrices.
SOLID-MATRIX LUMINESCENCE QUENCHING OF TETROLS ON FILTER PAPER BY HUMIDIFIED NITROGEN. W. Tjioe and R.J. Hurtubise, Department of Chemistry, University of Wyoming, Laramie, WY 82071-3838.

Tetrols are the metabolic products of benzo[a]pyrene-DNA adducts. The tetrols emit strong fluorescence in solution and on various types of solid matrices. With thallium acetate, they give strong room-temperature phosphorescence on filter paper. The quenching of the luminescence of the tetrols on filter paper was studied to provide information about the interactions of tetrols with the solid matrices. The phosphorescence from tetrols adsorbed on filter paper was more sensitive to moisture quenching than the fluorescence of the tetrols. The fluorescence lifetimes and intensities of all four tetrols changed little over the entire humidity range examined. In contrast, their phosphorescence lifetimes and intensities showed a different pattern of quenching after a certain weight percent of water was adsorbed on filter paper. Generally, the vulnerability of the phosphorescence intensities and lifetimes of tetrols to moisture quenching is related to the decrease of filter paper rigidity at higher moisture content. Preliminary results were obtained for the moisture quenching of the solid-matrix luminescence of benzo[a]pyrene-DNA adducts.

A COMPACT SOLID-STATE, Q-SWITCHED, DIODE PUMPED, Nd:YLF LASER USED IN A SIMPLE TIME-RESOLVED FLUOROMETER. Keith D. Grinstead, J. Fred E. Lyle, Purdue University, Chemistry Department, 1393 Brown Building, W. Lafayette, IN 47907-1968.

Recent improvements in an all solid state based, effectively frequency tripled, Q-switched, diode-pumped Nd:YLF laser has simplified several measurement schemes performed in our laboratory. This laser possesses properties which would make it useful in many applications in analytical chemistry requiring a high repetition pulsed UV source with high focusability. It’s physical size is ideal to replace Nitrogen lasers previously used in instruments. Also, it is extremely user friendly requiring only a key switch to turn on and normal wall outlet for power. No special facilities are needed with external cooling systems and no highly trained personal are required for operation. With these attributes, it easily allows for integration into mobile instruments. We will show the ease at which this laser was made into a simple fluorometer source. Also, the ease at which the data collection scheme for this instrument was developed using an Analytek series 2000B digital oscilloscope. The resulting data acquired was then transferred by a GPIB bus to the computer for processing giving a lower limit of detection of 10^-11 M for a biologically useful fluorophore.

EFFECTS OF DEUTERATED SODIUM ACETATE ON THE SOLID-MATRIX LUMINESCENCE PROPERTIES OF ADSORBED ORGANIC COMPOUNDS. S. M. Ramasamy and R.J. Hurtubise, Department of Chemistry, University of Wyoming, Laramie, WY 82071-3838.

Sodium acetate has been used in solid-matrix luminescence analysis to obtain luminescence from adsorbed compounds. In this work, sodium acetate (H3O) and deuterated sodium acetate (D3) were employed as solid matrices to study the fluorescence and phosphorescence properties of adsorbed anions of p-aminobenzoic acid, p-hydroxybenzoic acid and p-aminohippuric acid. For one of the phosphors, the changes with temperature in the phosphorescence intensity, phosphorescence lifetime and the ratio of phosphorescence intensity to phosphorescence lifetime have been interpreted in terms of differences in the properties of the solid matrices. The nature of triplet state decay on the two solid matrices for one of the phosphors was evaluated in terms of preexponential factor and activation energy terms. Also, from the phosphorescence lifetime data, some of the processes involved in the deactivation of the triplet state of the phosphors were identified. Evidence from diffuse reflectance infrared spectroscopy of the two matrices was obtained to determine the different isotopic forms of sodium acetate and deuterated sodium acetate.
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INVESTIGATION OF BINDING ENVIRONMENTS IN HUMIC SUBSTANCES USING FLUORESCENT PROBES. Sherry L. Hemmingsen, Linda B. McGown, Duke University, P. M. Gross Chemical Laboratory, P. O. Box 90348, Durham, North Carolina 27708-0348.

Humic substances play an important role in the binding and transport of both organic and inorganic chemical species in the environment. Therefore, investigation of the various binding environments offered by different types of humic substances should provide insight on how humic matter can alter the bioavailability of pollutants. These binding environments can be studied by using extrinsic fluorescent probes that cover a range of sizes, shapes, and solubilities. In this talk, we will present results for several fluorescence probes added to aqueous solutions of humic substances. The relative polarity of the probe microenvironment can be monitored by calculating a vibronic band intensity ratio (VBIR) from the fluorescence emission spectrum of the solubilized probe. The vibronic band intensity ratio is the intensity of the forbidden 0-0 transition relative to the intensity of an allowed transition. The intensities of the allowed transition bands are insensitive to changes in solvent polarity, while the band intensity of the vibronically forbidden transition varies significantly depending on the solvent environment. Since all solutions being studied are aqueous, changes in the VBIR value of the various probes will be a result of different humic-probe interactions. Further information about the humic-probe interactions is obtained from fluorescence lifetime studies.

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METABOLISM OF LEUKOTRIENE B$_4$ IN THE PRIMATE, Keith L. Clay, Bernard Fruteau de Laclos, and Robert C. Murphy. National Jewish Center for Immunology and Respiratory Medicine, 1400 Jackson St., Denver, Colorado 80206.

Leukotriene B$_4$ (5,12-dihydroxy-6,8,10,14-eicosatetraenoic acid) is a metabolite of arachidonic acid synthesized by the polymorphonuclear leukocyte (PMN). This eicosanoid has profound biological activity primarily being chemotactic for PMN. LTB$_4$ is metabolized by hepatocytes isolated from rat liver to a series of $\omega$-$\beta$-oxidation products suggesting rapid degradation of this eicosanoid by this organ. However, little is known about the metabolism of LTB$_4$ in the intact animal. Preliminary studies have been carried out investigating the urinary metabolites of LTB$_4$ following injection into monkeys. For these experiments, monkeys were anesthetized and LTB$_4$ was injected in a peripheral vein as a mixture of $^{13}$CLTB$_4$ and $[^3]$HTLB$_4$ (50/200 µg/kg). Urine was collected through an indwelling catheter at 1 hr periods on ice for a total of 8 hr post LTB$_4$ injection. Approximately 20% of the injected radioactivity was eliminated into urine during the 8 hr period. Of the total radioactivity, approximately one-third emerged into urine during the first hour collection, suggesting rapid elimination of metabolites. Following extraction and HPLC separation, several radioactive metabolites were found and their structures investigated using fast atom bombardment, electrospray ionization, and GC/MS techniques following derivatization to volatile derivatives. Of particular value was the synthesis of the pentafluorobenzyl ester and their El and ECI mass spectra. The overall goal of these experiments was to identify a major urinary metabolite that could be used to assess in vivo synthesis of LTB$_4$. This work was supported in part by a grant from National Institutes of Health (HL25785).
IDENTIFICATION OF LIPID PEROXIDATION PRODUCTS USING GC/MS AND FAB/MS/MS. Kathleen A. Kavaganich-Harrison and Robert C. Murphy, Department of Pediatrics, National Jewish Center for Immunology and Respiratory Medicine, 1400 Jackson Street, Denver, Colorado, 80206.

Peroxidation of lipids contributes to the damage sustained by an organism undergoing oxidative stress, such as may occur following a heart attack. The exact biochemical mechanisms by which damage occurs is not established. It has been suggested that the oxidative fragmentation of polyunsaturated fatty acids esterified in phospholipids (PL) produces molecules with platelet activating factor-like activity which causes activation of neutrophils that then adhere to the vasculature and undergo oxidative burst, causing more oxidative damage to nearby cells. It is also suggested that the formation of prostaglandin-like molecules formed by a free radical mechanism from PL esterified arachidonic acid could be released from the PL and mediate oxidative damage. The low levels of such oxidatively modified PL and the complexity of the biological tissues in which they might be found necessitate sensitive and specific methodology in order to detect and identify such molecules to determine their possible roles in oxidative damage. To develop such methodology we oxidized palmitoyl-arachidonyl glycerophosphocholine and used FAB and tandem mass spectrometry to identify HPLC separated oxidized PL molecular species that gave a positive response in a neutrophil adhesion bioassay. Little has been published concerning the mass spectral characteristics of oxidized PL. Our results suggest that oxidized PL containing aldehydic moieties undergo facile reactions with the FAB liquid matrix leading to unique derivatives which provides a convenient way to confirm the presence of this functional group. Also, oxidized PL containing esterified dicarboxylic acids possess multiple sites for ionization leading to different types of collision induced dissociation product ions not seen in the mass spectra of non-oxidized PL. Prostaglandin-like molecules, dihydroxy eicosatetraenoic acids, and monohydroxy eicosatetraenoic acids were also detected esterified to PL. Base hydrolysis of the oxidized PL followed by derivitization and GC/MS analysis was used to obtain more structural information concerning the oxidized fatty acid moieties.

STRUCTURAL DETERMINATION OF A MODIFIED MEMBRANE LIPOPEPTIDE FROM MYCOBACTERIUM AVIUM BY USING ELECTROSPRAY, FAB, AND PRECURSOR ION SCANNING. Denise K. MacMillan and Robert C. Murphy, Department of Pediatrics, National Jewish Center for Immunology and Respiratory Medicine, Denver, CO 80206. Hee-Joo Park and Patrick J. Brennan, Department of Microbiology, College of Veterinary Medicine and Biomedical Sciences, Fort Collins, CO 80523.

Diseases caused by Mycobacterium avium, a common pathogen, are increasing in recent years, especially among patients already infected with the AIDS virus. Treatment with cycloserine effectively kills M. avium, perhaps by modifying a cell membrane lipopeptide and interrupting peptidoglycan synthesis. Side effects involving the patient's central nervous system limit the use of cycloserine, however.

To determine the structure of the lipopeptide, we used both electrospray ionization with single quadrupole mass analysis and FAB ionization with triple quadrupole mass spectrometry. Both techniques gave a molecular ion cluster of seven species, (m/z 1194, 1208, 1222, 1236, 1250, 1264, 1278). Amino acid and fatty acid analyses suggested that the lipopeptide was composed of an octapeptide acylated at the N-terminus by one of four saturated fatty acids: octadecanoic, eicosanoic, docosanoic or tetracosanoic acid. Tandem mass spectrometry product ion experiments gave a primary amino acid sequence as Phe–Nmv–Nmv–Phe–Ala–Nmv–Ala–Phe, where Nmv represents N–methylvaline. The individual species differ by the length of the fatty acyl chain and inclusion of one or more methyl groups along the peptide chain. Sites of methylation were revealed by precursor ion scans.
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USE OF FAB/SIMS TO MEASURE IRON ABSORPTION in vivo. David R. Flory, Leland V. Miller and Paul V. Fennessey. Departments of Pharmacology and Pediatrics, UCHSC, 4200 E. Ninth Avenue, Denver, CO 80262.

The mechanisms of non-heme iron absorption in the human are still unknown. The development of stable isotope techniques are necessary if in vivo human iron metabolism research is to expand. Fast Atom Bombardment Secondary Ion Mass Spectrometry (FAB/SIMS) is a sensitive and readily available tool in mass spectrometry. We have developed techniques to isolate iron from whole blood or erythrocytes in a form free of isobaric interferences. Human studies of iron metabolism with stable isotopes have been accomplished using both an infusion and oral dose protocol. Enrichments of body iron stores have been measured with the developed FAB/SIMS method and compared to published values. In an animal model, absorption has been measured using stable and radioactive iron isotopes simultaneously. In addition, we have modified the mass spectrometer for a wider range of acceleration voltages and a pulse counting electron multiplier with the appropriate computer/data system. These modifications have increased the sensitivity of measurement from 1-2 µg of iron to 50 ng of iron with equal sensitivity and precision.

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ABSTRACT NOT AVAILABLE

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ANALYSIS OF PHOSPHOSERINE OR PHOSPHOTHREONINE BY ELECTROSPRAY MASS SPECTROMETRY DURING ON LINE HPLC OF CHEMICALLY BETA ELIMINATED PEPTIDE MIXTURES. Katheryn A. Resing, Richard S. Johnson, Kenneth A. Walsh. Dept. of Chem. and Biochem., University of Colorado, Boulder CO 80303 and Dept. of Biochem., University of Washington, Seattle WA 98195

Electrospray mass spectrometry is the method of choice for analysis of post-translational modification of proteins. However, sequencing of phosphorylated peptides by collisional induced fragmentation (CID) is complicated by the preferential elimination of the phosphate with little or no fragmentation at peptide bonds. A procedure has been developed where a phosphopeptide is trypsinized, the peptide mixture is treated with BaOH to form dehydroalanine or dehydrothreoine at the phosphorylated residues, followed by on line mass analysis of the peptides during reverse phase HPLC. Confirmation of the specific site of phosphorylation is made by CID of the modified peptides. This technique allowed characterization of a peptide with six phosphoserines. The technique was also adapted for analysis of 20 pmol of a phosphoprotein using a 500 micron diameter capillary HPLC column. Combination of this technique with trypsinization of phosphoproteins out of SDS-PAGE gel strips or from blots allows analysis of impure protein samples.
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RECENT ADVANCES IN ATMOSPHERIC PRESSURE IONIZATION MASS SPECTROMETRY: HIGH FLOW RATES WITHOUT COMPROMISING SENSITIVITY. Mark Sanders, Iain Mylcheest, Mark Hall, Kuldip Mock, Finnigan MAT, 355 River Oaks Parkway, San Jose, California 95132.

The development of an Atmospheric Pressure Ionization (API) source capable of both Electrospray Ionization (ESI) and Chemical Ionization (APCI), provides a highly sensitive and routine detector for liquid chromatography, allowing the analysis of an enormous range of compounds. Previously API techniques have been limited in their ability to accommodate the high flows associated with conventional 4.6 mm and 2.1 mm columns and various splitting arrangements would have to be employed to scale down the flow to the mass spectrometer. This tends to be both time consuming and, in many cases, unreliable on a day to day basis. In other systems where splitting was not absolutely necessary, higher flow rates were accompanied by dramatic losses in sensitivity. This new technology allows the direct coupling of an LC while simultaneously maintaining high sensitivity. Examples of this Atmospheric Pressure ESI/APCI source coupled to a Finnigan TSQ700™ series quadrupole mass spectrometer via a heated capillary, tube lens, skimmer and RF-only octopole focusing element will demonstrate:

- High flow/high sensitivity ESI (up to 1 mL/min).
- High flow/high sensitivity APCI (up to 2 mL/min).
- Increased sensitivity for drug, biochemical and environmental compound analysis and quantitation by LC/MS and LC/MS/MS.
- The use of RF-octopole collision induced dissociation for controlled, high efficiency source fragmentation for ESI and APCI.

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ELECTROSPRAY MASS SPECTROMETRY OF "SMALL" BIOMOLECULES: COMPARISON WITH FAST ATOM BOMBARDMENT MASS SPECTROMETRY. Joseph A. Zirrollo, Department of Pediatrics, National Jewish Center for Immunology and Respiratory Medicine, Denver, CO 80206.

The introduction and development of Fast Atom Bombardment (FAB) mass spectrometry in the early 1980's significantly enhanced the mass spectrometrist's ability to analyze "large" polar biomolecules. These compounds included complex lipids, carbohydrates, peptides and oligonucleotides. This technique is a "soft" ionization process involving desorption of the under derivatized analytes from a matrix-covered surface which yields molecular weight information from singly-charged molecular ions. The major limitation of FAB was the relatively "low" mass range of only several thousand Daltons. This restriction was overcome by the development of Electrospray Ionization (ESI) mass spectrometry in the late 1980's. This technique also employs a "soft" ionization process, but yields multiply-charged molecular ions from an atmospheric spray in a high electric potential. With ESI the effective mass range of analysis was extended to several hundred thousand Daltons and the analysis of intact proteins and other complex biopolymers was realized. However, more recently ESI has been applied to the analysis of much smaller biomolecules (100 - 2000 u) in conjunction with on-line HPLC/MS. This mass range is compatible with FAB/MS and this paper compares the relative ion formation processes and ionization efficiencies of the two techniques with a variety of "small" biomolecules, including single amino acids and small peptides (10 - 20 residues), fatty acids and oxidized fatty acids, and enzyme cofactors such as Coenzyme A and NAD.
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Time-of-flight mass spectrometers (TOF-MS) are widely employed with a variety of ion sources for the study of large m/z ions. Principal advantages of TOF-MS include simplicity, high upper mass limits and high sensitivity. The typically low mass resolution which can be achieved with TOF-MS is a disadvantage for many applications. A variety of techniques have been employed to improve the mass resolution by compensating for some of the initial kinetic energy spread of the ions. These have included ion mirrors, pulsed ion extraction and ion energy filters (electric sectors). With pulsed laser ionization (MALD), continuous ion extraction coupled with high accelerating potentials (25-30 kV) are typically employed to minimize the effect of the initial ion kinetic energy distribution and provide improved ion detection efficiency for large m/z ions. Pulsed extraction of MALD generated ions offers a variety of potential advantages including mass resolution enhancement and metastable ion studies. To date, most pulsed extraction studies have involved relatively low extraction fields and low total ion energy which have poor performance for large m/z ions. Initial results will be presented for a prototype pulsed (3 kV) extraction ion source operating at 25 kV coupled with MALD ionization and a linear TOF-MS.

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LOW TEMPERATURE MATRIX ASSISTED LASER DESORPTION MASS SPECTROMETRY, John J. Lennon and Robert S. Brown, Chemistry Department, Colorado State University, Ft. Collins, CO 80523.

Matrix assisted laser desorption (MALD) mass spectrometry is increasingly finding applications in a wide range of fields. Its primary application to date has been for the characterization of large biomolecules. Increasingly, the mechanisms involved in this relatively new ionization technique are becoming better understood. Primary attention has been directed at understanding the exact role(s) of the matrix in the ionization process. This should lead to the identification of improved matrices. In this regard, we have constructed a low temperature sample probe which can be cooled down to the temperature of liquid nitrogen and can be floated at high accelerating potentials (30 kV). This has allowed us to examine the influence of matrix temperature on the threshold laser irradiance necessary for the onset of ionization. The required laser irradiance is found to increase significantly at low temperature. Additionally, this cooled probe has allowed us to compare the performance of 3-nitro phenol as both a liquid (room temperature) and solid matrix for MALD ionization. Preliminary results with "solid" solution matrices whose physical properties (e.g., molar absorptivity, pK_a) can be varied will also be presented.

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ABSTRACT NOT AVAILABLE
FLOWING AFTERGLOW STUDIES OF BORON HYDRIDE ANIONS
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Department of Chemistry, University of Colorado at Denver, Denver, Colorado 80217-3364.

Under electron impact boranes and carbonores generally undergo considerable fragmentation to yield variously hydrogenated C₃B₄⁻ and B₃⁻ anions (n = 1-3; m = 1-5) [1]. The separation of anions with a particular mass to charge ratio from the bulk of ionic species created from B₂H₆ and R₂C₄H₁₆ (R = Me, Et, SiMe₃) in the plasma of our FA-SIFT instrument [2] is complicated by the natural abundance of ¹¹B/¹⁰B = 4.0. We have overcome this problem by synthesising isotopically labelled ¹⁰B₂H₆, which has allowed us to generate and isolate nonclassical anions previously not observed in solution. The gas phase ion-molecule reactions of several of these anions, their basicity, and their collision-induced dissociation (CID) reactions will be described. For further characterization we have determined their structures using high level ab initio calculations.


CHEMISTRY OF LOW VALENT SILICON-CONTAINING ANIONS: CHEMISTRY OF THE SILYLIMIDATE ANION [H(SiO)NH]⁻ AND ITS PARENT ION [H₂(SiO)NH₂]⁻.
Joseph A. Hankin, Michèle Krempf, and Robert Damrauer, Department of Chemistry, University of Colorado at Denver, Denver, Colorado 80217-3364.

The Flowing Afterglow - Select Ion Flow Tube instrument allows generation of unusual ions which can be isolated for characterization and study. (VanDoren, J.M.; Barlow, S.E.; DePuy, C.H.; Bierbaum, V.M. J. Am. Chem. Soc. 1987, 109, 4412.) The gas phase chemistry of several low valent silicon-containing anions has been studied, most recently including ions [HSiS]⁻ and [HSiNH]⁻. (Damrauer, R.; Krempf, M.; O'Hair, R.A.J. J. Am. Chem. Soc. 1993, 115, 1998.) Anions with structures [H(SiO)NH]⁻ and [H₂(SiO)NH₂]⁻ have been characterized in the FA-SIFT instrument and further analyzed with ab-initio calculations. A current instrument upgrade involving a new triple quadrupole mass filter detector will also be discussed.

SIFDT-DRIFT STUDIES OF SULFUR ANION REACTIONS. Hack Sung Lee and Veronica M. Bierbaum,
Department of Chemistry, University of Colorado, Boulder, Colorado 80309-0215.

Rate coefficients and product distributions of ³⁴S⁻ + (CS₂, COS, H₂S) reactions as a function of center of mass energy from thermal to ~1 eV have been measured with our Tandem Flowing Afterglow SIFDT (Selected Ion Flow Drift Tube). S⁻ ions were created by EI (Electron impact Ionization) on unenriched CS₂ in the source flowing afterglow tube. The overall rate coefficients for CS₂ and COS decrease at low energies then increase at higher energies. The product distributions, however, show quite different energy dependences. Namely, the rate of chemion neutral reaction (isotope exchange reaction) shows a large negative energy dependence for CS₂ but a much smaller negative energy dependence for COS. The production rate of S₂⁺ shows noticeable difference between these two cases primarily due to energetics. The overall rate for H₂S does not show appreciable energy dependence. However the product distribution shows a large negative energy dependence for isotope exchange and a positive dependence for proton transfer and hydrogen atom abstraction. This study sheds some light on reaction mechanisms since isotope labeling exposes otherwise hidden reaction channels. An attempt has been made to interpret the data with theories such as RRKM/QET and PST along with a newly proposed classical trajectory method.
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GAS PHASE REARRANGEMENT OF THE ISOCYANOMETHYL TO THE CYANOMETHYL ANION. Christopher M. Hadad, Charles H. DePuy and Veronica M. Bierbaum, Department of Chemistry and Biochemistry, University of Colorado, Boulder, Colorado 80309-0215.

The gas phase negative ion chemistry of the isomeric nitriles, acetonitrile (CH$_3$CN) and methyl isonitride (CH$_3$NC), have been re-examined in a flowing afterglow-selected ion flow tube (FA-SIFT). There are only a few known cases of negative ion rearrangements. The isomeric nitrile anions do show different chemical reactivity with a variety of neutral rearrangements, thereby allowing for a definitive test of rearrangement upon anion formation. The effect of deprotonation exothermicity of acetonitrile and methyl isonitrile on the isomerization has been examined. The isomerization of the CH$_3$CN$^-$ and CH$_2$NC$^-$ anions have also been studied via high level ab initio calculations. The gas phase acidities of both isomeric anions have been re-examined both experimentally and theoretically, and good agreement has been obtained with both methods. The relative chemistry of both isomeric anions will be presented.

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The reactions of ketenyl, allenyl and some related anions with ketene, COS, CO$_2$ and CS$_2$ in the gas phase using a FA-SIFT (Flowing Afterglow-Selected Ion Flow Tube) apparatus are reported. Products and reaction mechanisms will be discussed. The results indicate addition and subsequent rearrangement through a four membered cyclic intermediate, similar to that suggested for the reaction of ketenyl anion with COS and CS$_2$. Nevertheless, in some cases, different intramolecular cyclizations of the primary adduct are in competition, allowing the study of comparative reactivities. Random $^{13}$C and deuterium labeling of the anions were also used to reveal the mechanisms of these reactions.

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DYNAMIC NUCLEAR POLARIZATION AT 140 GHZ (5 TESLA). Lino R. Becerra, Gary Gerfen, Brendan F. Bellew, David J. Singel$, and Robert G. Griffin

Francis Bitter National Magnet Laboratory and Department of Chemistry, Massachusetts Institute of Technology, Cambridge, MA 02139.

$^{a}$Department of Chemistry, Harvard University, Cambridge, MA 02138.

Dynamic nuclear polarization experiments have been performed at 140 GHz/210 MHz EPR/NMR frequencies. We have succesfully observed enhancements in polystyrene doped with the radical BDPA which are comparable to those obtained at lower fields (1.4 T) with the potential added advantage of higher resolution. The resolved solid effect has been observed for both $^1$H and $^{13}$C DNP experiments. The power and field dependance have been studied. The temperature dependance will also be discussed.

The key to the success of these experiments has been the implementation of a gyrotron - a high frequency high power microwave oscillator- for 140 GHz and its incorporation into the DNP/NMR experiment. The design and implementation of this device, as well as the possibility of extending the experiments to higher frequencies, will be discussed.
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CROSS-POLARIZATION AND DIPOLAR-DEPHASING MAS NMR EXPERIMENTS: QUADRUPOlar NUCLEI AND SOLID-STATE STRUCTURAL DETERMINATION.
Kel T. Mueller, Colin A. Fyle, Hiltraud Grondey, and Kirby C. Wong-Moon, University of British Columbia, Department of Chemistry, 2036 Main Mall, Vancouver, BC Canada V6T 1Z1

Cross-polarization MAS or dipolar-dephasing experiments such as TEDOR can detect dipolar connectivities to quadrupolar nuclei, while also taking advantage of the fast $T_1$ relaxation of quadrupolar spins to obtain spectra of spin-1/2 species which have inefficient relaxation mechanisms. Extensions of these techniques into two-dimensional heteronuclear correlation experiments provide maps of connected resonances. Examples from inorganic chemistry with $^{27}$Al/$^{31}$P, $^{27}$Al/$^{29}$Si, $^{17}$O/$^{31}$P or other spin pairs demonstrate these ideas. Related techniques have also been considered and will be compared and contrasted in their ability to provide connectivity information and internuclear distances in the solid state. A study of the parameters (the $T_{1\rho}$ and $T_{1\rho}$ values) affecting the cross-polarization dynamics in these systems has also been undertaken. Cross-polarization at other orientations of the spinning axis, with a subsequent hop of the spinning axis and MAS detection, has been studied for coherence-transfer from quadrupolar nuclei and we will describe situations where this method is found to be more efficient than conventional CPMAS.

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VARIABLE AMPLITUDE CROSS-POLARIZATION MAS NMR
Olve B. Peersen, Xiaoleng Wu*, May Han, Günther P. Metz, and Steven O. Smith,
Yale University, Department of Molecular Biophysics and Biochemistry and Department of Chemistry*, New Haven, CT 06511.

Magic angle spinning (MAS) severely affects proton cross polarization (CP) of dilute spins when the MAS frequency is comparable to or greater than the proton dipolar interactions in the sample. Under such conditions it becomes very difficult to find and maintain exact CP matching conditions because the normally broad Hartmann-Hahn matching curve is transformed into a series of sharp matching peaks. The most efficient CP matching condition is found when the l and S spin-lock field strengths differ by exactly the sample spinning speed, making the experiment very sensitive to changes in the MAS rate, amplifier output, or probe tuning. We have introduced a new method, Variable Amplitude Cross Polarization (VACP), that overcome these problems and makes it significantly easier to set up and execute CP-MAS experiments over a wide range of spinning speeds. In VACP one generates a number of different matching conditions during the contact time by simply modulating the amplitude of one of the two rf fields while the other remains constant. This increases the apparent CP matching width of the sample by several kHz, restoring flat matching curves to high speed spinning experiments, and recovers signal intensity lost in high speed CP-MAS experiments due to rf inhomogeneity across the sample coil.

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CPMAS SPECTRAL EDITING USING POLARIZATION INVERSION. Xiaoleng Wu and Kurt W. Zilm, Dept. of Chemistry, Yale University, 225 Prospect Street, New Haven, CT. 06511.

Spectral editing is very useful for simplifying complex spectra and in assigning NMR signals. This talk will describe one approach to complete spectral editing of C-13 CPMAS spectra of rigid solids. The pulse sequences used combine standard CP with polarization inversion (PI). In polarization inversion the phase of the proton spinlocking RF is inverted after the CP time. This causes the C-13 magnetization to flow back into the protons. If the initial CP time is long enough, the PI time can be chosen to null the CH signals, invert CH$_2$ signals, and somewhat attenuate the methyl and non-protonated carbon signals. Editing can be improved by using both a short CP and PI time. With the proper choice of these times an inverted CH$_2$ only sub-spectrum can be produced. In combination with other spectral editing schemes it is possible to generate sub-spectra containing only CH$_3$, CH$_2$, CH or C groups respectively. Since the PI methods rely on heat capacity ratios, rather than the relative strengths of dipolar couplings, these methods are less sensitive to molecular motion than many other spectral assignment techniques used for solids.
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1H AND 19F MULTIPLE-QUANTUM NMR DYNAMICS IN QUASI-ONE-DIMENSIONAL SPIN DISTRIBUTIONS IN APATITES. Gyunggoo Cho, Liam B. Moran and James P. Yesinovskii, Department of Chemistry, Michigan State University, East Lansing, MI 48824-1322 and Naval Research Laboratory, Code 6120, Washington, DC 20375-5342.

We have studied the MQ-NMR dynamics of uniformly-spaced proton spins in hydroxyapatite, Ca₃(OH)(PO₄)₂, and related compounds. A log-log plot of the effective size N vs. the preparation time for creation of even-order MQ coherences has a slope ("growth exponent") of 0.98 for short times, in agreement with the slope of 1.00 predicted for 1-D systems by the "incremental shell model" (Levy and Gleason, J. Phys. Chem., 96, 8125, 1992). At longer times the slope is 1.82, close to the value of 2.05 calculated for two-dimensional distributions using this model, presumably reflecting the incomplete isolation of the columns of protons. The experimental rates of growth are significantly faster than the model predicts. Hydroxyapatite deficient in hydroxyl groups as well as fluorohydroxyapatite solid solutions exhibit decreased rates of growth of MQ coherences. A 1-D cluster model involving random "defects" in the 1-D chains is developed to account for the experimental results. The 19F MQ spectra of a single crystal of fluorapatite at different orientations show oscillatory behavior of the zero- and two-quantum intensities, reflecting the presence of oriented 1-D clusters of small numbers of spins. Approaches to "tuning" the dimensionality of the 19F spin system in fluorapatite by observing the MQ behavior of selected isochromats in the powder pattern will be discussed.

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13C-19F DIPOLAR DEPHASING IN MONOFLUORINATED ORGANIC SUBSTANCES. Edward W. Hagaman, Chemistry Division, Oak Ridge National Laboratory, Oak Ridge, TN 37831-6201.

The conventional solid state CP/MAS 13C NMR spectra of non-polymeric monofluorinated organic substances exhibit dramatic homogeneous broadening of resonances of those carbons in close spatial proximity to the magnetic dipole moment of the 19F nucleus. Resonances of carbons directly bonded to 19F can broaden beyond recognition. 13C-19F dipolar dephasing is the 13C T₂ relaxation pathway and is promoted by efficient 19F magnetization diffusion. 19F and 13C T₂'s have been measured directly to delineate these processes. The principal broadening occurs through the 13C-19F dipolar interaction and has an r⁻³ carbon-fluorine internuclear distance dependence. The 13C-19F dipolar dephased 13C spectrum edits the full 1H, 19F doubly dipolar decoupled spectrum, using the strength of the 13C-19F dipolar interaction as the editing criteria. The 13C-19F dipolar dephasing experiment constitutes a highly selective method for fluoride functional group determination under high resolution conditions. The coincidental application of resonant 19F and 1H dipolar decoupling diminishes relaxation broadening in the 13C spectrum. Concurrent 1H and 19F decoupling must be an integral feature of high resolution CP/MAS 13C experiments on fluorinated organic materials performed at routine (< 6 kHz) MAS speeds. Research sponsored by the Division of Chemical Sciences, Office of Basic Energy Sciences, U.S. Department of Energy under contract DE-AC05-84OR21400 with Martin Marietta Energy Systems, Inc.

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SPIN-SPIN COUPLING PHENOMENA INVOLVING PHOSPHORUS.
Roderick E. Wasylchen, Klaus Eichele, Michael D. Lumsden, Kenneth Wright, and Gang Wu. Department of Chemistry, Dalhousie University, Halifax, Nova Scotia, Canada B3H 4J3.

NMR studies of solids offer experimentalists an opportunity to measure spin-spin coupling constants, J, involving spin-1/2, spin-S pairs, where S ≥ 1. In order to analyze the spin-1/2 NMR spectra of such spin systems one must recognize that the quadrupolar interaction may significantly perturb the pure Zeeman states of the quadrupolar nucleus. We have analyzed the 31P NMR spectra of several systems in which phosphorus is spin-spin coupled to a quadrupolar nucleus using a first order perturbation approach developed by Olivieri. In some systems we have found compelling evidence for anisotropy in the J-tensor. The implications of an anisotropic J-tensor will be reviewed.

Finally, the recoupling of "equivalent" 31P spin-pairs in the MAS spectra of solids will be discussed.

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THE APPLICATION OF NMR SHIFTS TO STRUCTURAL STUDIES OF GLASSES AND MINERALS. Raymond Dupree$^{1,2}$, Simon C. Kohn$^1$, $^1$Physics Department, University of Warwick, Coventry CV4 7AL, U.K., $^2$Physics Department, Oregon State University, Corvallis, OR 97333

The chemical shift is one of the most significant parameters that is used to obtain structural information about disordered systems such as glasses, thus it is important to know the reliability of shift structure correlations. The many correlations between the $^{29}$Si shift and structure that have been presented in the literature are critically examined with respect to their ability to predict the spectrum of tridymite (SiO$_2$), which has 12 Si sites, and of $\text{K}_2\text{MgSi}_2\text{O}_6$ leucite which has 10 Si sites. None of the correlations are able to accurately predict the spectra of these materials. Nevertheless they may be used to obtain some information on the Si-O-Si bond angle distribution in glasses, even though it is very sensitive to the differential of the $^{29}$Si shift variation with angle, which is even more uncertain than the shift variation itself. Despite these problems the information obtained is still likely to be more accurate than that deduced using scattering techniques. The results will be compared with those obtained recently using an alternate NMR method, 2D $^{17}$O DAS, [Farnan et. al. Nature 358 31 (1992)] which relies on the angular dependence of the electric field gradient parameters to deduce the bond angle distribution.

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CARBON-13 CHEMICAL SHIFT TENSOR DATA COMPARED WITH DIFFRACTION STRUCTURAL PARAMETERS USING QUANTUM MECHANICAL CALCULATIONS. David M. Grant, Rob Iuliuucci, Fang Liu, Julio C. Facelli, and Don W. Alderman, Chemistry Dept., Univ. of Utah, Salt Lake City, Utah 84112.

The development of a two-dimensional flipper probe for measuring chemical shifts in single crystals allows 50-100 magnetically unique carbon atoms per unit cell to be indexed. The symmetric chemical shift tensor, determined in this manner, provides six parameters per carbon atom that affect the Zeeman levels of a nuclear spin system with an accuracy of less than 0.5 ppm. These frequency shifts are intimately connected to the electronic structure in the vicinity of the nucleus, and quantum mechanical calculations of shift tensors now correlate to a high degree of dependability with the molecular structural parameters. While the absolute shielding calculations still suffer from electron correlation errors, the quantum mechanical methods exhibit sufficient consistency to predict systematic changes in bond distances at the 0.005 Å level, a value that is generally lower than corresponding uncertainties in typical diffraction data on molecules of this size. With future anticipated improvements in quantum calculations relating the shift data with molecular parameters, it is expected that theoretical chemical shift tensors will provide structural information that will complement, if not actually compete with, standard x-ray and neutron diffraction data. This work is illustrated with single crystal data on a variety of sugars and aromatic compounds. These data are readily interpreted with changes in bond distances, distortions in bond angles, conformational variations and hydrogen-bond effects. The theoretical calculations also establish necessary criteria for conveniently assigning the chemical shift tensor components.
MEASUREMENT OF INTERNUCLEAR DISTANCES IN ISOLATED PAIRS OF SPINS BY NMR; WHICH IS THE MOST APPROPRIATE "HARD" EXPERIMENT?

B.C. Gerstein and Marek S. Pruski, 229 Spedding Hall, ISU, Ames, IA 50011

There exist at least four experiments which can in principle provide the internuclear distance of an isolated pair of spins 1/2 via the NMR spectrum: (1) a single shot, in which shielding anisotropy and chemical shift are the major interactions; (2) nutation, in which the shielding anisotropy is averaged to zero and the dipolar interaction is scaled by a factor of 1/2; (3) symmetry adapted Carr-Purcell, Meiboom-Gill sequences with stroboscopic observation, which average shielding shielding anisotropy to zero, and scale the dipolar coupling by a factor calculable in principle, and (3) use of a spin-echo sequence in which the shielding anisotropy is re-focused to zero, and the time between the 90° excitation pulse and the 180° re-foocussing sequence is incremented to provide the dipolar oscillation pattern. The advantages and limitations of each will be discussed, with reference to results on a sample of poly(ethyleneterephthalate) doubly doped at the methylene carbons, and on a sample of doubly doped ethylene deposited on silica-supported Ru at 78K.

NMR IMAGING AND SCATTERING EXPERIMENTS FOR SOLID STATE SAMPLES, D. G. Cory, Department of Nuclear Engineering Massachusetts Institute of Technology, Cambridge, MA 02139

The spatial distribution of a solid material can be investigated directly by NMR imaging techniques, or indirectly by following the interruption of the translational motions of imbibed fluids by the solid’s boundaries. The imaging experiment resolution is limited by the linewidth of the sample, and we have been investigating coherent averaging approaches to reducing this linewidth in a pulsed gradient imaging experiment. The resolution of the diffusive scattering experiment is limited by the gradient strength, and we have been formulating a model free interpretation of the diffusion results. A compact and unifying analysis of these two methods will be discussed, and some recent results presented.
NMR IMAGING OF ANOMALOUS SOLVENT TRANSPORT IN GLASSY AND RUBBERY MACROMOLECULAR MATERIALS.* George D. Cody and Robert E. Boto, Chemistry Division, Argonne National Laboratory, 9700 S. Cass Avenue, Argonne, IL 60439.

Magnetic resonance imaging (MRI) microscopy provides an effective approach to investigate the phenomenon of non-Fickian or anomalous solvent transport in glassy macromolecular networks near their glass to rubber transition. A sample of polyethyl-methacrylate (PEMA) and a sample of high volatile A rank coal were selected as specimens. By resolving the spatial distribution of mobile protons associated with the solvent, one can distinguish between Fickian and anomalous transport mechanisms. In the former case at some intermediate time, an exponential concentration profile will be observed; in the case of anomalous transport, however, a steep solvent front is often observed. The glass transition temperature, T_g, of PEMA is on the order of 35°C. Dilution with methanol suppresses T_g to less than room T; accordingly, the transport of methanol in PEMA is expected to be anomalous. The high volatile A rank coal is also glassy at room temperature, while swelling in pyridine has been reported to suppress coal's T_g. The results of MRI microscopy confirm that the solvent transport behavior for both samples is anomalous and characterized by a sharp solvent front which moves at an essentially constant velocity. The results of this analysis form the basis of a model of anomalous transport in macromolecular solids which couples diffusion with the kinetics of a first order phase transition. Using this model, the dynamics of anomalous transport is parameterized through a displacement diffusion coefficient, D, a glass to rubber transition rate constant, β, and a critical concentration which initiates the phase transition. The determination of these three dynamic parameters yields fundamental information on the molecular structure of these materials.

*This work was performed under the auspices of the Office of Basic Energy Sciences, Division of Chemical Sciences, U.S. DOE, contract no. W-31-109-ENG-38.

SHORT T_2 MAGNETIC RESONANCE IMAGING STRATEGIES, David E. Axelson, Ken Green, Jon Goldman, Jim Posti and Arno Nauert, Petroleum Recovery Institute, 100, 3512-33 St NW, Calgary, Alberta, Canada T2L 2A6 and Bruker Analytische Messtechnik GmbH, Silberstreifen, D-7512 Rheinstetten -Po., Germany

Imaging of rigid solids (characterized by T_2's of less than 1 ms) requires the application of specialized pulse sequences and places severe strain on hardware performance (gradient strength, linearity and reproducibility; ramp/rise times, digitizer performance). In this talk we will discuss two of the avenues available to achieve better images of such materials. These examples will be taken from our own laboratory experiences with a Bruker Biospec-X 24/30 (2.35T, 30 cm diameter bore). Part 1 will illustrate the use of variable temperature MRI (ambient to >100°C) on a variety of materials to demonstrate both the advantages and disadvantages of such an approach. The behaviour of fluids in porous materials presents special problems with respect to relaxation time behaviour as a function of temperature. Part 2 will then discuss the application of a newly developed technique (single point imaging) that enables MRI to be effective for samples with T_2's greater than 20-50 microseconds on large bore horizontal magnets (without the use of MAS or multiple pulse techniques). Images of polyethylene will be discussed in this case.
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SOLID-STATE NMR IMAGING WITH MAGIC-ANGLE SPINNING, Yahong Sun, Marian Buszko, Herman Lock, and Gary E. Maciel, Department of Chemistry, Colorado State University, Fort Collins, Colorado 80523.

As one of the main attractive features of NMR imaging in the long term may be chemical selectivity or specificity via the chemical shift, we have recently focussed on incorporating MAS in our solid-state NMR imaging strategies. \(^1\)H and \(^{13}\)C imaging probes that incorporate MAS and circuitry that generates rotating gradients constitute the hardware focus of this work. \(^1\)H NMR imaging under MAS has been carried out in one spatial dimension (along the rotor axis) and in two spatial dimensions (transverse to the rotor axis), with and without homonuclear dipolar line-narrowing by the TREV sequence, which has favorable characteristics for incorporation into \(^1\)H CRAMPS imaging strategies. Analogous \(^{13}\)C CP-MAS imaging experiments seem promising for somewhat larger samples (e.g., diameter ~10 mm), where the enhanced chemical shift resolution is attractive. The characteristics of \(^1\)H and \(^{13}\)C MAS imaging approaches will be described.

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HIGH-RESOLUTION NMR OF COMPLICATED SOLIDS: BIOLOGICAL AND SYNTHETIC COMPOSITES AND COMPLEXES, Jacob Schaefer, Washington University, St. Louis, MO 63130

We have recently shown that narrow-line \(^{13}\)C, \(^{15}\)N, and \(^{31}\)P NMR spectra of lyophilized powders of 50-kD protein complexes are observed if the complex is freeze-quenched from buffered, dilute solution (Biochemistry, 1993, 32, 2868). Solid-state and solution-state chemical shifts can be matched indicating that the local pH and extent of hydration of the binding site are unaffected by the lyophilization, consistent with preservation of the native conformation of the binding site. After lyophilization, each protein molecule is isolated by more than 200 buffer molecules in a glassy, charge-stabilized, molecular composite. Distances from \(^{31}\)P and \(^{13}\)C labels of inhibitors to \(^{15}\)N labels in the protein are measured by rotational-echo double-resonance (REDOR) NMR. These distances are constraints in molecular dynamics simulations to generate a model for the complex. This illustrates the general strategy of determining the structure of a non-crystallizable protein complex using solid-state NMR if the crystal coordinates of the uncomplexed protein (or a homolog) are available. The distances between packed chains in polymer glasses can be determined by the same types of REDOR NMR experiments developed for protein complexes. The distances determined by \(^{13}\)C-\(^2\)H REDOR NMR, for example, define local packing in a polycarbonate glass for which diffraction experiments are impossible. Interfaces of blends of heterogeneous polymers like poly(p-fluorostyrene) and \(^{13}\)C-labeled polycarbonate can also be characterized quantitatively by REDOR NMR. The residual protons in perdeuterated polymers behave as a rare spin, and REDOR between isolated \(^1\)H,\(^{13}\)C pairs in perdeuterated polycarbonate reveal the average location of the ubiquitous 0.3% (by weight) water in glassy polycarbonate.

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ABSTRACT NOT AVAILABLE
SOLID-STATE NMR STUDIES OF PEPTIDES AND PROTEINS. Stanley J. Opella, Department of Chemistry, University of Pennsylvania, Philadelphia, Pennsylvania 19104-6323, U.S.A.

Recent developments in solid-state NMR spectroscopy for resolution and measurement of spectral parameters in polypeptides will be described. Experiments involving the hydrogen and nitrogen sites of peptide bonds are the primary focus of attention. Recent applications of solid-state NMR spectroscopy to peptides and proteins will also be described. Experimental studies of several membrane associated peptides and proteins in both oriented and unoriented samples will be presented.

SPIN RELAXATION, MOLECULAR MOTION AND MORPHOLOGY IN POLYMERS. Robert L. Vold and Gina L. Hootson, Department of Physics, College of William & Mary, Williamsburg VA 23187

Coupling between morphological heterogeneity and local motion in polymers is determined by the relative magnitudes of intra- and inter-molecular contributions to the local potential energy surface. Thus in glassy polymers, distributions in both the rates and amplitudes of local motions can arise from differences in local packing. We have used both $^{13}$C and $^2$H relaxation techniques to study such motion. In order to identify characteristics of motion which are uniquely associated with polymer morphology, it is useful to compare the spin relaxation data for polymers with those of corresponding monomer units and small molecule precursors. Such comparisons will be presented for high performance thermoplastic polyimides, and for bisphenol-A polycarbonate.


Intuitively we expect energy absorption in amorphous polymers to be related to movement of the polymer chains. Ring flipping is an easily detected local motion in bisphenol-A polycarbonate and other aromatic polymers that does appear to be connected to energy absorption. Still, establishment of a direct link between ring flipping and properties of bisphenol-A polycarbonate involving energy absorption, such as impact strength, is difficult, but a series of results obtained over of period of years helps to clarify the connection. The similarity of the energy barrier for ring flipping in various systems suggests that intermolecular interactions help to control ring flipping. These intermolecular interactions may be the key to energy absorption. Careful consideration of the molecular packing in a crystalline model for polycarbonate in which the rings flip suggest some ways in which intermolecular interactions may be important. Future progress in connecting ring flipping to bulk properties may require the development of special experiments that relate the NMR measurements directly to physical perturbations of the sample.
SOLID STATE NMR INVESTIGATION OF NEGATIVE EXCESS MIXING ENTHALPY IN PVE/PIP BLENDS. Kenneth J. McGrath, Joel B. Miller, C. Michael Roland, and Allen N. Garroway, Code 6120, Naval Research Laboratory, Washington, DC 20375-5000

Blends of poly(vinylethylene), (PVE), and 1,4-polyisoprene, (PIP), which are very high in 1,2-PVE microstructure exhibit a single, anomalously broad calorimetric and dynamic-mechanical glass transition. In contrast to these results, which suggest a phase segregated morphology, static $^1$H NMR studies demonstrate mixing on a segmental level. There are no specific interactions in PVE/PIP blends (which would give rise to a negative mixing enthalpy) and intermolecular forces are strictly dispersive in nature. However, miscibility extends to infinite molecular weight (where combinatorial entropy vanishes). This anomaly was investigated by probing the spatial intimacy of the neat and blended components through characterization of the NMR $^1$H-$^{13}$C cross polarization cross relaxation efficiency. The results are consistent with closer spatial packing of the components in the blend relative to neat PVE, and account for the negative excess enthalpy in this van der Waals blend.

A SOLID STATE DEUTERIUM NMR STUDY: EVIDENCE OF LARGE AMPLITUDE MOTION IN THE FURANOSE RING OF AN OLIGONUCLEOTIDE. Debra L. Mattiello* and Gary P. Drobny Chemistry Department, University of Washington, Seattle WA 98195

Solid state deuterium NMR has been used to follow the large amplitude motion of the furanose ring at the C9 (C21) position in the synthetic oligonucleotide, d(CCGGAATTC$^*$GCG)$_2$. Even though this DNA oligomer has been widely studied by X-ray and high resolution NMR methods, there is no agreement concerning the furanose ring dynamics. Semiempirical equations are often used to interpret high resolution NMR proton scalar couplings in terms of simple conformational equilibria. The present results indicate that the dynamics of sugar rings in DNA oligomers can be large in amplitude, and sequence dependent. Additionally, the conformational populations may not be those predicted by semiempirical equations. Evidence of large amplitude furanose ring dynamics has prompted the investigation of the orientation dependence of the relaxation rates of Zeeman and quadrupolar order as a direct measure of the spectral densities and a substantive test of motional models. This work emphasizes the valuable contribution that solid state NMR can make to the study of biopolymer conformation and dynamics and represents the first application of deuterium spin alignment techniques to the study of furanose ring motions in hydrated oligonucleotides.

THE DETECTION AND CHARACTERIZATION OF MOLECULAR INTERACTIONS IN POLYMER BLENDS USING SOLID-STATE NMR. Jeffery L. White, Peter A. Mirau, AT & T Bell Laboratories, Murray Hill, NJ 07974

Specific intermolecular or interchain interactions often determine whether two polymers form a miscible blend or phase separate. Recent developments in one- and two-dimensional solid-state NMR methods allow for the detection of both weak Van der Waals and stronger hydrogen-bonding interactions between the functional groups of component polymers in solid blends. Solid-state two-dimensional heteronuclear correlation (HETCOR) spectroscopy and one-dimensional windowless isotropic mixing (WIM) polarization transfer experiments rely on exploiting distance dependent heteronuclear dipolar interactions between carbons and protons. In this way, information about the relative spatial relationships between polymer chains and/or functional groups is obtained. These experiments provide a direct experimental probe of miscibility, and specific intermolecular interactions have been detected in several polymer blend systems. Similarly, solid-state nuclear Overhauser experiments (NOE) have been used to detect weak intermolecular interactions in polystyrene/poly(vinylmethyl ether) blends.
ABSTRACT NOT AVAILABLE

Assessing and Developing Pulse Sequences with Interactive Computer Graphics Jonathan Callahan and Gary Drobny
Chemistry Dept. University of Washington, Seattle, Washington 98195 USA

3D Computer graphics will be displayed which aid in the design of experiments. Applications of this approach will be demonstrated for the areas of flow-imaging, distance measurements in solids and broad-band deuterium excitation. An ongoing effort in this laboratory has used density matrix calculations to simulate a variety of magnetic resonance experiments in an attempt to understand how existing experiments can be optimized for certain spin systems or for particular experimental limitations. The optimization techniques we use supply the computer with adjustable pulse sequence parameters and a desired spin state at the end of the pulse sequence. The computer performs a search through the parameter space and returns the most successful parameters. Although this technique is often successful, it removes us from the discovery process and can leave us without a clear understanding of the etiology of pulse sequence performance. Recently we have combined computer visualization techniques with our simulations in an attempt to present the store of information we generate in a more palatable form. We have found that computer animations showing the evolution of the density operator in a series of three-dimensional subspaces of the full density operator space brings us back into the discovery process and greatly eases the communication of our ideas to others.

Visualization of Multidimensional NMR Data
Robert D. Johnson, Dominique Brodbeck, Richter Rafey
Almaden Research Center, IBM Research, 650 Harry Rd., San Jose, CA 95120

Three and four dimensional NMR experiments have greatly increased the importance of software for processing and data analysis. The advent of computers specifically designed for visualization of complex datasets is an exciting opportunity for NMR in this regard. We will show some preliminary work in visualizing multidimensional NMR data. A video will be shown, which merges molecular structures with a fly-by over the surface of an NMR experiment. The processing was done on an IBM POWER Visualization system, consisting of 32 parallel processors and a 20GByte disk array. Applications to animation, and display of multiple datasets will be discussed.
STRUCTURE AND SPIN DYNAMICS OF THE SILICA SURFACE, \textit{et al.} 
L-Suuer Chuang, David R. Kinney, and Gary E. Maciel, Department of Chemistry, Colorado State University, Fort Collins, Colorado 80523.

$^1$H and $^{29}$Si NMR studies have been carried out on a variety of silica gel samples with various degrees of dehydration or hydration and of $^2$H$_2$O exchange. $^1$H-$^1$H dipolar dephasing prior to $^1$H-$^{29}$Si cross polarization and $^1$H-$^{29}$Si dipolar dephasing following cross polarization are useful strategies for examining silicon environments of specific silanols. The $^1$H-$^{29}$Si cross-polarization spin dynamics of six dry, partially $^2$H$_2$O-exchanged silica gels indicate that each non-hydrogen-bonded single silanol is surrounded by several other single silanols and that each geminal silanol is surrounded by several single silanols to which it is hydrogen bonded.

SINGLE CRYSTAL PROTON NMR STUDIES OF LOW CONCENTRATION HYDROUS SPECIES IN MINERALS. \textit{Herman Cho*} and George R. Rossman†, *Molecular Science Research Center MSIN K2-20, Pacific Northwest Laboratory, Richland, Washington 99352 and †Division of Geological and Planetary Sciences MC 170-25, California Institute of Technology, Pasadena, California 91125.

A proton NMR investigation of natural single crystal garnets containing low levels (0.2 - 0.3 wt% H$_2$O) of OH has been performed as part of a study to ascertain modes of OH incorporation in crystalline silicates. The synthetic hydrogrossular powder, Ca$_3$Al$_2$(O$_4$H$_4$)$_3$, in which the SiO$_4^+$ $\leftrightarrow$ 4OH- replacement is the predominant, known form of OH- incorporation, has been investigated in parallel. The results of proton multiple-quantum NMR experiments, in combination with a moment analysis of the proton spin-echo envelope modulation, are shown to provide a way for obtaining a detailed picture of hydrogen cluster sizes and internuclear distances in systems containing isolated groups of hydrogen nuclei. These experiments indicate that the hydrous component in the natural grossulars occur in static configurations consisting of mainly two, inequivalent, closely spaced hydrogen nuclei, with an essentially isotropic range of spatial orientations. The 4OH- tetrahedral substitution is not implicated as the major hydrous species in any of the natural grossular results. IR studies of these same crystals are in accord with the NMR conclusions.

Proton and Deuterium MAS NMR of Zeolites

Larry W. Beck and James F. Haw
Department of Chemistry, Texas A&M University, College Station, TX 77843.

The proton NMR spectral properties of zeolites are of interest, because they could, if properly interpreted, provide information about Bronstead acidity. This talk will be a progress report on investigations of the properties of two common zeolites, HZSM-5 and HY. Variable temperature 1 and 2 D $^1$H experiments indicate a variety of magnetization exchange processes. This picture can be at least partially sorted out with a combination of relaxation studies, $^2$H MAS, and other experiments.
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27Al MAS NMR STUDIES OF SODIUM ALUMINATE SPECIATION AND THE MECHANISTICS OF ALUMINIUM HYDROXIDE PRECIPITATION UPON ACID HYDROLYSIS. John V. Hanna and Susan M. Bradley, aCSIRO Division of Coal and Energy Technology, P.O. Box 136, North Ryde 2113, NSW Australia, bDavy Faraday Research Laboratory, Royal Institution of Great Britain, 21 Albermarle St., London W1X 4BS, United Kingdom.

27Al MAS NMR investigations of sodium alunites and aluminium hydroxides formed through acid hydrolysis have been undertaken, with an OH/Al hydrolysis ratio range of between 5.3 and 2.8 under catalysis. Resources representing four, five and six coordinate aluminium moieties are observed, the intensities of which vary as a function of OH/Al Ratio. The dominant species above on OH/Al ratio of 4.4 appears to be a $Q^0$ Na[Al(OH)$_4$] salt depicted by a sharp resonance at 86.6 ppm. A second broader resonance at 71.3 ppm demonstrates the simultaneous existence of other four coordinate aluminium species linked through oxo bonds to other four coordinate aluminium species (e.g. $Q^4$ NaAlO$_2$), although a range of similar species (e.g. $Q^2$ Na[Al(OH)$_2$]) could also be present contributing to this vicinity of the $^{27}$Al chemical shift range. Between an OH/Al ratio of 4.4 and 4.1 a water soluble phase forms that contains both four and six coordinate aluminium. At OH/Al ratios of 4.0 and below a water insoluble phase exists possessing four, five and six coordinate species, the relative ratios varying with the degree of acid hydrolysis. The insoluble portion of the OH/Al = 3.9 sample reveals $^{27}$Al chemical shifts similar to those reported for $\gamma$-Al$_2$O$_3$ suggesting that a pseudo-spinel intermediate is the first phase involved in the crystallization of gibbsite. The observed five coordinate resonance probably results from species involved in the transformation of the pseudo-spinel phase to pseudo-boehmite prior to gibbsite precipitation.

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STRUCTURE AND DISORDER IN GLASSY IONIC CONDUCTORS, Kaj K. Olsen, Sandra L. Tagg, Randall E. Youngman, and Josef W. Zawczak, Department of Chemistry, Indiana University, Bloomington, Indiana, 47405, (812) 855-3994.

We have used several different two-dimensional NMR experiments to investigate the microstructure and disorder in glassy ionic conductors based on borate and phosphate. Using Variable Angle Correlation Spectroscopy (VACSY) we have determined not only the phosphate species present in different compositions of the silver phosphate-silver iodide system, but also the way in which each species is structurally disordered within each composition. In borate-based glasses we have used Dynamic Angle Spinning (DAS) to determine the boron and oxygen containing species, and again the way in which they are disordered as a function of added network modifier (sodium oxide or rubidium oxide).

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HIGH TEMPERATURE NMR OF CHALCOGENIDE GLASSES AND MELTS. Robert Maxwell and Helmut Eckert, Department of Chemistry, University of California, Santa Barbara, CA 93106.

The structural speciations of glasses as determined by room-temperature MAS and other solid state NMR techniques are the result of structural speciation equilibria locked in permanently at the glass-transition temperature. To gain further insights into these equilibria, and to understand them on the basis of equilibrium melt thermodynamics, variable temperature NMR studies are necessary on the molten states directly in-situ. This contribution reports such high-temperature $^{31}$P NMR studies of melts in the system phosphorus-selenium within the temperature range 25 °C ≤ T ≤ 600 °C. Using this approach, the following processes have been characterized in terms of thermodynamic parameters, rate constants, and activation energies: (1) equilibration between three- and four-coordinate phosphorus atoms, (2) network depolymerization associated with motional narrowing, (3) formation of $P_4S_3$ clusters, and (4) the chemical exchange of these clusters with residual P atoms of the molten state. The results of these studies are complemented by solid state NMR experiments including MAS-spin diffusion and 2-dimensional dipolar-chemical shift correlation (DICSY) experiments.

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PURE $^{14}$N NQR OF LARGE SPECIMENS
Michael L. Buess, Allen N. Garroway, James P. Yesinowski and Joel B. Miller,
Chemistry Division, Code 6120, Naval Research Laboratory, Washington, D.C.
20375-5342; SFA, Inc., Landover, MD 20875.

Large sample volumes may be employed to increase the signal-to-noise ratio of magnetic resonance signals. Such a strategy is particularly amenable to $^{14}$N pure nuclear quadrupole resonance (NQR), for which there is no externally applied magnetic field. The effects of transmitter power and coil size on signal detection sensitivity for $^{14}$N pure NQR are examined. The use of very large specimens in large RF coils is advantageous for particular circumstances for which the pure NQR resonance frequency is well-known, the spin-spin relaxation time is reasonably long, and a faithful rendition of the powder pattern is not essential. The steady state free precession (SSFP) pulse sequence has some benefits for the detection of NQR signals: when $T_2 = T_1$, one obtains a signal corresponding approximately to one-half the equilibrium magnetization on the time scale of $T_2^*$. These remarks are illustrated by model studies on an NQR spectrometer with a 300-liter RF coil.

SQUID-NQR OF NITROGEN-14 IN AMINO ACIDS AND SMALL PEPTIDES.
Ulrike Werner, Bruce Black, Marcia Ziegeweid, and Alexander Pines, Department of Chemistry, University of California, and Materials Science Division, Lawrence Berkeley Laboratory, Berkeley, CA 94720

We present a technique for the study of nuclear quadrupole resonance of $^{14}$N interacting with low electric field gradients as found, for example, in amino acids and small peptides. The high natural abundance of $^{14}$N (99.6%) makes this nucleus a promising local probe to obtain structural information concerning the nitrogen environment. However, the detection of the signal poses significant problems due to the low nitrogen quadrupole frequencies combined with the quenching of the magnetic moment of nuclei with spin I=1 in low magnetic fields. This technique employs a superconducting quantum interference device (SQUID) to detect small NMR and NQR signals directly at low magnetic fields. Sweeping a saturating rf-field through one nitrogen resonance while matching the proton Zeeman splitting to another nitrogen transition induces an observable change of magnetization of the sample via cross relaxation. Simultaneous excitation of an additional nitrogen resonances enhances the signal and helps to identify connected transitions. We demonstrate various properties of this technique with experiments on $^{14}$N in amino acids and small peptides. By studying a series of amino acids we can observe how the combination of the amino acids that form small peptides influences the local nitrogen environment.

FORCE DETECTION OF MAGNETIC RESONANCE: A NEW METHOD OF MR IMAGING
Costantino S. Yannoni, Daniel Rugar, Othmar Züger and John A. Sidles IBM Almaden Research Center, 650 Harry Rd., San Jose, CA 95120 and Department of Orthopaedics, University of Washington, Seattle, WA 98195

A fundamentally different method for detecting magnetic resonance has recently been proposed and demonstrated. Oscillating forces as small as $10^{-11}$N between spin magnetization in the sample and a magnetic field gradient generated by a nearby ferromagnetic particle can be measured by sensing the angstrom-scale vibration of a micromechanical cantilever. Since saturation of spin magnetization, which will change the force and concomitantly the motion of the cantilever, occurs only when the spins in the sample are at resonance, a plot of cantilever motion versus external dc field at the sample constitutes a magnetic resonance spectrum. We have thus detected the EPR spectrum of DPPH and, using the built-in gradient necessary for generating the force, have been able to obtain images of DPPH particles with $\sim 1 \mu$ resolution. Small magnetic particles can generate gradients as large as $10^{9}$T/m i.e. 100 gauss/Å, so that individual spins can be isolated for detection. The sensitivity of force detection at low temperatures using state-of-the-art cantilevers suggest that the detection of a single nuclear spin is possible.


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ABSTRACT NOT AVAILABLE

SITE-RESOLVED OPTICAL NMR OF GALLIUM ARSENIDE. J.Y. Hwang, J.A. Marohn, P.J. Carson, S.K. Buratto, D.N. Shykind, and D.P. Weitekamp, Arthur Amos Noyes Laboratory of Chemical Physics, California Institute of Technology, Pasadena CA 91125

The contribution of nuclear magnetic resonance to semiconductor science has been hampered by the inability of the usual methods to detect signals at the low abundance typical of dopant and defect sites. We will report on recent extensions of our method of time–sequenced optical NMR, which has proven to be applicable to optically relevant defects below the part–per–million level. Differences between nominally similar samples grown in different laboratories indicate that NMR can contribute to the identification of uncontrolled differences in the preparation of high purity material. By applying a variety of time–domain methods, the spectroscopic analysis of quadrupole–perturbed sites near defects has been improved. A feature of possible general interest is the extension of FID, nutation and multiple–pulse methods to low fields where the Zeeman and quadrupole terms of the spin Hamiltonian are comparable. This can provide greater spectral separation of sites than is possible in high field alone and requires a nonperturbative analysis in which the rotating–wave approximation is not made. Extension of these methods to optically–induced spin Hamiltonians and epitaxial structures will be discussed.

DYNAMICS OF OPTICAL ALIGNMENT OF NUCLEI IN HIGH MAGNETIC FIELDS. Matthew P. Augustine and Kurt W. Zilm, Dept. of Chemistry, Yale University, 225 Prospect Street, New Haven, CT. 06511.

The use of spin polarized Xe-129 as a polarization source for other nuclei appears to be a promising approach for enhancing the sensitivity of solid state NMR investigations of matrices, surfaces and interfaces. Successful implementation of this technique in chemical problems will require efficient production of spin polarized Xe-129. Work in our laboratory has recently focussed on using spin exchange collisions with optically pumped alkali atoms to produce spin polarized Xe-129 in high magnetic fields. Approaches to optimizing the Xe-129 polarization have been identified using a theory of optical pumping which borrows from well-known treatments of the transient Overhauser effect. This theory has been verified in experiments where either the gas phase concentration of alkali atoms or the laser power is varied. Indirect detection of the alkali atom optical spectrum via the NMR of the Xe-129 provides additional insight into optimal design of a system for producing spin polarized Xe-129. Approaches to chemically interesting applications will be discussed.
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CROSS POLARIZATION EXPERIMENTS WITH
LASER POLARIZED XENON

Materials Science Division, Lawrence Berkeley Laboratory, 1 Cyclotron Road, Berkeley, CA 94720
and Department of Chemistry, University of California, Berkeley, CA 94720

Preparation of highly spin-polarized xenon is now routinely available by contact with rubidium vapor optically pumped by conventional high power cw lasers. Up to \( \sim 5 \times 10^{20} \) xenon atoms can be pumped to polarizations of four orders of magnitude higher than thermal Boltzmann statistics. Xenon has previously been used as a probe of low surface area materials and is now being employed to enhance the sensitivity of other spins. A variety of polarization transfer schemes will be discussed including low field thermal mixing (Chem. Phys. Lett. in press), high field Hartmann-Hahn contact, and level crossing to quadrupolar nucl. Experimental results will be shown for molecules occluded in xenon solid and for polymer surfaces. High sensitivity optical detection of xenon NMR and its ability to probe surfaces of just a few square centimeters will also be discussed if time permits.

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DYNAMICS OF HYDROGEN ON A CATALYST SURFACE - A STUDY BY
SOLID STATE NMR. Frank Engelke, Sandeep Bhatia, Terry S. King, and Marek Pruski, Iowa State University and Ames Laboratory, Ames, IA 50011.

Different NMR methods have been used to probe the dynamic behaviour of hydrogen at the surface of silica supported ruthenium particles. In this study 'in situ' \(^1\)H NMR has been employed in a temperature range of 100 to 800 K and pressures of 0 - 700 Torr. Several types of hydrogen were found on the catalyst surface at various conditions. Of particular interest are three types of hydrogen adsorbed on the metal. We used spin-population labeling techniques ('hole-burning' using DANTE and 2D exchange NMR) to investigate exchange phenomena in the ms time range. Slower motions were studied using isotope labelling methods. The NMR data are correlated with the results of volumetric and heat of adsorption measurements.

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Recent Developments in In Situ MAS NMR of Reactions on Catalysts

James F. Haw, Eric Munson, David Murray, Teng Xu, David Ferguson, and Ali Kheir
Department of Chemistry, Texas A&M University, College Station, TX 77843.

This lecture will briefly cover two topics: resonance assignments in \(^{13}\)C MAS NMR studies of moderately complicated in situ reactions, and recent progress toward a systematic physical organic chemistry of zeolitic reactions. This methodology could potentially result in the discovery of new catalytic processes.
SOLID NMR INVESTIGATIONS OF $^{13}$C ADSORBATES ON POWDERED PLATINUM ELECTRODES. K. Fraszczuk, J. Wu and A. Wierczkowski, Department of Chemistry, University of Illinois at Urbana-Champaign, 1209 West California Street, Urbana, Illinois 61801, B. Montez and E. Oldfield, Department of Chemistry, University of Illinois at Urbana-Champaign, 505 South Mathews Avenue, Urbana, Illinois 61801.

NMR studies of adsorbed $^{13}$C-cyanide — a prototypical electrocatalyst poison — at a powdered-platinum electrode are reported. A 360 MHz ($^1$H) solid-state NMR instrument, single-channel NMR, a variable temperature option and a simple Helen spin-echo pulse sequence were used. The adsorbate was obtained via adsorption of $^{13}$C-enriched sodium cyanide on platinum from Na$_2$SO$_4$ at pH = 11 and at electrode potential 0.10 V vs. Ag/AgCl reference. The working platinum electrode was either clean metal powder or the powder diluted by glass. The latter procedure improved the penetration of the $rf$ into the sample. The observed lineshapes were axially symmetric and had an anisotropy, $\Delta$$\omega$, of ~400 ppm. At room temperature, the $^{13}$C powder pattern was poorly developed. In contrast, a clear powder pattern was seen at 20 K. The relaxation experiments as a function of temperature on frozen samples allowed us to probe the electronic density of states at $^{13}$C (via the Korringa relationship). Preliminary data on the electrode potential effect on the $^{13}$C-cyanide adsorbate are also presented. We expect that further work of this type is likely to advance understanding of the properties of molecules and ions in electric field of the solid/liquid, electrified interface.

NITROGEN CHEMISTRY ON SURFACES: HYDRODENITROGENATION AND NO$_x$ DECOMPOSITION. Jeffrey A. Reimer, Phil Armstrong, Adam Aylor, Alexis T. Bell, and Sarah Larsen, Materials Science Division, Lawrence Berkeley Laboratory, and Department of Chemical Engineering, University of California, Berkeley, CA, 94720.

NMR techniques have been used to study the structure and dynamics of nitrogen-containing molecules adsorbed on rhenium nitride metal surfaces. These studies demonstrate the dominance of the nitrogen lone pair in adsorbate-surface interactions as well as reveal a rich physics of adsorbate dynamics. The catalytic decomposition of NO$_x$ in copper exchanged ZSM-5 zeolites has also been investigated by silicon, nitrogen, and copper NMR. These studies show that the copper location within the zeolite, as well and the copper oxidation state, play important roles in directing catalytic activity.


For well over a decade, solid state NMR has made significant contributions to the understanding of zeolite structure and function. Even so, fundamental questions still remain which bear on the spectroscopy and chemistry of these materials. Our recent work has shown that $^1$H/ $^{29}$Si cross polarization can be applied successfully in a number of organic template-containing zeolites and we have investigated the role of the template and adsorbed water in that process. We find that relative intensities of CP and Bloch decay spectra are often in apparent conflict because of $T_1$ dispersion especially in cases with cryostographically inequivalent tetrahedral sites. For instance, in the zeolite mazzite we show that published $^{29}$Si intensities are seriously in error leading to apparent contradictions between $^{29}$Si and $^{27}$Al data and the published assignments.
SIDEBAND ANALYSIS IN DOR-NMR SPECTRA: J.P. Amoureux, E. Cochon, Université de Lille-1, F 59655, Villeneuve d’Ascq, Cédex, FRANCE, FAX: (33) 20.43.40.84

With respect to the MAS technique, the DOR technique allows a great increase in the spectral resolution for nuclei with semi-integer spins. However, this improvement is really observable only when the linewidth is mainly related to quadrupole interactions. Indeed, consequently to an imperfect synthesis, the sample may be ill crystallized. Each species is then subjected to a distribution of local surroundings more or less broadening the lines. In this case, or when the sample is in an amorphous or vitreous state, the DOR spectrum may then be as broad as with the MAS technique. When samples are well-crystallized, the DOR technique has to be used. However this technique suffers from the slow outer-rotor speed and the difficult knowledge of the induced quadrupole shift and thus of the real chemical shift. When the quadrupole interaction is small or moderate, few rotational lines (< 4) appear on the spectrum and the inner-rotor speed can be assumed "infinite". When the quadrupole interaction is large, many rotational lines exist and one must use the thorough description. In this case sufficient experimental data are available so that all quadrupolar and CSA parameters can be determined and therefore the real chemical shifts.

SOLID-STATE $^{207}$Pb NMR SPECTROSCOPY: SPECTROSCOPIC DILEMMAS AND CHEMICAL RESULTS. Cecil Dybowski,$^1$ Mark Hepp,$^1$ Matthew Smith,$^1$ Guenther Neu$^2$ and Dale Perry,$^3$

$^1$Department of Chemistry and Biochemistry, University of Delaware, $^2$Physikalische Chemie, Universität Dortmund, Dortmund, Germany, and $^3$Lawrence Berkeley Laboratory, University of California, Berkeley, California.

Lead has been important for many centuries in the production of materials used by humans, from pigments to superconductors. Recently, concern over adverse effects on human health has led to policies to try to eliminate it from the environment and limit its spread. Lead, like carbon, phosphorus, xenon, hydrogen and several others, is an element with an isotope having spin 1/2, and thus is readily susceptible to investigation with NMR spectroscopy. Quite a literature on the liquid-state NMR spectroscopy of organolead compounds exists, however the literature on solid lead compounds is more limited, with much of the older literature only reporting average chemical shifts.

The anisotropic solid-state NMR shifts are particularly appropriate to investigate the local chemical and physical structure of solid materials, and so we have begun to investigate the NMR properties of certain inorganic lead materials. Because of the rather large chemical-shift range, spectroscopic distortions arise in the analysis of data from lead materials, which we discuss. We also report trends in the derived NMR parameters that can be correlated with physical and chemical properties.
DISSOLUTION: PAST, PRESENT & FUTURE. Marvin Delgado, Bill Meneses, Bill Hanson, and Royal Hanson, Hanson Research Corporation, 9810 Variel Ave., Chatsworth, CA 91311.

Dissolution in the broad sense is more than simple measurement of the rate of solubility. It may be more accurately described as a physical test to predict delivery to a target area in the proper amount at the right time. With this definition it becomes a central tool available for practical application of innovations resulting from studies of biopharmaceutics and pharmacokinetics. Dissolution has progressed in application through simple single ingredient solid dosage forms into modified release complex dosage avenues including transdermal patches. It is on the threshold of further applications to other dosage form problem areas. (This presentation was originally given at FDA workshop, Cincinnati, Ohio, April 14, 1992. Reprints are available.)

GCMS OF VERY LONG CHAIN FATTY ACIDS IN PEROXISOMAL DISEASE. Adrian W. Pike and Paul V. Fennessey, Dept Pediatrics, UCHSC, 4200 E 9th Ave., Denver Colorado 80262

Peroxisomal disease can be subdivided into two major categories. One condition is where liver peroxisomes are either absent or decreased in number as a result of multiple enzyme defects. The other is where peroxisomes are normal with a genetic defect affecting a single peroxisomal enzyme. Biochemically, plasmalogen synthesis is decreased resulting in an accumulation of very long chain fatty acids in tissues and plasma. Aberration of VLCFA biosynthesis manifests itself both clinically and biochemically in several ways. Typically, impaired liver function, eye abnormalities and renal cysts are some of the anomalies seen. While Zellweger syndrome is the most severe form and results in death in the first year of life, there are other less severe forms of the syndrome. However, these may not become apparent until the third or fourth decade of life. GC has been the method of choice to distinguish the various forms of this disease using plasma and measuring fatty acid methyl esters. We have developed a GCMS technique that is more sensitive and precise and uses less plasma. Results from this study will be discussed.

GC/MS ANALYSIS OF PHENYTOIN URINARY METABOLITES. Robert K. Lantz and Patricia L. Sulik, Rocky Mountain Instrumental Laboratories, Inc. 456 S. Link Ln., Ft. Collins, CO 80524.

Phenytoin (Diphenylhydantoin - DPH) is an important anti-convulsant agent. In order that we be able to study its pharmacokinetics, it was necessary to develop a sensitive, reliable GC/MS assay for phenytoin and its phenolic metabolites, m- and o-hydroxy DPH, DPH catechol, O-methyl catechol DPH, and DPH-diol.

All of the relevant compounds were amenable to methylation using dimethylformamide dimethylacetal. Extracts were incubated for 30 minutes at 65°C, then injected into a splitless injector. Complete methylation of all available sites on the molecules, without decomposition of the sample, was achieved only with this combination of pre-column and intra-injector methylation. Extraction of parent and metabolites was performed by liquid-liquid extraction with pH7.2 phosphate buffer and diethyl ether. p-methyl DPH was the internal standard. Detection used a Finnigan ITDS ion-trap mass spectrometer following an HP 5890 GC with a J&W DB-5+ 0.32mm x 30m quartz capillary column.
COMPARISON OF AN AGAR DIFFUSION BIOASSAY AND HPLC FOR QUANTITATION OF DOXYCYCLINE IN SIMULATED GINGIVAL CREVICULAR FLUID. Carol J. Housley, Amy L. Taylor, Kenneth C. Godowski and Paul C. Reinhart. Atrix Laboratories, Inc., 2579 Midpoint Drive, Fort Collins, Colorado 80525

Local drug delivery systems containing antibiotics are under development for treating periodontal disease. To validate measurement of doxycycline (DOXY) released from the Atrigel™ system into gingival crevicular fluid (GCF), an in vitro comparison between agar diffusion bioassay (Gordon et al, 1980) and an HPLC method was performed. (GCF: a serum-like exudate from periodontal pockets). Periopaper® strips spiked with 1 µl of DOXY reference solutions in water and fetal bovine serum were used to simulate clinical GCF samples. The bioassay allowed DOXY to diffuse from the paper strips into Clostridium perfringens ATCC 13124-seeded sheep blood agar and inhibit hemolysin production causing zones of inhibition. For HPLC assay, DOXY was extracted into acidic water and analyzed by a C-18 column with UV detector. HPLC analysis range 300 µg/ml (1.2 µg/strip) to 5000 µg/ml (20 µg/strip). Bioassay analysis range was 0.64 µg/ml (0.64 ng/strip) to 8470 µg/ml (8.5 µg/strip). The presence of serum in DOXY solutions reduced bioassay values 27-64% but not HPLC. More variation in precision was observed in the bioassay than HPLC assay. Correlation between methods was high for DOXY spiked water solutions, lower for DOXY serum solutions. The difference may be that the bioassay detects active DOXY, HPLC detects total DOXY.

OPTICAL SPECTROSCOPY IN THE ANALYSIS OF POLYPEPTIDE STRUCTURE AND STABILITY. James Matsuura, Michael E. Powers, Thomas M. Foster, Heather A. Thomas, Jonathon J. Dormish, John F. Carpenter, Merrick L. Shively and Mark C. Manning. School of Pharmacy, University of Colorado Health Sciences Center, Denver, CO 80262.

With the advent of biotechnology, production of proteins for use as pharmaceuticals has become a reality. Consequently, there has been an increasing demand for capabilities to assess the structure and stability of proteins. We have found that both circular dichroism (CD) and ultraviolet (UV) absorption spectroscopy are useful tools for studying both the structure and physical stability of peptides and proteins. In addition to providing secondary structure information, we have shown that CD can be employed to monitor the denaturation of proteins as well as the concentration- and temperature-induced aggregation of polypeptides. Examples of these applications will be discussed. Another application of optical methods in the assessment of protein stability is to monitor aggregation by turbidometric measurements. This approach has been used in the evaluation of the thermoprotective effects of certain polymers in the heat treatment of certain proteases. Together, CD and UV absorption spectroscopy have proven to be powerful analytical techniques in the characterization of peptides and proteins.

This work is supported by gifts from Abbott Laboratories and Takeda Abbott Pharm.

ABSTRACT NOT AVAILABLE
A METHOD FOR THE PHARMACOKINETIC EVALUATION OF RACEMIC FENFLURAMINE AND ITS MAJOR METABOLITE NORFENFLURAMINE IN HUMAN PLASMA AND URINE USING HPLC ENANTIOMERIC SEPARATION AND QUANTITATION AT THE LOW NG/ML LEVEL VIA A PIRKLE-TYPE CHIRAL RECOGNITION APPROACH.

Jia-ning Zeng, Lin Dou, and Hans H. Stuting, Analytical Chemistry & Clinical Trials Departments, Roche Biomedical Laboratories, 69 First Avenue, Raritan, New Jersey 08869.

Fenfluramine HCl is a racemic secondary amine. There is considerable interest in the pharmacology of the racemate of the individual enantiomers, and of the corresponding major metabolite. Because therapeutic concentrations of fenfluramine HCl in human plasma are in the low ng/mL range and because the intact drug molecule has low to moderate ultraviolet absorbitivity, improving the sensitivity, and specificity, has been a primary analytical challenge. In the literature, the best stereo-specific method utilized GC with ECD or NPD detection, and having a limit of quantitation (LOQ) of 30 ng/mL plasma. Our newly developed methodology has a LOQ of 10 ng/mL, while using HPLC with a Pirkle-type chiral recognition approach.

Analysis of the in-vitro plasma calibration curve data and quality assurance samples showed an overall inter-assay precision of 5.50%, 6.17%, and 3.83%, for d-fenfluramine HCl, l-fenfluramine HCl, and d-norfenfluramine HCl, respectively. The LOQ was 10 ng/mL, for these analytes, with a 6.0%, 6.0%, and 3.0% RSD, respectively.

Analysis of the in-vitro urine calibration curve data and quality assurance samples showed similar data yet the LOQ was 25 ng/mL (increased linear dynamic range required).

Data generated from a limited post-validation study while analyzing clinical trials plasma specimens (approximately 100 trays and 3500 specimens) further support the initial validation data, and that the method is amenable to the needs of clinical trials investigations.

SEPARATION AND DETECTION OF CEPHALOSPORINS USING HPLC WITH PULSED ELECTROCHEMICAL DETECTION. Lawrence F. Welch, and Elizabeth K. Yun, Chemistry Department, Knox College, Galesburg, Illinois 61401.

The cephalosporins are a family of β-lactam antibiotics, similar in structure to the penicillins, that are widely prescribed for a variety of medical purposes. We have been able to oxidize these species on gold and platinum electrodes throughout a wide pH range. The general voltammetric response was attributed to oxidation at the sulfide site on the cephalosporin backbone; some members of the class have electroactive side chain groups that cause some alteration in voltammetric behavior. The application of Pulsed Amperometric Detection (PAD) and Integrated Pulsed Amperometric Detection (IPAD) allowed efficient detection of any of the cephalosporins in a flowing stream environment. This allowed coupling with reversed-phase HPLC to enable speciation and detection of the cephalosporins to sub-ppm levels. The detection scheme was demonstrated to be compatible with some gradient elution programs and applicable to porcine serum samples.

MOISTURE CONTENT OF HUMAN GROWTH HORMONE FORMULATIONS USING AN AUTOMATED KARL FISCHER TITRATION SYSTEM. John K. Towns, Ralph M. Riggin, Tom W. Miyakawa, and Dave A. Jackson, Lilly Research Laboratories, Eli Lilly and Company, Indianapolis, Indiana 46285

Automation of the coulometric Karl Fischer titration has allowed for the accurate, precise determination of moisture content of lyophilized hGH formulations in six different sample amounts and four different container sizes. This system utilizes a two-hole sampling probe/venting needle assembly that dispenses titrant into the sample container and withdraws sample solution through the rubber septum of the closed container. The sample is then dispensed into the titrator through the systems transfer lines. This approach eliminates erroneous results due to environmental moisture contamination or loss of material during the sample transfer process. This system is also equipped with a fixed loop valving system which facilitates the precise measurement of a defined amount of water to be dispensed into the titrator. This allows for an accurate assessment of system suitability that was lacking with commercial water standards due to inaccurate moisture content at the time of manufacture or from environmental moisture contamination of the standard under storage. Experimental design techniques were employed to optimize the system with respect to moisture content and analysis time.
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APPLICATIONS OF CALORIMETRY IN AN INDUSTRIAL ENVIRONMENT

Calorimetry is the science of measuring heat. Virtually any process (chemical reaction, formation of a solution, phase change, adsorption, etc.) is accompanied by an exchange of heat with its surroundings. Therefore, calorimetric techniques allow one to follow a wide range of very diverse processes and may be viewed as a "universal" analytical tool. The thermodynamic information one obtains from such studies also gives information on the driving forces for the process thus yielding fundamental insight valuable in optimizing processes. Calorimetry is of particular value in assessing potential rates of energy release in the manufacturing and handling of chemicals.

The presentation will illustrate a well-equipped industrial calorimetry laboratory and some typical applications that illustrate the power and versatility of calorimetric techniques. Included will be examples in the area of non-aqueous pKa determination, solubility and titrations of surfaces. The wide kinetic range of the technique (12 powers of 10) will be illustrated with examples of stopped-flow calorimetry and the use of high sensitivity heat-flow calorimetry to study slow decompositions. Increasing the effectiveness of the technique by combining calorimetry with GC-Mass Spectrometry in the study of gas phase catalysis will be presented. Finally, application in the assessment of potential hazards in production, storage and handling of industrial chemicals will be discussed.

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PULMONARY DRUG DELIVERY OF FINE AEROSOL PARTICLES FROM SUPERCRITICAL FLUIDS. Anthony E. Lagalante¹, Brooks M. Hybertson¹,², John E Repine¹, Connie J. Beehler¹, Kathryn S. Rutledge¹, Robert E. Sievers², ¹Webb-Waring Institute for Biomedical Research, University of Colorado Health Sciences Center, Denver, CO 80262, and ²Cooperative Institute for Research in Environmental Sciences and Department of Chemistry and Biochemistry, University of Colorado, Boulder, CO 80309

Better methods for delivery of pharmacologic agents directly to and via the lung are needed. α-tocopherol (vitamin E) was chosen as a model compound to deliver based on its protective effects in cell membranes against lipid peroxidation. Vitamin E was dissolved in supercritical carbon dioxide and allowed to expand through a restrictor nozzle forming 0.3 to 3 µm diameter droplets. Particle size was determined using scanning electron microscopy and a laser diffraction particle size analyzer. The decompressed aerosol stream was diluted with gaseous oxygen and directly administered to rats via inhalation. Lung levels of vitamin E were quantitated using high performance liquid chromatography. Results show a 150% and 400% increase in vitamin E lung levels resulting from 10 and 30 minute dosings, respectively. A comparison of aerosol deposition in the central and peripheral regions of the lung was studied. The supercritical fluid drug delivery (SFDD) method holds potential for pulmonary delivery of many other drugs, and does not require the use of chlorofluorocarbon propellants.

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PHOTOSTABILITY OF PHARMACEUTICALS-INSTRUMENTAL APPROACH. Lawrence A. Bard, Heraeus DSET Laboratories, Inc. 45601 North 47th Avenue, Phoenix, Arizona 85027-7042

The sensitivity of pharmaceuticals to light at various wavelengths is an important but not commonly evaluated parameter. Most common materials used by industry are subjected to lightfastness tests. The standardization of protocols for paints, plastics, textiles, agricultural chemicals and other every day products have led to acceptable performance criteria and correlations between natural conditions and accelerated devices. Recent cooperations on an international level regarding the evaluation of pharmaceutical sensitivity to light is an encouraging sign. Experience by other industries can greatly assist in developing drug safety guidelines. This paper discusses the proper measurement of light, available sources to simulate sunlight, summary of standards in industry, recommended procedures currently under consideration, and introduces manufactured devices with accessories to meet the specifications.
PROBING MOLECULAR STRUCTURE IN THE FROZEN STATE AND DURING LYOPHILIZATION WITH INFRARED SPECTROSCOPY.
Richard L. Remmele, Cecil Stushnoff, and John F. Carpenter*, Dept. of Horticulture and Biochemistry, Colorado State University, Fort Collins, CO 80523.
*School of Pharmacy, University of Colorado Health Sciences Center, Denver, CO 80262.

Using a custom-built low-temperature internal reflectance accessory, infrared spectra can be acquired in real-time during lyophilization and used to observe protein structure in the frozen state. Additionally, this approach can delineate between soluble and precipitated aggregates. Qualitative information from second-derivative resolution enhancement of the amide I band has provided additional insight into the mechanism of freeze-induced denaturation of phosphofructokinase (0.5 mg/ml). This technique was also used to permit direct examination of phase behavior, sucrose band perturbations, and structural information about lysozyme during dehydration. For lysozyme in the presence of sucrose (which acts as a lyoprotectant), a devitrification event at -45°C was observed. Amide I and II bands for lysozyme lyophilized with and without sucrose showed distinctively different structural routes during the process. In comparing the final dried state for the two treatments, the state attained in the presence of sucrose exhibited a structure which resembled the native hydrated state more than that without. Both dried products (although different structures), upon rehydration regained full activity. The examples presented provide evidence for both physical and structural information about the process which can be used to optimize protein formulations in the dried state.

THE PREPARATION AND ANALYSIS OF NATIONAL INSTITUTE FOR STANDARDS AND TECHNOLOGY (NIST) SOIL STANDARD REFERENCE MATERIALS (SRMs). Stephen A. Wilson, Paul H. Briggs, and Steve Mee, U.S. Geological Survey, PO Box 25046 MS 973, Denver, Co. 80225

Under a cooperative arrangement between the U.S. Geological Survey (USGS) and NIST, three SRMs have been developed which represent a baseline soil (SRM 2709), and soils moderately (SRM 2711) and highly contaminated (SRM 2710) with heavy metals. The guidelines followed for site selection, method of collection, physical preparation procedures used, and criteria followed to evaluate SRM homogeneity will be discussed. Results of major and trace element analysis from USGS and NIST laboratories will be presented for 40 elements. Discussions will focus on the extended concentration ranges of selected elements including As (18-626 ppm), Cd (0.38-42 ppm), Cu (34-2950 ppm), Pb (19-5532 ppm), Zn (106-6952 ppm) and their usefulness in analytical, environmental, and geochemical exploration studies.

Were you aware that vast portions of the Mancos Shale in the western United States contain over 1 oz/ton platinum and other precious metals? That gold (boiling point: 2967°C) readily vaporizes during fire assaying at 1000°C? Promotions for fraudulent mining ventures are replete with these and similar abuses of analytical chemistry. In some cases, the actual analytical work is done by legitimate labs who have been sent unrepresentative samples or whose reports have been altered. In other cases, promoters with new, "secret" processes claim to detect and recover precious metals unamenable to detection by established methods. Such ventures frequently came to the attention of the SEC and other law enforcement agencies. Legitimate labs can help expose these alchemists for what they are by (1) keeping archival copies of all analytical reports, especially those performed for unfamiliar clients; (2) reporting instances where they smell a rat; (3) participating in public education, particularly of the media; and (4) being willing to testify as experts in civil or criminal trials. Alchemists and their client promoters frequently employ a barrage of pseudo-science and arcane, technical-sounding verbiage. To be effective, counteractive measures must use of plain, bottom-line English and emphasize the underlying reality of chemical and physical processes.

*The authors' views are their own and do not necessarily reflect the views of the Commission or other members of its staff.

ABSTRACT NOT AVAILABLE

PROBLEMS WITH THE LUCAS CELL AS AN ANALYTICAL TOOL. Henry F. Lucas, Lucas Laboratory, Inc. 2860 Hopi Dr. #1A, Sedona, AZ 86336

The Lucas cell is frequently used in the analysis of radon-in-air, $^{222}$Rn in water and $^{226}$Ra by the emanation method. There are problems with the Lucas cell which limit the accuracy unless precautions are taken. The Lucas cell is thermoluminescent, which results in an increased pulse height at short times after start of counting. The effect is to give a detection efficiency which declines with time after last exposure to either daylight, fluorescent or even some incandescent lights. The magnitude will vary with the counting system, but can be as high as 10%. Fortunately, the thermoluminescent pulse, which is time coincident with that from the alpha particle is NOT detected by the newer photomultiplier tubes with the bi-alkali photocathode. Ideally, a single Lucas cell filled with $^{222}$Rn will have the same counting efficiency and background counting rate on multiple counting systems. The effect of photomultiplier resolution, zero-intercept, gain and linearity will all be described. Rather than have different detection efficiencies and background counting rates for every cell on every counting system, a suggested procedure for the set-up of multiple counting systems will be described.

Improvements will be discussed that allow a more accurate, faster, and cheaper method for alpha spectrometry. Specific applications will be discussed, especially $^{222}$Rn in drinking water. Counting times are dramatically reduced over other methods due to a system counting efficiency of 100%. Due to the system's high resolution, the $^{222}$Rn and $^{218}$Po peaks are completely resolved from the $^{214}$Po peak. This allows immediate counting of the $^{222}$Rn peak alone or counting additional peaks after proper ingrowth. Other samples, such as soils, oils, effluents, bioassay, and biological, are easily analyzed with no sample self-absorption and no possibility of sample cross-contamination. This entire system is inexpensive, small, light-weight, and ideally suited for mobile laboratories as well as analytical labs.

AMERICIUM AND PLUTONIUM ANALYSIS OF ENVIRONMENTAL SAMPLES.
Robert Mero, Colorado Department of Health, 4210 East 11th Avenue, Denver, Colorado, 80220.

In 1992 the Colorado Department of Health implemented a new procedure for the analysis of actinides in water, soil, and air filters. The procedure, used by Argonne National Laboratory, involves the use of "TRU-Spec" ion exchange resin in conjunction with Bio-Rad AG1X-2 anion exchange resin to achieve matrix interference elimination and chemical separation of the actinides of interest. The procedure has produced analysis results comparable to the previous method for plutonium (described by Talvitie in Anal. Chem., 1972). The new method is advantageous in many ways, including savings of both time and reagents. The major benefit, however, has been the ability to perform americium analysis on the same aliquot of sample. As a result, a slight increase in labor has produced double the number of analytes obtained per sample.

NEW DEVELOPMENTS IN ALPHA SPECTROMETRY: LIQUID SCINTILLATION METHODS
W. Jack McDowell, and Betty L. McDowell, ETRAC, Inc., 1009 Alvin Weinberg Drive, Oak Ridge, TN 37830.

Present concerns regarding alpha-emitting radionuclides in the environment have led to increased demand for rapid, accurate, and sensitive methods for alpha determination in soils, water, air, and plant and animal tissues. Conventional methods of plate counting have serious limitations when faced with large numbers of samples and a constraining time frame. New embodiment of liquid scintillation methods appear to be poised to step into the gap and provide for this need. New methods of sample preparation and new detector/electronics configurations allow rapid sample preparation, virtually complete rejection of beta/gamma events (99.95%), extremely low background (0.001 cpm), 100% counting efficiency (a factor of ~7 less counting time than surface-barrier detectors), alpha energy identification, and high sensitivity. Available instrumentation will be discussed and several sample preparation procedures will be given that are superior to and more rapid than most methods for plate preparation yet give good energy resolution and very accurate analyses. Methods for sample preparation and determination of uranium, plutonium, the transplutonium trivalent actinides, radium, radon, and polonium will be given that allow sensitivities of less than 1 pCi per liter or kilogram with accuracies of 1% or better. Some comparisons of various instrumentation and sample preparation approaches will be presented.
BASIS FOR THE EICHROM COLUMN-CERENKOV COUNTING RADIOSTRONIUM PROCEDURE DEVELOPED AT THE YANKEE ATOMIC ENVIRONMENTAL LABORATORY, David E. McCurdy, Ashok D. Banavali and Edgar M. Moreno, Yankee Atomic Electric Company, 580 Main Street, Bolton, MA 01740, (508) 779-6711

The Yankee Atomic Environmental Laboratory (YANEL) provides radiochemistry support services for the U.S. nuclear power industry for the determination of the radioactive content of various effluent (10 CFR 50) and waste stream (10 CFR 61) matrices. Of the 16 specific long-lived radionuclides requiring quantitative evaluation, the radiostrontium analysis (\(^{89}\)Sr and \(^{90}\)Sr) is typically one of the more time consuming and troublesome techniques to conduct routinely. Prior to 1992, the radiostrontium method of choice at YANEL was the classical purification and isolation of SrCO\(_3\), and Y oxalate for counting in a beta particle counter. This technique provided excellent quantitative analyses and resolution of the isotopes for \(^{89}\)Sr to \(^{90}\)Sr ratios in the range of 0.10 to 80. However, the technique was very time consuming requiring approximately 12 hours of chemistry per sample batch. With the availability of the new EICHROM extraction chromatographic materials, the YANEL staff developed a unique chemistry - instrumentation technique that maintains the desired quantitative accuracy for the wide spectrum of expected isotopic ratios and, at the same time, decreases the processing time by a factor of three. This paper shall describe the basis for the technique design, the specificity and limitations of the key elements, and the boundary conditions and decontamination factors investigated. The Cerenkov nuclear instrumentation and mathematical resolution of the technique shall be discussed.


The fraction of \(^{222}\)Rn atoms generated from \(^{226}\)Ra decay that are released into pore spaces in rock or soil is termed the radon emanation coefficient, or emanating power, of the material. A soil's parent-rock mineralogy and chemistry controls the initial concentration and distribution of radionuclides in the soil as well as how the rock interacts with climate to form the soil—this determines the soil's emanating power and radon transport characteristics. The USGS Laboratory Soil Radon Collector (LSRC) was designed to determine radon emanation coefficients of relatively undisturbed soil samples. An important advantage of this method is that it preserves the structure and grain-to-grain relationships in the soil samples. The LSRC is a sealed apparatus containing a chamber with an air-filled volume of 100 cm\(^3\) at one end. Relatively undisturbed cylindrical soil cores, approximately 5.5 cm in diameter by 6.5 cm long, are collected using a commercially available soil corer with a removable soil-core sleeve. The ends of the LSRC are fitted onto the soil-core sleeve and the apparatus is allowed to stand for 21 days to allow the soil-gas radon to approach secular equilibrium in the sampling chamber. A gas sample is then extracted with a syringe, counted in an alpha scintillation counter, and compared with the radium content of the soil sample (determined by gamma spectrometry) to calculate the emanation coefficient. The design of the LSRC and soil corer permits the determination of other important soil properties from the same sample, including porosity, bulk density, soil moisture content, permeability, and petrologic and geochemical properties. The LSRC was designed to collect radon gas for the purpose of measuring radon emanation coefficients in soil and weathered rock samples, but it can be used to sample and analyze any gases generated by a soil sample, including methane and human-generated gaseous toxins.

CALCULATIONS OF THE LOWER LIMIT OF DETECTION. T. B. Borak and T. B. Kirchner, Colorado State University, Fort Collins, CO 80523.

The Minimum Detection Limit or Lower Limit of Detection following radiochemical analysis is often derived using simplifying assumptions. For example, the most popular formula:

\[
LLD = 2.71 + 4.65\sigma_B
\]

Eq(1)

is based on the assumption that each sample is paired with an appropriate blank and that the underlying uncertainties in each of these can be described by distributions that are simultaneously Poisson and Normal. This paper will briefly review the definition of Lower Limit of Detection and discuss the various assumptions used in the derivation of Eq(1). We also present values of LLD computed when these basic assumptions are not satisfied. Specifically this will include the situation when background counts are low, resulting in distributions that are Poisson but not Normal. This will be extended to include other skewed distributions of sample and background such as Log-Normal. Simulation modeling techniques will be discussed that can include the propagation of other uncertainties that can occur as a result of analytical chemistry and sample collection.

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SELECTION OF FORMULAS AND TECHNIQUES FOR DETERMINING MEASUREMENT DETECTION LIMITS IN RADIOMETRIC ANALYSIS, Robert W. Terry, Radiation Control Division, Colorado Department of Health, 4300 E. Cherry Creek S. Drive, Denver, Colorado 80222-1530.

Making a choice for a specific formula or technique for determining measurement detection limits in radiometric analysis requires consideration of the information needs of the laboratory's client. Selection generally is determined by the government agency for which the information is being prepared, or by the academic or work experience of the investigators who will use the measurement data. In any case laboratory personnel should have a thorough understanding of the formulas and techniques that are employed by the laboratory and of alternative procedures for determining detection limits.

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EVALUATION OF CONTROLS FOR THE ASSURANCE OF QUALITY DATA IN A RADIOCHEMISTRY LABORATORY. J. S. Morton, U.S. Department of Energy, Radiological and Environmental Sciences Laboratory, 785 Doe Place, Idaho Falls, Idaho 83401-1562

The paper describes the controls implemented by the United States Department of Energy at the Radiological and Environmental Sciences Laboratory (RESL) to secure data quality. A description of the analytical instrumentation and methodology employed by RESL is provided. The results of an intercomparison program with the National Institute of Standards and Technology are provided to demonstrate traceability to a primary source. A description of the methods and techniques used to insure quality control on a daily basis are given. The techniques used to evaluate the sources of uncertainty are reviewed and specific examples cited. The intercomparison programs operated by RESL are discussed.

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THE ROLE OF THE EPA RADIATION QUALITY ASSURANCE PROGRAM IN THE MEASUREMENT QUALITY ASSURANCE ACCREDITATION PROGRAM FOR RADIOASSAY LABORATORIES. Terence M. Grady, U. S. Environmental Protection Agency, P. O. Box 93478, Las Vegas, NV 89193-3478

As the nature and extent of radiological contamination becomes better documented and more public, radioanalytical laboratories are faced with a constantly expanding variety of new and difficult analytical requirements. Concurrent with those requirements is the responsibility to provide customers, regulatory officials or the public with defensible data produced in an environment of verifiable, controlled quality. To meet that need, a quality assurance accreditation program for radioassay laboratories has been proposed by the American National Standards Institute. The standard will provide the organizational framework and functional requirements needed to assure the quality of laboratory outputs. Under the proposed program, the U.S. Environmental Protection Agency's Laboratory Intercomparison Program plays a key role as a reference laboratory. The current and proposed roles of the EPA Intercomparison Program are discussed, as are the functional relationships between EPA, the accrediting organization and the service and monitoring laboratories.
QUALITY CONTROL FOR NUCLEAR ANALYTICAL MEASUREMENTS IN LABORATORY AND PRODUCTION ENVIRONMENTS, Richard S. Seymour, Terry Beal, William H. C. Clark, and Geoff Gleason, Oxford Instruments, P.O. Box 2560, Oak Ridge, TN 37831-2560 USA.

Accountability/defensibility of results to customers and management and customer certification of laboratory services are two important driving forces behind the development and implementation of QA/Q programs in the nuclear analytical laboratory. The associated quality control measurements are performed archived, and plotted using manual or automated methods provided with many analytical instruments. Important calibration and performance parameters monitored include those that are affected by instrument performance and those that directly affect the analysis and hence accuracy of the measurement method. C measurements for low background alpha/beta gross counting, alpha spectroscopy, and gamma spectroscopy are presented examining the source of variation being monitored and its relationship to accuracy and precision. Misinterpretation of QC data resulting from the inherent instrument drift and individual counting error are examined. Special treatment for QC parameters that are performed daily, such as instrument gain, is presented. Modern QC software employs statistical process control (SPC) techniques that are intimately related to laboratory QC objectives and can provide hypothesis testing of cause and effect in addition to prevention. Use of Shewart (X-bar) charts and frequency distributions to display run charts, pseudo-control charts, and control charts are contrasted for their applicability to these measurements.

ANALYTICAL METHODS SUPPORTING THE RADIONUCLIDE IN DRINKING WATER REGULATIONS. Paul B. Hahn and Stephen H. Pia, U. S. Environmental Protection Agency, P. O. Box 93478, Las Vegas, Nevada 89193-3478

The Office of Ground Water and Drinking Water of the U. S. Environmental Protection Agency has proposed updated regulations for radionuclides in public drinking water supplies. The regulations are due to be promulgated in October 1993. The major impact on the drinking water suppliers will be the limits for naturally occurring radionuclides, especially radon, whose maximum contaminant level (MCL) is proposed at 300 picocuries per liter. Analytical techniques for the measurement of radon, radium 226 and 228, uranium, strontium 89 and 90 and gamma emitting radionuclides will be discussed as will gross alpha and gross beta screening measurements used to avoid costly specific analyses when levels are below regulatory concern. Expected performance criteria of laboratories conducting compliance analyses can be estimated from past intercomparison studies and interlaboratory collaborative tests conducted at this laboratory. Limitations of proposed methods, such as determining compliance at levels approaching the MCL, using a mass measurement to estimate uranium activity, and computing an adjusted gross alpha value to estimate unknown alpha emitters will also be discussed.

USING HIGH RESOLUTION DETECTORS AND LOW SYSTEM BACKGROUND TO IMPROVE SENSITIVITY AND PRECISION IN GAMMA SPECTROMETRIC MEASUREMENT, Robert W. Terry and L.A. (Tony) Harrison, Radiation Control Division, Colorado Department of Health, 4300 E. Cherry Creek S. Drive, Denver, Colorado 80222-1530.

The cost of acquisition and maintenance of large, high-performance hyperpure germanium (HPGe) detectors justifies the additional cost of acquiring system components that afford the highest resolution available and of using shielding that will reduce background radiation to a minimum. The Colorado Department of Health operates a gamma spectrometric measurement facility that controls both resolution and background radiation in order to achieve the highest sensitivity and precision presently available for these types of measurements. Comparative data is provided to demonstrate the effects of resolution and background radiation on measurement sensitivity and precision.
REMOTE GAMMA-RAY SPECTROSCOPY WITH SATELLITE DATA TRANSMISSION.
Colin G. Sanderson, Environmental Measurements Laboratory, U.S. Department of Energy,
376 Hudson Street, New York, New York 10014-3621.

Since 1963 the Environmental Measurements Laboratory (EML) has maintained a worldwide network of surface air sampling stations. At these stations, airborne particles are collected on highly efficient polypropylene filters from about 8,000 m$^2$ of air each week. The filters are then analyzed for gamma-ray emitting radionuclides, and the resulting spectral data are transmitted to polar orbiting Argos satellites, transferred to the ground station, and recovered via a telephone link by EML's computer. Remote atmospheric measurement systems (RAMS) developed by EML are composed of a lead shielded 12.7 cm x 10.2 cm diameter NaI(Tl) detector with $^{241}$Am doping for gain stabilization, a programmable multichannel analyzer, a programmable transmitter and a laptop computer. The computer controls the entire system data flow, and provides the flexibility for easy modification of the controlling parameters. Transmitted gamma-ray spectral data are unfolded on EML's computer using linear least-squares analyses. The latest version of RAMS includes mechanically-cooled germanium detectors (35% efficiency), with energy resolutions that are a factor of 40 times better than NaI. Therefore, data reduction is simpler and the limits of detection are lower. In addition, these new systems use geostationary satellites that can receive 649 bytes of data each hour and a complete 1800 channel spectrum in 7 h. The orbiting Argos satellites allow only 32 bytes every three minutes, but because they are not always within view of our transmitters, actually take on average 24 to 48 h to recover a complete 196 channel NaI gamma-ray spectrum.

STREAMLINING AND AUTOMATION OF RADIOANALYTICAL METHODS AT A COMMERCIAL LABORATORY.
James T. Harvey, James W. Dillard, IT Corporation, 9000 Executive Park Drive, Suite A-110, Knoxville, Tennessee 37923.

Through the careful planning and design of laboratory facilities, incorporation of modern instrumentation and robotics systems, properly trained and competent laboratory associates can efficiently and safely handle radioactive and mixed waste samples. This paper addresses the potential improvements radiochemistry and mixed waste laboratories can achieve utilizing robotics for automated sample analysis. Several examples of automated systems for sample preparation and analysis will be discussed.

A LIMITATION OF GROSS-BETA ACTIVITY IN ENVIRONMENTAL STUDIES OF GROUND WATER.

We evaluated gross-beta activity as an indicator of beta-emitting isotopes in ground water for more than 800 samples from five areas across the United States. In four areas--the Carson River basin of Nevada, the Puerco River basin in northern Arizona and New Mexico, the Central Oklahoma aquifer, and the Piedmont Province of New Jersey--gross-beta activity is an unsatisfactory indicator because the largest contributor to the gross-beta activity is ingrowth of uranium-238 progeny. In a fifth area, the Atlantic coastal plain of New Jersey, gross-beta activity is a satisfactory measurement of the beta-emitting isotopes naturally present in the ground water. Gross-beta activity has been used as a screening technique for beta-emitting isotopes in ground water since the early 1950's. Originally designed for detection of radioactive releases from nuclear facilities, gross-beta activity is widely used in environmental studies of water. However, ingrowth of beta-emitting radionuclides, which can occur during the period between sample collection and sample analysis, limits the use of this measurement of radioactivity in environmental studies. In particular, two uranium-238 progeny (thorium-234 and protactinium-234) reach 90 percent of secular equilibrium within about 100 days. These beta-emitting progeny can grow in samples after collection, as indicated by a 2:1 ratio of uranium-238 to gross-beta activity in most of the samples from four of the five areas. One exception is the Coastal Plain of New Jersey, where the ground water contains low uranium activities. Other radionuclides that contribute to the gross-beta activity are potassium-40 and radium-228. In four areas, these isotopes generally contribute less than one-half of the gross-beta activity in ground water, with potassium-40 contributing more beta activity than radium-228. In contrast, dissolved radium-228 and potassium-40 are the largest contributors of gross-beta activity in the ground water of the Coastal Plain of New Jersey.
MEASURING THE CONTRIBUTION OF $^{222}$Rn IN WELL WATER TO INDOOR AIR BY LONG-TERM AND CONTINUOUS MONITORING. Peter F. Folger, Richard B. Wanty, Philip Nyberg, and Eileen Poeter, U.S. Geological Survey, MS 916, Denver, CO 80225

Indoor $^{222}$Rn concentrations were measured using α-track detectors, charcoal canisters, and continuous monitors to determine the amount of airborne $^{222}$Rn liberated from well water. Detectors were placed in rooms near water use (bathrooms, kitchens, etc.) and away from water use (bedrooms or living rooms), assuming that airborne $^{222}$Rn concentrations in water-use rooms would be higher if waterborne $^{222}$Rn contributes significantly to $^{222}$Rn in indoor air. Radon-222 in tap water was analyzed by liquid scintillation.

Our results show that water-use contributions of $^{222}$Rn are masked when soil-gas contributions are high (>50 pCi/L in the basement), regardless of the $^{222}$Rn concentrations in the well water. In those cases, continuous-monitoring results indicate that diurnal fluctuations in the soil-gas $^{222}$Rn exceed measurable increases from water use. However, houses with high ratios of $^{222}$Rn-in-water to $^{222}$Rn-in-soil gas show statistically significant contributions from water use.

A $^{222}$Rn mitigation system was installed in one house, decreasing basement $^{222}$Rn concentrations from more than 150 to less than 3 pCi/L. Then, continuous monitoring clearly recorded tenfold increases from 4 to 40 pCi/L in the laundry room due to water use. Charcoal canister results from a 7-day exposure following mitigation also indicate that water use significantly increased airborne $^{222}$Rn on the upper levels of the house.

THE FORT ST VRAIN INDEPENDENT SPENT FUEL STORAGE INSTALLATION RADIATION MONITORING PROGRAM - RESULTS TO DATE TED J. BORST, CHP PUBLIC SERVICE CO OF COLORADO, 16805 WCR 19 1/2, PLATTEVILLE, CO 80651

The Fort St Vrain Nuclear Generating Station was permanently shut down in August of 1989. Prior to initiating the decommissioning of the facility, the spent nuclear fuel had to be removed from the site. In accordance with a pre-existing agreement with the Department of Energy, plans were made to ship the fuel to the Idaho Nuclear Engineering Laboratory (INEL), as had been done following three reactor refuelings in the past. Due to legal challenges initiated by the Governor of Idaho, however, it became impossible to ship the fuel to the INEL. In order to provide for the removal of the spent fuel from the reactor and allow component removal and decommissioning activities to begin, an Independent Spent Fuel Storage Installation (ISFSI) was constructed northeast of the station on company property. The facility was licensed by the Nuclear Regulatory Commission. Loading of spent fuel into the ISFSI began in December of 1991 and was completed in June of 1992. A radiation monitoring program was established prior to loading spent fuel into the ISFSI, encompassing direct radiation and air monitoring. This presentation will describe the design features of the ISFSI along with the results to date of the radiation monitoring program.
EFFECTS OF URANIUM-MINING RELEASES ON GROUND-WATER QUALITY IN THE PUERCO RIVER BASIN, ARIZONA AND NEW MEXICO. Peter C. Van Metre, U.S. Geological Survey, 8011 Cameron Road, Austin, Texas 78754-3898.

The Puerco River of Arizona and New Mexico, a tributary of the Little Colorado River, received effluent from uranium-mine dewatering operations from 1960 until 1961 and from 1967 until 1986 when mining ceased. Activities of dissolved gross alpha, gross beta, uranium, and radium were increased in streamflow as far as 140 kilometers downstream from the mines. Mine dewatering and an accidental release caused by a tailings-pond dike failure on July 16, 1979 released an estimated 560 metric tons of uranium and 310 curies of gross-alpha activity to the river. The purpose of this study was to evaluate contamination of ground water in the alluvial aquifer under the Puerco River by radionuclides from uranium-mining releases. In 1989, a zone of large concentrations of dissolved uranium in ground water under the river extended about 65 kilometers downstream from where mine effluents entered the river. Large concentrations of uranium in the alluvial aquifer are caused principally by releases from mine dewatering, as indicated by uranium isotope ratios of near 1.0 in mine-dewatering effluent compared with ratios of about 1.5 in native ground-water. The distribution of uranium in ground water was affected by flow directions between the stream and aquifer. Concentrations of uranium in the aquifer were reduced by sorption of uranium onto sediments. Ratios of uranium-238 to uranium-234 to thorium-230 of greater than about 1.5 indicate excess uranium compared to the thorium progeny. Excess uranium on streambed sediments and on some well cores from 5 to 10 meters from the streambed, indicate sorption of uranium.


Dissolved radium-228 and radium-226 are present in high concentrations in the unconfined Kirkwood-Cohansey aquifer system in the New Jersey Coastal Plain. Concentrations of these isotopes in nine samples of ground water and associated sediment were compared to evaluate sediment as a source of dissolved radium. Isotopic ratios could not be calculated or constrained for two of the water samples because the detection limit for radium-228 is higher than that for radium-226. Concentrations of radium-228 and radium-226 in the ground water (maximum, 5.9 and 13 picocuries per liter, respectively) increased with decreasing pH (correlation coefficient (r) = -0.74 and -0.63, respectively) but showed no correlation with the radium content of the sediment. Concentrations of radium-228 and radium-226 in sediment ranged from 0.056 to 0.84 pCi/g (picocuries per gram) and from 0.11 to 1.3 pCi/g, respectively, and were higher in silty sand than in sand. Radium-228/radium-226 ratios were higher in sand than in silty sand and ranged from 0.43 to 1.73 (median, 1.00). Radium-228/radium-226 ratios in the water ranged from 0.30 to 4.31 (median, 1.07), and increased with the ratios of these isotopes in the adjacent sediment (r = 0.59). These data indicate that radium leaches from the sediment in acidic water—a potential problem in unconfined aquifers in the Coastal Plain of the eastern United States.
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GAMMA RAY AND ELEMENTAL ANALYSES OF SEDIMENTS TO OBTAIN DEPOSITIONAL HISTORIES IN THE LOUISIANA COASTAL MARSHES. John R. Meriwether, James N. Beck, Scott F. Burns and Ronald H. Thompson, University of Southwestern Louisiana, Lafayette, LA 70504-4210.

Cores from sediments in the Chenier plain of the Louisiana coastal marshes have been analyzed as a function of depth. The word Chenier derives from the French for the oak groves frequently found on the ridges embedded in the marshy plain. Study sites included White, North and Calcasieu lakes and open marsh near Chenier au Tigre. The concentration of non-equilibrium $^{210}$Pb (with a half life of 22 years) resulting from the fallout of the decay products of $^{222}$Rn in the atmosphere provides a chronology of the sediments over the last 100 years. The $^{210}$Pb concentration was determined by the measurement of the 46.5 keV gamma ray for each core segment (10 cm diameter, 2 cm deep). Sample self absorption corrections were derived from the measurement of the transmission of gammas from an external $^{210}$Pb source through each core segment. The $^{210}$Pb depth profile was analyzed using the Constant Rate of Supply model. The concentrations of a suite of thirty elements was measured by neutron activation analysis and atomic absorption spectroscopy in each core segment. The depositional pattern of barium, for example, illustrates an interesting event in the history of oilfield drilling in the region. The concentration of barium in a core from White Lake peaks sharply in the early 1930’s. Drilling fluids were either discharged directly into the lagoon or someone upset a barge!

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Since 1952, iodine-129 has been released to the environment by nuclear-fuel reprocessing activities at the Idaho National Engineering Laboratory. An estimated 0.56 to 1.18 curies of iodine-129 have been contained in wastewater disposed to wells and infiltration ponds at a nuclear-fuel reprocessing facility. Because of its 15.7 million-year half-life, background concentrations of iodine-129 in the Snake River Plain aquifer from natural production and the atmospheric testing of nuclear weapons is needed to evaluate the long-term effects of wastewater disposal. Ground- and surface-water samples were collected at 16 sites not affected by wastewater disposal. The samples were analyzed for iodine-129 using accelerator mass spectrometry (AMS). The AMS method is two to six orders of magnitude more sensitive than the neutron-activation method and provides an effective tool to determine background concentrations. Iodine-129 concentrations in water from four springs and nine wells on, and three streams tributary to the plain ranged from (1±1)x10$^{-7}$ to (8.1±0.6)x10$^{-6}$ picocuries per liter (pCi/L). The mean concentration was (3.3±0.5)x10$^{-6}$ pCi/L and the standard deviation about the mean was 2.1x10$^{-6}$ pCi/L. At the 95-percent confidence level, background concentrations of iodine-129 from the 16 sites are less than or equal to 6.8x10$^{-6}$ pCi/L.
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USING RADON-222 AND TRITIUM CONCENTRATIONS TO IDENTIFY STREAM-REACHES RECEIVING GROUND WATER DURING LOW FLOW, OWL CREEK BASIN, WYOMING. Kathy Muller Ogle, U. S. Geological Survey, Water Resources Division, 2617 East Lincolnway, Suite B, Cheyenne, WY 82001

Changes in radon-222 and tritium concentrations were used to qualitatively identify specific stream reaches where ground water was contributing to streamflow in a study conducted by the U. S. Geological Survey in cooperation with the Shoshone and Northern Arapaho Tribes. The concentrations of radon-222 and tritium were especially useful where differences in instantaneous discharge were less than measurement errors. Radon-222, as a gas, dissipates into the air under atmospheric pressure. Generally, the concentration of radon-222 in streams is relatively low compared to its concentration in ground water. An increase in radon-222 concentration from an upstream to a downstream measurement site indicates that ground-water inflow is occurring in the reach. Tritium is a conservative constituent that moves with water without being affected significantly by geochemical reactions or fractionation. Changes in stream concentration of tritium can be used to identify reaches where ground-water inflow contributes to streamflow if the concentration of tritium in ground water is different from the stream.

Radon-222 and tritium concentrations and instantaneous discharge were measured during low flow in 1991 at 16 sites on Owl Creek and its major tributaries. The streams drain a 505-square-mile basin in north-central Wyoming. One stream reach in the basin where ground water was contributing to streamflow was identified by changes in the concentration of radon-222 and tritium, and three additional reaches were identified by changes in the concentration of radon-222.

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The Carson River Basin is an internally drained basin within the semi-arid northern Basin and Range physiographic province. Uranium concentrations in the ground water vary three orders of magnitude as a result of a variety of geochemical conditions and the impact of man's activities. The hydrologic and geochemical conditions present in the Carson River basin appear similar to settings in other areas of the arid west and, therefore, may be indicative of conditions in other western basins. In the upper part of the Carson River basin, dissolved uranium activities in ground water are generally less than 10 picocuries per liter (pCi/L). Uranium is released by weathering of granitic and acidic volcanic rocks within the Sierra Nevada batholith and sedimentary deposits in the basins derived largely from those rocks. Results of alpha radiography indicate that uranium and its alpha-emitting progeny in the ground water are deposited on mineral coatings and fine-grained sediment, some of which are transported by fluvial processes. Uranium initially released by weathering is also adsorbed by sedimentary organic matter. Uranium transport within the basin is due, therefore to both solute and sediment transport. The highest measured uranium activities in ground water are in shallow ground water in the downstream end of the Carson River basin, where concentrations locally exceed 300 pCi/L. The shallow aquifer matrix consists, in part, of sediments derived from the upper parts of the basin that have uranium-bearing coatings. As a result of a rise in the water table due to local irrigation, uranium is being released from the sediments into the ground water. The release of uranium appears to result from the reaction of the iron and manganese oxide coatings with sedimentary organic matter. This releases uranium from these phases and produces anoxic, but low, sulfide water.

1 This abstract was first published in 1990 in Eos, American Geophysical Union Transactions, v. 71, no. 43, p. 1305.

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The introduction of extended range "n-type" Germanium gamma-ray spectrometers extends the useful energy range of detection from 5 keV to more than 2000 keV. The efficiency calibration of extended range detectors over the energy range from about 5 keV to 2000 keV introduces special problems that are not encountered with typical "p-type" coaxial germanium detectors. The effect of coincidence summing on efficiency calibrations will be discussed with examples of summing effects on efficiency curves using traditional gamma-ray mixtures. Precautions that must be taken to ensure the accuracy of measurements over a wide energy range in a single measurement will be discussed. Alternatives for the calibration and use of extended range germanium detectors for routine radiological measurements will be presented.

Robotic grippers (both motor-driven and pneumatic) work by applying a force to the gripping fingers so that the object can be grasped and lifted. Generally, laboratory robotic grippers are designed to grasp and lift small vials and small bottles with less than 100-milliliter (mL) capacity. Sample bottles used at the U.S. Geological Survey National Water Quality Laboratory range from 100 to 1,000 mL. The larger sizes (for example, 500 and 1,000 mL) cannot be lifted using commercial laboratory, pneumatically activated grippers. To enhance gripping and lifting capacity, a robotic gripper was modified with vacuum-activated suction cups. Vacuum was supplied to the system with a computer-controlled miniature vacuum pump. Four suction cups were mounted at the ends of two small (2-inch) pivoting axles (two suction cups per axle), and the axles were attached to the ends of the gripper fingers. Allowing the suction cups to pivot during the closing procedure ensured a tangential fit of the suction cups to the bottle surface independent of bottle circumference. It is necessary that the suction cups contact the surface of a bottle so an airtight seal is formed. Rigidly mounted (that is, non-pivoting) suction cups do not contact all bottle sizes at a tangent to the circumference of the bottle. The modified gripper with pivoting suction cups can easily grasp and lift 1,000 mL-bottles.


Three robotics applications have been developed for analysts at the National Laboratory for Environmental Testing to increase the throughput of samples, to decrease the number of handling operations and to improve overall analytical precision for tedious, repetitive operations. The approach was to employ a general purpose, robotic arm made by CRS Plus Inc. The first application presented water samples to a Flow Injection Analyser in moderately rapid succession. The second prepares samples for the digestion process in the Total Kjeldahl Nitrogen analysis. The third dispenses samples into trays for Total Phosphorus analysis. In each case, the process begins with the field sample bottle. The paper describes and discusses the robotics in these applications.

A ROBOTIC SYSTEM OPTIMIZED FOR CHEMICAL ANALYSIS, John Rollheiser Hewlett-Packard, 24 Inverness Place East, Englewood, Colorado 80112

A robotic system has been developed which automates sample preparation and analysis in a broad range of laboratory applications. The need for automation in our laboratories continues to grow because of increased sample loads, high labor costs and declining skilled labor pool. Reliable automated systems offer increased sample throughput, reduced sample rework, improved quality of results and better worker safety. This robotic system was designed specifically for laboratory automation and is highly flexible and programmable to perform a complex tasks. The product offers a number of advantages including: 1) designed for operation on a standard laboratory bench, 2) interfaces with standard laboratory equipment, 3) operates with advanced software, 4) modular software and hardware simplifying modification and support, 5) repeatable, reliable and rugged. To help analytical laboratories meet ever increasing challenges, this system was design to operate within an overall strategy of laboratory automation called the Unified Laboratory. The goal is to transform the laboratory from a series of isolated instruments into an integrated, interactive system. This approach brings together analytical instruments and computers through standardization of software and networking.
RECENT ADVANCEMENTS IN LABORATORY ROBOTICS, John P. Connelly and R. B. Jamieson, Zymark Corp., Zymark Center, Hopkinton, MA 01748

The analytical laboratory takes in samples and produces data. Over the last decade laboratory automation has improved this process of preparing samples and producing data by providing greater throughput, capacity, precision and accuracy. Today, the integrated sample preparation and analysis robotic system has changed dramatically in design and concept from the early robotic sample preparation systems.

Recent advancements in system integration and in peripheral workstation design have redefined the role of the robot. Greater intelligence is now available in the robot peripherals. Many analytical instruments are now being interfaced directly to the robotic system. Data can now be dynamically linked from the sample preparation and analysis system to application software, spreadsheets, LIMS, etc.

Examples from Chemical, Pharmaceutical, and Environmental applications will be used to illustrate the following topics:

- Changing role of the robot
- Synergy between standard and custom workstations
- Integration of analytical instruments through RS 232 interfaces
- The growing role of active intelligent peripherals
- Flexible robotic work environment

AUTOMATED ACID DIGESTION SYSTEM FOR THE PREPARATION OF SAMPLES BY APPROVED PROCEDURES. Leatrice A. Kaplan, David C. Yaworsky, Diane S. Layne, Chuck L. Horn, Virginia Power System Laboratory, 11201 Old Stage Road, Chester, VA 23831. Rodney A. Stockton, SLR Systems, P.O. Box 1265, 2950 George Washington Way, Richland, WA 99352.

A general description of an automated hot plate acid digestion system will be presented. The system is currently capable to performing 14 approved procedures for the preparation of water or solid samples for inorganic analyses. These analyses include inductively coupled plasma, flame, graphite furnace and mercury. The robot is also used in glassware preparation. Throughput is method dependent ranging between 50 and 180+ samples per day. Technician interaction is method dependent averaging 3 hours per day. Technician interaction involves bar-coding sample and digestate bottles, replenishment of reagents and consumables, and glassware maintenance. The system is based upon the Hewlett Packard ORCA robot. Virginia Power System Laboratory is using this robotic system to support the utility's operations and environmental monitoring activities. Benefits of the system include increased sample throughput, reduced staff exposure to hazardous materials, reduced sample contamination, enhanced quality control, and a more efficient use of staff.

PLANNING LABORATORY AUTOMATION USING ACCURATE COMPUTER SIMULATION. Michael G. Dodson, Jonathan T. Smalley, and Stanley L. Owseley, Jr., Pacific Northwest Laboratory (PNL)¹, P. O. Box 999, Richland, Washington 99352.

Automation which has been prevalent in many sectors of the economy is finally beginning to appear in the chemistry laboratory. The technology which includes robots and other programmable devices can be assembled into stand alone production cells. Such cells hold the promise of increased productivity, greater accuracy and chain of custody data tracking. The development is generally an area where the client chemists feel uncomfortable procuring a never-been-seen-before automated bench costing several hundred thousand dollars. PNL, the Department of Energy (DOE) research and development contractor on the Hanford Site, has been involved on a project called Contaminant Analysis Automation (CAA) which is focused on the automation of chemistry laboratories associated with remediation of DOE sites. A task at PNL within the CAA program has been the development of computer-based system simulations. These simulations are designed to reduce the uncertainty by building accurate, functional three-dimensional computer models. These models look and act exactly like the real system. The viewer can not only see and understand the automated bench, but can also discern what throughput can be expected from the finished system. ¹PNL is operated for the U.S. Department of Energy by Battelle Memorial Institute under Contract DE-AC06-76RAL 1830.
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AUTOMATION OF EPA MICROWAVE DIGESTION METHODS 3015 AND 3051 FOR TRACE METALS ANALYSIS. John Alexander, Katherine Adams, Jesse Campbell, and Stacey Butler, ICF Kaiser Engineers, 7411 Beach Drive E., Port Orchard, WA 98366.

A robotics system has been developed to perform microwave digestion of environmental samples following SW846 Draft Methods 3015 and 3051. The system consists of a Zymark robot with custom work stations and a CEM microwave digestion oven. Software provided by the National Institute of Standards and Technology (NIST) provides a generic computer interface which controls the Zymark robot and the CEM microwave oven. Digestion protocols and conditions are downloaded from a computer file and can be updated or modified for different procedures. The system utilizes Teflon™-lined digestion vessels capable of withstanding pressures up to 200 psi. In contrast to labor-intensive manual procedures, automated microwave digestion improves efficiency by decreasing digestion time and limiting analyst involvement to adding sample to microwave vessels and transferring digestates to analytical containers. Utilizing barcode readers and analytical balances interfaced to the central computer, sample identification, weight, reagent addition, digestion loss, and final dilution data is stored electronically. Preliminary tests indicate that precision of the automated digestion system is comparable or better than manual microwave methods, digestion losses are routinely less than 1%, accuracy is improved due to less analyst involvement, and up to 75% less labor time is required. These tests also indicate that day-to-day precision and accuracy do not markedly change.

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EVOLUTION OF A ROBOTICS SYSTEM FOR WASTEWATER ANALYSIS. Tracie A. Lango and Robert L. Casselberry, Rohm and Hass Bristol Plant, Analytical Development, P.O. Box 219, Bldg. 40A, Bristol, PA 19007.

A typical week in the Water Lab at Rohm & Haas Bristol Plant might see 300-400 clean and wastewater samples processed for standard tests like pH, chemical oxygen demand (COD), biochemical oxygen demand (BOD), suspended solids, and total organic carbon (TOC). In 1988 a system was designed with the help of engineers from Source For Automation (SFA) to automate a portion of the routine wastewater testing done in the Water Lab. A decision was made to automate the less-complicated methods first; pH and COD, following with several BOD methods, and ending with TOC to complete the testing cycle.

The robots, hardware, and miscellaneous instrumentation are integrated using RS232 protocol and dedicated workstations running compiled source code. The overall coordination of the workstations is handled with a 'Supervisor' computer running a spreadsheet interface program. This allows for easy modification of the daily sampling schedules by the analysts, if necessary, without the requirement of programming skills.

This system has undergone considerable modification since the first pump was installed back in 1988. This discussion will detail the major stages of evolution, including validation and performance issues, and highlight the significant achievements realized by the system.

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GAS CHROMATOGRAPHIC ANALYSIS OF GENTAMICIN AND NEOMYCIN RESIDUES IN RAW MILK. Susan B. Clark, Jeffrey A. Hurlbut, and Carolyn A. Geisler, U.S. Food & Drug Administration, Building 29, Denver Federal Center, Denver, Colorado 80225-0087.

A rapid and sensitive gas chromatographic method for the simultaneous determination of gentamicin and neomycin in raw milk is described. Sample preparation includes acid extraction, ion exchange column clean-up of extract, a two-stage derivitization, and a toluene extraction with a water wash. Recoveries, CV's, detection limits, and experimental conditions are presented.
LC/MS CHARACTERIZATION OF MALACHITE GREEN AND METABOLITES Sherri B. Turnipseed, José E. Roybal, Austin R. Long, Food and Drug Administration, Animal Drugs Research Center, Denver Federal Center, Denver, CO 80225-0087

Malachite green (MG) is a triphenylmethane dye used as a topical antiseptic by the aquaculture industry to control fungal growth in captive fish populations. MG has been shown to be carcinogenic, therefore it is important to monitor any residual dye in fish tissue. Mass spectral characterization of malachite green and leucomalachite green (LMG), a metabolite of MG which has a long lifetime in muscle, is necessary to develop methods confirming their presence in incurred tissue. MG and LMG were analyzed by particle beam LC/MS (EI and CI) and by using a thermospray LC/MS interface. While the response for these compounds was excellent using either method of ionization (50 ng scan and 5 ng SIM), the particle beam spectra yielded more useful fragment information which can be used for the confirmation of MG and LMG in fish. Using both the thermospray and particle beam interfaces, MG is partially reduced to the leuco form. The ratio of the cation/leuco forms of the dye is dependent on source conditions such as temperature and pressure.

DETECTION OF KETONES AND ALDEHYDES BY HPLC/UV USING 2,4-DINITROPHENYLHYDRAZINE. Jeffrey A. Hurlbut, Robert K. Munns, Jose E. Roybal, and Austin R. Long, Food and Drug Administration, Animal Drug Research Center, Denver Federal Center, P.O. Box 25087, Denver, CO 80225-0087.

2,4-Dinitrophenylhydrazine (24DNPH) was investigated as a potential precolumn derivatizing agent for ketones and aldehydes using HPLC separation and UV detection. 24DNPH readily reacts with ketones and aldehydes and produces a hydrazone which strongly absorbs at 366 nm. These hydrazones are separated on a C-18 five micron column using methanol/water as the isocratic mobile phase, and they are readily detected in the picomole region. Derivatization conditions; effect of HCl concentration; effect of ketone/aldehyde concentration; effect of time; typical detection limits; linear concentration ranges; effect of reaction solvents; purification of the 24DNPH; and formation of cis versus trans products were all investigated. The suitability of using 24DNPH as a derivatizing agent in the trace detection of ketones and aldehydes is discussed.

A METHOD FOR THE DETERMINATION OF THIONIN, A METABOLITE OF METHYLENE BLUE, IN MILK BY VIS/LC. Jose E. Roybal, Robert K. Munns, David C. Holland, Jeffrey A. Hurlbut, and Austin R. Long, Food and Drug Administration, Animal Drug Research Center, Denver Federal Center, P.O. Box 25087, Denver, CO 80225.

A liquid chromatographic (LC) method with detection at 603nm is presented for the analysis of Thionin in milk. The procedure consists of extraction of milk with acetonitrile, hydrolysis of the extract to release thiazine complex, partitioning of thionin from basic aqueous solution into methylene chloride and VIS/LC analysis. LC analysis is performed by isocratic elution with a buffered mobile phase using a Phenomenex CN (cyano) column with detection in the visible absorbance mode (VIS/LC) at 603nm. Recovery of thionin from fortified control milk at 5.35, 10.7, 21.4 and 53.5ppb was 60.9% (%CV = 7.12), 54.3% (%CV = 12.2), 57.0% (%CV = 5.23) and 51.3% (%CV = 9.73), respectively. The overall recovery was 56.0% (%CV = 10.5). The method was applied to methylene blue-incurred milk at post-dosing times of 8, 24, 32, 48, 56 and 72 hours. The average residual thionin in the 72 hour post-dosing milking was 26.6ppb.
SIMULTANEOUS DETERMINATION OF NITROFURAZONE AND FURAZOLIDONE IN SHRIMP (PENAEUS VANNAMEI) MUSCLE TISSUE BY LIQUID CHROMATOGRAPHY WITH UV DETECTION.
Heidi S. Rupp, Robert K. Munns, and Austin R. Long, U.S. Food and Drug Administration, Animal Drugs Research Center, PO Box 25087, Denver Federal Center, Denver, CO 80225.

A liquid chromatographic (LC) method was developed for the simultaneous determination of nitrofurazone (NFZ) and furazolidone (FZD) in shrimp muscle tissue. The drugs were extracted from the tissue with acetonitrile and the lipids and lipophilic pigments were removed from the extract with hexane. The remaining acetonitrile extract was evaporated by using rotary evaporation and the resultant residues were dissolved with HPLC-grade water, applied to a pre-conditioned C18 SPE column, and eluted with acetonitrile. The acetonitrile eluant was then dried under nitrogen, and the resultant drug residues were dissolved with mobile phase and filtered. The drugs were determined by LC using a C18 reversed-phase (ODS Hypersil) column, a mobile phase of acetonitrile-1% aqueous acetic acid (25:75, v/v), and a photodiode array ultraviolet detector at 375 nm. NFZ and FZD were each determined in shrimp tissue at each of five spiking levels (64, 32, 16, 8, and 4 ng drug/g tissue). Absolute recoveries ranged from 70.6 to 78.4%, and relative standard deviations ranged from 4.0 to 13.6%. The limit of detection of pure standard of each drug was approximately the equivalent of 1 ng drug/g tissue, and the limit of determination in a sample was 4 ng drug/g tissue.

DETERMINATION OF THE ANTI-Coccidial DRUG, HALOFUGINONE IN EGGS
BY LIQUID CHROMATOGRAPHY. David C. Holland, Robert K. Munns, Jose E. Roybal, Jeffrey A. Hurlbut, and Austin R. Long, Food and Drug Administration, Animal Drug Research Center, Denver Federal Center, P.O. Box 25087, Denver, CO 80225-0087.

A liquid chromatographic (LC) method is described for the determination of 5-100 ppb halofuginone (HFG) in eggs. Halofuginone is extracted from eggs as the free base with ethyl acetate, followed by cleanup on an acidic Celite 545 column. A Waters C-18 column is used for LC separation with UV determination at 243 nm. The isocratic mobile phase is a mixture of acetonitrile/water/ammonium acetate buffer and acetic acid. The interassay average recovery from eggs was 90.4%, with a standard deviation (SD) of 5.11 and a coefficient of variation (CV) of 5.65%.


Indoor radon and its decay products are recognized as a major potential threat to public health. The Environmental Protection Agency (EPA) recommends that indoor radon should not exceed 4 picocuries per liter (pCi/L) for residences. Soil is the primary source of radon in the indoor environment. Knowing soil-gas radon concentrations allows a prediction to be made of indoor radon concentrations. If soil-gas radon is 500 picocuries per liter or more, there is a moderate probability that indoor radon will exceed EPA's action level; if the soil-gas radon exceeds 2,500 picocuries per liter, there is a high probability. Methods were developed and tested so that radon soil gas measurements could be conducted quickly and inexpensively in the field. A survey was performed in Prince Georges County, Maryland, where indoor radon was not expected to be high because of the nature of the sedimentary materials, which consisted mostly of sand with minor pockets of clay. Of the three age systems for formations included in this study, Cretaceous, Tertiary and Quaternary, the Tertiary formations have the highest soil-gas radon concentrations, with the potential for indoor values to exceed the EPA action level. This premise has been supported by subsequent indoor radon measurements.
EPR STUDIES OF THE GLASSY BEHAVIOR OF PROTEINS
Heinz-J. Steinhoff, Klaus Lieutenant, and Christine Karim, Institute of Biophysics, Ruhr-University Bochum, 4630 Bochum, F.R.G.

The motions of protein bound spin label side chains are studied using hemoglobin and lysozyme as model proteins of known structure. While surface side chain motions provide information on solvation, the motion of buried residues informs about fluctuations of the protein structure. The dependence of the nitroxide reorientational fluctuation rates and amplitudes on temperature, viscosity of the solute, and hydration of the protein has been measured for different spin label locations. Molecular dynamics simulations performed on spin labeled hemoglobin in vacuo and in aqueous environment have been used to predict the influences of the nitroxide ps-fluctuations on the experimental EPR spectra for lyophilized samples and samples in aqueous solution. Reorientational oscillations in the ps time scale appear to be the essential mechanism of the side chain motion for temperatures below 200 K. Activated reorientational transitions in the ns-time scale indicate the onset of functional important fluctuations of the protein above temperatures of 200 K. The dependence of these activated processes on temperature and viscosity cannot be adequately accounted for by simple laws in accordance with theories of Eyring or Kramers. However, similarities to the dynamics in glasses are obvious and may be understood on the basis of the picture of the hierarchy of conformational substates introduced by Frauenfelder.


The general method for determination of preservatives specified in the USP was evaluated for two formulations of Fluorouracil. The USP gas chromatographic method requires a silanization step and extraction with ether during sample preparation. An alternate simple, rapid, and precise HPLC method for the above analysis has been developed. No silanization or extraction steps are needed and separation was achieved utilizing an isocratic mobile phase. The USP gas chromatographic method was compared to the HPLC method. The HPLC method will be discussed and its advantages over the USP method will be summarized. Validation data for the HPLC method demonstrating method precision, specificity, linearity, ruggedness, and accuracy will also be presented.

HEADSPACE GC ANALYSIS OF RESIDUAL ORGANIC SOLVENTS IN PHARMACEUTICAL MATERIAL USING DIETHYLENE GLYCOL AS SAMPLE DILUENT. Chen-Hwa Hui, Burroughs Wellcome Co., 3030 Cornwallis Road, Research Triangle Park, NC 27709 (919) 248-3755

A static headspace GC method was developed for the quantitation of organic volatile impurities (methanol, acetonitrile, ethanol, acetone, 2-propanol, diethyl ether, tetrahydrofuran, chloroform, ethyl acetate, butanol, toluene and dimethyl formamide) in a drug substance. Diethylene glycol (DEG) was used as the sample diluent in this study. DEG is a good solvent for salts and neutral compounds. Additionally, the high boiling point of DEG allows a broad range of solvents to be analyzed using the static headspace GC method. The effects of heating temperature and equilibration time for the standards and the bulk drug were studied. Also, the reproducibility and recovery were examined. The calibration curve was linear. A limit of detection of below 100 ppm was achieved for all solvents except DMF. The practical limit of quantitation of DMF was 0.1% w/w with respect to a sample preparation of 25mg/ml solution.
HEADSPACE CAPILLARY GAS CHROMATOGRAPHIC DETERMINATION OF RESIDUAL SOLVENTS IN PHOSPHOLIPIDS, Lynne-Marie Cavallaro, Bristol-Myers Squibb Pharmaceutical Research Institute, P.O. Box 191, One Squibb Drive, New Brunswick, NJ 08903-0191 (USA).

Often raw materials used in the manufacturing of pharmaceuticals are supplied by various vendors. Qualification of these materials is necessary to ensure the purity of the final product. This paper describes the application of headspace gas chromatography (HSGC) to the residual solvent profiling of L-alpha-dimyristoylphosphatidylglycerol (DMPG), a phospholipid used in the manufacturing of a novel pharmaceutical product currently under development. HSGC has been shown to be suitable in qualifying DMPG produced by various vendors utilizing different synthetic schemes. Levels of residual methanol, ethanol, acetone, isopropanol, diethyl ether, hexane, chloroform and toluene are quantified in a single preparation. HSGC was used to provide increased sensitivity and a sample aliquot free of matrix. DMPG is dissolved in 1-butanol and placed in an automated headspace sampler. An aliquot of the headspace is transferred via a thermostated transfer line into the split injector of the GC equipped with a flame ionization detector. The method was shown to be linear over several orders of magnitude with a relative standard deviation for replicate preparations of less than 5%. The average recovery of spiked sample solutions ranged from a low of 101% to a high of 106% for all levels and components investigated. For all of the components of interest (excluding chloroform), the detection limit (DL) and the minimum quantifiable limit (MQL) were calculated to be <0.002% w/w and <0.004% w/w, respectively. The DL and MQL for chloroform were determined to be 0.003% w/w and 0.01% w/w, respectively.


Within Martin Marietta's Analytical Services Organization (ASO), epoxy samples have traditionally been analyzed by high-performance ion chromatography (HPIC) using a bomb-prep method. Erratic sulfate results prompted an experimental 10% methanol preparation dissolution method to be used with subsequent analysis by HPIC. An HPIC method with isocratic separation and micromembrane suppression is discussed in this paper. This method is specifically for the determination of sulfur as sulfate and fluoride in an epoxy curing agent. The new method will be used as a replacement for a current production laboratory bomb-prep HPIC method. Matrix interferences caused by Parr Bomb combustion products were eliminated using this method. A precision and bias study was done to document the effectiveness of the new method.


DETERMINATION OF SELECTED CARBOXYLIC ACIDS AND ALCOHOLS IN GROUNDWATER BY GAS CHROMATOGRAPHY/MASS SPECTROMETRY, Jon Belhoffer and Cindy Ferguson, U.S. Environmental Protection Agency, National Enforcement Investigation Center, Bldg. 53, Box 25227, Denver Federal Center, Denver, Colorado 80225

A simple, rapid, and specific method for the determination of selected carboxylic acids and alcohols in water samples by gas chromatography/mass spectrometry (GC/MS) will be presented. The key aspect of the method is the direct injection of water samples onto a DB-FFAP column, which has an acidified polyethylene glycol phase. The use of a DB-FFAP column allows for the analysis of a broad array of polar compounds, including aliphatic carboxylic acids, aromatic carboxylic acids, aliphatic alcohols, and phenols. Overall, the method provides good precision, low bias, and a linear instrumental response over two orders of magnitude for alcohols and three orders of magnitude for carboxylic acids, with a detection limit for most compounds of less than 10 mg/L.


Complete determination of the constituents present within hazardous waste samples is often necessary for source identification, determination of storage compatibility, or determination of the potential for environmental transport. While methods exist for the convenient determination of most common anions, direct determination of hydroxide ion, via titration, is subject to interferences. In particular, if samples contain high concentrations of Cr (VI) ions, the Cr(VI) species are titrated along with the hydroxide ion. Fortunately, the determination of hydroxide ion can be indirectly accomplished by determining both the total alkalinity and the chromium (VI) ion concentration of the sample. The key to the success of this strategy is the fact that a linear relationship exists between the quantity of acid required to reach an appropriate endpoint and the Cr (VI) ion concentration.

MID- VERSUS NEAR- INFRARED IN THE STUDY OF HIGH MOISTURE SAMPLES: ADVANTAGES, DISADVANTAGES, AND COMPLEMENTATION. James B. Reeves, III, Ruminant Nutrition Lab, LPSI, ARS, USDA, Bldg. 200, Rm 218, BARC-East, Beltsiville, MD 20705.

Near infrared (NIR) spectroscopy has gained wide popularity for the determination of the composition of feedstuffs. Efforts with non-dried samples, such as silages, have not been as successful as with dry samples. Examination of spectra of high moisture samples has shown a wide variety of water induced degradative influences on NIR spectra. The objective of this work was to examine the advantages and disadvantages of each spectral region (Mid- and Near- IR) for the study of high moisture samples. Results with aqueous solutions has shown that less spectral distortion when subtracting water from Mid-IR spectra than from NIR spectra. It was also easier to produce high quality spectra in the Mid-IR by using attenuated total reflectance than by using transmission in the NIR. While Mid-IR spectra showed changes (induced by water, pH, physical state, and ionic strength) similar to those found in the NIR, there appears to be more total available information in the MID-IR even in the presence of water. Finally, the use of spectral changes in the two spectral regions offers an opportunity to relate NIR spectra to specific energy vibrations and to carry out band assignments by utilizing the vast knowledge available about IR bands.
THE USE OF LABORATORY ROBOTICS FOR THE CHEMICAL DECOMPOSITION OF GEOLOGIC MATERIALS IN THE DETERMINATION OF MERCURY BY COLD VAPOR ATOMIC ABSORPTION SPECTROPHOTOMETRY. Richard M. O'Leary, Stephen Wilson, and Philip Hageman, U.S. Geological Survey, Box 25046 MS973, Denver, Co 80225

A laboratory robotics method is presented for the chemical decomposition of rocks, soils, stream sediments and plants prior to the quantification of Hg by cold-vapor atomic absorption spectrophotometry (CVAAS). The robotics system dispenses 2 mL concentrated nitric acid and a 0.5 mL sodium dichromate solution (25%) into disposable tube containing a preweighed 0.1 g sample and places the tube in a heating block at 100°C for 2 hrs. Following the digestion the solution is brought to a 12 mL volume with deionized water using an optical sensor, mixed with a magnetic stirrer and returned to the sample rack. The mercury concentration is then determined by CVAAS with a limit of determination of 0.02 ppm. Studies comparing robotics and the manual procedure for: 1) Productivity; 2) Precision; 3) Accuracy using Standard Reference Material (SRM) from the National Institute of Standards and Technology (NIST); and 4) Cost recovery, will be presented.

DISTANCE MEASUREMENTS IN CARBON-13 NMR: APPLICATION TO DNA
Thomas P. Jarvie, Gershom M. Wolfe, Jonathan Callahan and Gary P. Drobny
Department of Chemistry, University of Washington, Seattle, WA 98195

The ability to measure distances between carbon atoms in DNA and RNA (in non-crystalline and therefore more natural forms) would aid in determining the sequence specific, local structure in these important molecules. In DNA and RNA, one of the most common and most easily labelled groups is the carbonyl. Measurement of weak dipole-dipole couplings in the presence of the large CSA of carbonyls presents a challenge. Techniques that involve magic angle spinning and rotor synchronous rf pulses to eliminate the effect of CSA while reinstating the dipole-dipole coupling will be presented. Experimental results on carbon-13 labelled test molecules as well as on labelled DNA will be presented. Additionally the results are compared to computer simulations.

HIGH-RESOLUTION NMR CHARACTERIZATION OF SOLIDS : J.P. ANOUREUX,
Université de Lille-1, F 59655, Villeneuve d'Ascq, Cédex,
FRANCE, Fax : (33) 20.43.40.84

Quadrupolar nuclei (I=1/2) compose approximately 3/4 of the elements in Nature. Unfortunately these nuclei are often difficult to observe in solid-state NMR, as a result of the couplings between their electric quadrupole moments and the electric field gradients to which they are subjected. The effects of these quadrupole interactions are very great on satellite transitions but much smaller on the central transition. Satellite-transition analyses on powder-samples are only possible when quadrupole interactions are moderate. When this is true, MAS technique greatly improves the resolution. Unfortunately, the simultaneous existence of CSA and quadrupole interactions with different PAS may render difficult the analyses of MAS spectra. Two different techniques (DAS and DOR) have been proposed for obtaining narrow lines on nuclei with semi-integer spins subjected to strong quadrupole interactions. Both methods are based on the same principle : samples are rotating around one axis which reorients itself with respect to Bo. Recently a new one-dimensional method (VAST) using classical probes with fixed rotors has been proposed for spin 3/2 subjected to very strong quadrupole interactions. Three of these methods (MAS, DOR and VAST) will be presented and some of their limitations discussed.
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MAGIC-ECHO AND SPIN-WARP MICROIMAGING OF POLYMERS BELOW AND ABOVE THE GLASS TRANSITION TEMPERATURE.

Winfried Kuhn, Peter Barth, Siegfried Hafner
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During the last few years NMR imaging has been applied sucessfully to less rigid polymeric materials. In our group parameter selective 2D and 3D imaging sequences have been used to investigate aging processes and crosslink density inhomogeneities in technical rubber materials and the penetration and diffusion of water in epoxy resins. Conventional imaging methods however are restricted to materials with linewidths less than 3 kHz such as elastomers far above glass transition temperature. For real rigid solids special sequences are needed to reduce the linewidth of the proton signal. We have applied the Magic Echo Phase-encoding Solid Imaging (MEPSI) method to investigate aged rubber samples below the glass transition temperature. This extends the studies on aging processes by parameter selective imaging also to this temperature range. Furthermore, we have studied the uptake and distribution of water in electronic semiconductor devices. The MEPSI sequence will be discussed in comparison to more demanding solid state imaging sequences and the results will be shown.

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$^{129}$Xe NMR IN SOLIDS: SHIELDING TENSORS AND DYNAMICS

J. A. Ripmeester, C. I. Ratcliffe, I. Moudrakovsky, Steacie Institute for Molecular Sciences, National Research Council of Canada, Ottawa, Ont. K1A OR6, Canada, and H. Tabbara, H. Graves Smith and C. Detellier, Dep't of Chemistry, University of Ottawa, Ottawa, Ont. K1N 8N5, Canada

In the course of developing an understanding of chemical shifts of $^{129}$Xe trapped in solids there is a considerable advantage to studying materials with small pores for which anisotropic chemical shifts are observable. Anisotropic chemical shifts are reported as a function of loading for xenon trapped in ALPO-11 and tetramethylammonium exchanged montmorillonite. For ALPO-11, the shifts vary continuously with loading, and can be interpreted in terms of a statistical model where there is fast exchange for three distinct xenon populations. For montmorillonite, the anisotropy tends to approach a constant value at higher loading. For materials which exhibit more than one site for xenon (Na mordenite, Ag exchanged A zeolite, Decadodecasil-3R ), both 1 and 2D methods have been used to study exchange processes.
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CHARACTERIZATION OF POLYCRYSTALLINE V₂O₅ BY SOLID-STATE ⁵¹V-NMR:
C. Fernandez, J.P. Amoureux, P. Bodart, Université de Lille-1,
F 59655, Villeneuve d'Ascq, Cédex, FRANCE, FAX : (33)20.43.40.84

Vanadium oxides have been extensively studied due to their importance as
industrial catalysts. Many studies have shown that supported V₂O₅ on TiO₂ (anatase) is
a superior catalyst to unsupported crystalline V₂O₅ for the selective oxidation of
hydrocarbons. But the exact nature of the mechanism by which the titania support
modifies the catalytic properties of V₂O₅ is not well understood. ⁵¹V-NMR may give
interesting informations about the local structure of V₂O₅. However, previous studies
of such systems have shown that static-powder sample resonance is very broad and
featureless ; MAS has to be used. When numerous sidebands are observed, the comparison
of the sideband intensities with the results of numerical simulations yields accurate
informations about the anisotropic (shielding and electric field gradient) interactions
and their relative PAS orientations. However, the MAS technique can only be fully
exploited, if it is paired with sophisticated procedures for the spectral analysis
taking into account all instrumental distortions : dead-time, coil quality factor, RF
pulse length. We have completely determined these two anisotropic interactions on V₂O₅
and V2O5 on TiO2. By the way, we have shown that the two PAS relative orientations
cannot be completely determined, due to the fact that powder samples are used.

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DYNAMICS OF SUBSTITUTED ADAMANTANES : A NMR STUDY, J.P. Amoureux,
R. Decressain, E. Cochon, Université de Lille-1, F 59655
Villeneuve d'Ascq, Cédex, FRANCE, FAX : (33) 20.43.40.84

Substituted adamantanes are composed of highly symmetrical rigid molecules.
At room temperature, these compounds are in a plastic phase ; which means that the
molecules are translationally ordered and orientationally disordered. The dynamics of
these compounds can easily by analysed in NMR by the relaxation times. Rotational
diffusions (BPP model) are nearly always assumed in liquids. In solids, the
reorientations must simultaneously take into account the lattice and molecule
symmetries (Frenkel model). We have analysed the dynamics of several substituted
adamantanes by T₁z and T₁p relaxation times with variable temperature. If only one
single relaxation time is considered, the BPP model nearly always appears exact. On the
other hand, the simultaneous refinement of several different relaxation times often
leads to a bad quantitative agreement with this model, particularly at low temperature.
This model only gives an approximate description of the solid-state dynamics because
only an averaged residence time is considered. In opposite, the Frenkel model with its elaborate description can bring the value of
the different residence times especially if several different spins are considered with
different magnetic fields.
CHEMICAL STRUCTURE COMPARISONS OF DISSOLVED HUMIC SUBSTANCES IN VARIOUS AQUATIC ENVIRONMENTS USING PROTON NUCLEAR MAGNETIC RESONANCE (\textsuperscript{1}H NMR) SPECTROMETRY Ted I. Noves and Jerry A. Leenheer, U. S. Geological Survey, 5293 Ward Rd., Arvada, CO 80002

Approximately 80\% of dissolved humic substances are uncharacterized and consist of complex altered residues of plant, animal, bacterial and fungal origin. However, interesting trends were noted in \textsuperscript{1}H NMR spectra obtained from humic substances sampled from widely divergent lake and river environments, including several unique "end members" (aquatic environments that have a simpler biogeochemical origin for dissolved humic substances than typical surface waters). Five \textsuperscript{1}H NMR peak regions were measured in this study to elucidate the structure of humic substances. Two regions are important indicators of origin and degree of degradation, in various aquatic environments. The aromatic proton region of \textsuperscript{1}H NMR (7.3-8.0 PPM) provides an indication of the source of humic substances (i.e. allochthonous versus autochthonous origin). The region representing methyl, methylene, and methine protons on carbons attached to aromatic rings or to adjacent carbonyl carbons (2.3-3.2 PPM) indicates the degree of degradation for a particular aquatic environment. By studying "end member" humic substances and more typical heterogenously produced humic substances, in an integrating environment such as the Mississippi River, a clearer understanding of the diagenesis of compounds in natural water can be realized.
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