38TH ROCKY MOUNTAIN CONFERENCE ON ANALYTICAL CHEMISTRY

final PROGRAM AND Abstracts

JULY 21-26, 1996

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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VENDOR WORKSHOP SCHEDULE

<table>
<thead>
<tr>
<th>Vendor</th>
<th>Sunday 7/21/96</th>
<th>Wednesday 7/24/96</th>
<th>Thursday 7/25/96</th>
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<td>Bruker</td>
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<td>Varian</td>
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<td>Waters</td>
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<td>Mac-Mod</td>
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CONFERENCE LOCATION

Technical sessions and the exhibition for the 38th Rocky Mountain Conference on Analytical Chemistry will be held in the Hyatt Regency Denver Hotel, 1750 Welton Street, Denver, Colorado 80202.
## SYMPOSIA SCHEDULE

<table>
<thead>
<tr>
<th>Room</th>
<th>Sunday 7/21/96</th>
<th>Monday 7/22/96</th>
<th>Tuesday 7/23/96</th>
<th>Wednesday 7/24/95</th>
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<td>Moulin Rouge</td>
<td>NMR</td>
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<tr>
<td>Royal</td>
<td>Lumin.</td>
<td>Lumin.</td>
<td>Pharm.</td>
<td>Pharm.</td>
<td>Waters</td>
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<tr>
<td>Florentine</td>
<td>Bruker</td>
<td>Bruker</td>
<td>FTIR</td>
<td>FTIR</td>
<td>ICP-MS</td>
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<td>Skogerboe</td>
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<td>Atomic Spec.</td>
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<tr>
<td>Imperial Ballroom</td>
<td>Exhibits</td>
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<tr>
<td>Imperial Foyer</td>
<td>General Posters</td>
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<td>General Posters</td>
<td>General Posters</td>
<td>General Posters</td>
</tr>
</tbody>
</table>

Room locations can be found on the map on the back cover of this program.
SYMPOSIA ORGANIZERS

ATOMIC SPECTROSCOPY
Gary Rayson
New Mexico State University
Department of Chemistry
Las Cruces, NM 88003
(505) 646-5839 fax: (505) 646-2649

CHROMATOGRAPHY
Richard Burrows
Quanterra Environmental Services
4955 Yarrow St.
Arvada, CO 80002
(303) 421-6611 fax: (303) 431-7171

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

Robert Wershaw
U.S. Geological Survey
MS408, 5293 Ward Road
Arvada, CO 80002
(303) 467-8280 fax: (303) 467-8240

ELECTROCHEMISTRY
Chuck Martin
Colorado State University
Department of Chemistry
Ft. Collins, CO 80523
(970) 491-0271 fax: (970) 491-1801

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Maria Tikkanen
Assoc. of California Water Agencies
910 "K" Street, Suite 250
Sacramento, CA 95814
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MASS SPECTROMETRY
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Hauser Laboratories
5555 Airport Road
Boulder CO 80301
(303) 443-4662 fax (303) 441-5803

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University of Denver
Department of Chemistry
Denver, CO 80208
(303) 871-2980 fax: (303) 871-2254

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Department of Chemistry
Denver, CO 80208
(303) 871-3102 fax: (303) 871-2254

FTIR / NIR / RAMAN SPECTROSCOPY
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University of Denver
Department of Chemistry
Denver, CO 80208
(303) 871-4404 fax: (303) 871-2932

Dwight Smith
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Department of Chemistry
Denver, CO 80208
(303) 871-2938 fax: (303) 871-2932

GENERAL POSTERS
Mary Cast
National Water Quality Lab
U.S.G.S.
5293 Ward Road
Arvada, CO 80002
(303) 467-8135 fax: (303) 431-8331

ICP-MS
Howard Taylor
USGS
3215 Marine Street
Boulder, CO 80303
(303) 541-3007 fax: (303) 447-2505

RADIOCHEMISTRY
Ann Mullin
USGS NWQL
5293 Ward Road
Arvada, CO 80002
(303) 467-8235 fax: (303) 467-8240
ORGANIZERS OF THE 38TH ROCKY MOUNTAIN CONFERENCE

CONFERENCE CHAIRMAN
Glenda Brown
U.S. Geological Survey
National Water Quality Laboratory
5293 Ward Road
Arvada, CO 80002
(303)467-8122 fax (303)431-8331

EXHIBITS AND VENDOR WORKSHOPS
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RFETS
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Golden, CO 80402-0464
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(email) 75057.2324@compuserve.com

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(303) 277-2931

AUDIO-VISUAL
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U.S. Geological Survey
National Water Quality Laboratory
5293 Ward Road.
Arvada, CO 80002
(303) 467-8147 fax: (303) 431-8331

SOCIAL EVENTS
Chuck Bates
Geneva Pharmaceuticals, Inc.
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Box 446
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(303) 438-4469 fax (303) 466-7935

ROCKY MOUNTAIN CONFERENCE INFORMATION
(303)843-9174
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email: barb.coles@hauser.com
SYMPOSIA ORGANIZERS

LUMINESCENCE
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(314) 537-6004 fax: (314) 537-6806

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(303) 530-1169 fax: (303) 530-1169

Patricia Sulik
Rocky Mountain Instrumental Labs
456 South Link Lane
Ft. Collins, CO 80524
(303) 530-1169 fax: (303) 530-1169

QUALITY ASSURANCE
Carl Craig
Sievers Instruments
6185 Arapahoe St.
Boulder, CO 80303
(303) 444-2009 fax: (303) 444-9543

UPCOMING CONFERENCE DATES

August 2-9, 1997 Hyatt Regency Denver
July 25- August 1, 1998 Hyatt Regency Denver

ACCOMODATIONS FOR DISABILITIES

If you have a disability and may require accommodations in order to fully participate in
cconference activities, please contact the Registration Desk. We ask your cooperation in
notifying us as soon as possible of your need for accommodation. While every effort will be
made to meet attendees' needs, we cannot guarantee the availability of accommodations in
response to requests received after July 8, 1996.

SPEAKER PREPARATION ROOM

The Gold Room is provided as a speaker preparation room for your convenience. The room has
a slide projector and overhead projector available for authors to prepare for their speech if they
desire. Please be considerate of others when using the room, as it is on a first-come, first-
served basis.
REGISTRATION

Admission to all technical sessions, vendor-sponsored users groups and the exhibition is by the name badge for the 38th Rocky Mountain Conference. Conference fees are payable by check (denominated in $US, only drawn on a U.S. Bank) made payable to the Rocky Mountain Conference. Visa and Mastercard are also accepted.

REGISTRATION FEES - 1996

<table>
<thead>
<tr>
<th>On Site</th>
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<tbody>
<tr>
<td>Regular (entire conference and exhibitions)</td>
<td>$100.00</td>
</tr>
<tr>
<td>One Day (specify day: M, T, W, R) includes exhibitions</td>
<td>$55.00</td>
</tr>
<tr>
<td>Retired / Unemployed</td>
<td>$35.00</td>
</tr>
<tr>
<td>Full Time Student - Regular (student ID required)</td>
<td>$35.00</td>
</tr>
<tr>
<td>Student - One Day (specify day: M, T, W, R)</td>
<td>$15.00</td>
</tr>
<tr>
<td>Additional Vendor (beyond 3)</td>
<td>$45.00</td>
</tr>
<tr>
<td>Exhibition Only (non-vendor)</td>
<td>$15.00</td>
</tr>
<tr>
<td>Rockies Baseball: 7:05 pm (evening), Wednesday, July 24 against the New York Mets. Tickets are limited!</td>
<td>$5.00</td>
</tr>
</tbody>
</table>

REFUNDS: Requests for refunds of conference fees must be received by July 8, 1996.

REGISTRATION TIMES

On-site registration for the 38th Rocky Mountain Conference will be held in the Imperial Ballroom Foyer of the Hyatt Regency Denver during the following hours:

<table>
<thead>
<tr>
<th>Day</th>
<th>Hours</th>
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<tbody>
<tr>
<td>Sunday, July 21</td>
<td>4:00 p.m. - 8:00 p.m.</td>
</tr>
<tr>
<td>Monday, July 22</td>
<td>7:30 a.m. - 3:30 p.m.</td>
</tr>
<tr>
<td>Tuesday, July 23</td>
<td>7:30 a.m. - 3:30 p.m.</td>
</tr>
<tr>
<td>Wednesday, July 24</td>
<td>7:30 a.m. - 3:30 p.m.</td>
</tr>
<tr>
<td>Thursday, July 25</td>
<td>8:00 a.m. - 10:00 a.m.</td>
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SOCIAL PROGRAM AT THE HYATT REGENCY DENVER

SCHEDULE OF EVENTS

<table>
<thead>
<tr>
<th>Day</th>
<th>Event</th>
<th>Hours</th>
</tr>
</thead>
<tbody>
<tr>
<td>Sunday, July 21</td>
<td>Registration Mixer</td>
<td>4:00 p.m. - 8:00 p.m.</td>
</tr>
<tr>
<td>Monday, July 22</td>
<td>Exhibition</td>
<td>10:00 a.m. - 5:00 p.m.</td>
</tr>
<tr>
<td>Monday, July 22</td>
<td>General Posters</td>
<td>3:00 p.m. - 5:00 p.m.</td>
</tr>
<tr>
<td>Monday, July 22</td>
<td>Conference Reception</td>
<td>5:00 p.m. - 7:00 p.m.</td>
</tr>
<tr>
<td>Tuesday, July 23</td>
<td>Exhibition</td>
<td>9:00 a.m. - 5:00 p.m.</td>
</tr>
<tr>
<td>Wednesday, July 24</td>
<td>Exhibition</td>
<td>9:00 a.m. - 2:00 p.m.</td>
</tr>
<tr>
<td>Wednesday, July 24</td>
<td>Rockies Baseball</td>
<td>7:05 p.m. first pitch</td>
</tr>
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REGISTRATION NIGHT MIXER

A cash bar will be open in the Imperial Ballroom Foyer of the Hyatt Regency Denver on Sunday evening, July 23, from 4:00 - 8:00 p.m. Plan to meet other conference attendees and beat the Monday rush to pick up your conference badge and final program.
CONFERENCE RECEPTION
On Monday evening, July 22, from 5:00 to 7:00 p.m., all attendees are cordially invited to join us for cocktails and hors d’oeuvres at the Hyatt Regency in the Imperial Ballroom. The exhibition will be open this evening and submissions from the General Poster session will be available for viewing. Enjoy music performed by last year’s favorite, Blue Heaven.

ROCKIES BASEBALL
A limited number of seats are available for the Wednesday evening game with the New York Mets at Coors Field in downtown Denver. Tickets are only $5.00. The game begins at 7:05 p.m. Contact the Registration desk for directions to Coors Field.

MESSAGE CENTER
Incoming telephone messages for conferees will be posted on the Conference Message Board, near the conference registration booth. The telephone number is (303) 295-1234. Indicate that the individual is attending the Rocky Mountain Conference so the message can be posted in the proper area.

VISITOR INFORMATION
Contact the Guest Services in the main lobby of the Hyatt Regency Denver for suggestions about the large number of activities that are available 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.

RESTAURANT SERVICE
The Hyatt Regency Denver has an excellent restaurant in the hotel. In addition, Guest Services in the main lobby has sample menus and suggestions for casual to elegant dining experiences throughout the Denver area.

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 at the A.C.S. booth during the conference for review by prospective employers. Employers may then select qualified job applicants to arrange an interview or further meeting. Job applicants should provide a local telephone number where they can be contacted during the conference, or they may check for messages at the A.C.S. booth. Employers may also post current job openings on the bulletin board located near the A.C.S. booth.
EXHIBITORS FOR THE 1996 ROCKY MOUNTAIN CONFERENCE

The Rocky Mountain Conference exhibition provides an opportunity to see and discuss the latest in analytical instrumentation, supplies, and services. Many vendors will be on hand to display and demonstrate their latest products.

Exhibit Hours:
Monday 10:00 a.m. to 5:00 p.m.
Tuesday 9:00 a.m. to 5:00 p.m.
Wednesday 9:00 a.m. to 2:00 p.m.

The following exhibitors will be in attendance
(as of June 7, 1996).

Analytical Instrument Recycle
Advanced Chemistry Development, Inc.
Allen Scientific Glass, Inc.
American Chemical Society, Colorado Section
Bruker Instruments, Inc.
Finnigan MAT
Fisons Instruments / VG Elemental
Hamilton Co.
Hauser Laboratories
Hewlett Packard
High Purity Standards
Hiltech
JEOL USA, Inc.
3M Company
Mac-Mod Analytical
Mattson Instruments
Micro-Now Instrument Co., Inc.
Micromass, Inc.
Morgan Scientific
Nicolet Instruments
Otsuka Electronics USA, Inc.
Oxford Instruments, Inc.
Perkin-Elmer Corp.
Resonance Research, Inc.
Resonance Technologies, Inc.
Scientific Supply
Society for Applied Spectroscopy
Supelco, Inc.
Thermo Jarrell Ash
Update Instruments, Inc.
Varian Associates, Inc.
Waters Corporation
Webster Associates
Western Analytical
Wilmad Glass
SHORT COURSES

(Sponsored by the Colorado Section of the American Chemical Society)
to be held in conjunction with the 38th Rocky Mountain Conference

Analytical Inductively Coupled Plasma-Emission AES and ICP-MS       July 25-26, 1996
Fee: $400, ACS or SAS member, $450, non-member           Faculty: Howard E. Taylor
The course presents the basic principles, techniques and analytical applications of ICP-AES and ICP-MS
to chemists, biochemists, chemical engineers, analysts, QA managers, clinicians; anyone who wants to
know about the use and applications of this versatile instrumentation. Beginning with the theory of
atomic spectrometry and a discussion of the state-of-art instrumentation and data processing techniques,
specialized sample introduction methods are then discussed including laser ablation, ultrasonic, and slurry
nebulization. These techniques are applied to the analysis of isotopes used in the study of tracers,
geochronology, and quantitation by isotope dilution.

Quality Assurance/Quality Control in the Analytical Testing Laboratory    July 25-26, 1996
Fee: $400, ACS or SAS member, $450, non-member            Faculty: Steve Callio and John Gillis
This course addresses the important principles of quality assurance as applied to the analytical testing
laboratory. Beginning with a fundamental discussion of the functions and practices that are essential to
generating and documenting high-quality analytical data, an in-depth description is then presented
covering the establishment and continuous improvement of laboratory QA programs and specific QC
practices. Attendees will also learn how to develop better laboratory practices essential to document
laboratory performance and what to ask for in negotiating for the performance of laboratory testing
services.

Introduction to Polymer Science             July 25-26, 1996
Fee: $400, ACS or SAS member, $450, non-member        Faculty: Dr. Bonnie J. Bachman
This introductory course is aimed at all individuals who work with polymers and need to have a basic
knowledge and understanding of polymer fundamentals. Topics discussed include definitions and
nomenclature used in the polymer industry, the classification of polymers, polymer synthesis, key
properties of polymers, and methods used to characterize polymers. Additionally, the fabrication,
modification, and important property-structure relationships of polymers are discussed.

For short course information, contact:
Dr. Gary Clapp                          Dr. Joe Zirrolli
Hauser Laboratories                     Hauser Laboratories
5555 Airport Blvd.                      5555 Airport Blvd.
Boulder, CO 80301                        Boulder, CO 80301
Tel: (303) 443-4662                     Tel: (303) 443-4662
Fax: (303) 443-5803                     FAX: (303) 443-5803
email: j.zirrolli@hauser.com
VENDOR WORKSHOPS

Bruker Instruments, Inc. 4th Annual Rocky Mountain Conference Workshop on Solid-State NMR

Bruker Instruments will host a workshop dedicated to solid-state NMR on Sunday, July 21, 1996 at the Hyatt Regency Hotel. New developments and products from Bruker will be presented, along with experimental results presented by users of Bruker instrumentation. All NMR spectroscopists with an interest in solids are encouraged to attend, regardless of whether they are familiar with Bruker Instruments or not. This should be an excellent opportunity to find out more about the current capabilities and future directions of Bruker in solids, and also for you to share your ideas on what you would like to see us offer in the future.

If you plan to attend, or would like more information, please call Doug Burum at (508) 667-9580 ext. 120.

Varian Associates: Varian NMR Instruments 5th Solids State Users Conference

Varian Solids Systems’ owners and users are invited to a users’ conference on Sunday, July 21, 1996. The conference will consist of presentations from both Varian personnel and Varian spectrometer users. Varian applications scientists, R&D engineers, and sales representatives will be present at this half-day conference. This is an excellent opportunity for long-term Varian customers to gather for an afternoon of stimulating scientific interaction, and for an evening of dining as guests of Varian.

For registration material, please call Ms. Bee Sehrt in Palo Alto, CA at 1-800-356-4437 #3 ("Events Line"). Please indicate if you wish to make a presentation. For other information regarding this conference, please call lain Green at 314-725-5862.

Waters Chromatography: Strategies For Faster Hplc Method Development

Using pharmaceutical compounds as examples, this seminar explains the importance of column quality on method development criteria. Optimizing the solvent and the column with respect to precision, accuracy, limit of quantification, specificity, ruggedness, and robustness are necessary for confidence in the method. These six criteria make up the parameters of Method Validation. It doesn't need to take that long if you know the simple rules of FAST HPLC METHOD DEVELOPMENT!

This seminar will be held Wednesday afternoon, July 24, 1996. To make reservations, call Denise Kent at (800) 252-4752 ext. 6987.

Otsuka Electronics USA Inc. Chemagnetics® Instruments

7th Annual Solid-State NMR Spectroscopy Workshop

Dates: Friday, July 26th and Saturday, July 27th

Locations: Thursday night, Friday Elkhom Lodge, Estes Park, Colorado
Saturday Otsuka Electronics USA Inc.
2607 Midpoint Dr.
Ft. Collins, CO 80525

This will be an informal workshop focusing on the nuts & bolts of NMR. Friday includes a number of speakers, informal discussions, a mixer and dinner at the Elkhom Lodge. Saturday will include a day of lab work on various solids NMR techniques at the Otsuka Electronics headquarters in Fort Collins. Transportation to Fort Collins will be provided by Otsuka from Estes Park. There is no fee to attend the workshops, however local accommodations and meals are the attendee’s expense. Space is limited, so please respond as soon as possible. For further information contact Dr. Jim Frye, (970)484-0428 or email jimf@otsuka.com
SYMPOSIUM ON ATOMIC SPECTROSCOPY
Organized by Gary Rayson

Tuesday, July 23, 1996

Gary Rayson, presiding

8:30 Opening Remarks and Announcements

8:40 INVITED SPEAKER: The Production, Transport and Fate of Sample Aerosols in ICP-OES and ICP-MS: From Fundamental Studies to Practical Analysis to Elemental Speciation, John W. Olesik, Department of Geological Sciences, The Ohio State University. (1)

9:20 Mechanistic Studies in an Axially Viewed ICP Used for Absorption Measurements, Carl E. Hensman and G. D. Rayson, Department of Chemistry and Biochemistry, New Mexico State University. (2)

9:40 Break

10:20 Analysis of Oils for Halogens and Nitrogen by ICP-AES in the VUV Region, G. N. Coleman, C. Harris, M. O'Boyle, R. Starek, and J. D. Steiner, VG Elemental. (3)

10:40 New Wave for Sample Preparation, Edward E. King, W. E. Jennings, and D. Manchester, CEM Corporation. (4)

11:00 The Development of a Portable Hazardous Waste Monitor, A. J. R. Hunter, M. E. Fraser, L. G. Piper, and S. J. Davis, Physical Sciences, Inc. (5)

11:20 Impact of Operation Parameters for an Inductively Coupled Argon Plasma Axial Viewing Absorption Technique, Gary D. Rayson and C. E. Hensman, Department of Chemistry and Biochemistry, New Mexico State University. (6)

11:40 Influence of Robust Plasma Operating Conditions on Detection Limits in an Axially-Viewed Inductively-Coupled Plasma, G. N. Coleman, C. Harris, M. O'Boyle, and R. Starek, VG Elemental, (withdrawn)

12:00 Lunch

SYMPOSIUM ON CHROMATOGRAPHY
Organized by Richard Burrows

Chromatography papers have been included in the Environmental Chemistry Symposium.

SYMPOSIUM ON COMPOSTING AND SUSTAINABLE AGRICULTURE
Organized by Cal Kuska and Robert L. Wershaw

Wednesday, July 24, 1996

Robert Wershaw and Cal Kuska, presiding

1:00 Performance of Compost on Agricultural Crops, Robert Rynk, Biological and Agricultural Engineering Department, University of Idaho, Moscow, ID. (8)

1:20 Recycling Nutrients from Crop Residues for Space Applications, Richard Strayer and Cheryl Atkinson, NASA, Kennedy Space Center, FL. (9)

1:40 Small-Volume Composting, Cheryl Atkinson, NASA, Kennedy Space Center, FL. (10)

2:00 Intrinsic Odor Generation by Composting Food Wastes, Michael A. Cole, Department of Natural Resources and Environmental Sciences, University of Illinois, Urbana, IL. (11)

2:20 Break

2:50 Composting of Hazardous Waste From Agricultural By-Products with Animal Origin, Laszlo Alexa and Sandor Der, University of Agricultural Sciences, Godollo Pater, Hungary. (12)
Farmers and Transition: Learning Approaches to Sustainable Agriculture Through Narratives, Kim L. Staritzky, Cornell University, Ithaca, NY. (13)

Community Planning for Sustainability through Renewable Carbon Management, Jim McNelly, Naturtech Composting Systems, Inc., Saint Cloud, MN. (14)

Community Supported Agriculture, Paul Magedson, Good Earth Organic Farm, Celeste, TX. (15)

Composting as a Means of Integrating Seafood and Food Processing By-Products Management, M. Y. Minkara, T. B. Lawson and G. A. Breitenbeck. Louisiana State University, Baton Rouge, LA. (16)


SYMPOSIUM ON ELECTROCHEMISTRY
Organized by Charles R. Martin

Monday, July 22, 1996

Session I Charles R. Martin, presiding

8:30 Opening Remarks and Welcome, Charles Martin

8:35 Anodic Stripping Voltammetric Assays at Hg-coated Diamond Thin Film Electrodes, G.M. Swain and S. Alehashem, Department of Chemistry, Utah State University, Logan, UT. (18)

9:00 An Experimental Comparison of Marcus vs. Mulliken-Hush Theory, D. Derr, S. Ferrere, C.M. Elliott, Department of Chemistry, Colorado State University, Ft. Collins, CO. (19)

9:25 Electrochemically Modulated Liquid Chromatography: Applications and Retention Processes, En-Yi Ting, M.S. Abdel-Latif and M.D. Porter, Microanalytical Instrumentation Center, and Ames Laboratory, USDOE, Iowa State University, Ames, IA. (20)

9:50 The Electrochemical and Structural Characterization of Diamond-coated and Hydrogenated Glassy Carbon Electrodes, J. Xu and G.M. Swain, Department of Chemistry, Utah State University, Logan, UT. (21)

10:15 Break

10:45 Monitoring Homogenous Electron Self-exchange Kinetics Using Stable Isotopes, M.E. Ketterer, G.E. Kozerski, M.A. Fiorentino, J. Song, Department of Chemistry, John Carroll University, University Heights, OH. (22)


11:35 Magnetic Field Control of the Interfacial Potential Distribution and Voltammetric Currents Using Microelectrodes, H.S. White, J. Lee, S.R. Ragsdale, X. Gao, Department of Chemistry, University of Utah, Salt Lake City, UT. (24)

12:00 Lunch

Session II, Henry S. White, presiding

1:15 The Electrochemical Response of Anodically Polarized Diamond Thin Film Electrodes, M.C. Granger, G.M. Swain, Department of Chemistry, Utah State University, Logan, UT. (25)

1:40 Optimization of an Amperometric Sensor for Neutral Organiccs in Aqueous Solution Based on Conducting Polymer Modified Electrodes, S.M. Hendrickson, C.M. Elliott, Department of Chemistry, Colorado State University, Ft. Collins, CO. (26)

2:05 Controlled Creation of Defects in Alkanethiol Monolayers, T.A. Tanzer, R. H. Terrill, and P.W. Bohn, Department of Chemistry, University of Illinois, Urbana, IL. (27)

2:30 Enzyme Facilitated Transport, B. Lakshmi, and C.R. Martin, Department of Chemistry, Colorado State University, Ft. Collins, CO. (28)

2:55 Break


4:10 Improved Charge Transfer Kinetics at Polypyrrole/Nafion Composite Thin Films, B.L. Hirsche, J. Xu, and G. M. Swain, Department of Chemistry, Utah State University, Logan, UT. (31)

4:35 Potential-induced Changes in the Surface Morphology of (100) n-InP Samples Photochemically Etched, D.A. Stoltz and L. Crescato, Instituto de Fisica, UNICAMP, Campinas-SP, Brazil. (32)

SYMPOSIUM ON ENVIRONMENTAL CHEMISTRY
Organized by Maria W. Tikkanen

Financial Support provided by Finnigan MAT

Monday, July 22, 1996

Maria W. Tikkanen, presiding

8:30 Opening remarks

8:35 Cleanup of Metallic Contaminants using Supercritical Carbon Dioxide Extraction with an Inexpensive Chelating Agent, Edwin F. Holcombe, Anthony F. Lagalante, Jefferey A. Merkel, Wendy A. Andersen, Barbara A. Watkins, and Robert E. Sievers, Department of Chemistry & Biochemistry and CIRES, Campus Box 215, University of Colorado, Boulder, CO 80309. (33)

8:55 Total Microwave Sample Preparation for Environmental Analysis, W. Gary Engelhart, Milestone MLS, 7289 Garden Road #219, Riviera Beach, FL 33404. (34)

9:15 Trace Element Analysis in Saline Samples using ICP-MS after Automated Chelation Concentration, Rob Henry, Dagmar Koller, Tom Rettberg, Fisons Instruments, 1812 Mapleton Ave., Boulder, CO 80304. (35)


9:55 Anthropogenic Lanthanides in the Environment? Michael E. Ketter and Blake L. Ohlson, Department of Chemistry, John Carroll University, University Heights, OH 44118. (37)

10:15 Break

10:35 INVITED SPEAKER IN ENVIRONMENTAL CHEMISTRY

Immobilized Polyamino Acids for Trace Metal Pre-concentration and Remediation, James A. Holcombe, Holly Autry, Maury Howard and Fabian Rorif, University of Texas at Austin, Chemistry Department, Austin, TX 78712. (38)

11:15 Different Sample Preservation Schemes as Used in the Determination of Total and Speciated Arsenic in Water, M.W. Tikkanen, Association of California Water Agencies, 910 K St., Sacramento, CA 95814 and A. Eaton, Montgomery Watson Laboratory, 555 E. Walnut St., Pasadena, CA 91101. (39)


12:00 Lunch
Afternoon Session:

Maria Tikkanen, presiding

Analytical Chemistry in a Drop, Purnendu K. Dasgupta, Department of Chemistry and Biochemistry, Texas Tech University, Lubbock, TX 79409-1061. (41)

Automated Mercury Preparation and Analysis at Parts per Trillion, Sergei Leikin and Ben Moshiri, Questron Corp., 4044 Quakerbridge Road, Mercerville, NJ 08619. (42)

Historical Record of Stratospheric Ozone by Quantification of Thymine Dimers in DNA from Pollen Grains Found in Ice Cores, Jill K. Gregory, John W. Birks, and Kathy L. Rowlen, University of Colorado, Department of Chemistry, Campus Box 215, Boulder, CO 80309. (43)

Polymer Inclusion Membranes with Macrocyclic Carriers - a New Simple Way for Preconcentration of Toxic Elements, John D. Lamb and Alexander Y. Nazarenko, Brigham Young University, Department of Chemistry and Biochemistry, C100 BNSN, Provo, UT 84602. (44)

Detector Alternatives for Halogenated Volatiles, Richard Burrows and Mark Bruce, Quanterra Environmental Services, 4955 Yarrow St., Arvada, CO 80002. (45)

The Role Of Molecular Size and Flexibility in Humic Acid Associations, Regginal R. Engebretson, and Ray von Wandruszka, Department of Chemistry, University of Idaho, Moscow, ID 83844. (46)

The Devil’s in the Details - Surprising Problems in Environmental Chromatography, Jeff Cornell and Alan Quick, Quanterra Environmental Services, 4955 Yarrow St., Arvada, CO 80002. (47)

Waste Reduction through the Electrodialytic Purification of Acids, Alex F. Schreiner, Schreiner & Associates, Inc., 1322 State St., DeKalb, IL 60115. (48)

Morning Session:

Edward T. Furlong, Presiding

8:35 Opening Remarks

Invited Speaker in Environmental Mass Spectrometry

Analysis of Pesticides by Combined on-line Trace Enrichment/Post-column Photolysis/LC-MS/MS in Water and Food Samples, Dietrich Volmer, Institute for Marine Biosciences, 1411 Oxford St., Halifax, Nova ScotiaB3H 3Z1, Canada. (49)


Increasing Liquid Chromatographic Performance in the Environmental Lab, Stuart A. Oehrle, Water Corp., 34 Maple St., Milford MA 01757. (51)

HPCL Detection of Chemical Indicators of Human Pollution in Water, Elizabeth A. Piocos, and Armah A. De la Cruz, U.S. Environmental Protection Agency, 26 W. Martin Luther King Drive, Cincinnati, OH 45268-1320. (52)

10:15 Break

Fundamentals of Capillary Electrochromatography and Applications, Tom Keel, Hewlett Packard Company, 24 Inverness Place East, Englewood, CO 80112, and David Heiger, Hewlett Packard Company, 2850 Centerville Road, Wilmington, DE 19808-1610. (53)

Simplified Design of a Temperature Programmable Multi-Mode Injection System, Jesse Crocket Butler and Terry Rankin, Finnigan Corporation, 2215 Grand Ave. Parkway, Austin, Texas 78728-3821. (54)


19TH INTERNATIONAL EPR SYMPOSIUM
Organized by Sandra S. Eaton and Gareth R. Eaton

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Sunday, July 21, 1996

5:45 Meet in hotel lobby for bus transportation to open house at the University of Denver.
- Bruker will present a brief overview of EPR equipment on exhibit at conference.
- Plan to join us for a light supper. Bruker will provide the usual refreshments.
- There will be demonstrations, tutorials, and exhibits of our spectrometers including:
  - A new cross-loop loop-gap resonator
  - Low-frequency spectrometers including bridges operating at 150-300 MHz, 1-2 GHz, 2-4 GHz, and 4-8 GHz.
  - Spin echo EPR
  - Bruker ESP380E
  - Programmable Timing unit and human interface in Visual Basic
  - Saturation recovery with the EG&G 9825 digitizer
- For details see http://www.du.edu/~seaton/eprsym.html

Monday, July 22, 1996

Session I, Gold Medal Award Session
K. McLauchlan presiding

8:30  Opening Remarks and Welcome, Sandra S. Eaton
8:35  Presentation of International EPR Society Gold Award to Professor Kev Salikhov by Prof. Keith McLauchlan, President of International EPR Society.

8:45  Award Address: Theoretical Approach to the Analysis of Arbitrary Pulses in EPR Experiments, K. Salikhov and J.H. Freed, Zavoiski Institute, Kazan and Cornell University. (57)
9:30  Radical Re-encounter Probabilities Inside the Geminate Cage, R. B. Eveson and K. A. McLauchlan, Oxford University, England. (58)

10:10  Break
10:40  Saturation Recovery and Multi-Quantum Studies of Spin Exchange, J. S. Hyde, Medical College of Wisconsin. (59)
11:20  Presentation of International EPR Society Young Investigator Award to Dr. Gunnar Jeschke by Prof. Keith McLauchlan, President of International EPR Society
11:25  Award Address: Hyperfine Spectroscopy, G. Jeschke, Swiss Federal Institute of Technology, Switzerland. (60)
12:00  Lunch
Session II, M. K. Bowman presiding

1:30 Presentation of International EPR Society Silver Award to Klaus Mobius by Prof. Keith McLauchlan, President of International EPR Society

1:35 **Award Address: Time-Resolved High-Field EPR/ENDOR in Photosynthesis Research, K. Mobius, Freie Universitat Berlin, Germany.** (61)

2:15 **EPR/ENDOR Studies on Porphyrin and Chlorin Cation and Anion Radicals: Consequences for the Efficiency of Biomimetic Model Compounds for Photosynthesis, M. Huber, M. Fuhs, J. L. Sessler, and K. Mobius, Freie Universitat Berlin, Germany and University of Texas at Austin.** (62)

2:40 **Multifrequency Pulsed EPR Studies of Nitrogen Hyperfine Coupling in the Primary Donor P700 of Photosystem I: Implications for Electronic Structure, M. Mac, G. T. Babcock, and J. McCracken, Michigan State University.** (63)

3:00 Break

3:30 **Pulsed EPR Investigations of "Iron-only" Hydrogenases: a Histidine Residue is Involved in the Deactivation of the H-Cluster, P. J. van Dam, E. J. Reijerse, and W. R. Hagen, University of Nijmegen, the Netherlands.** (64)

3:55 **Pulsed EPR Studies of the Type 1 Copper Centers: A Retrospective, C. Bender and J. Peisach, Albert Einstein College of Medicine.** (65)

4:20 **Distance Measurements Using Double Quantum Two Dimensional Fourier Transform Electron Spin Resonance, S. Saxena and J. H. Freed, Cornell University.** (66)

4:40 **Using 2D EPR Exchange Spectroscopy to Investigate Early Events in Protein Folding, C. J. Stenland and G. L. Millhauser, University of California - Santa Cruz.** (67)

5:00 Conference Mixer and Instrument Exhibits

**Tuesday, July 23, 1996**

Session III, Nitric Oxide in Biology and Medicine

D. J. Singel, presiding

8:30 Presentation of International EPR Society Silver Medal in Biology/Medicine to Ronald P. Mason by Keith McLauchlan, President International EPR Society

8:35 **Award Address: Metabolism of Hydroxyurea to Nitric Oxide, R. P. Mason, J. J. Jiang, and S. J. Jordan, NIEHS.** (68)

9:05 **Targets of Nitric Oxide in the Rat Gastrointestinal Tract, W. Chamulitrat, N. V. Skrepnik, and J. J. Spitzer, Louisiana State University Medical Center.** (69)

9:35 **EPR Spectroscopy and Imaging of Nitric Oxide Formation in the Heart, J. L. Zweier, P. Wang, A. Samouilov, and P. Kuppusamy, The John Hopkins Medical Institutions.** (70)

10:05 Break

10:35 **In Vivo and In Vitro Nitric Oxide Spin Trapping Study on Pharmacologic Effects of Nitrones, Y. Kotake, T. Miyajima, M. S. West, D. R. Moore, and L. A. Reinke, Oklahoma Medical Research Foundation and University of Oklahoma Health Sciences Center.** (71)

11:05 **Detection and Quantitation of Nitric Oxide in the Tissue Using Electron Paramagnetic Resonance, S. T. Ohnishi, Philadelphia Biomedical Research Institute.** (72)

11:35 **Protective Effect of Nitric Oxide (NO) and Nitroxyl Anion (NO−) Donors Against Myocardial Ischemia, B. Kalyanaraman, Medical College of Wisconsin.** (73)

12:05 Lunch

Session IV, H. Halpern, presiding

1:30 **Detection and Imaging of Spin-Trapped Nitric Oxide Using PEDRI, D. J. Lurie, B. Fichtlscherer, I. Seimenis, M. A. Foster, and A. Mulsch, Aberdeen University, UK and Johann Wolfgang Goethe University Clinic, Germany.** (74)

1:55 **Gated EPR Spectroscopy and Imaging of the Beating Heart, P. Kuppusamy, M. Chzhan, and J. L. Zweier, Johns Hopkins Medical Institutions.** (75)
Direct Detection of Paramagnetic Metal Ions and Spin Adducts in Whole Living Animals, K. J. Liu, J. Jiang, X. Shi, and H. M. Swartz, Dartmouth Medical School and NIEHS. (76)

2:45 Break

Session V, Posters, S. S. Eaton presiding

300 - 4:00 Authors Present for Posters Labeled A
4:00 - 5:00 Authors Present for Posters Labeled B

(Posters are listed alphabetically by presenting author)

A The Role of Cytokines and Nitric Oxide in the Inflammatory Response Produced by Sulfur Mustard (HD), C. M. Arroyo, U.S. Army Medical Research. (77)

B A Three-Stage Helical Resonator/Bandpass Filter for Pulsed EPR Spectroscopy at Low Frequency, C. Bender, Albert Einstein College of Medicine. (78)

A ESR Imaging of a Spin Labelled Dextran (TEMPO-DX) in Mice, S. Kazama, G. Takashige, H. Yoshioka, T. Ogata, J. Koscielniak, and H. J. Berliner, Yamagata University and Ohio State University. (79)

B An EPR Probe for the Detection of DNA Bending, R. S. Keyes, Y. Y. Cao, E. V. Bobst, and A. M. Bobst, University of Cincinnati. (80)

A A 17.5 GHz Two Dimensional Fourier Transform ESR Spectrometer, P. P. Borbat, R. H. Crepeau, and J. H. Freed, Cornell University. (81)


A Adjoint and Time Reversal Properties of Spin Hamiltonian Tensor Operators, H. A. Buckmaster and R. Chatterjee, University of Victoria and University of Calgary, Canada. (83)

B A 9 GHz CW-EPR Variable Temperature Study of Monocrystalline 1-Benzyl 4-Hydroxy Piperidine, R. Krzyniowski, M. Pawlicka, Z. Kuczynski, J. Kudynska, and H. A. Buckmaster, Adam Mickiewicz University, Poland and University of Victoria, Canada. (84)

A Continuous Wave EPR Studies of Integer Spin Manganese Dimers, K. A. Campbell, D. Wright, W. H. Armstrong, and R. D. Britt, University of California-Davis and Boston College. (85)

B An APL Software for the Simulation of ESR Spectra of Fluid, Viscous, and Rigid Systems, C. Chachaty, AFAPL/GARPE, France. (86)


B Spin Lattice Relaxation of Copper Acetylacetone in Liquid Solution, T. Christidis, W. Francisz, and J. S. Hyde, American University of Beirut, Lebanon, Jagiellonian University, Poland, and Medical College of Wisconsin. (88)


B Protonation and Stability of Nitroxide Free Radicals in Strong Acids, W. Damerau, A. Rockenbauer, and K. Hideg, Max Delbruck Center of Molecular Medicine, Germany. (90)

A Cross-Peak Lineshape of Two-Dimensional Pulsed EPR Spectra of Disordered S=1/2,1=1 Spin System, S. A. Dikanov and M. K. Bowman, Battelle Pacific Northwest National Laboratory and Institute of Chemical Kinetics and Combustion, Russia. (91)

B CW and Pulsed EPR Study of Orthophosphoric and Boric Acid Modified y-Alumina, R. I. Samoilova, S. A. Dikanov, A. V. Fionov, A. M. Tyryshkin, E. V. Lunina, and M. K. Bowman, Pacific Northwest National Laboratory, Institute of Chemical Kinetics and Combustion, Russia, and Moscow State University, Russia. (92)

B How Big Can a Small Hyperfine Coupling Be in Mints ENDOR? P. E. Doan and B. M. Hoffman, Northwestern University. (94)

A Structural Changes Induced in p21 ras upon GAP Binding as Probed by ESEEM Spectroscopy, C. T. Farrar, D. J. Halkides, and D. J. Singel, Massachusetts Institute of Technology and Montana State University. (95)

B An ESR and CIDEP Study of the Photochemistry of 2,2'-Biphenol in Aqueous Solution, P.-Y. Jiang and R. W. Fessenden, University of Notre Dame. (96)

A EPR Characterization of Ni(III)-Tetracyanate in Disordered Sample, Using One- and Two-Dimensional ESEEM Techniques, G. Filep and J. McCracken, Michigan State University. (97)


B In vivo EPR Detection and Imaging of Endogenous Nitric Oxide by Using a 700 MHz EPR and DTCS-Fe Complex as a Spin Trapping Reagent, S. Fujii, T. Yoshimura, H. Yokoyama, F. Takayama, K. Oikawa, and H. Kamada, Institute for Life Support Technology, Japan, Oita Medical University, Japan, and Yamagata Research Institute of Technology, Japan. (100)

A EPR Study of Radical-Anions Generated from Phosphaalkenes Bound to a Heterocycle, M. Geoffroy, A. A. Badri, and A. Jouaiti, University of Geneva, Switzerland. (101)


A EPR Investigation of the Kinetically Competent Intermediate Formed in Ribonucleotide Reduction: Evidence for a Thiol Radical-Cob(II)alamin Interaction, G. J. Gerfen, S. Licht, J.-P. Willems, B. M. Hoffman, and J. Stubbe, MIT and Northwestern University. (103)

B Pulsed EPR Study of Low Spin K[Mn(CN)6], D. M. Gingell and R. D. Britt, University of California - Davis. (104)

A “VESE-ENDOR Study of Vanadyl Model Complexes, C. Grant, J. Ball, and R. D. Britt, University of California - Davis. (105)

B Macroyclic Effects on Alkali Metal Reduced Shiff Base Cryptands on the EPR Time Scale, A. S. Ichimura, Q. Xie, L.P. Szajek, J.E. Jackson, J.L. McCracken, and J.L. Dye, Michigan State University. (106)

A Matched Two-Pulse ESEEM- An Application of a New Description of Non-Ideal Microwave Pulses, G. Jeschke and A. Schweiger, Swiss Federal Institute of Technology. (107)


A A New One-Electron Oxidant: The Stable Free Radical CB3, > Me, , B.J. King and J. Michl, University of Colorado. (109)

B Davies ENDOR and HYSCORE Measurements of Carotenoid Cation Radicals on Silica-Alumina Solid Support, L. D. Kispert, A. S. Jeevarajan, and P. Hofer, University of Alabama and Bruker Analytische Messtechnik, Germany. (110)

A EPR Characterization of Cu(II) Ions in Single Crystals of Thallium Cobalt Sulphate Hexahydrate, M. Krishna, National Physical Laboratory, India. (111)


A Melanotropic Peptides - Lipid Bilayer Interaction: A Spin Label and Circular Dichroism Study, M.H. Biaggi, K. A. Riske, and M.T. Lamy-Freund, Universidade de Sao Paulo, Brazil. (113)
B Free Radical Intermediates in the Maillard Reaction, R. V. Lloyd, University of Memphis. (114)


B EPR Spectroscopy of S-Nitroso Hemoglobin, B. P. Luchsinger, J. Bonaventura, J. S. Stamler, and D. J. Singel, Montana State University and Duke University Medical School. (116)

A A Human-Scale Free Radical Imager Using Field-Cycled PEDRI, D. J. Lurie, M. A. Foster, D. Yeung, and J. M. S. Hutchison, University of Aberdeen. (117)

Tuesday evening - Dinner to recognize recipients of International EPR Society Gold and Silver Medals: All attendees are invited, see information on http://www.du.edu/~seaton/eprsym.html.

Wednesday, July 24, 1996

Session VI P.M. Lenahan, presiding

8:30 Presentation of International EPR Society Silver Medal in Instrumentation/Physics to Joharm-Martin Spaeth by Keith McLauchlan, President International EPR Society

8:35 Award Address: Electrical Detection of EPR and ENDOR of Defects in Semiconductors, M. Spaeth, S. Greulich-Weber, and B. Stich, University of Paderborn, Germany. (118)

9:15 ENDOR at 95 GHz on Shallow Centres in Semiconductors, O. G. Poluektov, M. T. Bennebroek, T. Matsimoto, A. Arnold, P. G. Baranov, and J. Schmidt, University of Leiden, the Netherlands. (119)


10:00 Break - last day to see exhibits

10:40 Pulsed Electron Spin Resonance Studies of Cu(II) Sites and Adsorbate Interactions Ion Exchanged into Silicoaluminophosphate Type 18, T. Wasowicz, S. J. Kim, S. B. Hong, and L. Kevan, University of Houston and Korea Institute of Science and Technology. (121)


11:35 SOPHE - New Methodologies for the Analysis of Randomly Orientated EPR Spectra, G.R. Hanson and D. Wang, The University of Queensland, Australia. (123)

12:00 Lunch

Session VII, W. Trommer presiding

1.30 In vivo EPR Detection of Rat Hemoglobin Thiyl Radical Adduct, J.J. Jiang, R. P. Mason, S. J. Jordan, K. J. Liu, and H. M. Swartz, NIEHS and Dartmouth Medical School. (124)

1:50 Aqueous Microviscosity of Murine Sarcomas and Normal Legs in vivo with Low Frequency EPR: Implications for MRI and the Physiology of Tumors, H. J. Halpern, G. V. R. Chandramouli, E. D. Barth, D. J. Grdina, and B. A. Teicher, University of Chicago and Harvard Medical School. (125)


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

(Posters are listed alphabetically by presenting author)

C Aminoxyl Radical Dosimetry: Quantitative Determination of Radiation-Induced Transient Free Radical Yields by EPR, K. P. Madden, University of Notre Dame. (127)

D FT-EPR Study of the Photochemistry of Some Organometallic Complexes, D. Martino, C. J. Kleverlaan, H. van Willigen, and A. Osham, University of Massachusetts at Boston and Universiteit van Amsterdam, the Netherlands. (128)

C Damage to Cu, Site of Cytochrome c Oxidase in Samples Purified by Affinity Column Chromatography, S. M. Monroe, G. R. Eaton, and S. S. Eaton, University of Denver. (129)


C Magnetic Interactions and Aromatic Ring Stacking: An EPR Study with the Two Systems dichlorobis- and dibromobis-l-phenyl-3,5-dimethylpyrazole, O.R. Nascimento, A.J. Costa-Filho, C. Munte, M.P.D. Mattioli, and R. Calvo, Instituto de Fisica de Sao Carlos, Brazil, Institute de Quimica de Araraquara-UNESP, Brazil, and Universidad Nacional del Litoral-Santa Fe, Argentina. (131)

D Spin Labeled Taxol Analogues Reveal Microtubule Assembly, R. Nicholov, Winnie Y. Ho, and F. DiCosmo, University of Toronto, Canada. (132)

C Two-Dimensional In-Vivo Imaging using Radiofrequency Longitudinally-Detected ESR (LODESR Imaging), J. Nicholson, M. A. Foster, F. J. L. Robb, J. M. S. Hutchison, and D. J. Lurie, University of Aberdeen, UK. (133)


C Low-Magnetic-Field Pulsed DNP Relaxometry, B. Odintsov, R. L. Belford, and R. B. Clarkson, University of Illinois and Zavoisky Institute, Kazan. (135)

D EPR Spin Trapping of Ammonium Dinitramide (ADN) Radicals from Aqueous Phase ADN Decomposition and Liver Enzyme Metabolism, M. D. Pace, L. Steel-Goodwin, K. W. Dean, and A. J. Carmichael, Naval Research Laboratory, Wright-Patterson Air Force Base, and Armed Forces Radiobiology Research Institute. (136)

C Direct Measurement of Zero Field Splitting of Divalent Nickel in a One-Dimensional System by High Frequency - EPR Spectroscopy, L. Pardi, L.-C. Brunei, J. Redijk, and F.B. Hulsbergen, National High Magnetic Field Laboratory and Leiden University, the Netherlands. (137)


C Low Temperature Integer Spin Q-Band Spectrometer for Metalloprotein Studies, D. T. Petasis and M. P. Hendrich, Carnegie-Mellon University. (139)

D Protein Folding of Spin Labeled Yeast Iso-1-Cytochrome c: Probed by Rapid Mix, Stopped-Flow EPR, K. Qu, J. Vaughan, J. S. Fetrow, A. Sienkiewicz, and C. P. Scholes, Polish Academy of Science, Poland and SUNY Albany. (140)


C Pulsed EPR, ENDOR, and ESEEM of Mixed Valence Mn Model Compounds and the PS II Oxygen Evolving Complex, D. W. Randall and R. D. Britt, University of California - Davis. (143)

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D Electron Paramagnetic Resonance Study of an Electride: Li(Cryptand[2.1.1]) Electride, K.A. Reidy-Cedergren, J.L. Dye, and J. McCracken, Michigan State University. (144)

C A "HYSCORE" Investigation of the VO(Salicylaldoximine)2 Complex. Characterization of Nitrogen Coordination and Intramolecular Hydrogen-Bonding, E. J. Reijerse and J. I. Martinez, University of Nijmegen, the Netherlands and Universidad de Zaragoza, Spain. (145)

D A Systematic Analysis of 1D and 2D ^N-ESEEM Spectra: Application to a Nitrogen Coordinated Oxo-Vanadium Complex, E. J. Reijerse, A. M. Tyryshkin, and S. A. Dikanov, University of Nijmegen, the Netherlands, Institute of Chemical Kinetics and Combustion, Russia, and Battelle Pacific Northwest National Laboratory. (146)

C Crossed-Loop Resonator Structure for Spectroscopy, a New Type of Bi-Modal Resonator, G. A. Rinard, R. W. Quine, and G. R. Eaton, University of Denver. (147)

D Modelling the PEDRI Enhancement as a Function of [O2], F. J. L. Robb, I. Nicholson, and D. J. Lurie, University of Aberdeen, UK. (148)

C A Small-Bore FC-PEDRI Imaging System, F. J. L. Robb, J. M. S. Hutchison, I. Nicholson, and D. J. Lurie, University of Aberdeen, UK. (149)

D Complexation of Copper(II) with Carbonate Ligands in Frozen Aqueous Solution as Studied by CW and Pulsed EPR, P. M. Schosseler, B. Wehrli, and A. Schweiger, Swiss Federal Institute of Technology. (150)

C Nutation-Frequency-Correlated ESR Spectroscopy, S. Stoll, G. Jeschke, Z. Madi, and A Schweiger, Swiss Federal Institute of Technology, Switzerland. (151)

D Dark Magnetic Resonance, E. C. Hoffmann, G. Jeschke, and A. Schweiger, Swiss Federal Institute of Technology, Switzerland. (152)

C Double-Stacked Dielectric Ring Resonator for Sensitive EPR Measurements of Biological Samples - Theory and Praxis, M. Jaworski, A. Sienkiewicz, and C. P. Scholes, Polish Academy of Sciences, Poland and SUNY Albany. (153)

D Right Angle Spinning (RAS) EPR, G. A. Sierra and A. Schweiger, Swiss Federal Institute of Technology, Switzerland. (154)


D A Visual User Interface Using the Origin® Environment for an ESR Spectrometer, R. S. Henry and H.J. Sipe, Jr., Hampden-Sydney College. (156)

C Does EPR at 95 GHz Indicate the Distribution of Small Nitroxide Probes in a Phospholipid Bilayer? A. I. Smirnov, R. B. Clarkson, and R. L. Belford, University of Illinois. (157)

D High-frequency (95 GHz) EPR Spectroscopy to Characterize Spin Adducts, T. I. Smirnova, A. I. Smirnov, R. B. Clarkson, R. L. Belford, Y. Kotake, and E. G. Janzen, University of Illinois and Oklahoma Medical Research Foundation. (158)


D Electron and Nuclear Relaxations in Paramagnetic Metal Ion Complexes, S. K. Sur, Charlottesville, VA. (160)

C EPR Kinetic Studies of the LDL Oxidation Process Driven by Free Radicals, M. Schneider, A. M. Jentzsch, W. E. Trommer, and H. K. Biesalski, Universitat Hohenheim, Germany and Universitat Kaiserslautern, Germany. (161)

D Q-Band ENDOR of the Electronic Structure from Copper-Containing Nitrite Reductase, A. Veselov, K. Olesen, A. Toffanin, J. P. Shapleigh, and C. P. Scholes, SUNY Albany and Cornell University. (162)

C Spin-Lattice Relaxation in Paramagnetic Rhodium Hexacyanide - Process and Mechanism, C. A. Coelho Neto and N. V. Vugman, Universidade Federal do Rio de Janeiro, Brazil. (163)

D Extracting Magnetic and Electric Data from Dysonian Lines, L. Walmsley, Universidade Estadual Paulista, Brazil. (164)


C Determination of g Values in Titanium-Doped Sapphire by Very High Turning Angle Nutation Experiments, M. Wilier and A. Schweiger, Swiss Federal Institute of Technology, Switzerland. (167)

Wednesday evening - Chinese dinner, see poster area for details

Thursday, July 25, 1996

Session IX, J.A. Weil, presiding

8.30 Pulsed EPR at High Frequencies: Why and How, M. K. Bowman and Yu. D. Tsvetkov, Pacific Northwest Laboratory and Russian Academy of Sciences, Russia. (168)

9:00 EPR with Mirrors: A Broadband Millimeter Wave EPR Spectrometer, K. A. Earle, D. S. Tipikin, and J. H. Freed, Cornell University. (169)


10:15 Break

10:30 Modification and Use of a CW EPR Spectrometer for Measuring Relaxation Times in the Laboratory and Rotating Frame, C. S. Yannoni, R. D. Kendrick, J.-M. Vieth, J. Wegener, and D. Rugar, IBM Almaden Research Center and University of Dortmund, Germany. (172)

11.00 Probe-Pulse Detection, E. C. Hoffmann, G. Jeschke, and A. Schweiger, Swiss Federal Institute of Technology, Switzerland. (173)

11:30 Progress and Prospects in Magnetic Resonance Force Microscopy, C. S. Yannoni, IBM Almaden Research Center. (174)

12:00 Lunch

Thursday lunch and afternoon: Bruker User's Group. Please register at the Broker booth in the exhibit area and contact Dr. Arthur Heiss for information about location and program. Also visit http://www.bruker.com and browse the EPR section.

SYMPOSIUM ON FTIR/NIR/RAMAN SPECTROSCOPY

Organized by Abdul R. Chughtai and Dwight M. Smith

Financial support provided by ASI Applied Systems, Millersville, MD.

Monday, July 22, 1996

Session I, Dwight M. Smith, presiding

8:30 Opening Remarks

9:05 Invited Speaker: On-line Monitoring and Control of Batch and Fed-Batch Bioreactors Using Mid-IR Spectroscopy, Janice Phillips, Department of Chemical Engineering, Bioprocessing Institute, Lehigh University, Bethlehem, PA 18015. (176)

9:50 Simplification of FTIR Spectra by Rotational Cooling of Molecules Entrained in a Supersonic Molecular Beam Expansion, Steven W. Sharpe, Robin McDowell and Thomas Blake, Battelle Pacific Northwest National Laboratory, Richland, WA 99352. (177)

10:20 Break

10:45 Recent FTIR Studies of Black Carbon (Soot) Surface Reactivity, Abdul R. Chughtai, Brian K. Konowalchuk, Christakis A. Sergides, Maher M. O. Attaya, and Dwight M. Smith, Department of Chemistry, University of Denver, Denver, CO 80208. (178)

11:15 A Diffuse Reflectance FTIR Study of CO Oxidation Catalysts in Stoichiometric Mixtures of Carbon Monoxide and Oxygen, Kenneth G. Brown, Donna S. Duarte, Department of Chemistry and Biochemistry, Old Dominion University, Norfolk, VA 23529; and Billy T. Upchurch and David R. Schryer, NASA-Langley Research Center, Hampton VA 23681. (179)

11:45 A Diffuse Reflectance FTIR Study of the Reductive Pretreatment of CO Oxidation, Kenneth G. Brown, Donna S. Duarte, Department of Chemistry and Biochemistry, Old Dominion University, Norfolk, VA 23529 and Billy T. Upchurch and David R. Schryer, NASA-Langley Research Ctr., Hampton VA 23681. (180)

12:15 Lunch

Session II, Abdul R. Chughtai, presiding.


2:00 High-Temperature Raman Spectra of 9,10-Dihydroanthracene and Stilbene Vapors and Melts, Jaan Laane, Kevin Morris, Kristjan Huller, WheYi Chiang, and Arnold del Rosario, Department of Chemistry, Texas A&M University, College Station, TX 77843-3255. (182)

2:30 Applications of Polarized FTIR Spectroscopy in Ferroelectric Liquid Crystals, Cheol Soo Park, W. G. Jang, and N. A. Clark, Department of Physics, University of Colorado, Boulder, CO 80309-3900. (183)

3:00 Break

3:30 Infrared Studies of Conformational Isomerism in Some Acrylates and Acrylic Acids, MaryKay Orgill, Scott P. Leary, and Noel L. Owen, Department of Chemistry and Biochemistry, Brigham Young University, Provo, UT 84602. (184)

4:00 Raman and Photoacoustic FTIR Studies of Polymers Synthesized in Microgravity, Kenneth G. Brown and Karen S. Burns, Department of Chemistry and Biochemistry, Old Dominion University, Norfolk, VA 23529; Billy T. Upchurch, NASA-Langley Research Center, Hampton, VA 23681. (185)

Tuesday, July 23,1996

Session III, Abdul R. Chughtai, presiding.

9:00 Opening Remarks

9:05 Study of Lifetime Stability of Thiol Coated SERS Substrates, Timothy O. Deschaines, and Keith T. Carron, P.O. Box 3838, Chemistry Department, University of Wyoming. Laramie, WY 82071. (186)

9:35 Development of a Selective SERS Substrate for the Detection of Illicit Drugs, Roberta A. Sulk, Robert C. Corcoran, and Keith T. Carron, P. O. Box 3838, Chemistry Department, University of Wyoming. Laramie, WY 82071. (187)

10:05 Applications of Near-Infrared Spectroscopy to Breath Analysis: Potential Use in the Diagnosis of Disease, Steven W. Sharpe, Robert Sams, Karla Thrall, and James Toth, Battelle Pacific Northwest National Laboratory, Richland, WA 99352. (188)

10:35 Break
11.00 *Measurement of Benzene in Gasoline Using Near- or Mid-Infrared Spectra*, James E. Tackett, Marathon Oil Company, P.O. Box 269, Littleton CO 80160. (189)

11:30 *Real Time Detection Of VOC's at a Wastewater Treatment Plant using Long Path FTIR and Ultraviolet Spectroscopy*, Phillip A. Russell, L/E WWTP, Englewood, Colorado 80110, Amber Hodgson and Donald H. Stedman, Department of Chemistry and Biochemistry, University of Denver, Denver, CO 80210. (190)

12:00 Concluding Remarks (Dwight M. Smith).

**GENERAL POSTER SYMPOSIUM**

Organized by Mary E. Cast

Monday, July 22, 1996

3:00 - 5:00 Authors Present for Posters

(Posters are listed alphabetically by presenting author)

*The Determination of Bromate in the Presence of Haloacetic Acids by Ion Chromatography-Inductively Coupled Mass Spectrometry*, Carol A. Brockhoff, John T. Creed, and *Matthew L. Magnuson*, US Environmental Protection Agency, National Exposure Research Laboratory, Human Exposure Division, 26 W. Martin Luther King Drive, Cincinnati, OH 45268. *National Research Council Postdoctoral Associate.* (191)

*Low Energy Lamp for GRO-DRO with a Tandem PID/FID*, Jesse Crockett Butler, Terry Rankin, Finnigan Corp., 2215 Grand Ave. Parkway, Austin, TX 78728-3812. (192)

*Blood Alcohol Analysis by Static Headspace with Dual FIDS/Megabore Capillary Columns*, Jesse Crockett Butler, Terry Rankin, Finnigan Corp., 2215 Grand Ave. Parkway, Austin, TX 78728-3812. (338)

*StatiStafic Headspace Analysis of Residual Solvents in Pharmaceuticals Using FID and Tandem PID/FID*, Jesse Crockett Butler, Terry Rankin, Finnigan Corp., 2215 Grand Ave. Parkway, Austin, TX 78728-3812. (339)


*Bromate in Drinking Water; Trace Level Determination by Ion Chromatography*, B. Lo, and K. Subramanian, Bureau of Chemical Hazards, Environmental Health Directorate, Ottawa, Canada. (195)

*Novel Buffer/Additive Combinations in EKC Affording Fast, High Resolution Separations with Improved Detectability*, J.R. Mazzeo, E.R. Grover, and M.E. Swartz, Waters Corporation, 34 Maple Street, Milford, MA 01757. (196)

*Analysis of Nitramine and Nitoraromatic Explosives by Capillary Electrophoresis*, S.A. Oehrle, Waters Corporation, 34 Maple Street, Milford, MA 01757. (197)

SYMPOSIUM ON ICP-MS
Organized by Howard E. Taylor

Tuesday, July 23, 1996

Howard Taylor, Presiding


1:50 *Technology Advances in the Application of Quadrupole ICP-MS to the Routine Analysis of Semiconductor Materials*, R. Henry, P. Sigsworth, and T. Rettberg, Fisons Instruments, Boulder, CO. (201)

2:00 Break

2:30 *The Role of Interferences in the Determination of Trace Metal Concentrations by ICP-MS and What to Do About It*, R. A. Antweiler and H.E. Taylor, U.S. Geological Survey, Boulder, CO. (202)


TECHNICAL SYMPOSIUM IN HONOR OF PROFESSOR RODNEY K SKogerboe

A special technical symposium honoring the career of Professor Rodney K. Skogerboe, Professor of Chemistry, retired, Colorado State University. No abstracts are available for this session.

Wednesday, July 24, 1996

Howard E. Taylor, presiding

1:00 Introductory Remarks


1:45 *LC-MS-MS Analysis of AMT, a Toxic Metabolite of AZT*, Pat Sulik, and Robert Lantz, Rocky Mountain Instrumental Labs, Ft. Collins, CO. (206)

2:15 *Analysis of Oils for Halogens and Nitrogen by ICP-AES in the VUV Region*, Geoff N. Coleman, C. Harris, M. O’Boyle, R. Starek, and J.D. Steiner, VG Elemental, Beverly, MA. (207)

2:45 Break
Fred E. Lichte, presiding
3:00 Use of Isotope Dilution-Inductively Coupled Plasma-Mass Spectrometry to Determine Mercury in Natural Water Samples, David Roth and H.E. Taylor, U.S. Geological Survey, Boulder, CO. (208)
3:30 Diagnosis by Molecular Methods, Joseph E. Bonelli, Sterling Regional Medical Center, and Department of Pathology, University of Colorado School of Medicine, Denver, CO. (209)
4:00 Analysis of Tree Rings by Laser Ablation ICP-MS, Fred E. Lichte and Larry Gough, U.S. Geological Survey, Lakewood, CO. (210)
4:30 Closing Remarks, Rodney K. Skogerboe.

LUMINESCENCE SYMPOSIUM
Organized by DeLyle Eastwood and Robert J. Hurtubise

Monday, July 22, 1996
Robert J. Hurtubise, Presiding
8:30 Opening Remarks
8:35 Characterization of Benzo(a)pyrene-DNA Adducts Via Solid-Matrix Luminescence and Solution Fluorescence, R.J. Hurtubise and S.W. Tjoe, Department of Chemistry, University of Wyoming, Laramie, WY 82071. (211)
9:00 Detection of Polycyclic Aromatic Hydrocarbon-Hemoglobin Adducts for Human Exposure Monitoring, Christian Hackl, Ainsley Weston, Jutta Lintelmann, and Antonius Kettrup, GSF-Forschungszentrum fuer Umwelt und Gerundheit, Institut fuer Oekologische Chemie, Postfach 1129, D-85758 Oberschleissheim, Germany, Environmental Health Sciences Center, Mount Sinai Medical Center, New York, NY 10029, USA. (212)
9:25 Metal-Ligand Complexes as a New Class of Long-Lived Fluorophores for Protein Hydrodynamics, Ewald Terpetschnig, Henryk Szmacinski, Henryk Malak, and Joseph R. Lakowicz, Center for Fluorescence Spectroscopy, Department of Biological Chemistry, University of Maryland at Baltimore, 108 North Greene Street, Baltimore, MD 21201. (213)
9:50 Lifetime-Based Sensing in Highly Scattering Media, Henryk Szmacinski and Joseph R. Lakowicz, Center for Fluorescence Spectroscopy, Department of Biological Chemistry, University of Maryland at Baltimore, 108 North Greene Street, Baltimore, MD 21201. (214)
10:15 Break
10:40 Interactions of Polymers with Luminescent Metal Complexes and Organic Dyes. Design of Useful Analytical Systems, J.N. Demas, Wenying Xu, Kristi Kneas, and Sari Benmeir, Department of Chemistry, University of Virginia, Charlottesville, VA 22901; B.A. DeGraff, Department of Chemistry, James Madison University, Harrisonburg, VA 22807; Ming Wu, Peter M. Goodwin, Rhett L. Affleck, and Richard A. Keller, Chemical Science and Technology Division, Los Alamos National Laboratory, Los Alamos, NM 87545. (215)
11:05 Oxygen Sensor Based on the Quenching of Room-Temperature Phosphorescence Intensity of Phenanthrene (D.) Adsorbed on Whatman IFS Filter Paper, S.M. Ramasamy and R. J. Hurtubise, Department of Chemistry, University of Wyoming, Laramie, WY 82071. (216)
11:30 Development of Near-Infrared Fluorescent Tracers for Immunoassays, Anand Swamy, Abraham George, and Gabor Patonay, Department of Chemistry, Georgia State University, University Plaza, Atlanta, GA 30303. (217)
12:00 Lunch
DeLyle Eastwood, Presiding

2:00 Remarks

2:05 Stochastic Adsorption Kinetics at Liquid/Solid Interfaces: Measuring Rate Processes near the Single-Molecule Limit, Richard L. Hansen and Joel M. Harris, Department of Chemistry, University of Utah, Salt Lake City, UT 84112. (218)


3:20 Break

3:45 Brewster Angle and Fluorescence Microscopy of Electric-Field-Perturbed Langmuir Films, Matthew Jones and Paul W. Bohn, Department of Chemistry, University of Illinois at Urbana-Champaign, Urbana, IL 61801. (221)

4:10 Novel Luminophores for Cation Sensing Based on Re(I) 2,2-Bipyridine and 1,10-Phenanthroline MLCT Excited States, Yibing Shen and B. Patrick Sullivan, Department of Chemistry, University of Wyoming, Laramie, WY 82071. (222)

4:35 Steady-State Fluorescence of Polystyrene in Supercritical Carbon Dioxide, Ming Li and Frank V. Bright, Department of Chemistry, State University of New York at Buffalo, Buffalo, NY 14260-3000. (223)

SYMPOSIUM ON MASS SPECTROMETRY

Organized by Joseph A. Zirrolli

Tuesday July 23,1996

Joe Zirrolli, Presiding

8:25 Opening Remarks

8:30 Invited Speaker: Flights of Fancy, Chris Enke, Department of Chemistry, University of New Mexico, Albuquerque, NM 87131-1096. (224)


9:50 Protein Sequencing Using MALDI In-Source Metastable Decay Ions, Duane C. Reiber and Robert S. Brown, Department of Chemistry and Biochemistry, Utah State University, Logan, UT 84322-0330. (226)

10:10 Break

10:30 High Resolution MALDI Time-of-Flight Mass Spectrometry, Robert S. Brown, Duane C. Reiber, Edward E. Durrant, and Jinhua Feng, Department of Chemistry and Biochemistry, Utah State University, Logan, UT 84322-0330 (227)

10:50 The Effects of Ethanol on the Metabolism of Prostaglandin E, in Rat Hepatocytes, Joseph A. Hankin and Robert C. Murphy, Department of Pediatrics, National Jewish Center for Immunology and Respiratory Disease, 1400 Jackson Street, Denver, CO 80206. (228)

11:30 Nonenzymatic Formation of Biologically Active Eicosanoids during Lipid Peroxidation, Lisa M. Hall and Robert C. Murphy, National Jewish Center for Immunology and Respiratory Disease, 1400 Jackson Street, Denver, CO 80206. (230)

11:50 Characterization of Several New Substituted Cinnamic Acids as Matrices for MALDI, Jinhua Feng and Robert S. Brown, Department of Chemistry and Biochemistry, Utah State University, Logan, UT 84322-0300. (343)

SYMPOSIUM ON NMR


Financial Support Provided by:

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- Monsanto Company
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Monday, July 22, 1996

Session I, Solid-State Chemistry

Clare Grey, Presiding

8:25 Welcoming Remarks, Joel Garbow

8:30 $^{19}Xe$ and $^{129}Xe$ as Probes of Void Space in Solids, I. L. Moudrakovski, C. J. Ratcliffe, and J. A. Ripmeester, Steacie Institute for Molecular Sciences, National Research Council of Canada, Ottawa, Ontario, K1A 0R6, Canada. (231)

9:00 Surface Bonding, Chain Dynamics and Order in Self-Assembled Monolayers: Solid-State NMR Studies, L. Reven, W. Gao, A. Badia, and L. Dickenson, Department of Chemistry, McGill University, Montreal, Quebec, H3A 2K6, Canada. (232)

9:30 Solid State NMR Investigations of the Three Dimensional Structures of Zeolite-Sorbate Complexes, H. Grondey, C. Fyfe, A. Lewis, and A. Diaz, Department of Chemistry, University of British Columbia, Vancouver, B.C., V6T1Z1, Canada. (233)

10:00 Break

10:40 Studies on Porous Silicon Surface by $^{29}Si$ CPMAS NMR, W. K. Chang, M. Y. Liao, and K. K. Gleason, Department of Chemical Engineering, Massachusetts Institute of Technology, Cambridge, MA 02139. (234)

11:10 Two-Dimensional $^{29}Si$ Nuclear Magnetic Resonance Investigations of the Structure of Alkali-Silicate Glasses, P. J. Grandinetti, P. Florian, P. Zhang, and J. F. Stebbins, Department of Chemistry, Ohio State University, Columbus, OH 43210; Department of Geology, Stanford University, Stanford, CA. (235)

11:40 Characterization of Disordered Materials by a Combined Quadrupole NMR Methodology, M. E. Smith, Department of Physics, University of Kent, Canterbury, Kent, CT2 7NR U.K. (236)

12:00 Lunch

Monday, July 22, 1996

Session II, Environmental Science / Geochemistry

Robert Wind, Presiding

1:30 Investigation of Cesium Promoted Catalysts by Low Temperature Solid State NMR, P. D. Ellis, E. Hughes, and J.M. Koons, Batelle Pacific Northwest National Laboratory, Richland, WA 99352. (237)
2:00 Cadmium Complexation by Suwannee River Fulvic Acids, C. K. Larive, M. D. Morton, A. Lankford, and W. R Carper, Department of Chemistry, University of Kansas, Lawrence, KS 66045; Department of Chemistry, Wichita State University, Wichita, KS, 67260. (238)

2:30 Probing Dynamics in a Novel Polymer Electrolyte, D. B. Zax, S. Wong, and H. Hegemann, Department of Chemistry, Cornell University, Ithaca, NY 14853. (239)

3:00 15N NMR Study of the Adsorption of NO and NH3 on Titania-Supported Vanadia Catalysts, S. Hu and T. M. Apple, Department of Chemistry, Rensselaer Polytechnic Institute, Troy, NY 12180. (240)

3:20 Break

Session III Quadrupoles
Robert Wind, Presiding

3:50 15N NMR of Broad Powder Patterns: Reorientation-Induced Redistribution of Isochromats and RotIsseRIe NMR, E. A. Hill and J. P. Yesinowski, Code 6120, Naval Research Laboratory, Washington, DC 20375. (241)

4:20 Rotation Induced Adiabatic Coherence Transfer and Its Applications to High Resolution NMR of Quadrupolar Spins, D. Rovnyak, G. Wu, and R. G. Griffin, Francis Bitter Magnet Laboratory and Department of Chemistry, Massachusetts Institute of Technology, Cambridge, MA 02139. (242)

4:40 Indirect Detection of Nitrogen-14 Relaxation in Molecular Crystals, Peptides and Proteins Via Two Dimensional CP-MAS Exchange NMR Spectroscopy, B. Herreros, G. S. Harbison, and R. K. Shoemaker, Department of Chemistry, University of Nebraska, Lincoln, NE 68588. (243)

Tuesday, July 23, 1996

Session IV, Polymers
Jeff Reimer, Presiding

8:30 Polarized NMR Signals Result from Electron Transfer in Photosynthetic Reaction Centers, A. E. McDermott and M. Zysmilich, Department of Chemistry, Columbia University, New York, NY 10027. (244)

9:00 Molecular Conformation and Phase Structure of Solid Polymers and Polypeptides Investigated by 2D NMR, K. Schmidt-Rohr, Department of Polymer Science & Engineering, University of Massachusetts, Amherst, MA 01003. (245)

9:30 Structures of Peptides and Polypeptides in the Solid State as Studied by High Resolution NMR Spectroscopy, I. Ando, Department of Polymer Chemistry, Tokyo Institute of Technology, Tokyo 152, Japan. (246)

10:00 Break

10:40 Morphological Study of a Sulfonated Poly(styrene)/Poly(amide) Blend Using Solid-State NMR, D. L. VanderHart, Y. Feng, C. C. Han, and R. A. Weiss, Polymers Division, National Institute of Science and Technology, Gaithersburg, MD 20899; University of Connecticut, Storrs, CT. (247)


11:40 A 15N and 19F REDOR Characterization of HF Doped "N-Polyaniline, M. Espe, B. Mattes, and J. Schaefer, Department of Chemistry, Washington University, St. Louis, MO 63130; Los Alamos National Laboratory, Los Alamos, NM 87545. (249)

12:00 Lunch
Session V, Poster Session
James Yeshinowski, Presiding

2:00-4:30

MAS-NMR Analysis of $^5$V in Solids, C. Fernandez, Y. Dumazy, J. P. Amoureux, A. R. Grimmer, and L. Delevoye, Université de Lille I LDSMM - CNRS URA 801, F59655 Villeneuve d'Ascq, France. (250)

Optimization of Solid-Echos for Strong Quadrupole Interactions, Y. Dumazy, J. P. Amoureux, C. Fernandez, and L. Delevoye, Université de Lille I LDSMM - CNRS URA 801, F59655 Villeneuve d'Ascq, France. (251)

Obtaining Connectivity and Distance Information between Spin-1/2 and Quadrupolar Nuclei, Y. Ba, F. I. Poshni, C. P. Grey, and T. Gullion, Department of Chemistry, State University of New York, Stony Brook, NY 11794-3400; Department of Chemistry, Florida State University, Tallahassee, FL 32306. (252)

How To Calculate the Evolution of Large Systems of Coupled Spins-1/2, A. D. Bain and R. S. Dumont, Department of Chemistry, McMaster University, Hamilton, Ontario, L8S 4M1, Canada. (253)

NMR Studies of Yttrium Trihydride, J. J. Balbach, M. S. Conradi, and T. J. Udovic, Department of Physics, Washington University, St. Louis, MO 63130; National Institute of Science and Technology, Gaithersburg, MD 20899. (254)

Chemical-Shift Selective Imaging of Molecular Probes Used in Porosity Determinations, R. E. Botto and R. E. Gerald, Chemistry Division, Argonne National Laboratory, Argonne, IL 60439. (255)


$^{19}$F NMR Investigations of Glass Ceramics Containing Fluoroapatites, M. Braun and C. Jana, Institut fur Optik und Quantenelektronik, Max Wien Platz 1, D-07743 Jena, Germany; Otto-Schott-Institut fur Glaschemie, Fraunhoferstrabe 6, D-07743, Jena, Germany. (257)

Automated Analysis of Complex Hydrocarbons Using NMR, L. W. Dennis, Exxon Chemical Company, Baytown, TX 77522. (258)

Cross Polarization from Quadrupolar Nuclei Under MAS, S. M. De Paul, M. Ernst, L. M. Bull, S. Wang, J. Shore, J. F. Stebbins, and A. Pines, Materials Science Division, Lawrence Berkeley National Laboratory; Department of Chemistry, University of California, Berkeley, CA 94720. (259)

Solid-State NMR Studies of Bismuth Molybdate Catalysts, M. C. Douskey and E. J. Munson, Department of Chemistry, University of Minnesota, Minneapolis, MN 55455. (260)

Solid-State $^1$H NMR Spectroscopy of Celluloses and Mushroom Parts, E. A. Kegerise, E. J. Gaffney, and C. Dybowski, Department of Chemistry, University of Delaware, Newark, DE 19716. (261)


Broadband Cross Polarization at High Speed Magic Angle Spinning by Using Phase Modulated 'Meandering' Spin Lock, R. Fu, P. Pelupessy, and G. Bodenhausen, Center for Interdisciplinary Magnetic Resonance, National High Magnetic Field Laboratory, Tallahassee, FL 32310. (263)

Solid-State $^1$C NMR Investigation of Sugar Ring Conformations in the Dickerson Sequence, [d(CGCCGATTCGCG)], K. B. Geahigian, J. Stringer, J. M. Miller, and G. P. Drobny, Department of Chemistry, University of Washington, Seattle, WA 98195. (264)
Motionally Averaged REDOR, J. M. Goetz and J. Schaefer, Department of Chemistry, Washington University St. Louis, MO 63130. (265)

Comparison of TRAPDOR, REDOR, and REAPDOR. L. Chopin and T. Gullion, Department of Chemistry, Florida State University, Tallahassee, FL 32306. (266)

Structural Investigations of Electrode Glasses by Multinuclear NMR: Novel Interpretations of $^{27}$Al and $^{11}$B NMR Spectra, K. Herzog, B. Thomas, and C. Jager, University of Mining and Technology, Institute of Analytical Chemistry, Freiberg/Sa., Germany; Friedr. Schiller University, PATF, Jena, Germany. (267)

Solid-State NMR Studies of Membrane-Bound Peptides, D. J. Hirsh, J. Blazyk, and J. Schaefer, Department of Chemistry, Washington University, St. Louis, MO 63130; Department of Chemistry and College of Osteopathic Medicine, Ohio University, Athens, OH 45701. (268)

$^{27}$Al->$^{65}$Cu SEDOR NMR Study of Cu-ZSM5 Catalyst Using a Single-Input Double-Tuned Circuit, S. Hu, J. A. Reimer, and A. T. Bell, Center for Advanced Materials, Materials Sciences Division, Lawrence Berkeley National Laboratory; Department of Chemical Engineering, University of California, Berkeley, CA 94720. (269)


Multidimensional $^{31}$P NMR Investigations of Solids, C. Jager, P. Hartmann, M. Feike, and H. W. Spiess, Freidrich Schiller University, PATF, Max Wien Plate 1,07743, Jena, Germany; Max Planck Institute for Polymer Research, POB 3148,55021, Mainz, Germany. (272)

Characterization of the Lewis Acid Sites in Zeolite XY, with Probe Molecule Trimethylphosphine and $^{31}$P/ $^{27}$Al Double Resonance NMR, H.-M. Kao and C. P. Grey, Department of Chemistry, State University of New York, Stony Brook, NY 11794-3400. (273)

The Use of Gradients in Magic Angle Spinning Spectroscopy, W. E. Maas and D. G. Cory, Bruker Analytical Systems, Inc., Billerica, MA 01821; Department of Nuclear Engineering, Massachusetts Institute of Technology, Cambridge, MA 02139. (274)

High Resolution Multiple Quantum Magic Angle Spinning NMR of Quadrupolar Spins, L. Marinelli, J. Harwood, and L. Frydman, Department of Chemistry, University of Illinois, Chicago, IL 60607. (275)


$^{59}$Co Magic-Angle Spinning NMR Studies of Hexacoordinated Porphyrin Complexes, A Medek, V. Frydman, and L. Frydman, Department of Chemistry, University of Illinois, Chicago, IL, 60607. (279)

Solid-State Dipolar-Dephasing NMR Experiments: Isotropic Transforms and Pure Dipolar Spectra, K. T. Mueller, D. J. Aurentz, and T. P. Jarvis, Department of Chemistry, Pennsylvania State University, University Park, PA 16802; Curagen Corporation, Branford, CT 06405. (280)


Variable Temperature NMR Relaxation Studies of Asphalts, D. A. Netzel, F. P. Miknis, J. L. Soule, and A. E. Taylor. Western Research Institute, Laramie, WY 82070; Chemical and Petroleum Engineering Department, University of Wyoming, Laramie, WY 82071. (284)

Fluorine NMR of Colchicine and Paclitaxel Complexes with Tubulin, M. D. Poliks, B. M. Poliks, I Pardes, H. Eichelberger, and S. B. Hastie, State University of New York, Binghamton, NY 13902; IBM Corporation, T37/Materials Science, Endicott, NY 13760. (285)

Study of Structural Units in Glassy and Crystalline xNa^S + (1-x)B& by MAS and 2D-MQ MAS 'B NMR, S.-J. Hwang C. Fernandez, J. P. Amoureux, D. P. Lang, J. Cho, S. W. Martin, and M. Pruski, Ames Laboratory, Ames, IA 50011; Universite de Lille I Villeneuve d'Ascq F-59655, France; Iowa State University, Ames, IA 50011. (286)

Multi-dimensional Solid-State NMR Spectroscopy of Peptides, A Ramamoorthy, L. M. Giersch, and S. J. Opella. Department of Chemistry, University of Pennsylvania, Philadelphia, PA 19104; Department of Chemistry, University of Massachusetts, Amherst, MA 01003. (287)


Construction of Broadband Heteronuclear Cross Polarization Sequences via Numerical Optimization, N. S. Rao and N. Reddy, NMR Center, Department of Medical Genetics, University of Toronto, Toronto, Canada; NMR Laboratory, Indian Institute of Chemical Technology, Hyderabad, India. (289)

Solid State NMR of Transition Metal Complexes Supported on Silica and Alumina: Analytical Tool in Organometallic Chemistry, A. Rebrov and Y. Oprunenko, NMR Laboratory, Topchiev Institute of Petrochemical Synthesis, Moscow, Russia. (290)

NMR Imaging of Liquid Crystalline Polymer Fluid Flow Through a 4-to-1 Contraction, Y. Song, K. Scheirngug, S. J. Muller, and J.A Reimer, Center for Advanced Materials, Materials Sciences Division, Lawrence Berkeley National Laboratory; and Department of Chemical Engineering, University of California, Berkeley. CA 94720. (291)


Structures of Cycloolefinic Copolymers, Studied by NMR Spectroscopy, B. Sperlich, J. Ruotoistenmaki, and M. Mikola-Santala, Technical Research Center of Finland, Biologinkuja 7, PL 1401,02044 VTT, Finland. (294)
Multidimensional Correlation Spectroscopy in Rotating Solids Via Dipolar Recoupling, B.-Q. Sun, P. R. Costa, C. M. Rienstra, J.-G. Hu, P. T. Lansbury, Jr., J. Herzfeld, and R G. Griffin, Department of Chemistry, Brandeis University, Waltham, MA; Francis Bitter Magnet Laboratory and Department of Chemistry, Massachusetts Institute of Technology, Cambridge, MA 02139. (295)


Proton NMR Studies of Nearly Homoionic Forms of Clinoptilolite, J. A. Happe, R L. Ward, and R T. Pabalan, Lawrence Livermore National Laboratory, University of California, Livermore, CA 94550; Center for Nuclear Waste Regulatory Analyses, Southwest Research Institute, San Antonio, TX 78238. (297)


NMR Studies of Aramide Polymers in Solid and Fluid Phases, M. Zhou, V. Frydman, and L. Frydman, Department of Chemistry, University of Illinois, Chicago, IL 60607. (299)

Tuesday Evening, July 23, 1996 7:30 - 9:30 p.m.

VENDOR POSTER SESSION
James Yesinowski, Presiding

Wednesday, July 24, 1996

Session VI, Robert W. Vaughan Memorial Symposium
Joel Garbow, Presiding


9:30 Small Forward Steps in Solid-State NMR, Experimental and Computational, J. S. Waugh, Department of Chemistry, Massachusetts Institute of Technology, Cambridge, MA 02139. (301)

10:10 Break

10:40 Simple NMR Experiments on Complex Systems, J. J. H. Ackerman, Department of Chemistry, Washington University, St. Louis, MO 63130. (302)

11:20 Determination of the Nitrogen Composition in Coal: Back to Dynamic Nuclear Polarization, R. A. Wind, R J. Pugmire, P. D. Ellis, and D. M. Grant, Battelle Pacific Northwest National Laboratory, Richland, WA 99352; University of Utah, Salt Lake City, UT 84112. (303)

12:00 Lunch

Session VII, Magnetic Resonance And Simulations
Hans Thomann, Presiding

1:30 NMR Studies of Structure and Dynamics in Urea Inclusion Compounds, R L. Void and G.L. Hoatson, Departments of Applied Science and Physics, College of William & Mary, Williamsburg, VA 23187. (304)

2:00 Solid State NMR of Ligand Binding to Electrocatalyst Surfaces and to Heme Proteins, E. Oldfield, W. Arnold, P. Debrunner, A.C. de Dios, R Havlin, H. Le, M. McMahon, J. Pearson, R Salzmann, R Srinivasan, M. Wodjeski, J. Day, J.J. Wu, P. A. Vuissiez, J.P. Ansermet, and A. Wieckowski, School of Chemical Sciences, University of Illinois, Urbana, IL 61801; Ecole Polytechnique Federale de Lausanne, Institut de Physique Experimentale, CH-1015 Lausanne, Switzerland. (305)
2:30 **Understanding NMR of Reactive Species Using Calculations of Structures, Energies and Chemical Shifts**, James F. Haw, Department of Chemistry, Texas A&M University, College Station, TX 77843. (306)

3:00 Break

Session VIII. Decoupling, Recoupling, Exchange

Hans Thomann, Presiding

3:30 **Solid-State Exchange NMR Spectroscopy Applied to Molecular Guest Dynamics in Zeolites**, D. J. Schaefer, D. E. Favre, and B. F. Chmelka, Department of Chemical Engineering, University of California, Santa Barbara, CA 93106. (307)

4:00 **Limits of High Resolution Proton NMR in Solids**, B. C. Gerstein, T. Taki, R. Pugmire, M. Solum, and D. M. Grant, Iowa State University, Ames, IA 50011; Tokushima University, Tokushima, Japan; University of Utah, Salt Lake City, UT 84112. (308)

4:20 **Heteronuclear Decoupling and Spin Coherence Lifetimes in Rotating Solids**, C. M. Rienstra, A. E. Bennett, B. Sun, and R G. Griffin, Francis Bitter Magnet Laboratory and Department of Chemistry, Massachusetts Institute of Technology, Cambridge, MA 02139; Laboratory of Chemical Physics, National Institutes of Health, Bethesda, MD 20892. (309)


Thursday, July 25, 1996

Session DC, New Techniques

Lucio Frydman, Presiding

8:30 **Deuterium NMR of Paramagnetic Materials and Magnetically Ordered Bilayers**, R R Vold, R S. Prosser, J. A. DiNatale, and J. S. Hwang, Department of Chemistry and Biochemistry, University of California, La Jolla, CA 92037. (311)


10:00 Break


11:00 **High Field CPMAS NMR: Problems and Prospects**, A Mehta, B. Touging, S. Burns, X Wu, I. Wu, and K. W. Zilm, Department of Chemistry, Yale University, New Haven, CT 06511. (315)

11:30 **3Q and 5Q-MAS-NMR Spectroscopies of AI**, J. P. Amoureux, C. Fernandez, L. Delmotte, Y. Dumazy, and L. Delevoye, Universite de Lille I, LDSMM - CNRS URA 801, F59655 Villeneuve d'Ascq, France. (316)

12:00 Lunch

NMR Abstracts available at http://www.cchem.berkeley.edu/~jargrp/rmc.html
SYMPHOSIUM ON PHARMACEUTICAL ANALYSIS
Organized by Michael Cutrera, Robert K. Lantz, and Patricia L. Sulik

Tuesday, July 23, 1996

Robert Lantz, presiding

8:55 Opening Remarks
9:00 Software Validation and Design Control, Marc Goodman, Noblitt & Rueland, Irvine, CA 92714. (317)
10:05 HPLC/MS/MS Analysis of Pharmaceutical Phospholipids and Degradants, Robert K. Lantz and Patricia L. Sulik, Rocky Mountain Instrumental Laboratories, Ft. Collins, CO. (318)
10:30 The Concomitant Detection of Picogram Levels of Steroids from Human Plasma by LC/MS/MS, Alan Breau, P-E SCIEX Corp., Foster City, CA. (319)
10:55 Break
11:15 The Role of Amino Acids in Fetal Growth, Adrian Pike, P. V. Fennessey, M. Timmerman, and G. Meschia, Department of Pediatrics and Physiology, UCHSC, Denver, CO 80262. (320)
11:40 Detection of Artemisinin by Derivatization with Diaso Dyes, Michael Green, Nisha Gandhi, G. Daniel Todd, and Dwight Mount, Centers for Disease Control, Atlanta, GA. (321)
12:00 Lunch

1:30 An Investigator's Point of View: Significant GMP Deviations, Terri L. Dodds, Field Operations Branch, FDA, Denver, CO. (322)
2:00 Aseptic Drug Production Quality Control and its Effect on GMP During Audits of the Pharmaceutical Industry, Steven C. Madzo, Field Operations Branch, FDA, Denver, CO. (323)
2:35 Solution Behavior of Human Corticotropin Releasing Factor, Jeffrey Meyer and Mark Manning, UCHSC, Denver, CO; Bert Ho, Neurobiological Technologies, Richmond, CA; Dan Snyder, Protein Solutions, Inc., Charlottesville, VA. (324)
3:00 A Novel Microwave Autoclave for Automation of Pharmaceutical Research Applications, W. Gary Engelhart, W. Lautenschlager, and Martin Metzger, Milestone MLS, Riviera Beach, FL. (325)

Wednesday, July 24, 1996

Mac-Mod Analytical Open Forum III

Preregistration is requested, call Pat Sulik, (303) 530-1169

8:30- 9:30 Choosing the optimum HPLC column and conditions for pharmaceutical analysis (340)
9:45-10:45 Choosing the optimum column configuration for pharmaceutical analysis (341)
11:00-12:00 When All Else Fails - Special Separation Techniques (342)

SYMPOSIUM ON QUALITY ASSURANCE
Organized by Carl Craig

This symposium has been cancelled for 1996 because of the concurrent American Chemical Society 12th Annual Waste Testing and Quality Assurance Symposium. We regret any inconvenience this may have caused.
SYMPOSIUM ON RADIOCHEMISTRY

Organized by Ann Mullin

Monday, July 22, 1996

Ann Mullin, presiding

8:10 Introductory Remarks

8:15 A New Approach to Gross Alpha Measurements Using Extraction Chromatography and LSC, Michael Fern, Anil Thakkar, Tom Kupka, and Jim Harvey, Eichrom Industries, Inc., Darien, IL; Chuck Passo, and Jock Thomson, Canberra Packard, Meriden, CT. (327)

8:45 Microwave Dissolution of Soils for Radiochemical Analysis, Richard Robinson, Richard Peters, Joseph Rodriguez, Yasser Ebaid, Catherine Hensley, Alice Slemmons, Claudine Armenta, Edward Gonzales, and Steve Goldstein, Los Alamos National Laboratory, P.O. Box 1663, MS K-484, Los Alamos, NM 87545. (328)

9:15 Who's Watching the Foxes as They Guard the Henhouse? (The State of Independent Evaluation of Radiochemical Data), Keith Wegner, QuantaLex, Inc., 300 Union Boulevard, Suite 600, Lakewood, CO 80228. (329)

9:45 The Distribution of Strontium Between Water and Sediment at the Idaho National Engineering Laboratory, Mike Liszewski, U.S. Geological Survey, INEL, MS-4148, P.O. Box 2230, Idaho Falls, ID 83403-2230. (330)

10:15 Break

10:45 Benefits of the DEEMS Data Deliverable, Terry McKibbin, Paragon Analytics, Inc., 225 Commerce Drive, Fort Collins, CO 80524. (331)

11:15 A Disposable Radon Emanation Flask, Henry F. Lucas, Lucas Laboratory, Inc., 2860 Hopi Drive MA, Sedona, AZ 86336. (332)

11:45 Lunch

1:30 A Fast, Accurate, and Sensitive Gross Alpha Method, Henry F. Lucas, Lucas Laboratory, Inc., 2860 Hopi Drive #1A Sedona, AZ 86336. (333)

2:00 When You're Hot, You're Hot (or Preventing Cross-Contamination and Exposure From High Activity Samples in an Environmental Laboratory), Ginny Whiteford, Accu-Labs Research, Inc., 4663 Table Mountain Drive, Golden, CO 80403-1650. (334)

2:30 Radium Separation and Measurement in Water Samples Using Empore Radium Rad Disks, Robert Shannon, Paragon Analytics, Inc., 225 Commerce Drive, Fort Collins, CO 80524. (335)

3:00 Break

3:30 Sequential Separation and Analysis of Sr-90 and Pb-210, Robert Jump, Paragon Analytics, Inc., 225 Commerce Drive, Fort Collins, CO 80524. (336)

4:00 Examination of Alpha Spectrometric Performance Data to Determine Statistically Reasonable Qualify Control Limits for Chemical Recovery, David Moody and Bob Thielke, QuantaLex, Inc., 300 Union Boulevard, Suite 600, Lakewood, CO 80228. (337)
1 THE PRODUCTION, TRANSPORT AND FATE OF SAMPLE AEROSOLS IN ICP-OES AND ICP-MS: FROM FUNDAMENTAL STUDIES TO PRACTICAL ANALYSIS TO ELEMENTAL SPECIATION. John W. Olesik, Laboratory for Plasma Spectrochemistry, Laser Spectroscopy and Mass Spectrometry, Department of Geological Sciences, The Ohio State University, 125 S. Oval Mall, Columbus, OH 43210

The production and efficient transport of aerosol into the ICP in a form that is effectively converted into free ions (for MS) or excited atoms or ions (for OES) is key to obtaining high sensitivity and low detection limits. When sample volumes are small, such as when ICP-MS is used to detect species in nanoliter samples separated by capillary electrophoresis (CE), the conversion of sample to signal must be highly efficient.

Plasma-sample interactions can affect the number of atoms or ions observed, the fraction that are excited and emit light, the fraction that are transported from the ICP to the MS detector and the formation of molecular oxide ions. Fundamental experiments focusing on individual drops of sample that address each of these processes and that point to the appropriate aerosol characteristics for practical analysis will be discussed.

The basis of elemental speciation using CE-ICP-MS will be briefly discussed. The importance of aerosol properties on CE-ICP-MS will be considered. Fundamental investigation of aerosol production and transport suggests that the main mechanism for loss of aerosol in the spray chamber is droplet collisions, coagulation and loss of large drops. The transport efficiency of even small drops is low (10% or less) when the sample uptake rate is 1 mL/min. When small sample uptake rates are used, the droplet number density in the spray chamber and drop collision frequencies are reduced leading to high aerosol transport efficiencies. Aerosol transport efficiencies of up to 87% were obtained using either standard or high efficiency nebulizers.

MECHANISTIC STUDIES IN AN AXIALLY VIEWED ICP USED FOR ABSORPTION MEASUREMENTS. Gary D. Rayson and Carl A. Hensman, Department of Chemistry and Biochemistry, New Mexico State University, Las Cruces, NM 88003

Previous studies have resulted in a fundamental understanding of the Inductively Coupled Plasma (ICP). The use of incident radio frequency (RF) applied power square wave modulation has allowed the recognition of several dominant mechanisms within the discharge. These mechanisms can be associated with excitation by energetic species, radial movement of the plasma gases and sample transport along the discharge. These observations and hypotheses have been realized utilizing analyte emission in a tangentially oriented ICP torch (i.e. emission was viewed perpendicular to the combined vector gas flow). The investigation currently undertaken in this laboratory is concerned with the feasibility of ICP atomic absorption as a commercial instrument. To this extent the torch is oriented along the optical axis and the incident radiation is passed through the central channel of the RF modulated discharge. Three distinct maxima have been observed 2 - 15 ms after an abrupt power decrease (1500 - 850 Watts). These maxima are temporally independent of modulation frequency. The use of mathematical deconvolution has allowed the approximation of the contributing peak parameters. The derived information from this study will be presented and discussed.

ANALYSIS OF OILS FOR HALOGENS AND NITROGEN BY ICP-AES IN THE VUV REGION. G.N. Coleman, C. Harris, M. O’Boyle, R. Starek, and J.D. Steiner, VG Elemental, 55 Cherry Hill Drive, Beverly MA 01915

The analysis of feedstocks and products for chlorine and nitrogen is of great importance to the petroleum industry, and there is growing interest in bromine and iodine. Unfortunately, most conventional methods are time-consuming and labor intensive. ICP emission spectrometry has the potential for rapid, cost-effective analyses, but halogen lines above 190nm are quite weak in the ICP spectrum. Recent developments in spectrometer optics allow the inclusion of sensitive deep vacuum ultraviolet (VUV) wavelengths in the Accuris, a 1.0m Paschen-Runge simultaneous spectrometer. Typical limits-of-detection for halogens are significantly less than 1mg/L in solution. The nitrogen limit-of-detection is limited by the absorption of atmospheric nitrogen into solution, but is typically 30mg/L The presentation will include design considerations and the use of the Accuris VUV for the analysis of lubricating oils.
NEW WAVE FOR SAMPLE PREPARATION. Edward E. King, William E. Jennings and Dennis Manchester, CEM Corporation, P.O. Box 200, Matthews, NC 28106-0200 (704) 821-7015

The application of microwave power for chemical digestion has become an accepted technique for sample preparation over the last decade. Currently, both open and closed vessel microwave systems are available to apply controlled microwave power to samples. A standard technique for applying power to multiple sample vessels is to monitor the temperature or pressure of a single "control vessel" while simultaneously irradiating multiple vessels. This process exposes all samples in the system to relatively equivalent radiation while controlling the amount of microwave power to the entire system based on the feedback from a single vessel. This procedure assumes that the bulk of the reactions occurring in all vessels are similar to the reaction occurring in the control vessel. As a result, good control of all reactions is established only if all samples in the system are similar. For years, precise control of all reaction vessels in a system has been sought since the application and control of this energy can dictate the extent and reliability of the chemical digestion process. This presentation will introduce a novel microwave system for accurate and controlled chemical digestion reactions. This new system incorporates unique microwave and temperature control mechanisms which allow precise control of the digestion process in all reaction vessels in the system. The design, optimization and use of this new system will be presented along with supportive time, temperature and analysis results. In addition, a review of the theoretical digestion process as applies to this new system will also be presented.


The overall objective of this program is to develop a portable monitor for hazardous waste that can be used in field tests on building materials. The project has been undertaken in response to demands for a real-time, on-site monitor that allows rapid decision-making during D&D operations. We have designed and are beginning to test a portable device to measure metals and radioactives in ambient aerosols and aerosols ablated from solid matrices.

The basis of the measurement is spark-induced breakdown spectrometry (SIBS), in which temporally resolved atomic emission is observed following vaporization of the particulate in an intense electrical discharge. Preliminary calibrations are being performed in tandem with a dry aerosol generator. Previous results from our laboratory indicate that this technique is capable of detecting levels of Pb, Cd, Cr and Hg in aerosols at or below the limits set by NIOSH and OSHA, and have been applied to simple and sensitive lead monitor for use at firing ranges. We are currently expanding our list of analytes to increase the possible uses for such an instrument.

IMPACT OF OPERATIONAL PARAMETERS FOR AN INDUCTIVELY COUPLED ARGON PLASMA AXIAL VIEWING ABSORPTION TECHNIQUE, Gary D. Rayson and Carl A. Hensman, Department of Chemistry and Biochemistry, New Mexico State University, Las Cruces, NM 88003

Recently, work within our laboratory has been concerned with the utilization of inductively coupled plasma (ICP) as an atom source for atomic absorption (AA) measurements. Previous studies by other researchers have concluded that the energetic environment is more suited to analyte emission measurements. It has been determined through our investigations that the conditions required for ICPAA are commercially feasible. Several dominant mechanisms within the plasma discharge have been realized. Specifically while using a ICP torch oriented along the optical axis and square wave modulation of the incident radio frequency (RF) applied power, analyte atomic absorption can be improved. The reduction of applied RF power via modulation affords a lower background emission signal. Concurrent with the reduction of contributing background signal three distinct atomic analyte absorbance maxima are observed. This enhancement in the analyte absorption can be related to an increase in the number density of ground state analyte atoms. The conditional parameters for enhanced atom absorption, precision and accuracy will be presented and discussed.
PERFORMANCE OF COMPOST ON AGRICULTURAL CROPS

Robert Rynk, Biological and Agricultural Engineering Department, University of Idaho, Moscow, ID 83844-0904. 208-885-7626

The emphasis of agricultural composting is shifting from compost production to compost use. This is a positive shift, reflecting farmers’ growing appreciation for the potential benefits of compost. While the collective experience from research projects and agricultural users of compost is somewhat inconsistent and confusing, several general observations and trends are apparent. Compost usually improves crop growth, though the effects are typically subtle and may be long term. Immediate benefits from compost often occur where the soil or fertility is otherwise lacking or where the compost suppress crop diseases. The best crop yields tend to result from a combined use of compost and chemical fertilizer. Crops sometimes suffer if the compost quality is poor or unsuited its intended use. Immaturity, high soluble salt content, and a high C:N are among the more common problems. Increasingly, users recognize the biological and soil-improving qualities of compost and appear less concerned with short-term yield effects. As an example, some compost suppliers market compost as a source of microorganisms rather than a source of nutrients. Users tend to apply compost at low application rates, to reduce their expenditure and/or hedge against possible quality problems. There is also greater awareness among users of compost ingredients, characteristics, and quality. Overall, the use of compost in commercial agriculture is increasing. Farmers are becoming more sophisticated in their knowledge and use of compost.

RECYCLING NUTRIENTS FROM CROP RESIDUES FOR SPACE APPLICATIONS. Richard F. Strayer, Ph.D. Dynamac Corporation, and Cheryl Atkinson, Ph.D. National Research Council, Kennedy Space Center, Florida

NASA will probably employ "sustainable agriculture" during extended-duration missions with sizable crews. The Advanced Life Support (ASL) program is developing regenerative systems capable of producing and recycling food, air (oxygen), and water for long-term human missions in space. The goal of the ALS Breadboard Project at Kennedy Space Center is to integrate and evaluate various components at a scale sufficient to demonstrate feasibility for further development and operation. Crops (i.e., wheat, white potato, soybean, and lettuce) are produced in a closed, controlled environment (20 m² growing area) with hydroponic cultivation systems to supply inorganic nutrients from crop residues, decompose soluble organic compounds (up to 25% of volatile solids from crop residues) and, hopefully, reduce levels of the refractive cellulose and hemicellulose. We have primarily employed conventional continuous stirred tank reactors, or CSTR, to accelerate aerobic crop residue decomposition with suspension cultures of mixed microbial populations. Up to 80% of inorganic nutrients (depending on the element) have been recovered from crop residues and recycled successfully back to the crop hydroponic culture systems. However, volume and mass requirements of CSTR, the "costs" relevant to space travel are probably too high for inclusion in an ALS. The next paper will examine composting as an alternative to CSTR for nutrient recycle in an ALS.

SMALL-SCALE COMPOSTING. Cheryl F. Atkinson, NASA, Mail Code MD-RES, Kennedy Space Center, Florida 32899, U.S.A.

Freeze-dried inedible potato biomass (roots, stems, and leaves) was composted thermophilically in small-scale (1 L) reactors for 21 days. The process was slower and carbon dioxide production was lower than that for fresh plant material. Average volatile solids were reduced by about 4%, however, layers with a moisture content of about 70% showed a reduction of about 10%. Levels of inorganic nutrients extracted with water comparable to those of aerobic bioreactors and should be sufficient to support plant growth. Subsequent studies will incorporate human solid wastes with freeze-dried plant biomass for two reasons: (1) Human solids are nutrient rich and have a large population of active microorganisms, which should speed up the composting process; (2) Space flights of extended durations will require processing of human solid wastes in a manner that will reduce levels of potentially pathogenic organisms (bacteria, viruses, ova, and parasites) and produce a non noxious end product, yet require a minimum of volume and mass. A small-scale continuous composter is currently being developed that could eliminate the start-up phase required in batch-type composting and, thus, reduce composting time to 3-5 days.
Odor problems are generally attributed to mismanagement of composting systems, with production of microbial fermentation products as a result of inadequate aeration and volatilization of ammonia and hydrogen sulfide being the most commonly cited operating difficulties. Food wastes are notoriously odorous, particularly if meat products are included in the process. Many of the odors that arise from food wastes are not the result of mismanagement of the microbial component, but rather are generated inevitably by release of volatile plant components, formation of metabolites by plant (not microbial) enzymes, and by chemical reactions of waste constituents. Thus, even the best-managed systems will still operate in an odor-generating mode. In terms of chemistry, the major classes of phytogenic odorous compounds are organosulfur flavor constituents, simple aromatics and terpenes, amines, and autooxidation products of fats and oils. Published work on plant flavor ingredients, volatile metabolites, and lipid autooxidation will be reviewed and proposed methods for odor management during food waste composting will be evaluated.

During the operation of agricultural farms several by-products with animal origin are developed that are considered as hazardous waste. The farms can sell these by-products only with high costs to ATEV (Animal Feed Processing Company). Therefore, farms depot the extremely infectious waste on their farmyard that may lead to environmental damage. One of the best solutions of eliminating this environmental problem is to compost these by-products.

In our project we developed the composting technology of rabbit fur in Galgamenti Cooperative farm at Tura.

Our main goals were the following:
- Measurement of chemical and micro biological parameters and analysis of the different phases of composting;
- Determination of reasons and time of nutrient losses;
- Development of a composting technology for the Galgamenti Cooperative farm at Tura.

In our project we have characterized the main four phases of composting with micro biological and chemical parameters. The pathogen microorganisms have perished during thermophyl phase because of the high temperature. In spite of the fact that the C/N ratio was an optimal 25:1, the nitrogen losses (in form of ammonia) were significant. We have reduced these losses with easily soluble C-sources.

In this paper I present a synthesis of 10 interviews with men and women farmers from across New York state, in which they discuss their new understanding of sustainable farming. The farmers in the study expressed a desire to "revolt" against the demise of the family farm which is steeped in a unique culture and value system. The "bottom line" for these farmers has shifted beyond the economic sphere to include the spheres of environment and health. Increasing numbers of women in extension and in the sustainable farming community describe their concern about the environmental impact of farming on the health of their families. Farmers interviewed shared a distrust of technology and a desire for a more holistic view of farming. Farmers desire a forum to increase their exposure to those who hold the "old wisdom" they feel is being lost. In the paper, I conclude that educators, extensionists and others in the agricultural sector should be encouraged to forge stronger links to knowledge sources within farmer networks - becoming facilitators instead of lecturers, that "learning by doing" can be woven into training and education and that mentoring and apprenticing are desired by these farmers within the "sustainable" agriculture movement.
COMMUNITY PLANNING FOR SUSTAINABILITY THROUGH RENEWABLE CARBON MANAGEMENT. Jim McNelly, Naturtech Composting Systems, P.O. Box 7444, Saint Cloud, MN 56302.

Renewable carbon wastes such as wastewater treatment biosolids, the organic fraction of the solid waste stream, and agricultural residuals are typically viewed as nuisance materials representing an environmental or economic liability to community officials but can be managed such that they become valuable local resources providing a foundation for development of a model sustainable community. The city of Hutchinson, Minnesota has implemented comprehensive renewable carbon management programs designed to educate residents, provide community materials management services, and promote consumption of value added commodities. Educational programs include an aggressive home composting education program and an elementary school soil ecology curriculum which are implemented through cooperation with regional environmental education and regulatory officials. Municipal services included the upgrade of centralized composting facility to recover leaves, brush, landscape trimmings, and grass clippings as well as installation of an in-vessel composting system for managing wastewater treatment biosolids and food byproducts from residents, schools, farms, and industries. Utilization of value added commodities include marketing of high grade compost products and mulch, using mulch and compost products in city park, highway, and forestry projects, and promotion of community gardening and farmers markets. This study outlines the procedures the City of Hutchinson went through to develop these educational, service, and demonstration activities, ranging from planning strategies for department heads to cooperate with other agencies, the use of regional and state resources, and step by step implementation strategies for each program.

COMMUNITY SUPPORTED AGRICULTURE. Paul Magedson, Good Earth Organic Farm, Rt. 2, Box 343, Celeste, TX 75423-9748.

Community supported agriculture (CSA) is finding its place in American agriculture. Members buy shares at the beginning of the year. The farmer delivers weekly fresh seasonal produce. Advantages to the farmer: He knows how much money he will make. He does not have to work on selling his produce each week of the growing year. The farmer can concentrate on growing the produce that his members want. Advantages to the consumer: They know where their food is coming from, but there is much more. The members are encouraged to come to the farm and participate in some kind of farm activity. This gives the member a sense of returning to his or her farm roots. It is good from them and good for the entire family. CSA is about taking care of the environment. Most of the farmers are organic and/or biodynamic. CSA is about education. Members learn how to pickle, dry, freeze, and other food storing techniques that are a mystery to most of us. As a CSA member, once a week you are presented with more vegetables than you would probably purchase at the store. You learn to eat like a farmer, seasonally and locally grown. You need three elements to start a CSA: 1) A farmer to grow the food. 2) A core group of members who volunteer with farm activities and special events. 3) The membership for financial support.

Four different food and industrial byproducts were evaluated for composting crawfish processing wastes: woodchips, rice hulls, bagasse, and bark. Relatively equal volume ratios of each of the bulking agents was mixed with crawfish wastes in bench scale reactors. Three replicates of each bulking agent were used. Compost temperature was continuously monitored, and moisture content was maintained within recommended ranges. Samples were collected and analyzed for C, N, NO3, NH4, and pH throughout the process. Physical properties such as volume and particle size reduction and water holding capacity were also measured. The results show a similar behavior in temperature variation, but the compost with rice hulls and bagasse maintained slightly higher temperatures. Crawfish decomposition was satisfactory with all bulking agents. The finished product for all mixtures is beneficial for use as a soil conditioner or can be reused for additional seafood waste composting.


The major constituents of leaves are cellulose, hemicelluloses, and lignin. Lesser amounts of lipids, proteins, phenolic compounds such as tannins, and polyester polymers such as cutin are also present. The oxidative degradation of leaves begins with senescence. During senescence concentrations of oxidative free radicals increase. This increase leads to peroxidation of lipids and most likely the partial depolymerization of lignin. Further oxidative degradation is brought about by extracellular enzymes secreted by fungi, bacteria, and other microorganisms. The sequence of enzymatic oxidative degradation of lignin is: ether fission leading to depolymerization, 0-demethylation, and hydroxylation followed by ring-fission, chain-shortening, and oxidative removal of substituents. Oxidative ring-fission leads to the formation of carboxylic acid groups on the cleaved ends of the rings, and in the process transforms phenolic groups into aliphatic alcoholic groups. Carbohydrate components are broken down into aliphatic hydroxy acids and aliphatic alcohols.

ANODIC STRIPPING VOLTAMMETRIC ASSAYS AT HG-COATED DIAMOND THIN FILM ELECTRODES

Shokoofeh Alehashem and Greg M. Swain
Department of Chemistry and Biochemistry, Utah State University
Logan, UT 84322

We report on the detection of Pb^{2+} and Cu^{2+} at Hg-coated diamond thin film electrodes using anodic stripping voltammetry in the flow injection analysis mode. Our preliminary investigations indicate that boron-doped diamond is superior to glass carbon for these types of assays due to a lower background current and more stable response. The sensitivity for Pb^{2+} detection at Hg-coated diamond and glassy carbon electrodes are similar but the limits of detection at diamond are at least an order of magnitude lower. Linear dynamic ranges from 10^{-10} to 10^{-8} M Pb^{2+} and limits of detection near 10^{-9} M (S/N=2) have been reproducibly observed at diamond. Details of the nature of Hg deposition and stripping on diamond will be reported as will results from the anodic stripping voltammetric assays for Pb^{2+} and Cu^{2+}. 

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AN EXPERIMENTAL COMPARISON OF MARCUS THEORY VS. MULLIKEN-HUSH THEORY

We have developed a series of binuclear complexes of the form Fe$_2$L, where L is a bisbipyridylalkane ligand. One bipyridine on each ligand coordinates to each metal, forming a rigid, triply-bridged, symmetric complex. Upon one electron oxidation of the initial tetra-cation, a very weak intervalence transition in the near IR has been observed for several complexes in the series. Calculation of $H_{12}$ (the coupling matrix element) from these bands by Mulliken-Hush theory gives an extremely low electronic delocalization for this "Creutz-Taube ion" like system. Marcus Theory allows us to predict the rate of thermal electron transfer from $H_{12}$, $X$ (reorganizational energy), and $r$ (donor-acceptor separation), all measurable quantities. Such considerations indicate the electron transfer rates are too fast to measure by NMR (the probe of choice) for the complexes studied so far. However, we believe the series can be extended to a point where $H_{12}$ can be determined from both an intervalence transfer band and a thermal electron transfer rate for one complex. Data supporting this will be presented. Being able to compare the results from the two different experiments on the same complex will be the litmus test of the compatibility of the Mulliken-Hush and Marcus theories.

ELECTROCHEMICALLY MODULATED LIQUID CHROMATOGRAPHY: APPLICATIONS AND RETENTION PROCESSES. En-Yi Ting, M. S. Abdel-Latif, and Marc D. Porter, Department of Chemistry, Microanalytical Instrumentation Center, and Ames Laboratory-USDOE, Iowa State University, Ames, Iowa 50011

A novel high performance liquid chromatographic system that incorporates electrochemical control of the stationary phase composition as a variable for optimizing separations has been developed. The electrochemically-modulated liquid chromatographic system consists of porous graphitic carbon particles acting as the working electrode in a HPLC column that has been converted into an electrochemical cell. Electrochemically-induced changes in the excess charge at the carbon surface prior to elution are used to manipulate the donor-acceptor and solvophobic interactions between the analytes and the stationary phase. Results using this system for the manipulation of the elution of a variety of aromatic analytes and biochemically important compounds will be presented. Details related to the development of the retention mechanism will be described.

THE ELECTROCHEMICAL AND STRUCTURAL CHARACTERIZATION OF DIAMOND-COATED AND HYDROGENATED GLASSY CARBON ELECTRODES

Jishou Xu and Greg M. Swain
Department of Chemistry & Biochemistry, Utah State University, Logan, Utah 84322-0300

There is a need to develop more chemically stable and corrosion resistant electrodes for use in electroanalysis, electrosynthesis, energy storage devices and electrochemical based toxic waste remediation. We present data which show that diamond-coated and hydrogenated glassy carbon surfaces exhibit: (i) background voltammetric currents approximately a factor of 5 less than polished glassy carbon; (ii) faradic currents as large or larger than polished glassy carbon; and (iii) a high degree of activity for long periods of time without conventional pretreatment. The lower background currents and comparable faradic currents lead to enhanced S/B ratios for redox analytes like FeCCN$^\text{IV}$ $^\text{V}$ $^\text{VI}$ $^\text{V}$ $^\text{IV}$ • Details of the film growth procedures will be presented along with electrochemical data and surface structural characterization data using SEM, STM/AFM, Raman spectroscopy and AES.
MONITORING HOMOGENEOUS ELECTRON SELF-EXCHANGE KINETICS USING STABLE ISOTOPES. Michael E. Ketterer, Gary E. Kozerski, Michael A. Fiorentino, and Jessica Song, Department of Chemistry, John Carroll University, University Heights, OH 44118.

The electron self-exchange rate constant, $k_{11}$, describes the equilibrium rate at which two members of a redox couple exchange an electron(s) with each other, and is a critical parameter in interpreting and predicting reactivities of various couples. Since the self-exchange process involves no net chemical change, direct measurement is not straightforward. A plausible but little-exploited approach is to incorporate stable isotope-labeled atoms into either the Ox or Red species, perform timewise separations of an Ox/Red reaction mixture, and monitor the change in stable isotope abundances of Ox and/or Red using mass spectrometry. We have recently exploited this approach using isotopic measurements with inductively coupled plasma mass spectrometry (ICPMS) to monitor the self-exchanges of slower reactions such as aquo Ti(III/I), Eu(III/II) and Fe(III/II) ions. Separations of Ox and Red may be accomplished using precipitation, solvent extraction, or HPLC. The latter is most attractive as the exchange can be monitored in real-time with a coupled HPLC-ICPMS experiment. The homogeneous and heterogeneous self-exchanges of aquo Fe(III/II) have been contentious subjects regarding mechanism and adiabaticity; our results confirm the validity of previously published homogeneous self-exchange rates. We are continuing to use this approach to study self-exchange reactions of various Ni(III/II) and Ru(III/II) couples.

PLASMA ENHANCED CVD OF AROMATIC AMORPHOUS CARBON FILMS FOR USE AS PROTECTIVE COATINGS ON ELECTROCHEMICAL ELECTRODES. Neil Mackie, Jeffrey R. Bottin, and Ellen R. Fisher, Department of Chemistry, Colorado State University, Fort Collins, CO 80523-1872

Conventional electrodes can not operate in corrosive environments at elevated temperatures or in radioactive surroundings. Thus, there is a real need for electrode coatings which can allow the electrode to function under these harsh conditions. Recently, thin diamond films have been shown as a promising material for this application. Diamond film growth, however, is extremely slow, usually taking as long as 24 hours to grow as little as 50 nm. In our laboratory, we have developed plasma enhanced chemical vapor deposition (PECVD) methods for producing novel amorphous aromatic hydrocarbon films. These films are grown from inductively coupled benzene and benzene/H$_2$ plasmas. In contrast to diamond film growth, we can produce very thick films in an extremely short time. For example, from a 100% C$_6$H$_6$ plasma, we measure deposition rates as high as 900 nm/min. Nonaromatic amorphous carbon is quite resistive, but we believe that the high degree of intact aromatic groups in our films increases their conductivity. Thus, these films are promising as protective coatings for electrodes. The physical, electrical and electrochemical properties of our films will be discussed.


Au and Pt microdisk electrodes (6.4, 12.5, and 25 urn radii) have been used to investigate the influence of a uniform external magnetic field on faradaic reactions. Magnetohydrodynamic flow adjacent to the microdisk surface results in an increase in steady-state limiting voltammetric currents for reduction and oxidation of both neutral and charged electroactive molecules. A mechanism for the magnetic-field effect at microdisks is presented that considers the force arising from the divergent radial flux of electrogenerated ions through a uniform magnetic field. Viscous drag on the field-accelerated ions results in convective fluid flow that alters the rate at which electroactive molecules are transported to the surface. Both lateral and cyclotron fluid motion can be established within a microscopic volume element (0.2 to 30 nL) near the electrode surface depending on the orientation of the magnetic field with respect to the microdisk. In low ionic strength solutions, the external magnetic field also reduces the electrostatic driving force for electron-transfer. This magnetic field-induced reaction overpotential is shown to result from a steady-state displacement of charge-balancing electrolyte ions at the electrode/solution interface. Potential applications of magnetic field effects using microelectrodes for ion-focusing, trapping, and switching will be discussed.
The Electrochemical Response of Anodically Polarized Diamond Thin Film
Electrodes

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Repeated potential cycling of diamond thin film electrodes to +2.0V vs SCE in acidic media
produced little change in the electrochemical response of these materials. The diamond surfaces
were extremely corrosion resistant under the imposed electrochemical conditions while glassy carbon
experienced severe oxidation and pitting. Potential cycling was performed in 0.1M HC10, from -0.4
to +2.0V vs SCE for up to 150 cycles. Cyclic voltammetry and ac impedance analysis were used to
evaluate the background current response before and after cycling. Cyclic voltammetry was also used
to measure the heterogeneous electron rate constants for Fe(CN)$_6^{3-}$/Fe(CN)$_6^{4-}$, IrCl$_6^{3-}$/IrCl$_6^{4-}$,
ascorbic acid, dopamine, benzoquinone, and 4-methyl catechol before and after cycling. Results from these
electrochemical studies as well as from in situ AFM and Raman microprobe characterizations of the
surface topography and microstructure will be presented.

OPTIMIZATION OF AN AMPEROMETRIC SENSOR FOR NEUTRAL ORGANICS
IN AQUEOUS SOLUTION BASED ON CONDUCTING POLYMER MODIFIED
ELECTRODES. Susan M. Hendrickson and C. Michael Elliott, Department of
Chemistry, Colorado State University, Fort Collins, CO 80523-1872.

Shifts in the cyclic voltammetry of conducting polymer films in aqueous solutions
containing trace neutral organics are currently being developed for amperometric sensing. The
majority of our studies have focused on the ability of poly(N-methylpyrrole) films to
detect dichloromethane in aqueous electrolyte solution. Before optimization efforts, this
system was found to detect dichloromethane in aqueous solution over four orders of
magnitude in concentration, 1 mg/mL to 0.1 |ag/mL, without preconcentration or dilution.
Variables which are being investigated to improve the detection limit of this sensor include
film thickness, flow rate and applied potential. Results will be presented describing the
relationship between these variables and the film's charge response. Thus far, optimization
has been successful at lowering the detection limit of dichloromethane by one order of
magnitude in concentration to 10 ppb.

CONTROLLED CREATION OF DEFECTS IN ALKANETHIOL MONOLAYERS.
Troy A. Tanzer, Roger H. Terrill, and Paul W. Bohn. University
of Illinois, 600 S. Matthews Ave, Urbana, IL 61801.

Self-assembled monolayers (SAMs) have received much attention due
to their applicability to many systems under study. The ability to
form defect structures in SAMs that are well-defined in number density,
morphology, and size would be valuable in the construction of model
systems of membranes and lithography. In addition, reproducible and
well-defined defects could lead to well-controlled and well-defined
mixed-monolayer systems. We have been working on two methods of
forming defects in monolayers. The first method used UV photolysis
of the Au-S bond to create random defects in the monolayer. The
intensity and exposure time can be varied to control defect numbers.
The second method uses partial electrochemical reductive desorption
to create nucleated defects in the monolayer. Adjustment of the
vertex potential and delay can be used to control the number of defects.
A variety of techniques are used to determine the size and shape of the
defects created by these two methods.
Facilitated transport occurs in cell membranes which have transport proteins as carrier molecules to transport amino acids and sugar into the cell. This has been demonstrated in synthetic membranes for gas separation using synthetic carrier molecules. Other kinds of separations have also been done using liquid membranes.

Our idea is to use enzyme without the coenzyme as a carrier molecule to facilitate the transport of the molecules to which the enzyme is specific to. We use 0.4 microns polycarbonate membrane and grow polypyrrole plugs of 1 micron electrochemically. We load the enzyme in, and grow polypyrrole in nonaqueous medium to form plugs on the other side too.

When alcohol dehydrogenase is loaded we notice ethanol flux is larger than phenol as the enzyme is specific to ethanol. We have shown facilitated transport with aldehyde dehydrogenase. Next, we loaded enantioselective enzymes and we are able to see selectivity for the enantiomer to which the enzyme is specific.


Advanced oxidation processes (AOPs) transform organic pollutants into less toxic compounds via illumination with UV light. We are interested in an APO that implements the use of a reusable photocatalyst, titanium dioxide (TiO2), with long-wavelength UV light, thus permitting the sun to be used as the light source. By using the TiO2/UV APO, the possibility exists of practical systems requiring only sunlight, air, and photocatalyst to treat waste streams that contain many harmful pollutants. The main problem with treatment of wastes using semiconductor photocatalysts is low photoefficiency, which causes solar-based reactors to be large and slow, and lamp-based reactors to be energy-intensive. Recent research at the University of Colorado has demonstrated that the photoefficiency of illuminated TiO2 slurries can be dramatically increased by controlled periodic illumination (CPI) of the photocatalyst rather than constant illumination. A laminar flow slurry reactor was constructed that allowed TiO2 particles traveling along the reactor trough passed into and out of illuminated zones. Results indicated that photoefficiencies increased by 500% when the illumination time was 40 ms followed by a dark period of 1.5 sec. Attempts to achieve CPI via fluid mixing in a Taylor vortex photocatalytic reactor will also be described. A rotating ring/disk electrode (RRDE) was used to demonstrate that the effects of CPI on photoefficiency can be observed using TiO2 films adhered to solid substrates. Raman microscopy using... is being developed as a tool for investigating the molecular factors responsible for the CPI effect.

INVESTIGATION OF ELECTROCHEMICAL TECHNIQUES AVAILABLE FOR FLUORIDE ANALYSIS: AN IMPROVED FLUORIDE ION SELECTIVE ELECTRODE. Steven L. Monroney, Hach Company, 5600 Lindbergh Drive, Loveland, CO 80539

A brief history of electrochemical, primarily potentiometric, fluoride analysis is discussed with an eye toward providing the drinking water analyst a reliable method for aqueous fluoride ion quantitation. A sampling of various methods developed over the last 40 years is provided, including spontaneous current methods, single crystal lanthanum fluoride membrane electrodes, Pungor type membranes, optical-fiber sensors, and ISFETS. Some limitations and advantages of the techniques are covered. Duplication of prior potentiometric work with Pungor type membranes was conducted with variable success. Causes for premature failure of commercial probes were investigated with the focus primarily on the interaction of design elements. The cause was identified as degredation of an epoxy seal. Inner filling solution was found to pass through leakage pathways in the epoxy where delamination occurred. The crystals return to Nernstian behavior after removal from PVC probe housings displaying sub-nernstian slopes and adhered onto new ones. Fabrication techniques that would optimize the doped lanthanum fluoride single crystal electrode were investigated. It was concluded that molding the plastic housing directly to an electroactive crystal could be achieved and useable lifetime of probes extended at least twofold.
IMPROVED CHARGE TRANSFER KINETICS AT POLYPYRROLE/NAFION COMPOSITE THIN FILMS

Blayne L. Hirsche, Jishou Xu and Greg M. Swain
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There is much technological interest in the use of conducting polymers due to the materials' electronic, electrochemical and optical properties. These polymers can be reversibly switched from conducting to insulating in aqueous electrolyte solutions depending on the applied potential. However, the rate of charge transport (i.e., switching rate) is often limited by mass transport of solvent and counter balancing electrolyte anions within the polymer microstructure. Our group has attempted to improve the rate of charge transport by co-depositing films of Nation and polypyrrole on glassy carbon. The idea is to combine the ionomeric properties of Nafion with the electronic properties of polypyrrole to produce a composite thin film with improved solvent/electrolyte transport characteristics. The cyclic voltammetric response of these composite films as a function of the pyrrole/Nafion ratio, deposition conditions and electrolyte composition will be discussed.

POTENTIAL INDUCED CHANGES IN THE SURFACE MORPHOLOGY OF (100) n-InP SAMPLES PHOTOELECTROCHEMICALLY ETCHED. David A. Soltz* and Lucila Cescato, Instituto de Fisica, UNICAMP 13083-970 Campinas-SP, BRAZIL

This study concerns the surface morphology of (100) n-InP samples photoelectrochemically etched in 1 M HCl using uniform white light. The photoelectrochemical etches were strongly anisotropic and resulted in the production of microstructures, the size and shape of which depended on the charge density and applied potential, respectively. At more positive etching potentials V-grooves aligned along the [OIL] axis were formed, delineated by the (111) and (111) indium etch stop planes, whereas etching at more negative potentials resulted in the formation of rectangular shaped pits oriented along the [OIL] axis. These pits were composed of large (111) and (111) indium etch stop planes and a more complex stepped structure which was analyzed in detail. We explain the relationship between the etching potential and the resulting structures by calculating the distribution of photogenerated minority carriers in the region below the surface of the semiconductor. At more positive etching potentials the holes are drawn rapidly to the surface where they participate in the dissolution reaction, whereas at more negative etching potentials the collection of minority carriers is less efficient, and the diffusion profile extends further into the bulk. This allows for the exposure of non-illuminated etch stop planes found in the stepped structure. Formation of the complex structure may also increase the efficiency of carrier collection, since the mean distance that a hole must travel to a reacting surface is reduced.

CLEANUP OF METALLIC CONTAMINANTS USING SUPERCRITICAL CARBON DIOXIDE EXTRACTION WITH AN INEXPENSIVE CHELATING AGENT. Edwin F. Holcombe, Anthony F. Lagalante, Jeffrey A. Merkel, Wendy A. Andersen, Barbara A. Watkins, and Robert E. Sievers, Department of Chemistry and Biochemistry and CIRES, Campus Box 215, University of Colorado, Boulder, CO 80309.

Supercritical fluid technology is a rapidly growing area of interest with great promise for environmental cleanup operations. Supercritical carbon dioxide (SF-CO$_2$) dissolves many organic contaminants, and, when used in conjunction with chelating agents, can also remove metal ions from aqueous solutions. Our work has focused on the use of an inexpensive chelating agent, 2,2,7-trimethyl-3,5-octanedione, or H(tod). In the past, we have demonstrated the solubility of a number of transition metal and lanthanide (tod) complexes in pressurized CO$_2$, including copper(II), iron(III), chromium(III), europium(III), and erbium(III). In addition, we have achieved high rates of extraction for copper(II) and iron(III) from aqueous solution with H(tod) using moderate CO$_2$ temperatures and pressures. Our current work focuses on the extraction of lanthanide ions from aqueous solution using H(tod). If the metal ions used as mixed waste surrogates in our studies behave similarly to other radioactive and non-radioactive metals, these exploratory studies indicate that it may be feasible to use SF-CO$_2$, together with H(tod), to remove actinides as well as other metals.

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TOTAL MICROWAVE SAMPLE PREPARATION FOR ENVIRONMENTAL ANALYSIS. W. Gary Engelhart, Milestone MLS 7289 Garden Road # 219, Riviera Beach, Florida 33404

To date microwave digestion methods have only focused upon reducing the time of a single step in the overall sample preparation process for atomic spectroscopy. The preliminary sample drying and final acid evaporation/concentration steps have remained unaddressed. This is also true of the current generation of U.S. EPA microwave digestion methods; 3015, 3051, CLP-SOW. Another limitation is that these methods are leaching procedures utilizing only nitric acid. Consequently the methods do not allow for recovery of all 26 RCRA toxic elements, nor use of all atomic spectroscopy techniques. Recent innovations now make it possible to perform every step of the sample preparation process in a microwave workstation. This Total Microwave Sample Preparation concept reduces overall sample prep time, manual handling, and need for multiple apparatuses; vacuum drying oven, digestion system and water or sand bath. On July 25th, 1995 the U.S. EPA Office of Solid Waste proposed a new method for inclusion in the SW-846 manual of approved methods for evaluating solid wastes. U.S. EPA Method 3052 for soils, flyash, sediments, sludges, and oil contaminated soils is the first official method to utilize Total Microwave Sample Preparation principles. This performance based method overcomes limitations of earlier methods, achieving recovery of all 26 toxic elements with digestate solutions suitable for analysis via FLAAS, CVAAS, GFAAS, ICP-OES and ICP-MS. The underlying principles of Total Microwave Sample Preparation will be presented along with a synopsis of U.S. EPA Method 3052.

TRACE ELEMENT ANALYSIS IN SALINE SAMPLES USING ICP-MS AFTER AUTOMATED CHELATION CONCENTRATION. Rob Henry, Dagmar Roller, Tom Rettberg, Fisons Instruments, 1812 Mapleton Avenue, Boulder, CO 80304, USA.

ICP-MS has been used for the analysis environmental samples since 1984, however limitations on the dissolved solids content of the samples have restricted its use for the direct analysis of saline solutions. Sample preconcentration and separation techniques can often lead to incorrect data due to contamination but with the advent of sophisticated sample handling systems the complete analysis can be automated.


The National Water Quality Laboratory analyzes approximately 4,000 surface- and ground-water samples for nonpurgeable suspended organic carbon. These analyses are useful in assessing the potential oxygen demand and the carbon particulate load caused by organic material in environmental water samples. The analytical method uses high-temperature wet-chemical oxidation and infrared analysis. An aliquot of water is filtered through a 0.45-micrometer silver filter. The retained organic carbon-containing particulate matter is oxidized using phosphoric acid and potassium persulfate in a sealed glass ampoule at elevated temperatures. The CO2 evolved during oxidation is directly proportional to the concentration of chemically oxidizable, nonpurgeable organic carbon in the sample. Precision, accuracy, recoveries, variations caused by sample types, and a summary of losses measured throughout the field-extraction process are presented. The method detection limit for routine analysis is 0.2 milligram per liter.
ANTHROPOGENIC LANTHANIDES IN THE ENVIRONMENT? Michael E. Ketterer and Blake L. Ohlson, Department of Chemistry, John Carroll University, University Heights, OH 44118.

The lanthanides (Ln's) represent a series of elements which are well-known to geochemists and geologists; nevertheless, few studies have made use of information contained in the Ln signature to assess anthropogenic impact or sources of pollutants in the environment. Recent studies in marine sediments (Sholkovitz et.al., ES&T 1991, 25, 310-316) and atmospheric aerosols (Anderson et.al., ES&T 1992, 26, 1368-1375) clearly demonstrate that Ln emissions may be derived from catalyst substrates used in oil refining and possibly automotive catalytic converters. The anthropogenic perturbation is characterized by significant enrichments of light Ln's; this enrichment is consistent with the addition of a Ln signature of commercial bastnasite-type ores to the usual crustal signature. We are examining Ln pattern in Lake Erie estuarine sediments as well as in urban aerosols in an effort to observe a similar signature. The "anthropogenic" Ln's, if present, are associated with particles less than 2 um; therefore, particle size classification is important to remove the large, obscuring contribution from ordinary crustal materials. Airborne particulates are digested using nitric-hydrofluoric-perchloric acids and sediments are dissolved using acid digestion or fusion with KOH. Inductively coupled plasma mass spectrometry (ICPMS) provides a convenient and reliable means of determining all Ln's.

IMMOBILIZED POLYAMINO ACIDS FOR TRACE METAL PRECONCENTRATION AND REMEDIATION, James A. Holcombe, Holly Autry, Maury Howard and Fabian Rorif; Department of Chemistry; University of Texas at Austin; Austin, TX 78712

The ideal ion exchanger for trace metal remediation and preconcentration have very similar requirements, with many of the requirement appearing to be contradictory, i.e., "strong binding with easy release".

- The binding constant for the target metal should be large;
- The exchanger should be highly selective for user-defined target metals;
- The exchanger should be reusable (i.e., exhibit a long lifetime);
- The extracted metal should be easily released from the exchanger without destroying its future use;
- The synthesis/production of an exchanger for a new target metal should be easily accomplished.

It is our goal to take advantage of natures metal binding system which is known to a) exhibit a high level of selectivity, b) accommodate different target metals using different "designs", and c) provide on-demand release of the bound ion. In Nature, this is generally done using only 21 different building blocks, i.e. the amino acids. Unfortunately, natural proteins are either costly to purchase or time consuming to extract. However, they provide a useful "philosophical base" from which to contemplate the fabrication of a flexible biomolecular chelator that is made from polymers comprised of amino acids. This talk will discuss the work done with poly-L-cysteine, a linear chain of cysteines (ca. 50 residues) that has been immobilized on glass for use in preconcentration and could be used in remediation. The current work will discuss how this material can be used to form a "template" for a particular target metal and how that target metal can be altered. Thus providing flexibility in design, and selectivity.

DIFFERENT SAMPLE PRESERVATION SCHEMES AS USED IN THE DETERMINATION OF TOTAL AND SPECIATED ARSENIC IN WATER, M.W. Tikkanen, Association of California Water Agencies, 910 K St., Sacramento, CA 95814 and A. Eaton, Montgomery Watson Laboratory, 555 E. Walnut St., Pasadena, CA91101.

Determination of the species of an analyte is often required when toxicity or treatment techniques are being evaluated. The drinking water standard for arsenic is currently being considered for revision by EPA. The current MCL for arsenic is 50 µg/L, characterized as total arsenic. But, both health effects studies and development of treatment methodologies for a revised standard necessitate knowledge of the form of the arsenic in the source water. This paper will detail preservation schemes used in recent studies to determine low level arsenic concentrations of total arsenic as well as arsenic(III) and arsenic (V) in a number of source water samples. Analysis of samples preserved with nitric acid, hydrochloric acid, ascorbic acid and l-cysteine are compared. Analytical methods used included LSE-GFAAS, CT-HG-AAS, and HG-ICPMS. Results from interlaboratory analyses of these samples will be discussed.
DEVELOPMENT OF AN IMPROVED METHOD FOR THE DETERMINATION OF ARSENIC AT LOW LEVELS IN BIOLOGICAL MATRICES. Ruth L. Hund.
American Water Works Association Research Foundation, 6666 W. Quincy Avenue, Denver, CO. 80235, X. Chris Le. 13-103 Clinical Sciences Building, University of Alberta, Edmonton, AB. T6G2G3

Recent epidemiological studies on arsenic carcinogenicity have caused increased concern over the levels of arsenic in drinking water and re-evaluation of the current maximum contaminant level (MCL) of 50 ug/L. The USEPA is considering a new MCL between 0.2 and 20 ug/L primarily based on a linear extrapolation of an epidemiological study in Taiwan. Although a relationship between arsenic and human cancer seems likely at high levels, extrapolation to predict potential impact at low levels in the United States has several inherent uncertainties. Efforts to develop exposure dose-response relations, and the mechanisms(s) of toxic response depend on accurate quantification of arsenic species in large numbers of blood and urine samples. Currently available analytical methods to quantify arsenic species are too time-consuming and expensive to use in studies requiring large numbers of samples. This project will develop or improve current methods using atomic fluorescence spectrometry to quantify inorganic and arsenic species in blood and urine. In addition, it will develop or improve methods that preserve arsenic species.

ANALYTICAL CHEMISTRY IN A DROP Purnendu K. Dasgupta
Department of Chemistry, Texas Tech University, Lubbock, TX 79409.

The freshness of air after a shower has a long been a favorite allegory of the literati. Raindrops do indeed act as effective scavengers of trace gases. In the laboratory, drops can be formed, on either a static or a dynamic basis with a degree of reproducibility that taxes the capability of extant instrumentation to characterize. Evaporating Liquid drops/films automatically discriminate against particles - a phenomenon termed Diffusiophoresis due to Stefan flow. This presentation will focus on the use of drops and films for the measurement of trace gases in conjuration will direct optical/electrochemical probing or automated analysis by Suppressed Conductometric Capillary Electrophoresis Systems (SuCCESS). Measurement of gases such as H2O2, HCHO, S02, HN03, organic acids, etc. will be discussed. Solvent extraction using a single drop will be demonstrated in a video format.

AUTOMATED MERCURY PREPARATION AND ANALYSIS AT PARTS PER TRILLION
Sergei Leikirt and Ben Moshiri, Questron Corporation, 4044 Quakerbridge Road, Mercerville, New Jersey 08619.

In this paper we will present application results and recoveries for a Mercury Digestion by Microwave Technology along with Mercury Analysis by cold-vapor fluorescence. Although the EPA protocol in the United States has called for CVAA analysis of Mercury, this technique has been absolutely by the requirements for lower detection limits. At ppt levels, factors other than sensitivity of the instruments become first order considerations Purity of the chemicals; cleanliness of the environment; dynamic range and recovery of the analyzer; and reproducibility of the preparation step all grow in importance. A new microwave preparation system has been developed to interface with fluorescence detector in order to better serve the requirements of ppt levels. In this paper we will discuss this technique and present the results of preparation analysis.
HISTORICAL RECORD OF STRATOSPHERIC OZONE BY QUANTIFICATION OF THYMINE DIMERS IN DNA FROM POLLEN GRAINS FOUND IN ICE CORES

Jill K Gregory. John W. Birks, Kathy L. Rowlen, University of Colorado, Department of Chemistry, Campus Box 215, Boulder, CO 80309

The flux of biologically damaging ultraviolet-B radiation (280-320 nm) reaching the earth's surface is strongly affected by the ozone column. Ozone acts as a shield to prevent UV-B radiation from damaging the DNA of organisms and causing cell mutation or death. The primary form of UV-B induced damage in DNA is the formation of thymine dimers. If two thymine nucleotides are adjacent on a strand of DNA photodimerization by a (2+2) cycloaddition occurs to form a thymine dimer (TT). The thymine dimer to thymine ratio (TT/T) can be used to determine UV-B exposure of the DNA. Two independent derivatization/chromatographic methods have been developed for analyzing the TT/T ratio. The first method uses HPLC for separation and 4-(bromomethyl)7-methoxycoumarin as a fluorescent derivatizing agent. The limit of detection obtained was picomoles, but can be improved through the use of a microbore HPLC column coupled with laser induced fluorescence. The second is a GC method in which the derivatizing agent is the strongly electron capturing molecule, pentafluorobenzylbromide. The limit of detection obtained was 0.6 femtomoles. Mass spectrometry was used to confirm the identity of the derivatization products in both reactions. The sensitivity of each technique is sufficient for the analysis of DNA photodamage in pollen grains from the ice cores. The preservation of DNA in ice core pollen will allow us to determine a long term record of UV-B radiation, which in turn will be an indication of past ozone levels.

POLYMER INCLUSION MEMBRANES WITH MACROCYCLIC CARRIERS - A NEW SIMPLE WAY FOR PRECONCENTRATION OF TOXIC ELEMENTS.

John D Lamb and Alexander Y. Nazarenko, Brigham Young University, Department of Chemistry and Biochemistry, C100 BNSN, Provo, Utah 84602

A new polymer material composed of cellulose triacetate as support, o-nitrophenyl octyl ether as plasticizer (solvent) and dicyclohexano-18-crown-6 as carrier, is proposed as a solid extractant for metal ion sorption and as a membrane material for ion transport. Selective extraction and transport of Pb(II) was observed. Influence of the source solution composition on sorption and transport processes was investigated. A diffusion-limited transport model has been found to accurately describe metal ion transport by dicyclohexano-18-crown-6. The polymer inclusion membranes are easy to prepare in the laboratory, and they may be useful in separation and preconcentration procedures for Pb, Tl, Hg determination.

DETECTOR ALTERNATIVES FOR HALOGENATED VOLATILES.

Richard Burrows and Allen N. Quick Jr., Quanterra Environmental Services, 4955 Yarrow Street, Arvada, Colorado 80002; Mark L. Bruce and Timothy J. Lavey, Quanterra Environmental Services, 4101 Shuffel Drive, NW, North Canton, Ohio 44720.

Electrolytic conductivity detectors (ELCD) have been used for many years in the GC analysis of volatile organic analytes. Methods 8010 and 8021 list the ELCD as the detector of choice. While the ELCD is more specific than the electron capture detector (ECD), chromatographic performance is degraded by the liquid transfers involved. Thus, short-term reproducibility may suffer and raise detection limits. The limited linear range of the detector can require frequent dilutions for common samples. Long-term stability is limited and leads to more frequent recalibration than other common GC detectors. Alternative approaches to halogenated volatiles are available, including a relatively new detector technology based on thermionic emission (Halogen Specific Detector, XSD®) and Mass Spectrometric detection. This paper presents comparative results from ELCD, XSD® and MS detectors for spike and real world samples. GC peak shape will be examined in particular as well as general performance characteristics such as accuracy and precision, linearity, analyte specificity and sensitivity to water. The impact of improved chromatographic performance on productivity measures such as turnaround time and capacity will also be examined.
THE ROLE OF MOLECULAR SIZE AND FLEXIBILITY IN HUMIC ACID ASSOCIATIONS, Regginal R. Engebretson and Ray von Wandruszka, Department of Chemistry, University of Idaho, Moscow, ID 83844

Size and flexibility are expected to play a major role in the ability of humic acid (HA) molecules to coil up and form pseudomicellar structures in aqueous solution. The influence of these molecular features was investigated by subjecting HA solutions to ultraviolet radiation, causing them to break into smaller pieces and/or develop additional unsaturation that results in a loss of flexibility. Large, flexible HAs were greatly affected by this treatment, as evidenced by changes in fluorescence behavior of a fluorescent probe added to the solution. The ability of HA to form hydrophobic domains was greatly reduced, as was the influence of cations on the secondary structure of the aqueous molecules. Size exclusion chromatography bore out conclusions drawn from the fluorescence studies, and variations in a recently developed Association Index provided further confirmation.

THE DEVIL’S IN THE DETAILS—SURPRISING PROBLEMS IN ENVIRONMENTAL CHROMATOGRAPHY Jeffery L. Cornell, Richard Burrows, Ph.D., and Allen N. Quick, Jr., Quanterra Inc., 4955 Yarrow Street, Arvada, CO 80002.

Many instrument and column vendors are attempting to provide additional value to environmental laboratories by providing "solutions" for a given regulated method. These "solutions" typically specify instruments, columns, temperature and pressure programs, and other operating parameters to meet the method performance criteria. In general, the operating parameters are developed by skilled chromatographers and the intent is to reduce the need for highly skilled personnel in the laboratory. However, the vendor is typically not in a good position to test the "solution" under the additional stresses of high production work with highly varied sample matrices. This paper will illustrate some of the details that needed to be resolved before method 8260 on a HP 5972 GC/MS system was optimized to a level suitable for production work, including resolution of effects due to co-elution of target compounds with water and methanol.

WASTE REDUCTION THROUGH THE ELECTRODIALYTIC PURIFICATION OF ACIDS Alex F. Schreiner, Schreiner & Associates, Inc., 1322 State St., DeKalb, IL. 60115.

The electrodialytic purification of acids is achieved through membrane based cells. The particular case study presented is the purification of chromic acid plating baths and nitric acid stripping solution. The membrane used was a Nafion® 417 perfluoromer available from DuPont. The comparison of the lab and industrial results are presented for both systems.

The evaluation focuses on the extraction efficiency expressed in grams per amphours (g/Ahrs), but will also discuss the different parameters which effect this efficiency. The specific contributions of ion mobility, complex formation, thermodynamics of the cation selective membrane, and physical properties of a cell to the extraction efficiency and selectivity are investigated.

The applications towards in process recycling and waste reduction for metal finishers are contrasted to the typical waste disposal methods.
ANALYSIS OF PESTICIDES BY COMBINED ON-LINE TRACE ENRICHMENT/POSTCOLUMN PHOTOLYSIS/LC-MS/MS IN WATER AND FOOD SAMPLES. Dietrich A. Volmer. Institute for Marine Biosciences, 1411 Oxford Street, Halifax, N.S. B3H 3Z1, Canada

Several ionization techniques were evaluated with respect to their suitability in the LC-MS determination of a large number of pesticides. An on-line trace enrichment was combined with LC-MS detection allowing both selective identification and detection down to the lower ppt-level in water samples. Comparisons were made between thermospray, particle-beam, electrospray and APCI. The methods were evaluated by the usual criteria for the validation of analytical methods, e.g. selectivity, recovery, linearity, precision and ruggedness. A major problem commonly associated with LC-MS was also addressed, the interlaboratory standardization of LC-MS methods. Results from an interlaboratory study investigating several LC-MS interfaces of different makes are presented. This study proves conclusively that standardized methods can be obtained under LC-MS with different interfaces and mass spectrometers. Furthermore, a new approach for the confirmatory analysis is discussed since the special value of LC-MS techniques lies in the field of structural information and confirmation. The most common LC-MS interfacing techniques yield primarily molecular weight information. That is, little fragmentation is observed to confirm the structure of the analyte. Alternatively, on-line postcolumn photolysis can be used to induce dissociations. This offers a means of producing structurally significant ions. Examples for the trace confirmatory analysis of pesticides in food sample extracts by means of photolysis LC-electrospray-MS are shown in this paper.


Nitroaromatic and nitramine explosives and their degradation products are potentially hazardous environmental contaminants. Their toxicity and mutagenicity in humans and biota and potential for environmental mobility have been demonstrated. Production, storage, disposal, and ordnance testing at military facilities for the past 50 years have extensively contaminated soil and water. Explosives contamination is usually characterized by high-performance liquid chromatographic (HPLC) separations with ultraviolet detection, or by electron-capture detection or mass spectrometric detection of gas chromatographic separations of soil, sediment, or water samples. We compared the performance characteristics of photodiode-array (PDA) detection, and selected-reaction-monitoring tandem mass spectrometric (SRM) detection of nitroaromatic and nitramine explosives in HPLC separations of environmental extracts isolated using solid-phase extraction. Selected-reaction monitoring provided low nanogram-per-liter (ng/L) quantitation levels, increased sensitivity, and enhanced specificity. Photodiode-array detection provided wide quantitation ranges (100 to 40,000 ng/L) and indicated the presence of uncharacterized compounds. Together, PDA and SRM detection provide quantitation ranges from 10 to 40,000 ng/L for selected explosives and their degradation products in environmental samples.

INCREASING LIQUID CHROMATOGRAPHIC PERFORMANCE IN THE ENVIRONMENTAL LAB
Stuart A. Oehrle. Waters Corporation, 34 Maple St., Milford, MA 01757

Analysis of environmentally important samples was accomplished using a new generation of liquid chromatographic (LC) equipment. This system, called Alliance, is completely integrated to include both the solvent and sample management components of an LC. This allows one to easily validate and transfer methods between different systems with little if any modifications of the method. Several examples of environmentally important samples analyzed by Alliance will be shown. These include PAH'S, explosives, paraquat/diquat, and ions in drinking and wastewater. Gradient and isocratic reproducibility between injections will be shown as well as the ease of methods transfer between different systems.
HPLC DETECTION OF CHEMICAL INDICATORS OF HUMAN POLLUTION IN WATER.

Elizabeth A. Piocos and Armah A. de la Cruz, U.S. Environmental Protection Agency, National Exposure Research Laboratory, 26 W. Martin Luther King Drive, Cincinnati, Ohio 45268-1320

Delays and uncertainties associated with the conventional microbial indicators of human contamination in water have prompted interest to search for specific, rapid, and sensitive methods to better define water quality. Nonmicrobial human by-products, such as caffeine, coprostanol, and urobilin have been proposed as alternative markers of human pollution in water. A reversed-phase HPLC with diode array detection has been developed to simultaneously detect all three compounds in water samples. A library of chromatograms of other compounds which can interfere with the analysis has been established. A pretreatment and preconcentration of water samples to improve the detection sensitivity will be also presented. This method shows promise as a supplemental and/or alternate indicator of human contamination which can better define water quality and predict the risk of disease outbreaks.

FUNDAMENTALS OF CAPILLARY ELECTROCHROMATOGRAPHY AND APPLICATIONS. Jom Keel, Hewlett-Packard Company, 24 Inverness Place East, Englewood, Colorado 80112; David N. Heiger, Hewlett-Packard Company, 2850 Centerville Road, Wilmington, Delaware 19808.

Capillary electrochromatography (CEC) is a hybrid of HPLC and CE, employing CE-size capillaries packed with HPLC packing. This results in separation efficiency like CE and selectivity like LC. In CEC, solvent transport is achieved by electroosmotic flow (EOF) instead of the hydraulic flow like in HPLC. The advantage of using EOF is that the column efficiency increases because of the plug-flow profile and the ability to use smaller particles than those used in HPLC. CEC can be used for neutral as well as charged solutes. General theory, instrumental and experimental aspects, and applications of CEC will be reviewed.

SIMPLIFIED DESIGN OF A TEMPERATURE PROGRAMMABLE MULTI-MODE INJECTION SYSTEM. Jessie Crockett Butler and Terry Rankin, Finnigan Corporation, 2215 Grand Avenue Parkway, Austin, Texas 78728-3812.

Temperature programmable inlet systems have been available to the chromatographer for several years. Early versions were simple extensions of traditional duckbill cold on-column injectors. More recent versions employ complicated pneumatics and cryogenic capabilities to extend the useful applications for these inlets. Most recently, large volume injections have become the exciting application for this class of inlet systems. While the newer designs have given more capability, many designs are quite complex. The author will describe the design of a simpler Temperature Programmable Inlet (TPI). This new universal inlet may be used as a conventional split/splitless injector, cool on-column inlet and large volume injector for trace analysis. Some topics that will be addressed are: solvent selection optimization and boiling point cutoffs. Data will be presented to show the improvement in thermally labile component analysis by using the cool on-column mode, enhanced detectability with large volume injections and the elution of high temperature analytes through temperature programming of the inlet.
COMPARISON OF WHOLE-EXTRACT-SPECTROPHOTOMETRIC METHODS AND COUPLED-
CHROMATOGRAPHIC-SPECTROPHOTOMETRIC METHODS FOR CHLOROPHYLL DETERMINATION
IN PERIPHYTON. Paul P. Soliven, Bruce D. Anderson, and Edward T. Furlong, U.S. Geological Survey,
National Water Quality Laboratory, 5293 Ward Road, Arvada, Colorado 80002.

Accurate and precise chlorophyll determinations are essential to state and national water-quality monitoring
programs. Several different analytical methods are used to determine chlorophyll, including fluorometric,
spectrophotometric/trichromatic, and high-performance liquid chromatographic (HPLC) methods. In order to
reconcile chlorophyll concentration data gathered from these different methods, we compared methods to evaluate
how chlorophyll concentrations determined by U.S. Geological Survey (USGS) National Water Quality Laboratory
(NWQL) methods compared with data produced by the previously mentioned methods. These analytical methods
were systematically compared using replicate periphyton samples collected from two regions of the United States.
Three of the methods compared used whole-extract-spectrophotometric analysis, while two of the methods used
coupled-chromatographic-spectrophotometric analysis. Results show that, in general, coupled-chromatographic-
spectrophotometric methods produce lower chlorophyll a concentrations than whole-extract-spectrophotometric
methods in replicate samples. Measured chlorophyll concentrations for the methods considered were, in descending
order, as follows: trichromatic, spectrophotometric, fluorometric, isocratic HPLC, and gradient HPLC methods.
These differences are explained by the fact that HPLC methods chromatographically separate chlorophyll
degradation products from native chlorophylls a and b, rather than using optical/acidification techniques to correct
for the presence of chlorophyll degradation products.

CAPILLARY ION ANALYSIS: A POWERFUL TECHNIQUE FOR ANALYZING
INORGANIC AND SMALL ORGANIC IONS IN ENVIRONMENTAL MATRICES
Stuart A. Oehrle, Joseph P. Romano, James A Krol, and Gary J. Fallick, Waters Corporation,
34 Maple St., Milford, MA 01757

Capillary ion analysis (CIA) is a capillary electrophoretic technique which is optimized for the rapid
analysis of low-molecular weight inorganic and organic ions. Anion analysis using this technique is
rapid (less than 5.5 minutes), with little sample preparation required. A chromate based electrolyte
employing indirect UV detection at 254nm was used for anion analysis. An electroosmotic flow
modifier is added to the electrolyte as well which reverses the normally cathodic direction of the
osmotic flow and thus augments the separation. Using this electrolyte several different aqueous
samples of environmental interest were analyzed. Comparison of anion amounts found using CIA,
conventional suppressed ion chromatography (IC), and wet-chemical methods was done with good
correlation between these techniques.

THEORETICAL APPROACH TO THE ANALYSIS OF ARBITRARY PULSES IN
MAGNETIC RESONANCE EXPERIMENTS. K. M. Salikhov and J. H. Freed,
Zavoiski Physical-Technical Institute, Sibirskey trakt IO/7, Kazan, Russia and Baker
Laboratory of Chemistry, Cornell University, Ithaca, NY 14853-1301.

Using model systems we investigated method for analysis of arbitrary pulses, i.e. pulses
of arbitrary magnitude. This approach is then applied to typical EPR sequences.
RADICAL RE-ENCOUNTER PROBABILITIES INSIDE THE GEMINATE CAGE.

58 R. B. Everson and K. A. McLauchlan. Physical and Theoretical Chemistry Laboratory, Oxford University, England.

An important property in determining the reaction probability of radicals formed geminately, and in controlling the magnitude of the effects of magnetic fields on chemical reactions, is the probability that radicals formed together subsequently re-encounter in the geminate cage after an initial separation. This is also relevant to the creation of electron spin and nuclear spin polarization in the radicals and products, respectively. A method will be described, using CIDEP phenomena, which (uniquely) gives precisely this information. This represents an example of using magnetic resonance to study the fundamental processes in the physical chemistry of radical reactions in solution.

SATURATION RECOVERY AND MULTI-QUANTUM STUDIES OF SPIN EXCHANGE.

59 James S. Hyde. Medical College of Wisconsin, 8701 Watertown Plank Road, Milwaukee, Wisconsin 53226

Spin exchange in liquid phase spin label systems results in multi-exponential saturation-recovery signals that can be difficult to deconvolve. Multi-quantum EPR methods may result in improved data. The experimental parameter space consists of the signal intensities of each hyperfine line as a function of microwave power, spin concentration, viscosity, microwave frequency and harmonic number. The numerator of the MQ-EPR signal intensity varies as $T_2^2(Tr^n)$ where $n$ is the harmonic number. It is hypothesized that the ratio of the high field to low field signal height of the 3 quantum transition ($n=1$) divided by the same ratio for the 5 quantum transition ($n=2$) will exhibit a high sensitivity to spin exchange. It is further hypothesized that Q-band will be a specially favorable frequency for this experiment. Q-band MQ-EPR has recently been demonstrated in this laboratory and experiments are in progress. Spin exchange of spin labels with very rapidly relaxing species presents a different challenge. These bimolecular events result in a change in the apparent value of $T$. MQ-EPR signals at 2 or more harmonics offers an opportunity, but it appears that absolute consistency of signal intensities is required for both harmonics. Instrumentation to accomplish this will be described.

HYPERFINE SPECTROSCOPY. Gunnar Jeschke. Laboratory of Physical Chemistry, Swiss Federal Institute of Technology, 8092 Zurich, Switzerland.

The resolution of conventional solid-state EPR spectroscopy is usually quite poor, even in single crystal work. The situation can be changed drastically by using ENDOR or ESEEM techniques, where nuclear rather than electron spin transitions are measured. For systems with many nuclear spins the number of transitions is again large; in particular where nuclear spins larger than 1/2 are concerned. The resolution of ENDOR and ESEEM is then again poor and assignment ambiguities may occur. The resolution can however be further improved and the assignment ambiguities overcome by a novel method, termed hyperfine spectroscopy, that directly measures frequencies representing the hyperfine splittings. In such an approach, each group of equivalent nuclear spins is represented in the spectrum by only one peak at the hyperfine frequency, irrespective of the nuclear and electron spin quantum numbers. The lost information on the nuclear Zeeman and quadrupole interactions can be reintroduced in two-dimensional (2D) experiments. In this contribution 1D and 2D pulse EPR methods for the measurement of hyperfine spectra and hyperfine-correlated ENDOR and ESEEM spectra will be presented. The approaches are based either on the transfer and detection of selectively excited nuclear coherence (HYEND experiment) or on the transfer of nuclear coherence excited and detected by chirped radio frequency pulses (chirp hyperfine spectroscopy). The 2D experiment resulting from the latter method can be generalized for the use with other nuclear coherence generators and detectors. The underlying principles of these techniques will be discussed and the advantages demonstrated by experiments on both ordered and disordered systems.
TIME-RESOLVED HIGH-FIELD EPR/ENDOR IN PHOTOSYNTHESIS RESEARCH. Klaus Mobius, Department of Physics, Free University Berlin, Arnimallee 14, D-14195 Berlin, Germany

For the elucidation of the spatial and electronic structures of the donor and acceptor ion radicals involved in primary photosynthesis 3 mm (W-band, 95 GHz) high-field EPR/ENDOR studies on the primary donor cation radicals P⁺* (bacteriochlorophyll dimer), the acceptor anion radicals Q⁻* (quinones), and the charge-separated radical pairs (P⁺' - Q⁻") in photosynthetic bacteria and biomimetic model systems have been performed. In favorable cases, the increased electron Zeeman interaction in high-field EPR leads to spectra with resolved g-tensor and hyperfine tensor components even in disordered samples. Pulsed high-field EPR directly reveals anisotropic contributions from librations of quinones to T₂ relaxation due to specific H-bonding. Laser flash-induced time-resolved high-field EPR spectra are spin-polarized and allow an unambiguous determination of the relative orientation of the g-tensors of donor and acceptor parts. Thereby high-precision structure information is obtained on the electron transfer pigments after light-induced charge separation. The results will be discussed with regard to structure-function relationships in primary photosynthesis.

EPR/ENDOR STUDIES ON PORPHYRIN AND CHLORIN CATION AND ANION RADICALS: CONSEQUENCES FOR THE EFFICIENCY OF BIOMIMETIC MODEL COMPOUNDS FOR PHOTOSYNTHESIS Martina Huber”, Michael Fuhs, Jonathan L. Sessler, Klaus Mobius”

Biomimetic model compounds for the light induced electron transfer processes occurring in photosynthesis frequently consist of porphyrins as electron donors (D) covalently linked with quinones as acceptors (A). One of the goals of investigating these systems is to gain understanding of the mechanistic aspects concerning the efficiency of charge separation. With respect to studying the influence of electronic factors, EPR/ENDOR methods are of prime importance. In porphyrins which act as photoexcited donors, cation and anion radicals need to be measured to probe the relevant orbitals (HOMO and LUMO). Often spectroscopy on the anion radicals presents substantial problems due to the effects of static and/or dynamic Jahn-Teller distortions. The spectral manifestations of these effects are investigated as a function of the porphyrin substituents, and significant differences are seen in asymmetrically substituted porphyrins. The final goal, to obtain local information on HOMO and LUMO coefficients, was attained in two cases. The implications for the expected efficiency of model compounds based on these porphyrins are discussed. As a result, the optimum position at which the acceptor should be attached to the porphyrin in covalent model compounds can be determined.

MULTIFREQUENCY PULSED EPR STUDIES OF NITROGEN HYPERFINE COUPLINGS IN THE PRIMARY DONOR P₇₀₀⁺ OF PHOTOSYSTEM I: IMPLICATIONS FOR ELECTRONIC STRUCTURE Michelle Mac, Gerald T. Babcock and John McCracken

In higher plants and cyanobacteria, the photosynthetic process requires the interplay of two membrane bound pigment-protein reaction centers, Photosystem I and II (PSI and PSII). In each of these, the primary photochemical event proceeds via the light induced generation of a chlorophyll a cation radical species. These specialized chlorophylls initiate a series of unidirectional electron transfer events that ultimately either oxidize water (PSII) or reduce NADP⁺ (PSI). To understand better both the initial charge separation and subsequent electron transfer events, it is imperative that the geometric and electronic structures of the cofactors be determined. Recent X-ray crystallographic studies have shown that the primary donor, P₇₀₀⁺, in its ground state consists of a dimer of chlorophyll a; the electronic structure of the cation radical, however, remains elusive. It has been suggested, on the basis of comparisons to the primary donors in bacterial systems and recent ENDOR and ESEEM studies on 'N enriched P₇₀₀⁺', that the unpaired electron is delocalized either monomerically or highly asymmetrically over the two halves of the dimer. We have used multifrequency ESEEM, ENDOR and spectral simulations of the experimental data to determine the nitrogen hyperfine and quadrupole coupling constants for P₇₀₀⁺ containing either natural abundance 'N or enriched isotopically with 'N.
PULSED EPR INVESTIGATIONS OF "IRON-ONLY" HYDROGENASES: A HISTIDINE RESIDUE IS INVOLVED IN THE DEACTIVATION OF THE H-CLUSTER

Pieter J. van Dam, Eduard J. Reijerse and Wilfred R. Hagen
Department of Molecular Spectroscopy, University of Nijmegen, Toernooiveld 1, 6525 ED Nijmegen, The Netherlands.

Hydrogenases are metallo-enzymes involved in redox reactions with molecular hydrogen. They use hydrogen as receptor or donor with the basic reaction: \( \text{H}_2 \rightarrow 2\text{H}^+ + 2\text{e}^- \). The active H-cluster of the "Iron-only" hydrogenases from *M. elsdenii* and *D. vulgaris* has been investigated with ESEEM and HYSCORE spectroscopy. In both proteins the coordination of nitrogen nuclei to the cluster was confirmed. One set of quadrupole interaction parameters \( K = 4.83 \text{ MHz}, T_J = 0.13 \) is similar to that measured on hydrogenase obtained from *C. pasteurium*. The high quadrupole coupling constant suggests coordination of an unusual type of nitrogen. Taking into account that a diatomic cofactor has been found for other hydrogenases we propose that a small cofactor, i.e. N2 or CN~ must be present.

The inactivated hydrogenase from *D. vulgaris* (generated by O2 or CO exposure) shows \(^{14}N\text{-ESEEM signals which are consistent with an imidazole interaction. Its parameters are similar to those measured on Rieske type iron-sulfur clusters. Since a histidine nearby the cluster is conserved in the known amino acid sequences of Fe-hydrogenases the assumption is made that this histidine plays a role in the hydrogen reduction/oxidation. The inactivation of the enzyme is thus accompanied by the coordination of the imidazole ring to the H-cluster."

PULSED EPR STUDIES OF THE TYPE I COPPER CENTERS: A RETROSPECTIVE. Chris Bender, Jack Peisach. *Albert Einstein College of Medicine, Bronx, NY.*

ESEEM studies of several Type I copper proteins have been concluded and analyzed in the context of the Mims density matrix formalism and ab initio molecular orbital calculations. Our findings indicate that despite close similarities among the nuclear quadrupole interaction parameters and double quantum transition, there are distinguishing features in the spectral region typically assigned to the combination lines. Spectral simulations of a \( (S = V_2, I_x = I_y = I_z = 1) \) system reveal that the combination lines' shape is indicative of the relative orientation of the superhyperfine tensor axes. These simulations likewise reveal a graphical method of determining the superhyperfine parameters from multifrequency experiments. Ab initio calculations yield spin density distributions within a Type I center model and have been compared with Cu(imid) results. Our finding indicate that the imidazole spin density is strongly correlated to axial ligand coordinates and charge polarization within the complex.

DISTANCE MEASUREMENTS USING DOUBLE QUANTUM TWO DIMENSIONAL FOURIER TRANSFORM ELECTRON SPIN RESONANCE. Sunil Saxena and Jack H. Freed, Baker Laboratory of Chemistry, Cornell University, Ithaca, New York 14853.

Measurement of distance in biomolecules has become an important area of research due to its potential of elucidating structural properties. Conventional methods using continuous wave electron spin resonance (CW ESR) so far rely on obtaining observable differences in spectral features due to large dipolar and/ or exchange couplings. Hence they are restricted to distances less than 15 Å. Double quantum Fourier transform electron spin resonance (2D FT-ESR) has the advantage that the dipolar couplings can be selectively extracted, using simple pulse sequences and phase cycling (by analogy to well known NMR methods). Double quantum 2D FT-ESR experiments on a poly-proline peptide spin labeled at both ends, are reported. A distance of 21 Å between the spin labels was found, in agreement with earlier measurements using fluorescence energy transfer. This method can, potentially, be used to measure distances as large as 50-60 Å.
ESR and spin labeling has demonstrated its utility in probing the structure and dynamics of peptides in aqueous solution through single and double labeling studies. These investigations focused on the conformation of secondary structural elements such as helices. With some of the details known of how primary structure, solvent and other factors influence the conformation of helical peptides, we are investigating how these factors control the association of helical peptides in solution. ESR is ideally suited to investigate association phenomena through Heisenberg spin exchange, which is a measure of the rate of collision between spin labeled sites on two macromolecules. The framework lattice model of protein folding indicates that secondary structure forms rapidly and thus steers these elements to make tertiary contacts. How the helical macrodipole influences association is a fundamental question in protein folding. By labeling the N and C termini of helical peptides, the influence of the helical macrodipole on the rates of collision can be directly measured. In turn, these relative collision rates can be used to determine the energetics of parallel and antiparallel alignment.

The metabolism of nitrovasodilators such as glyceryl trinitrate and nitroprusside to NO provides the active moiety of these drugs. This process is not limited to the known nitrovasodilators, but also occurs with nitroaromatic antimicrobials. The administration of hydroxyurea to rats at pharmacological doses formed detectable nitrosyl hemoglobin (HbNO), which increased with dose as detected from whole blood. At higher doses, nitrosyl hemoprotein complexes could also be detected in liver biopsies. Microsomal incubations of hydroxyurea with NADPH and hemoglobin also formed HbNO complexes, indicating a possible role for cytochrome P-450 in this nitric oxide formation. Since nitric oxide inhibits ribonucleotide reductase, the rate-limiting enzyme in DNA synthesis, nitric oxide may be an active moiety of hydroxyurea's antineoplastic activity, although hydroxyurea is also thought to act directly on ribonucleotide reductase.

Recent data show the elevation nitric oxide synthase activity in colonic mucosa of patients with ulcerative colitis and Crohn's disease. We therefore evaluate the role of nitric oxide and its targets in experimental models of gastrointestinal (GI) inflammation. Nitric oxide binds strongly to endogenous proteins (forming nitrosyl complexes), thereby facilitating the direct detection of nitric oxide production in vivo. EPR spectra measured at 77°K exhibited nitrosyl complexes in the small intestine and colon of rats after intravenous endotoxin injection or intraluminal administration of 2,4,6-trinitrobenzene sulfonic acid (TNBS). In studies with endotoxin, oxidative stress biomarkers were determined as mucosal reduced thiols and lipid peroxidation. These parameters were attenuated by pretreatment of nitric oxide synthase inhibitors indicating that nitric oxide [or its product(s) such as peroxynitrite] may contribute to oxidative injury. In studies with TNBS, our data show that TNBS was metabolized through the redox cycling of TNBS by GI flavoproteins to TNBS radical with concomitant superoxide radical production. This endogenously produced superoxide may regulate the expression of inducible nitric oxide synthase at later time as the GI damage became apparent. Our approach in utilizing tissue proteins as endogenous traps of nitric oxide to monitor patho-and physiological changes will be discussed.
Alterations of nitric oxide, NO, formation in biological tissues are important in the pathogenesis of tissue injury. In ischemic tissues, such as the heart, where there is a lack of flow large quantities of NO are formed by both the enzyme nitric oxide synthase (NOS) as well as by enzyme independent mechanisms. We have applied EPR spectroscopy to measure the mechanisms of NO generation in the ischemic heart using the spin trap Fe(II)-N-methyl-D-glucamine dithiocarbamate (Fe-MGD$_2$) or by direct binding to intrinsic heme proteins both of which give rise to characteristic triplet EPR signals which enable definitive measurement of NO’ formation. While only trace NO triplet signals were seen prior to ischemia, during ischemia these signals greatly increased. With short ischemic durations of 30 min or less, inhibition of NOS decreased NO formation, however, inhibition was incomplete and with increasing durations of ischemia less than 50% inhibition was seen. When hearts were labeled with $^{15}$N nitrite and then subjected to ischemia prominent doublet signals were observed, demonstrating that during ischemia nitrite was directly reduced giving rise to large amounts of NO’. 3D spatial EPR imaging of NO generation in the heart was performed at L-band and enabled mapping of NO with submillimeter resolution. These EPR techniques are shown to have great utility enabling both in-vitro and in-vivo measurements and imaging of nitric oxide.

**IN VIVO AND IN VITRO NITRIC OXIDE SPIN TRAPPING STUDY ON PHARMACOLOGIC EFFECTS OF NITRONES.** Yashige Kotake, Takashi Miyajima, Melinda S. West, Danny R. Moore, and Lester A. Reinke

Free Radical Biology and Aging Research Program, Oklahoma Medical Research Foundation, Oklahoma City, OK 73104.

department of Pharmacology and Toxicology, College of Pharmacy, University of Oklahoma Health Sciences Center, Oklahoma City, OK 73190.

Nitrone spin traps such as phenyl N-tert-butyl nitrone (PBN) have shown a variety of pharmacologic effects in animal models, including the prevention of endotoxin-mediated death and reversal of age-related parameters. The involvement of nitric oxide (NO) in these pharmacologic effects has been suggested. Using an EPR NO-spin trapping method with an iron-dithiocarbamate complex (iron-MGD) as the NO-spin trap, we have studied the effect of nitrones on endotoxin-induced NO generation in vivo in rodents. When PBN was administered before endotoxin injection, there was a significant reduction in the amount of NO-spin adduct in the liver tissue as well as in the biliary efflux, and the reduction was dose dependent. PBN also decreased NO generation from activated mouse peritoneal macrophages in vitro. Reduced expression of inducible NO synthase (iNOS) and its mRNA was obtained in the presence of PBN, indicating that PBN is an inhibitor of iNOS induction. Other nitrones, especially lipophilic nitrones showed similar inhibition.

**DETECTION AND QUANTITATION OF NITRIC OXIDE IN THE TISSUE USING ELECTRON PARAMAGNETIC RESONANCE.** S. Tsuyoshi Ohnishi, Philadelphia Biomedical Research Institute, 100 Ross and Royal Roads, King of Prussia, PA 19406

Using diethyldithiocarbamate and iron as spin trapping agents [A.F. Vanin et al.], we have measured the tissue level of nitric oxide (NO). In the rat brain, it increased from a normal level of 1 uM to 5 uM within a few minutes of mild hypotension, suggesting that the increase was to secure blood flow to protect tissues. The level exceeded 10 uM in global ischemia. After a short ischemia time, it quickly returned to the normal level upon reperfusion. However, after longer ischemia, the NO level remained high during the reperfusion phase [with Sato, Tominaga and Ohnishi]. This raises the possibility of producing peroxyhitrite during the reperfusion, thereby causing reperfusion injury. We have performed 3-dimensional imaging of NO in the rat brain [Collaboration with P. Kuppusamy and J.L. Zweier].

Applying this EPR NO-trapping technique, we have also shown that NO was produced when the rat was exposed to carbon monoxide [with S. Thom and H. Ischiropoulos] or ozone [with D.L. Laskin]. Viral infection or autoimmune diseases also increased the production of NO [with D.C. Hooper & H. Koprowski].
PROTECTIVE EFFECT OF NITRIC OXIDE (NO) AND NITROXYL ANION (NO\textsuperscript{\textminus}) DONORS AGAINST MYOCARDIAL ISCHEMIA. B. Kalyanaraman. Biophysics Research Institute, Medical College of Wisconsin, 8701 Watertown Plank Road, Milwaukee, WI 53226.

There is now much interest in the rational design of a new class of mechanism-based anti-ischemic drugs that can release nitric oxide (\textquoteleft NO\textquoteright) in a controlled fashion. \textquoteleft NO donors show a broad spectrum of pharmacological activities toward cardiovascular disorders. In this study we have evaluated a number of structurally-different *NO donors (nitrosoglutathione, spermine NONOate, etc.) and nitroxyl anion (NO\textsuperscript{\textminus}) donor as protective agents against myocardial ischemia in isolated rat heart. Angeli's salt (HN2O3\textsuperscript{\textminus}) was used as the source of an NO\textsuperscript{\textminus} species. Nitronyl nitroxides, scavengers of •NO and NO\textsuperscript{\textminus}, antagonized the protective effect of \textquoteleft NO donors and Angeli's salt. Using myoglobin as an intracellular *NO trap, we investigated the formation of nitrosylmyoglobin (MbNO) in intact ischemic hearts. In this talk, I will discuss the following: (1) the mechanism of \#NO release from nitrosoglutathione in isolated hearts, (2), the mechanism by which nitronyl nitroxides antagonize the protective effect of \textquoteleft NO and NO\textsuperscript{\textminus} donors, and (3) the role of NO\textsuperscript{\textminus} and N2O in the myocardial protection elicited by Angeli's salt.

DETECTION AND IMAGING OF SPIN-TRAPPED NITRIC OXIDE USING PEDRI
David J. Lurie, Birgitt Fichtlscherer, Ioannis Seimenis, Margaret A. Foster and Alexander Mulschf
Dept. of Bio-Medical Physics, Aberdeen University, Foresterhill, Aberdeen, UK and \^Centre of Physiology, Johann Wolfgang Goethe University Clinic, Theodor-Stern-Kai 7, 60590 Frankfurt/Main, Germany

Nitric Oxide (NO) is an important signal and effector molecule which is generated from L-arginine by specific enzymes, is released from nitrovasodilators and exhibits a plethora of biological actions. Existing detection methods for NO analyse tissue or fluid samples by indirect biochemical methods or \textit{ex-vivo} EPR spectroscopy, and cannot easily be used to study the production or decay of NO \textit{in-vivo} in response to stimuli. We have investigated the feasibility of detecting and imaging spin-trapped nitric oxide using Proton-Electron Double-Resonance Imaging (PEDRI), a combination of NMR imaging with ESR which has the potential for imaging free radicals in large animals or even in humans. The spin-trapping technique is based on the formation of paramagnetic mononitrosyl-iron complexes with diethylthiocarbamate (DETC) or dinitrosyl-iron complexes with unknown endogenous ligands. Model compounds were studied in order to determine if PEDRI would have sufficient sensitivity to image the spin-adducts \textit{in-vivo}. Paramagnetic dinitrosyl-iron-glutathione complex (DNIC-GSH) was formed by the anaerobic reaction of FeS0 \textsubscript{4} with a large excess of GSH in the presence of NO gas. PEDRI experiments conducted at 10 mT with an EPR irradiation at 288 MHz showed that it was possible to image the complex at concentrations as low as 15 \textmu M with good SNR. Recent \textit{in-vitro} experiments involving the perfusion of rat livers with sodium nitroprusside have also yielded sufficient trapped nitrosyl-iron radicals to allow PEDRI imaging. These results indicate that it should be possible to image NO production \textit{in-vivo}, and we are currently working towards this goal.

GATED EPR SPECTROSCOPY AND IMAGING OF THE BEATING HEART
Periannan Kuppusamy, Michael Chzhan, and Jay L. Zweier
Molecular and Cellular Biophysics Laboratories, Division of Cardiology and the EPR Center, Johns Hopkins Medical Institutions, 5501 Hopkins Bayview Circle, Baltimore, MD 21224

\textit{In vivo} or \textit{ex vivo} electron paramagnetic resonance imaging, EPRI, has been established as a powerful technique for determining the spatial distribution of free radicals and other paramagnetic species in living organs and tissues. While instrumentation capable of performing EPR imaging of free radicals in whole tissues, and isolated organs has been previously developed, it was not possible to image rapidly moving organs such as the beating heart. We have, therefore, developed EPR instrumentation capable of performing gated-spectroscopic and imaging measurements on isolated beating rat hearts at L-band. A synchronized pulsing and timing system was developed enabling gated acquisitions of up to 2.56 images per cycle, with rates of up to 16 Hz. The temporal and spatial accuracy of this instrumentation was verified using a specially designed beating heart-shaped phantom with acoustically driven sinusoidal motion at a cycle rate of 5 Hz. Gated EPR spectroscopy and imaging were performed on a series of isolated rat hearts perfused with nitrooxide spin labels. These hearts were paced at a rate of 6 Hz with either 16 or 32 gated images were per cardiac contractile cycle. The images enabled visualization of the time dependent alterations in the free radical distribution and anatomical structure of the heart which occurs during the cardiac cycle.
Transient paramagnetic metal ions and free radicals have been postulated to have important roles in the development of ischemia-reperfusion damage, cancer, aging, and other types of uncontrolled oxidation. They certainly have roles in many normal physiological processes, ranging from intermediates in enzyme states to roles as effectors (especially nitric oxide, and perhaps, superoxide). The toxicity of certain drugs and chemicals also may be mediated by free radical reactions. Due to the very reactive nature of these species, however, they are generally very short-lived in vivo. Most of the approaches to detect these species in biological systems use in vitro systems, isolated organs, or in vitro analyses of free radicals generated in vivo. We report here the direct observation in vivo of a transient paramagnetic metal ion, Chromium(V), and a spin adduct, DMPO/SO$_3^-$, using low frequency EPR (1.2 GHz, L-band). These results suggest that in vivo EPR may provide an important new avenue for obtaining biologically valid and pertinent data for the still expanding and often controversial field of the role of oxidative damage and free radical reactions in biology and medicine.

Cytokines play a major role in both acute and chronic inflammatory processes. Irritants including sulfur mustard (HD) are thought to cause release of primary cytokines such as interleukin-1 (IL-1) and tumor necrosis factor-alpha (TNF-α) from epidermal cells. These primary cytokines, in turn, stimulate the production of other cytokines by cells in the dermis (fibroblasts, macrophages, endothelial cells, and mast cells). Only then is the inflammatory process fully developed. We have determined by immunocytochemistry the levels of interleukin-1 beta (IL-1β) in culture human epidermal keratinocytes (NHEK) following exposure to HD. Human skin keratinocytes express significant numbers of IL-1 receptors as determined by the PredictCTM Interleukin-1 (3 kit, an enzyme-linked immunosorbent assay (ELISA) procedure. Exposure of NHEK (~10$^6$ to 10$^7$ cells, to HD (2 mM) and preincubation for 90 min. at 37°C results in significant changes in IL-1 activation. In neonatal NHEK exposed to HD, IL-1β is decreased. Conversely, in adult breast NHEK exposed to HD, IL-1β is increased. In addition, ELISA experiments were conducted to determine whether vesicating agents such as half-mustard (H-MG) may induce the release of tumor necrosis factor in human monocytes (THP-1). The results indicate that TNF-α is rapidly synthesized in H-MG stimulated THP-1 cells. The effect peaks at 400 to 600-fold above non-stimulated levels 1 to 2 hours after stimulation. Nitric oxide (NO) has been implicated as the effector molecule that mediates IL-3. To confirm the involvement of NO in the expression of the IL-1 receptor, EPR spectroscopy was employed. EPR detectable iron-nitrosyl complex in NHEK exposed to HD (1 mM for 18 h) was measured. Our results show the release of NO during IL-1 cytokine expression when keratinocytes are exposed to HD. Moreover TNF-α may play a role as a biochemical marker for pathophysiological changes induced by vesicating or related agents. Based upon this work, it appears possible that IL-1 and TNF-α could be used as specific markers for epidermal cytotoxicity in mechanistic studies of the toxicity of HD and in defining interventive and therapeutic regimen against HD vesication.

A THREE-STAGE HELICAL RESONATOR/BANDPASS FILTER FOR PULSED EPR SPECTROSCOPY AT LOW FREQUENCY. Chris Bender. *Albert Einstein College of Medicine, Bronx, NY.*

Helical resonators are commonly used as bandpass filters in communications circuits, and the attraction for adopting these structures for EPR is that they can readily be engineered for low $Q$, high pass band applications (as desired in pulsed EPR). Because the helix surrounds the sample and (if properly designed) the resonant field is quite uniform within the windings, the structure has the added advantage of a high filling factor. A three-stage structure is reported for operation at C-band in a transmission mode. The coils are wound on fused silica tubing, and each occupies a cylindrical chamber that is open to the adjoining chambers). The central silica tube houses the sample during operation, whereas the adjoining two resonators each feature a micrometer controlled fused silica rod for tuning. Coaxial feeds comprise the interface to the transmitter and receiver of the spectrometer.
The obstacles to obtaining strong, clearly resolved images have been the short in vivo lifetimes of most commercial spin probes. These spin probes should possess low or negligible toxicity, overall metabolic stability, and long in vivo retention times. The nitroxide group 2,2,6,6-tetramethylpiperidine-l-oxyl (TEMPO) was covalently bound to a dextran to produce a novel spin probe, TEMPO-dextran (TEMPO-DX), which circulates for long time periods in animals without metabolic destruction. The optimum dose was about 2-3g/kg (0.3ml of 15% TEMPO-DX solution for a 20g mouse), yielding a final TEMPO-DX concentration of 4.0-5.0 x 10^-3 M in the blood circulation. The in vivo ESR signal of TEMPO-DX in the mouse was reduced 50% within about 50 minutes after administration and was stable in both the blood circulation and the urine. L-band three-dimensional ESR images of TEMPO-DX specific organs were calculated for specific organs. The relatively efficient transport through the kidney suggests that the molecular weight of the modified dextran was reduced after synthesis from 100-200kDa to less than ca 40kDa.

AN EPR PROBE FOR THE DETECTION OF DNA BENDING. Robert S. Keyes, Ying Y. Cao, Elizabeth V. Bobst, and Albert M. Bobst. Department of Chemistry, University of Cincinnati, Cincinnati, OH 45221.

Sequence specifically spin-labeled 15mer duplexes containing AATT or AAATT were prepared enzymatically. The location of the spin label L (L = DUAP, a deoxyuridine analog spin-labeled in position C5 which places the nitroxide into the major groove) was changed by selecting appropriate 15mer templates. The EPR spectra of the 15mers containing AATT are all similar, while the AAATT-containing 15mer produced a line shape with significant additional line broadening. The dynamic cylinder motional model (Keyes and Bobst, Biochemistry 34, 9265 (1995)) was used to interpret the EPR data. In this model, the DNA dynamics are grouped into overall and internal contributions. These two classes of motion are considered to be decoupled due to their difference in rate. While the overall motion consists of global tumbling of the DNA cylinder which is described hydrodynamically, the internal dynamics consist primarily of spin-labeled base librations which are characterized by an order parameter S. Applying this model to the EPR data indicates that the AAATT sequence has a larger S value than the AATT sequence. X-ray structures of oligomers containing these two sequences suggest that they bend toward the major groove (Young et al., Biophys. J. 68, 2454 (1995)). In view of the x-ray data, the increase in S for AAATT as compared to AATT implies a greater bend for the former sequence (supported in part by GM 27002).

A 17.5 GHz TWO DIMENSIONAL FOURIER TRANSFORM ESR SPECTROMETER. 

As part of an ongoing program in developing multifrequency Pulsed and CW ESR instrumentation at Cornell, a heterodyne 17.5 GHz Fourier Transform ESR spectrometer was constructed. It operates at a 9.2 GHz intermediate frequency and employs the X-band quadrature phase shifters and detectors optimized at this frequency. Dual-channel pulse-forming circuitry was implemented to obtain minimal pulse separation, reduce interpulse interaction and further increase the number of available pulse sequences. Performance of the spectrometer is demonstrated with different resonant structures and compared with the existing X-band FT ESR spectrometer where a low-Q bridged loop-gap resonator is normally used. As model systems we studied nitroxide spin-probes in the slow-motional regime by means of 2D-ELDOR experiments. Multifrequency 2D-ELDOR enables better determination of molecular motion, can extend the slow-motional regime, and enables shorter dead-times and better sensitivity for limited volume samples.

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Iron-sulfur proteins are a wide group of proteins containing polymeric clusters [2Fe-2S], [3Fe-4S], [4Fe-4S] in which the iron ions are tetrahedrally coordinated, generally with bridging sulfide ions and cysteinyl residues as ligands. One of the remarkable properties of iron-sulfur proteins is the wide range of redox potential variations exhibited even by the proteins containing clusters with essentially the same structure. Among the other possible factors affecting the redox potential are the orientation of cysteine ligands and hydrogen bonds relative to the cluster. One way to characterize them is through the proton location in these structural units.

For the study of the protons surrounding the paramagnetic forms of iron-sulfur clusters in proteins such magnetic resonance techniques as NMR and ENDOR spectrosopies are widely used. In the present work we describe the application of two-dimensional ESEEM spectroscopy called HYSCORE to the reduced [2Fe-2S] cluster in ferredoxin from the red marine algae Porfira umbilicalis. After deuterium substitution of the exchangeable protons we obtained highly resolved orientationally-selected HYSCORE spectra with four pairs of cross-peaks from strongly coupled unexchangeable protons. We assign these protons to the P-CH₂ protons of cysteine ligands. The analysis of the cross-peak lineshapes allows separate determination of isotropic and anisotropic couplings of these protons. The isotropic couplings of each p-proton determined the dihedral angle between the planes Fe-S-C and S-C-H.

Our data show that HYSCORE is very suitable technique for the detection of weak structural differences between the proteins or their oxidation states via the measurement of the proton hyperfine couplings.

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ADJOINT AND TIME REVERSAL PROPERTIES OF SPIN HAMILTONIAN TENSOR OPERATORS. H.A. Buckmaster* and R. Chatterjee** Department of Physics and Astronomy, *University of Victoria, P.O. Box 3055, Victoria, B.C., Canada. V8W 3P6 **The University of Calgary, Calgary, AB, Canada T2N 1N4.

The adjoint and time reversal properties of the angular momentum tensor operators used to describe the electron and nuclear Zeeman, zero field splitting and hyperfine interactions terms in spin Hamiltonian parameterization of electron paramagnetic resonance and ENDOR data are reviewed. An analysis of the various definitions that exist is presented which reveals that most of the arguments used to determine the selection rules for these operators are invalid. A self consistent formalism approach is outlined which can be used with both conventional and generalized spin Hamiltonians to determine those terms which are allowed by the crystalline electric field paramagnetic ion site symmetry as well as order these terms as a function of the rank of the external magnetic field operator.

A 9 GHz CW-EPR VARIABLE TEMPERATURE STUDY OF MONOCRYSTALLLINE 1-BENZYL 4-HYDROXY PIPERIDINE. R. Krzymiński*, M. Pawlicka*, Z. Kruczyński*, J. Kudynska** and H.A. Buckmaster**. *Institute of Physics, Adam Mickiewicz University, 65614 Poznan, Poland. **Department of Physics and Astronomy, University of Victoria, P.O. Box 3055, Victoria, B.C., Canada. V8W 3P6.

This poster reports on the progress that has been achieved in the study of molecular dynamics in acceptor-hydrogen bridge-donor molecular structures using EPR spectroscopy. Temperature measurements were made on monocristalline 1-benzyl 4-hydroxy piperidine which was Y-irradiated with a 150 kGy dose at 293 K. It was found that the ionizing radiation generates a free radical by removal of one hydrogen from the CH₂ group in the bridge connecting the benzene and piperidine rings. The hyperfine splitting parameters and the unpaired electron densities were determined. The linewidth was found to be temperature dependent with an anomalous behaviour indicative of a solid-solid structural phase transition. The hyperfine splitting parameters were also found to be strongly temperature dependend.
CONTINUOUS WAVE EPR STUDIES OF INTEGER SPIN MANGANESE DIMERS

Kris A. Campbell, David Wright, William H. Armstrong, and R. David Britt

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The exact structure of the tetrameric manganese cluster which comprises the oxygen-evolving complex (OEC) of photosystem II is still unknown. The currently proposed OEC models consist of manganese cluster configurations in which the manganese oxidation states give rise to an integer spin system. Thus, to further characterize the structure of the manganese cluster of the OEC, we have measured the continuous wave (CW) EPR spectra of various integer spin manganese dimer model compounds. In addition, we have measured the CW EPR spectra of the OEC in its dark stable state (SI) in an attempt to observe the presence of an integer spin system. The integer spin CW EPR spectra was collected using parallel polarization of the applied magnetic field. The temperature dependence of the CW EPR spectra was also investigated. This data provides information concerning the relative populations of the ground and excited states, which in turn will describe the mechanism of coupling between Mn atoms and the coupling parameters. The temperature dependence data also allows determination of the axial and rhombic crystal field splitting parameters.

AN APL SOFTWARE FOR THE SIMULATION OF ESR SPECTRA OF FLUID, VISCOUS AND RIGID SYSTEMS.

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A software written in APL language, has been implemented on PC computers for the simulation of ESR spectra of isotropic and anisotropic systems. This software, available on request, covers a wide range of applications of ESR to physical-chemistry and biophysics: simulation of the spectra of $S = 1/2$ and $S > 1$ species in rigid matrices for any relative orientation of the $g$, hyperfine coupling or ZFS tensors, simulation of high resolution spectra in liquids as well as calculation of linewidths or spectral shapes for the fast or slow tumbling regimes of spin probes. For the latter, the effect on the spectral shapes of the exchange rates between two or three sites can be also calculated. Most of the programs include a module for the non-linear least squares fit of experimental spectra, using the Levenberg-Marquardt's algorithm(1). In the case of a paramagnetic species undergoing multiple internal motions such as a flexible biradical, the dynamics of internal and tumbling motions can be obtained by similar procedures from the ESR alternating linewidths and the nuclear relaxation rates in a parent diamagnetic molecule (1, 2)


A PULSED BROAD BAND RADIO FREQUENCY EPR SPECTROMETER FOR BIOLOGICAL APPLICATIONS.

R. Murugesan, S. Subramanian, R. Tschudin, M. Cherukuri, 1 School of Chemistry, Madurai Kamaraj University, Madurai, India; RSIC, Indian Insitute of Technology, Madras, India; laboratory of Chemical Physics, NIDDK, NIH, Bethesda, MD 20892; Radiation Biology Branch, NCI, NTH Bethesda, MD 20892.

A pulsed EPR spectrometer operating in the range of 200-400 MHz corresponding to a magnetic field of about 5 to 17 mT has been built. The spectrometer is designed for the study of lossy biological samples and it operates in a pulsed mode collecting and summing free induction decays at very high speed, subsequent Fourier transformation producing the spectra. The instrument is based on a modular design incorporating, wherever possible, commercially available sub-systems and is capable of being operated in a 2-channel (quadrature) mode. A unique gated cascaded preamplifier has been constructed and integrated with the homodyne receiver arm for very fast signal recovery. A set of 2 axes gradient coils has also been integrated with the spectrometer for spatial resolution and imaging of the distribution of suitable free radicals in biological systems. Detailed description of the construction, operation and examples of the performance of the spectrometer are presented.
SPIN LATTICE RELAXATION OF COPPER ACETYLACETONATE IN LIQUID SOLUTION
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W. Froncisz, Institute of Molecular Biology, Jagiellonian University, Krakow, Poland
James S. Hyde, Biophysics Research Institute, 8701 Watertown Plank Rd, Milwaukee WI, 53226.

The spin lattice relaxation time $T_1$ of copper acetylacetonate Cu(AcAc)$_2$ in chloroform and chloroform-glycerol mixtures has been made using progressive saturation. Using a high efficiency loop-gap resonator LGR (A = 4.5) and a 500 mW microwave amplifier, the microwave power was gated. The gating was such as to maintain constant incident power on the resonator at about 35 mW, in order to avoid sample heating by the microwave power. By fitting the spectrum to four lorentzian lines, it was possible to extract the linewidths as a function of incident power and temperature. The relaxation times measured vary from 5-20 ns, depending on viscosity and temperature.

CLARIFICATION OF THE RELATIONSHIP BETWEEN FREE RADICAL SPIN TRAPPING AND CARBON TETRACHLORIDE METABOLISM IN MICROSOMAL SYSTEMS.
H. D. Connor, Kentucky Wesleyan College, Owensboro, KY, 42301, R. P. Mason, National Institute of Environmental Health Sciences, R. G. Thurman, University of North Carolina Dept. of Pharmacology, G. Chen, University of Guelph, J. L. Poyer, Oklahoma Medical Research Foundation, and E. G. Janzen, Oklahoma Medical Research Foundation.

It has been proposed that the C-phenyl-N-t-butyl nitrone/trichloromethyl radical adduct (PBN/-CCl$_3$) is metabolized to either the C-phenyl-N-t-butyl nitrone/carbondioxide anion radical adduct (PBN/-CO$_2$-) or the glutathione (GSH) and CCl$_4$ dependent PBN radical adduct (PBN/[GSH--CCl$_3$]). Inclusion of PBN/-CCl$_3$ in microsomal incubations containing GSH, nicotinamide adenine dinucleotide phosphate (NADPH), or GSH plus NADPH produced no electron paramagnetic resonance (EPR) spectral data indicative of the formation of either the PBN/[GSH--CCl$_3$] or PBN/-CO$_2$- radical adducts. Microsomes alone or with GSH had no effect on the PBN/-CCl$_3$ radical adduct EPR signal. Addition of NADPH to a microsomal system containing PBN/-CCl$_3$, presumably reduced the radical adduct to its EPR-silent hydroxylamine since no EPR signal was observed. The Folch extract of this system produced an EPR spectrum that was a composite of two radicals, one of which had hyperfine coupling constants identical to those of PBN/-CCl$_3$. We conclude that PBN/-CCl$_3$ is not metabolized into either PBN/[GSH--CCl$_3$] or PBN/-CO$_2$- in microsomal systems.

PROTONATION AND STABILITY OF NITROXIDE FREE RADICALS IN STRONG ACIDS.
Werner Damerau, Antal Rockenbauer, and Kalman Hideg, Max Delbruck Center of Molecular Medicine, Robert Rossle Str.10, D-13125 Berlin, Germany

Reaction of the nitroxides 2,2,5,5-tetramethyl-3-phenylpyrrolidine-1-oxyl (I) and 2,5,5-trimethyl-2-phenylpyrrolidine-1-oxyl (III) with concentrated H$_2$SO$_4$/HN0$_3$ leads to nitrations of the phenyl ring. Despite the drastic conditions during synthesis, the nitroxide moiety (>NO) of I and III, respectively, is recovered in the nitrated products II and IV. In 96 % sulfuric acid, for the nitroxides I and III an unusual EPR signal is observed having a large nitrogen coupling constant $a_N$ in the range of 20 G and a proton coupling in the range of 3 G. Correspondingly in the frozen solution a value $2A''_{OH} = 91$ G is measured. The EPR spectrum is assigned to the protonated form (>NOH$^+$) of I and III. Concentration of the protonated species is <0.1 % in concentrated sulfuric acid and becomes even smaller with increasing dilution. After neutralization complete recovery of I and III is observed. When nitroxide I is solved in a mixture of concentrated H$_2$SO$_4$/HN0$_3$, no EPR spectrum is measured but 100 % of the spin concentration is recovered in the form of the nitration product II after 30 min treatment followed by neutralization. It is concluded that the nitroxides I and III are transformed via their protonated forms into the diamagnetic oxonium ion which is then nitrated in the phenyl ring. Behavior of the nitroxides I - IV in sulfuric acid is compared with the behavior in concentrated hydrochloric and phosphoric acid. Implication for the use of spin labels is discussed.
CROSS-PEAK LINESHAPE OF TWO-DIMENSIONAL PULSED EPR SPECTRA OF DISORDERED S=1/2, 1=1 SPIN SYSTEM. Sergei A. Dikanov" and Michael K. Bowman, 'Macromolecular Structure & Dynamics, Environmental Molecular Sciences Laboratory, Pacific Northwest National Laboratory, Richland WA 99352, Institute of Chemical Kinetics and Combustion, Novosibirsk 630090, Russia.

The paramagnetic metal ions in synthetic complexes and active metal sites of metalloproteins are often ligated by several nitrogens with different hyperfine and quadrupole couplings. In such situation it is very difficult to interpret one-dimensional ENDOR and ESEEM spectra consisting of many nuclear frequencies due to congestion in the spectra and overlap of lines. A fruitful way to improve the spectral resolution is the use of pulse two-dimensional (2D) techniques. They may include three- and four-pulse (HYSCORE) sequences, a recently proposed six-pulse experiment as well as 2D coherent Raman beats. The general advantage of 2D techniques is connected with the creation of the cross-peaks whose coordinates are nuclear frequencies from opposite manifolds. The present work gives an analytical description of the orientationally-disordered contour lineshape for cross-peaks from nuclear spin 1=1 with arbitrary values of isotropic hyperfine interaction, nuclear Zeeman and quadrupole interaction in disordered systems. This approximation was used successfully in numerous cases for the interpretation of nitrogen one-dimensional spectra. The behaviour of the intensity of different cross-peaks is analyzed specifically for the HYSCORE spectra. The influence of anisotropic hyperfine interaction on the lineshape of cross-peaks is qualitatively discussed.

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CW EPR, pulsed ENDOR, one- and two-dimensional ESEEM techniques have been applied to study the influence of acid modifications of Y-A1.0, by H.P0, and H.B0, on the electron acceptor sites using the adsorbed probe molecules such as anthraquinone and o-chloranil. After the adsorption of anthraquinone on activated y-A1.0, the EPR spectra are the superposition of the radicals adsorbed on the surface and three paramagnetic complexes of anthraquinone at coordinatively-unsaturated aluminum sites of different structure. The isotropic hyperfine coupling with aluminum nuclei in these complexes is 3, 21, 28 MHz. The H.P0, treatment of y-A1.0, decreases the concentration of adsorbed radical and complexes with 3 and 21 MHz hyperfine coupling while H.B0, treatment yields only the complex with 21 MHz hyperfine coupling. The resolved EPR structure arises from two equivalent aluminums in this site. The ESEEM spectra show weak dipole-dipole interaction with "P and "B nuclei located in the second shell of paramagnetic complex.

Pacific Northwest National Laboratory is a multiprogram national laboratory operated by Battelle Memorial Institute for the U.S. Department of Energy under contract DE-AC06-76RLO 1830. This research was supported by Associated Western Universities, Inc. Northwest Division (AWU NW) under Grant DF-FG06-89ER-75522 or DE-FG06-92RL-12451 with the U.S. Department of Energy.
CHANGES IN OXYGEN CONSUMPTION DURING DEVELOPMENT: PC-12 CELL DIFFERENTIATION AND T-CELL ACTIVATION. Reef (Philip D., II) Morse, K. Dickerson, and B. T. Donovan. Departments of Chemistry and Biology, Illinois State University, Normal, IL 61790.

We are currently monitoring changes of respiratory rates during cellular development. For these studies, we have chosen the activation of cytotoxic T lymphocytes (which destroy infected cells with bursts of superoxide and peroxide), and the differentiation and apoptotic cell death induced by dihydroxyphenylalanine (DOPA), of PC-12 cells, a neurological precursor cell line. Respiratory rates are measured by changes in linewidth of TEMPOL spectra over time at various developmental stages. Using spectral deconvolution methods (Smimov and Belford, 1995), we can obtain respiration rates from low cell concentrations (10⁴ cells/ml) to eliminate the effects of cell crowding on respiration. At these low concentrations, linewidth changes due to respiration can be easily corrected for TEMPOL reduction. In addition, TEMPOL does not alter the developmental processes at the concentrations we use (10-100 mM). Our preliminary studies show that at 8x10⁵ cells/mL, respiratory rates of undifferentiated PC-12 cells were 4.4x10⁻³⁰ moles of oxygen/min/cell. TEMPOL reduction rates were 4.0x10⁻³⁶ moles of TEMPOL/min/cell, about 1% of the respiratory rate, and were independent of oxygen concentration. This indicates that TEMPOL reduction is probably not a direct function of electron transport activity. Studies on changes in respiratory rates induced by differentiation of PC-12 cells and activation of cytotoxic T lymphocytes are underway. We gratefully acknowledge the financial support of the Beta Lambda Chapter of the Phi Sigma Society and the Illinois State University Department of Chemistry, as well as the technical support of Dr. Alex Smimov, Illinois EPR Research Center, University of Illinois, Urbana-Champaign.

HOW BIG CAN A SMALL HYPERFINE COUPLING BE IN MLMS ENDOR? 94 Peter E. Doan, Brian M. Hoffman, Department of Chemistry, Northwestern University, Evanston IL 60208-3113.

It is almost axiomatic in articles concerning pulsed ENDOR applications that Mims ENDOR techniques are most useful in studies of systems with small hyperfine couplings and Davies ENDOR techniques are better applied when the hyperfine is large. What size hyperfine is small and what is large is actually dependent both upon the instrument and the sample, if the effective deadtime of the spectrometer is x μs, then a Mims ENDOR experiment always is preferred over a Davies for any set of hyperfine values that fall in 0 < A < 1/2x, (A in MHz). In this poster, we describe a technique that uses remote echo detection to decouple the x from the deadtime. This Refocused' Mims ENDOR technique bridges some gaps in performance in pulsed ENDOR studies, especially for A values in the 3-7 MHz range, where often neither a Davies nor a standard Mims ENDOR will give adequate signal-to-noise.

95 STRUCTURAL CHANGES INDUCED IN P21 RAS UPON GAP BINDING AS PROBED BY ESEEM SPECTROSCOPY. Christian T. Farrar, Christopher J. Halkides, and David J. Singel. Francis Bitter Magnet Lab, Massachusetts Institute of Technology, Cambridge, MA 02139, Institute of Molecular Biology, University of Oregon, Eugene, OR 97403, Dept. of Chemistry, Montana State University, Bozeman, MT 59717.

p21 ras acts as a molecular switch in the signal transduction pathway for cellular growth and differentiation. Conformational changes in p21 play an important role in the termination of the growth signal. These conformational changes are normally promoted upon the binding of the protein GAP which increases the intrinsic GTPase rate by 10⁵ fold. Functional models for the hydrolysis mechanism have to date been based solely on structural data from uncomplexed p21. Here we report the first structural study of the p21-GAP complex using Electron Spin Echo Envelope Modulation (ESEEM) Spectroscopy with ¹⁵N-Gly, ¹³Cp-Thr, and ²H₂p-Thr isotope labeling of p21. A dramatic conformational change is observed for a glycine residue upon GAP complexation. This result suggests a pivotal role for a glycine residue in GAP binding and nucleotide hydrolysis. Gly60 is the most likely candidate for this glycine residue. Large H and ¹³C Zeeman signals are also observed in the GAP complexed state indicating that Thr35, weakly coordinated in p21-GTP, moves closer to the Mn ion. Studies of a D57N ras mutant, in which the GAP dependent GTPase is abolished, with Hp-Thr and ¹⁵N-Gly labels provide further support for the importance of residue Gly60 in the GAP dependent GTPase. Based on a comparison of these preliminary studies of GAP bound p21 and isolated p21 mutant structures a model for the conformational change brought about by GAP binding of p21 is proposed.
AN ESR AND CIDEP STUDY OF THE PHOTOCHEMISTRY OF 2,2'-BIPHENOL IN AQUEOUS SOLUTION. Pei-Yun Jiang and Richard W. Fessenden. Radiation Laboratory and Department of Chemistry and Biochemistry, University of Notre Dame, Notre Dame, IN 46556-0579

Laser flash photolysis of 2,2'-biphenol in basic aqueous solutions in the absence and presence of electron scavengers and/or triplet quenchers was studied by time-resolved ESR and optical absorption spectroscopy. Photolysis results in ejection of electrons by mono- and biphotonic processes as well as formation of a triplet state. The triplet state is quenched by oxygen and electron acceptors such as fumarate, trans,trans-muconate, and bromoacetate. Chemically induced dynamic electron polarization (CIDEP) of the radicals derived from the quenchers was studied by TRESR. Electrons from the single photon process show absorptive ESR (A) as the result of radical pair CIDEP involving the singlet radical pairs of eₐq and the phenoxy radical (as is seen with other phenols). Electrons produced in the two photon step show emissive CIDEP (E) as a result of triplet radical pair and/or triplet mechanisms. Electron transfer in the triplet quenching step is proved by the A/E pattern of intensities of the radical products such as the (tri)anion radical of fumarate. This behavior is only possible if the anion radical is formed as one member of a radical pair. CIDEP by random encounters in the cross reaction of the anion radicals with the phenoxy radical was also studied.

EPR CHARACTERIZATION OF NI(III)-TETRACYANATE IN DISORDERED SAMPLES, USING ONE- AND TWO-DIMENSIONAL ESEEM TECHNIQUES
Gyorgy Filep. John L. McCracken, Department of Chemistry, Michigan State University, East Lansing, MI 48824

The stability of Ni(III) in the catalytic site of Ni-Fe hydrogenase enzymes has generated interest in the structure of various model complexes containing Ni(III). One of the simplest of these is the title compound, [Ni(III)(CN)₄(H₂O)₂]⁺. We have studied the shape of the contour lines obtained from hyperfine sublevel correlation spectroscopy (HYSCORE) experiments at g and obtained the hyperfine coupling parameters for samples prepared with ¹⁴N-containing samples in order to determine the nuclear quadrupole constants. This provides further insight into the electronic structure of a Ni(II) complex in a tetragonally elongated octahedral ligand field.

A PULSED EPR STUDY OF THE SUBSTRATE BINDING ENVIRONMENT OF PHOTOSYSTEM II. Dee Ann Force, Gary A. Lorigan, R. David Britt, Department of Chemistry, University of California, Davis, CA 95616-0935

We are using 3-pulse Electron Spin Echo Envelope Modulation (ESEEM) spectroscopy to probe the water-binding pocket of the Oxygen Evolving Complex (OEC) of Photosystem II. A series of small deuterated alcohols which vary in length and bulkiness have been added to PS II membranes. These alcohols are being studied at several concentrations to obtain an estimate of the pocket dimensions; the radial distance of the alcohol's deuterons to the manganese cluster of the OEC are obtained by simulating the ESEEM data.
The incorporation of boron and phosphorus into SiO₂ interlevel dielectric thin films in integrated circuit applications has been known to increase the reliability of devices under certain conditions. Although the macroscopic electronic properties of these films have been empirically related to the processing chemistry variables, little is known about the relationship between these variables and the point defects which dominate the electronic properties of interest. Extensive EPR studies of bulk borosilicate (BSG) and phosphosilicate (PSG) glasses have identified nearly a dozen paramagnetic phosphorus and boron related centers. Limited studies of unpatterned thin-film BSG and PSG have suggested that two of these centers might play a major role in device reliability improvements. We find that at least five paramagnetic centers may play significant roles in the electronic properties of these thin films. Using a combination of EPR and electrical measurements, and charge injection sequences, we have determined charge capture cross-sections of these centers. We find a striking correlation between the charge trapping behavior of these films and the densities of several paramagnetic centers. Our results suggest that several phosphorus-related centers act as electron-hole recombination centers, exhibiting very large capture cross-sections for both electrons and holes.

Work supported by Harris Semiconductor and Dynamics Research Corporation.

Nitric Oxide (NO) has been widely recognized as playing an important role in many biological processes. To elucidate a variety of actions of endogenous NO, information concerning the quantities and distributions of NO in cells, tissues and organs is essential. In this presentation, we demonstrate in vivo EPR imaging of endogenous NO produced in lipopolysaccharide (LPS)-treated mice employing the N-Dithiocarboxysarcosine (DTCS)-Fe complex and 700 MHz EPR spectrometer. We prepared a septic shock model by administering LPS to mice and attempted EPR imaging of endogenous NO that had been trapped by a DTCS-Fe complex in the abdominal region of the mice. About 8 hours after LPS administration we could detect the EPR signal of NO-Fe(DTCS)₂ formed in vivo and could obtain a 2-D EPR projection in the abdominal region of a live mouse. To our knowledge, this is the first example of EPR imaging of endogenous free radicals produced in vivo.
We report the electrochemical reduction of new molecules containing a furane or a thiophene ring bound to the carbon atom of a phosphaalkene moiety. This reduction is quasi-reversible in THF and occurs at -2039 mV (calomel electrode). The EPR spectra of the corresponding radical-anions could be obtained by reacting the phosphaalkene solution on a potassium mirror at 255K. In the liquid phase the proton and phosphorus coupling constants clearly show that the unpaired electron is delocalized on both the heterocycle and the -P=C< double bond. For the furane-containing radical anion ($^3\text{P}$)A$_{\text{iso}}$ is equal to 145 MHz while the couplings with four protons are equal to 18, 12, 11.5 and 4 MHz respectively. For the thiophene-containing anion ( P)A$_{\text{iso}}$ is equal to 137 MHz and couplings with four protons are also detected. The ( P)anisotropic coupling constants could be measured after the reduced solutions had been frozen. This hyperfine tensor is axial and indicates that 35% of the spin lies in a 3p orbital of the trivalent dicoordinated phosphorus atom.

EPR STUDY OF RADICAL-ANIONS GENERATED FROM PHOSPHAALKENES BOUND TO A HETEROCYCLE. Michel Geoffroy, Abdel Al Badri, and Abdelaziz Jouaiti. Department of Physical Chemistry. 30 Quai Ernest Ansermet, 1211 Geneva 4. Switzerland.

HIGH FREQUENCY EPR SPECTROSCOPY OF THE APOGALACTOSE OXIDASE RADICAL
Gary J. Gerfen, Brendan F. Bellew, Robert G. Griffin, David J. Singel, Christopher A. Ekberg and James W. Whittaker. Francis Bitter Magnet Laboratory and Department of Chemistry, MIT, Cambridge, MA 02139.

The activated form of galactose oxidase from the fungus Dactylium dendroides contains a single divalent copper ion which is antiferromagnetically coupled to a protein-based free radical. Chemical oxidation of the apoenzyme generates the free radical which is localized on a covalently cross-linked tyrosine-cysteine residue. This species, together with a model radical generated by UV-irradiation of o-methylthiocresol (MTC), has been studied by high frequency EPR spectroscopy (139.5 GHz/5 Tesla) in conjunction with molecular orbital calculations employing self-consistent local density functional (LDF) methods. The Zeeman interactions determined from the high frequency spectra of the apogalactose oxidase and the MTC model radicals are remarkably similar and support the assignment of the protein radical to a sulfur-substituted tyrosyl moiety. Molecular orbital calculations accurately reflect the experimental data. High frequency echo-detected EPR spectroscopy of the apogalactose oxidase radical resolves hyperfine splittings. Based on the molecular orbital calculations and EPR spectroscopic results presented here, together with results from previous experiments, the hyperfine splittings are assigned to two methylene protons - one derived from tyrosine and one from cysteine.

EPR INVESTIGATIONS OF A KINETICALLY COMPETENT INTERMEDIATE FORMED IN RIBONUCLEOTIDE REDUCTION: EVIDENCE FOR A THIYL RADICAL-COB(II)ALAMIN INTERACTION.
Gary J. Gerfen, Stuart Licht, Jean-Paul Willems, Brian M. Hoffman, JoAnne Stubbe. Francis Bitter Magnet Laboratory and department of Chemistry, MIT, Cambridge, MA 02139.

The ribonucleoside triphosphate reductase (RTPR) from Lactobacillus leichmannii requires adenosylcobalamin (AdoCbl) as a cofactor to catalyze the conversion of nucleotides to deoxynucleotides. RTPR has previously been shown to catalyze the homolytic cleavage of the carbon-cobalt bond of AdoCbl, and the resulting paramagnetic species has been characterized by rapid freeze-quench EPR spectroscopy. This study presents X- and Q-band EPR spectra of this intermediate, referred to as "active coenzyme B12." Modeling this species as a thyl radical coupled to cob(II)alamin by electron-electron exchange and dipolar interactions yields reasonable fits to spectra obtained at both EPR frequencies, while simulations that employ either a single spin model or Cob(II)alamin coupled to a different organic radical do not. This provides support for the intermediacy of a thyl radical in this system. The techniques employed here may prove generally useful in the simulation of similar spectra observed in other Bi2-dependent enzyme systems.
Continuous wave and pulsed EPR methods are used to study the oxygen evolving complex of photosystem II and its manganese model compounds in order to develop structural models. The tetramanganese OEC gives rise to a S = 1/2 ground state in the S2 state of the Kok cycle. Past studies have observed the EPR properties of S = 1/2 manganese model compounds in the form of antiferromagnetically coupled dimers. The model compound K4[Mn(CN)6] is the simplest low spin manganese complex to prepare and has a net spin S = 1/2. Using Electron Spin Echo Envelope Modulation (ESEEM) and Electron Nuclear Double Resonance (ENDOR) we have determined the nitrogen quadrupole parameters for K4[Mn(CN)6] and the 13C hyperfine coupling constant for K4tMn(3CN)6.

Vanadyl model complexes have been investigated by Electron Spin Echo-Electron Nuclear Double Resonance (ESE-ENDOR). The nuclear quadrupole coupling constants determined are sensitive to the coordination environment of the vanadyl ion. The information obtained is useful for the investigation of vanadyl interactions with biological molecules. Currently under investigation is the ribonucleoside-vanadyl complex that serves as a transition state analog for the ribonuclease enzyme.

The reaction of alkali metals with hexa-imine macrobicyclic cryptands with aromatic linking groups can be controlled stochiometrically to produce mono-, di-, and trianion salts. In solution, the macrobicycle mono-reduced ligand with a m-phenylene linkage displays a complex hfs pattern in cw-EPR experiments. The dominant hfs comes from the nitrogen and hydrogen nuclei of the imine moiety in addition to hfs from the alkali metal. Addition of cryptand[2.2.2] to the solution effectively separates the metal cation from the macrobicyclic monoanion collapsing the cw-EPR spectrum to a single line. The latter situation corresponds to solvent separated ion pairs, while the presence of hfs implies contact ion pairing in solution. To investigate the properties of a single strand of the macrobicyclic, a m-phenylene linked di-imine radical anion was prepared. A complex hfs pattern was observed but was not lost when cryptand[2.2.2] was present in solution. The difference between the bicyclic and acyclic cases demonstrates the importance of electron delocalization among the three strands of the macrobicycle taking place on the EPR time scale. EPR spectra of the di- and trianions were less amenable to interpretation, possibly due to complex ion pairing equilibria in solution. In addition, the results of solution ENDOR and ESEEM measurements of the frozen solution will be presented. Details of our method for fitting solution EPR spectra will be described.
MATCHED TWO-PULSE ESEEM- AN APPLICATION OF A NEW DESCRIPTION OF NON-IDEAL MICROWAVE PULSES, Gunnar Jeschke and Arthur Schweiger, Laboratory of Physical Chemistry, Swiss Federal Institute of Technology, 8092 Zurich, Switzerland

A new description of non-ideal microwave (raw) pulses acting on electron-nuclear spin systems is developed that is virtually free of restrictions on mw pulse durations and on the magnitude of the hyperfine coupling. The approach depends on a truncation of the Hamiltonian after two pre-diagonalization steps and provides new insight into a number of recently observed phenomena caused by pulse non-ideality, like nuclear coherence generation by a single mw pulse in the one-pulse coherent Raman beat (CRB) experiment, CRB without pre-excitation pulses, $K-2K$ primary nuclear spin echo formation, and hyperfine decoupling in spin-locked electron spin echo envelope modulation (ESEEM). It is found that forbidden coherence transfers are always maximum at the Hartmann-Hahn match, for which an expression is given that is valid for arbitrary hyperfine couplings and resonance offsets. In contrast to earlier theories we find that forbidden transfers exhibit a slow and oscillatory build-up, so that maximum transfer is achieved at flip angles considerably larger than $TC$. The theoretical results are applied to the design of matched two-pulse ESEEM experiments. Such experiments improve the sensitivity of two-pulse ESEEM for peaks at the hyperfine and basic nuclear frequencies considerably and allow for the discrimination of the two types of peaks. It is found experimentally that in favourable cases the signal enhancement factor may be larger than one order of magnitude and that matched two-pulse ESEEM is well suited for the detection of very weak modulations in the presence of very strong ones.

ELECTRON SPIN ECHO STUDIES OF SPIN POLARIZED RADICAL PAIRS IN PLANT PHOTOSYSTEMS. Asako Kawamori, Hideyuki Hara and Sergei, A Dzuba*. Faculty of Science, Kwansei Gakuin University, Nishinomiya 662, Japan and Institute of Chemical Kinetics and Combustion, Russian Academy of Sciences, Novosibirsk 630090, Russia.

Laser induced Spin polarized signals of radical pairs in plant Photosystem I and II have been studied by two pulse Echoes. The sine Fourier transformed line shapes of the obtained out of phase signals after laser flash have been analyzed for systems of dipolar and exchange coupled radical pairs P- Q". In Zn-substituted (for Fe) Photosystem II, the distance between P680 and the acceptor quinone Q, was estimated to be 29 A, with presence of some heterogeneity.

In Photosystem I natural and A^-substituted (2,3 di-bromo-1,4- naphthoquinone) particles gave the same distances of about 26 A for the radical pairs P700 A A. With an inversion $\tau$t-pulse 1 us after laser pulse, the life time of the spin polarized state was lengthened to several ms from several 10 us without the $\tau$t-pulse at 30 K.

A NEW ONE-ELECTRON OXIDANT: THE STABLE FREE RADICAL CB,Me,+

A stable radical, dodecamethylcarba-hemicloso-dodecaboranyl (1), has been prepared by one-electron oxidation of the cesium salt of the recently reported (King, B. T.; Janousek, Z.; Gruner, B.; Trammell, M.; Noll, B. C; Michl J. J. Am. Chem. Soc, 1996, 118, 3313) weakly coordinating anion CB,Me,+ (2), isolated, and characterized by single-crystal X-ray diffraction and spectroscopic methods including EPR. No ENDOR signal of 1 was observed down to 4 K. Radical 1 is a strong one-electron oxidant which affords the inert and weakly coordinating anion 2 upon reduction, providing a gentle method for the generation of salts of radical cations from oxidizable precursors in both polar and nonpolar solvents. This method has been used to generate a series of radical cations.
DAVIES ENDOR AND HYSCORE MEASUREMENTS OF CAROTENOID CATION RADICALS ON SILICA-ALUMINA SOLID SUPPORT. L. D. Kispert, A.S. Jeevarajan, and P. Hofer, (a) Department of Chemistry, The University of Alabama, Tuscaloosa, Alabama 35487, (b) Bruker Analytische Messtechnik, D-76287 Rheinstetten, Germany.

Carotenoids serve not only as photoprotect agents and accessory light harvestors in the photosynthetic apparatus, but also as antioxidants. Carotenoid cation radicals formed during oxidation can be produced chemically by a heterogeneous process on a silica-alumina catalyst. A previous ENDOR study of the cation radicals or canthaxanthin and 8'-apo-fi-caroten-8'-al on such supports revealed hyperfine coupling constants of only the methyl protons. We have now carried out Davies ENDOR and HYSCORE measurements using the Bruker ESP 380E FT-EPR spectrometer in attempts to obtain better spectral resolution for the carotenoid cation radicals on the silica-alumina disordered system. C-13 couplings have been observed in the HYSCORE spectra and are in general agreement with RHF-INDO/SP derived couplings. Comparisons of the various spectral measurements will be presented. This work was supported by the Division of Chemical Sciences, Office of Basic Energy Sciences, Department of Energy, under grant DE-FG-86ER13465.

EPR CHARACTERIZATION OF Cu(II) IONS IN SINGLE CRYSTALS OF THALLIUM COBALT SULPHATE HEXAHYDRATE. M. Krishna. EPR Group. Materials Characterization Division, National Physical Laboratory, New Delhi - 110 012, India.

EPR measurements on single crystals of Cu(II) ion doped in thallium cobalt sulphate hexahydrate have been performed over the temperature range 120 - 390 K at X-band (9.205 GHz). The angular orientation dependence of EPR spectra reveal that the impurity ions enter at the divalent cobalt site in the lattice, exhibiting two symmetry related equivalent complexes. The g- and A-tensors have been estimated and found to be axially symmetric and dependent on temperature. The ground state is suggested to be mainly $\alpha,\beta_-,\beta_+$ orbital. The Fermi contact (K) and covalency parameter (a) are evaluated from the principal parameters and indicate more covalency of the Cu(II) ion with the ligands at room temperature which further increases at the lower temperatures.

PHARMACOKINETIC AND PHARMACODYNAMIC STUDIES ON FREE AND MACROMOLECULE-BOUND NITROXIDES BY EPR SPECTROSCOPY AND IMAGING Periannan Kuppusamy, Li Ma*, Honghua Qin, Penghai Wang, Charles E. Trimble*, Jay L. Zweier, & Carleton J. C. Hsia National Institute of Environmental Health Sciences, Division of Cardiology and the EPR Center, Johns Hopkins Medical Institutions, 5501 Hopkins Bayview Circle, Baltimore, MD 21224; Synzyme Technologies, Inc., One Technology Drive, Suite E-309, Irvine, CA 92718

The development of stable nitroxyl radicals as free radical scavengers and antioxidant enzyme mimics for therapeutic use has been frustrated by their rapid bioreduction to the hydroxylamine form in vivo (Kuppusamy et al., Proc. Natl. Acad. Sci. 91, 3388, 1994). To address this problem we have created a new class of compounds by covalently linking nitroxides to biological macromolecules. We have recently reported that polynitroxylated (PN) albumin (PNA) can reoxidize the hydroxylamine back to nitroxide in vivo (Kuppusamy et al., Biochemistry, 1996, in press). We have prepared a PN hemoglobin derivative (PNH) for use as a red cell substitute, and particularly as a therapeutic agent for the reperfusion of ischemic tissue without reperfusion injury ("protected reperfusion"). This PNH is also capable of reoxidizing hydroxylamine to nitroxide in vivo. This indicates that it is capable of participating in redox reactions in the vascular space. Plasma PNH concentrations corresponding with bound nitroxide concentrations of up to 30 mM are well tolerated in the mouse and rat. The plasma half-life of the nitroxide when attached to the macromolecule is more than one hour, as compared with less than a minute for free nitroxide. The ability of PN molecules to maintain therapeutic plasma nitroxide levels for a prolonged period of time appears to be the basis for our observations of protection in animal models of free radical-mediated diseases including myocardial infarction, stroke, and ionizing radiation injury. (Supported by NTH grants 1 R43 HL 53860-01 and HL-38324)
The interaction of the native peptide α-MSH and the biologically more active analog [Nle\(^4\), D-Phe\(^7\)]-α-MSH with lipid vesicles was studied by spin label ESR spectroscopy and circular dichroism (CD). Using spin labels located at the membrane interface and at different depths along the acyl chain it was shown that the binding of both peptides to the membrane induces tighter lipid packing at all the monitored positions. However, the effect of the analog on the spin label ESR parameters was much more evident, and suggested that it penetrates farthest into the lipid matrix than the native molecule. Lipid partition coefficients were calculated based on the effect the peptides cause on the ESR spectra of spin labels incorporated in the membrane. For the biologically more potent peptide, the partition coefficient was found to be about four times greater than that of the native hormone. Furthermore, for the same concentration of peptide bound to the membrane, MSH-I was found to cause a greater effect on the membrane structure than α-MSH, in accord with its deeper penetration into the bilayer. CD results in aqueous solution and in the α-helix inducing solvent 2,2,2-trifluoroethanol, showed that the two peptides have somewhat different structures in solution, though similar conformational changes occur in both peptides as a result of their interaction with negatively charged vesicles or micelles. The higher peptide-lipid association constant and the deeper penetration of the analog into lipid bilayers could be related to its greater activity and/or prolonged action. (Financial support: FAPESP, CNPq and FINEP).

FREE RADICAL INTERMEDIATES IN THE MAILLARD REACTION, Roger V. Lloyd, Department of Chemistry, University of Memphis, Memphis, TN 38152

The Maillard (browning) reaction is an extremely complex reaction between amines and carbohydrates that ultimately yields poorly-defined, dark-colored polymeric end products. The initial stages, however, proceed via radical intermediates, which appear to be substituted dihydropyrazine cation radicals. Using glyceraldehyde or glycolaldehyde as the carbohydrate with an \(N, A^\text{dialkylethlenediamine}\) as the amine (alkyl = Me, Et, iPr) in aqueous buffer (Tris or phosphate), we have identified and characterized two series of dihydropyrazine radicals (a 1:1 sugar : amine product and a 2:2 product). In methanol (alkyl = iPr, tert-Bu) we have also observed nitroxide radicals in addition to the 2:2 product. The work is now being extended to the study of radical formation in mouse skin with solutions of dihydroxyacetone or glucose.


Superhyperfine couplings of \(N\) to the oxovanadium (vanadyl, \(V\,^0\)) cation have been well-characterized by ESEEM, in the case where nitrogen is an equatorial ligand. To date, however, there has been very little work published regarding axial nitrogen ligands to \(V\,^0\), and a full spectroscopic characterization of such ligands has yet to appear. In the present work, preliminary stimulated echo ESEEM measurements on a series of model complexes in 50% water/glycerol solution are described. Under proper conditions, the complexes form in solution in the same way as in single crystals. In each case, the axial ligand to \(V\,^0\) is a tertiary amine nitrogen, while equatorial ligands are various combinations of carboxylate, hydroxylate, water, carbonyl oxygen, and pyridine nitrogen. Simulations of the ESEEM data show that the isotropic component of the tertiary amine nitrogen's superhyperfine coupling is \(|\alpha| = 18\) MHz, and that this value is effectively independent of the equatorial ligands. These results have major implications for interpretation of recent measurements on \(V\,^0\) in proteins. For example, in chloroplast F1-ATP synthase, there appears to be a primary amino nitrogen axial ligand to the cation, at the M3 metal-binding site.
116 EPR SPECTROSCOPY OF S-NITROSO HEMOGLOBIN. Ben P. Luchsinger, Joseph Bonaventura, Jonathan S. Stamler and David J. Singel, Montana State University, Bozeman MT 59717 and Duke University Medical School, Durham, NC 27700

S-nitrosylation of \( \beta \) cys-93 confers upon human hemoglobin potent vasorelaxant activity that is subject to allosteric control by \( O_2 \) coordination and by the redox status of the heme iron. This allosteric regulation has motivated us to probe the structural basis by which the communication between the heme and sulfhydryl sites is conducted. We report the results of EPR and optical spectroscopic measurements that illuminate this pathway. These spectroscopic measurements also reveal chemical interactions that stem from the proximity of the nitroso-thiol and heme iron in S-nitroso hemoglobin.

117 A HUMAN-SCALE FREE RADICAL IMAGER USING FIELD-CYCLED PEDRI

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Proton-Electron Double-Resonance Imaging (PEDRI) has been developed over the last decade. An NMR image is collected while the ESR of a free radical of interest is irradiated. The Overhauser effect causes an enhancement of the NMR signal from parts of the sample containing free radicals, and these regions exhibit greater intensity in the final image. PEDRI has previously imaged nitroso free radicals in living, anaesthetised rats, using an imager operating at 100 Gauss, with EPR irradiation at 237 MHz (Phil.Trans.Roy.Soc.Lond. A 333, 453 (1990)). In scaling up the sample size, problems with rf penetration and heating occur, and an elegant solution is provided by Field-Cycled PEDRI (FC-PEDRI), where the applied magnetic field is switched rapidly between two levels during the pulse sequence (J.Magn.Reson. 84, 431 (1989)). EPR irradiation is applied at very low field (hence low frequency and power, plus good penetration) and NMR signal detection occurs at higher field (hence good SNR and image quality). We have constructed a whole-body sized FC-PEDRI imager to image free radicals in large animals and, potentially, in humans. The apparatus uses a whole-body permanent magnet (585 Gauss, 2.5 Mhz proton frequency) with an internal "field-offset" coil. Energising this coil lowers the applied field for the EPR irradiation period. We have used the FC-PEDRI imager to image the distribution and clearance of PCA nitroxide injected into anaesthetised, adult New Zealand White rabbits (~2 kg). EPR irradiation was at 30 Gauss at a frequency of 51 MHz. We believe that this is the first time free radicals have been imaged in any animal larger than a rat.

118 ELECTRICAL DETECTION OF EPR AND ENDOR OF DEFECTS IN SEMICONDUCTORS

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Conventional EPR and ENDOR methods are not suitable to investigate small concentrations of defects in thin epitaxial layers or small volumes such as one has in diodes, transistors etc. because of sensitivity problems. It is shown that EPR can be measured as a change in photoconductivity with very high sensitivity and even spatial resolution independent of the microwave frequency used, if the defect is involved in a kind of donor-acceptor recombination process. It has also been possible to measure ENDOR this way. Compared to conventional ENDOR, the ligand ENDOR signals were particularly intense when using electrical detection. This opens up new possibilities to study semiconductor defects, which will be illustrated with current examples.
ENDOR spectroscopy is a powerful technique for determining the electronic structure of paramagnetic centres in semiconductor materials. There are two principal limitations of conventional ENDOR spectroscopy: low sensitivity and low spectral resolution. These limitations may be partially overcome by using pulsed ENDOR at high magnetic field and high microwave frequencies. First of all, in pulsed experiments the ENDOR effect may be as large as ESR signal itself. Secondly, high absolute sensitivity and high spectral resolution can be achieved by going to high magnetic field. In this contribution we present the results of 95 GHz pulsed ENDOR/ESR studies of paramagnetic centres in two types of materials. The first study concerns the intrinsic shallow electron centre (SEC) in the AgCl. Here the analysis of the ENDOR spectra of the Ag and Cl nuclei enables us to establish the structure and reconstruct the envelope wave function. It appears that the intrinsic SEC is located on a Ag lattice position and trapped in the Coulombic field of two adjacent Ag ions symmetrically placed on a single cationic site. The second study concerns the shallow B acceptor in the C-enriched 6H-SiC crystals. Here the high frequency ESR/ENDOR results allow us to build a consistent model for the electronic structure of the centre. From a Si and C ENDOR study it is concluded that 60-70% of the spin density is distributed in the crystal with a Bohr radius of 2.2 A, a value that is in reasonable agreement with effective mass theory.

SYNTHESIS OF Bai-,K,Bi03 CERAMIC SPECIMENS: ELECTRON PARAMAGNETIC RESONANCE AND MICROWAVE ABSORPTION. Sushil K. Misra, Serguei I. Andronenko, Rosa R. Andronenko, Larisa P. Mezentseva, a) Physics Dept., Concordia University, 1455 de Maisonneuve Blvd W., Montreal H3G 1M8 Canada, b) Inst.of Silicate Chemistry, St. Petersburg 199155, Russia

Bai-,K,Bi03 ceramic samples were synthesized with many initial relative amounts of reagents. Chemical analysis revealed that only four values of x = 0.13, 0.25, 0.4, 0.5 with Ax = 0.03 were possible. EPR and microwave-absorption investigations of the synthesized ceramic specimens were carried out in the temperature range 4-100 K. In the two nonsuperconducting specimens x = 0.13, 0.25 the same two EPR lines at g = 2.09 and 4.25 were observed, whose intensities increased sharply below 40 K, likely due to the phase Bao,g75Ko,i25Bi0. Variation of the intensity of the line at g = 4.25 for the sample with x = 0.13 due to a transition within the energy levels belonging to the excited triplet state of hole pairs localized on the oxygen ions, in accordance with (1/T)exp(-Jp/T), yielded the value of the exchange constant Jp = 2.3±0.5 K. Low-field microwave absorption and X-ray diffraction by the superconducting specimens with x = 0.4, 0.5 reveal the presence of two different superconducting phases: one, with x = 0.375, possessing Tc = 16 K. Four possible configurations of the solid solutions Bai-,K,Bi0, have been proposed based on the present data.

PULSED ELECTRON SPIN RESONANCE STUDIES OF Cu(II) SITES AND ADSORBATE INTERACTIONS ION EXCHANGED INTO SILICOALUMINOPHOSPHATE TYPE 18. Tomasz Masowicz, Sun Jin Kim, Suk Bong Hong and Larry Kevan, University of Houston, Chemistry Department, Houston, TX 77204-5641, Korea Institute of Science and Technology, P.O. Box 131, Seoul 130-650, Korea.

The silicoaluminophosphate type 18 (SAPO-18) is a medium-pore molecular sieve and is of interest as a support for heterogeneous catalysts. A SAPO-18 material was synthesized with an Al: P: Si ratio of 10: 9: 1 with the silica substituting selectively only the phosphorus sites. Divalent copper ion exchanged into SAPO-18 from an aqueous solution of CuCl2 was used as a spin probe to examine its location in the ion-exchanged SAPO-18 and its interaction with small molecular adsorbates. To monitor the Cu(II) interactions with the local environment electron spin resonance (ESR) and three-pulse electron spin echo modulation was used. Taking advantage of the presence of 31P in the framework and based on 29Si MAS NMR results that Si is located only in phosphorus sites, 31p modulation has been used to determine the distance and number of P from the Cu(II) ion at various stages of hydration of the material. Using deuterium-labeled adsorbates including D2O, ND3, CD3OH and CH3OD and analyzing the D modulation from three-pulse electron spin echoes the distances between the CuH3 and the adsorbed molecules are derived. Additionally, the interaction with ND3 ammonia is supported by ESR results obtained for Cu(II)-15NH3, for which the 'N hyperfine interaction is resolved and reveals the number of interacting 'N.
RECENT IDENTIFICATION OF PARAMAGNETIC DEFECTS IN DIAMOND. J.M. Baker*,
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Superabrasives, Worthington, Ohio, USA.

Although EPR was first observed in diamond in 1954, only a few paramagnetic centres had been
assigned an unambiguous model by 1988. Since then, the use of ENDOR, initially mainly of 14N,
facilitated the characterization of many nitrogen containing defects. In the last two years, the availability
of diamonds of high purity and perfection, grown with enriched 13C content by chemical vapour deposition
and subsequent single crystal growth at high temperature and pressure, has revolutionised the study of
radiation induced defects. Following the identification of the negative vacancy by Isoya in 1992 using
ESEEM, we have used ENDOR and EPR to identify: (a) the optically excited 5A2 state of the neutral
vacancy, (b) a coupled system of nearest neighbouring [100] split interstitials, and (c) a coupled system of
two nearest neighbouring vacancies. The features of the magnetic resonance spectra which provide
unambiguous characterization will be reviewed, together with other information which can be deduced about
energy level structures, and the mechanisms and kinetics of formation and annealing, of the defects.

SOPHE - NEW METHODOLOGIES FOR THE ANALYSIS OF RANDOMLY ORIENTATED EPR
SPECTRA. Graeme R. Hanson and Deming Wang, Centre for Magnetic Resonance, The University of
Queensland, Brisbane, Queensland, Australia, 4072.

A new software package named SOPHE after the Sydney Opera House for computer simulation of
randomly oriented powder spectra in magnetic resonance will be described. A central feature of SOPHE is that
all interactions associated with the electronic and nuclear spins are treated equally through matrix diagonalisation.
In order to make this approach "workable", several new methodologies have been developed which include, a
novel partition scheme for partitioning the unit sphere, an interpolation scheme involving a combination of global
cubic spline and local linear interpolation and a segmentation method for handling multiple resonances between
given pair of energy levels. The SOPHE package can be used to simulate randomly orientated, solution and
single crystal EPR spectra arising from isolated paramagnetic spin systems (S^Vi) and complex coupled spin
systems (Sj, S^Vi). Representative examples will be shown.


IN VIVO EPR DETECTION OF RAT HEMOGLOBIN THIYL RADICAL ADDUCT.
JinJie Jiang, Ronald P. Mason, Sandra J. Jordan: Laboratory of Molecular Biophysics, National Institute of
Environmental Health Sciences, National Institutes of Health, Research Triangle Park, NC 27709; Ke Jian
Liu, Harold M. Swartz: Department of Radiology, Dartmouth Medical School, Hanover, NH 03755

The spin-trapping technique in conjunction with a low-frequency electron paramagnetic (QPR or ESR)
spectrometer was used to detect the hemoglobin thiyl free radical in living rats using a whole body resonator. The
hemoglobin thiyl free radical was formed following the intragastric (i.g.) administration of phenylhydrazine at the LD50
dose of 188 mg/kg. The hemoglobin thiyl free radical was then trapped by pre-injected 5,5-dimethyl-1-pyrrolineN-oxide
(DMPO), which formed the DMPO/hemoglobin thiyl free radical adduct in the blood. The time course of the in vivo
formation and disappearance of the spin adduct was followed. The DMPO/hemoglobin thiyl free radical was detected in
blood samples using 9.5 GHz (X-band) and 11 GHz (L-band) EPR at room temperature and 77 K. Pretreatment of rats
with ascorbate and diethylmaleate (DEM) decreased the signal intensity of the DMPO/hemoglobin thiyl free radical spin
adduct. The incubation of ascorbate and DEM at 37° C with rat blood containing preformed DMPO/hemoglobin thiyl
radical adduct showed that there was no effect of DEM on the free radical adduct concentration, while a significant effect of
ascorbate on the radical adduct concentration was observed. This study provided direct evidence of the formation of the
DMPO/hemoglobin thiyl free radical in vivo, and enabled us to study this formation in living animals free of any artifacts
that can occur when using ex vivo methods.
AQUEOUS MICROVISCOSITY OF MURINE SARCOMAS AND NORMAL LEGS IN VIVO WITH LOW FREQUENCY EPR: IMPLICATIONS FOR MRI AND THE PHYSIOLOGY OF TUMORS


Microviscosity is the highly localized viscosity measured with nitroxide EPR linewidth differences. The spin probe used is the nitroxide 4-protio-3-carbamoyl-2,2,5,5-tetramerdeutero-methyl-1-N-pyrrolin-1-lyoxy (mHCTPO) which distributes in the total body water. The spin probe was infused IP into C3H mice. High and low field manifolds were measured from mHCTPO localized in either mouse leg or a mouse leg bearing 12 mm FSA or NFSa fibrosarcomas. Extraction of the linewidths was accomplished with spectral fitting. Microviscosity was evaluated from the differences in the high and low field manifold linewidths. Calibration used fetal bovine serum albumen. Measurements now extend over a total of 38 tumors, 20 FSA and 18 NFSa fibrosarcomas. A total of 14 normal legs were also measured. No significant difference was seen between tumor types. The mean normal leg microviscosity was 2.9±0.3 cP. The mean tumor microviscosity was 1.8±0.1 cP. It is difficult to distinguish a relationship between size and microviscosity, consistent with the minimal necrosis in these tumors. A highly significant difference was seen between tumors and normal tissues. The magnitude of this difference is consistent with differences in transverse relaxation times (T2) measured in similar rodent tumors and normal tissues (soft tissue sarcomas and muscle in rats). Implications of this and other aspects of this viscosity difference will be discussed.

TRYPTOPHAN SPECIFICITY IN THE SELF-PEROXIDATION OF METMYOGLOBIN BY HYDROGEN PEROXIDE

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The protein-centered radical formed in the reaction between metmyoglobin and hydrogen peroxide was recently shown using electron spin resonance (ESR) spectroscopy and spin-trapping to be centered on a tryptophan residue. Recombinant wild-type metmyoglobin prepared using 13C-labelled tryptophan was used to positively confirm formation of a peroxyl radical on tryptophan. To determine which of the two conserved up residues forms the previously detected peroxyl radical, site-directed mutant sperm whale myoglobins were prepared in which trp-7, trp-14, or both were replaced with phe and the resultant mutant proteins were expressed and purified from Escherichia coli. The mutant myoglobins were oxidized with one equivalent of hydrogen peroxide per heme and frozen, and the direct ESR spectra of the frozen solutions were recorded. Peroxy radicals were detected after aerobic reactions between hydrogen peroxide and the wild type and trp-7-phe recombinant proteins, but when trp-14 was replaced by phe, the ESR spectrum of a peroxyl radical was replaced by that of an unknown species. Spectra obtained from the up mutants were compared to those obtained from mutant sperm whale myoglobins in which one, two, or all three tyrosine residues were replaced with phenylalanine and with the mutant protein in which the distal histidine residue was replaced with valine. Peroxy radicals were detected after aerobic reactions in all proteins that contained trp-14, although the signal was very weak in the his-64-val mutant. The results suggest that peroxyl radical formation occurs only at trp-14. The aerobic and anaerobic ESR spectra of the trp-14-phe mutant have identical features, suggesting that the radical detected in that mutant represents a secondary, electron hole on the protein which is used when trp-14 is unavailable. Our results confirm the spin-trapping-derived identification of a tryptophan residue as the site of detectable self-peroxidation of metmyoglobin.

AMINOXYL RADICAL DOSIMETRY: QUANTITATIVE DETERMINATION OF RADIATION-INDUCED TRANSIENT FREE RADICAL YIELDS BY EPR. Keith P. Madden, Notre Dame Radiation Laboratory, University of Notre Dame, Notre Dame, IN 46556-0579

Conventional field-modulation EPR techniques have long been used successfully to determine the concentration of persistent free radicals in a wide variety of systems. Transient free radical concentrations produced by ionizing radiation, however, have been more difficult to assess due to the lack of a reliable dosimeter. We have used the reduction of the aminoxyl radical TEMPONE (4-oxo-2,2,6,6-tetramethyl-piperidinooxy) in an aqueous solution containing 400 micromolar TEMPONE and 20 mM sodium formate as a dosimeter for in situ radiolysis ESR experiments to quantify the yield of radiation-induced free radicals in aqueous solutions. The G-values for the dosimeter in nitrous oxide- and nitrogen-saturated solutions indicate quantitative destruction of the aminoxyl radical corresponding to the yield of radiation-induced primary water transients. Due to the moderate relaxation time of the aminoxyl radicals, CIDEP is not a complicating factor in the use of this dosimeter.
FT-EPR STUDY OF THE PHOTOCHEMISTRY OF SOME ORGANO METALLIC COMPLEXES. Debora Martino, Cornells J. Kleverlaan, Hans van Willigen and Ad Osham. Chemistry Department, University of Massachusetts at Boston, Boston MA, 02125-3393, USA. Anorganisch Chemisch Laboratorium, Universiteit van Amsterdam, 1018 WV Amsterdam, The Netherlands.

A FT-EPR study was made of organic free radicals R* formed by pulsed-laser excitation of the organometallic complexes Re(R)(CO)(bpy) and Ru(R)(iPrDAB), with R = methyl, ethyl, isopropyl, benzyl, bpy and iPrDAB are bipyridyl and diisopropyl-1,4-diaza-1,3-butadiene, respectively. Information on the mechanism and kinetics of the photo-induced homolysis of the metal-R bond was obtained by studying the time evolution of the FT-EPR spectra given by the alkyl radicals. The spectra display CIDEP effects which are strongly solvent dependent. The origin of this effect will be discussed.

Acknowledgment: Financial support for this work was provided by the Division of Chemical Sciences, Office of Basic Energy Sciences of the US Department of Energy (DE-FG02-84ER13242).

DAMAGE TO CU, SITE OF CYTOCHROME C OXIDASE IN SAMPLES PURIFIED BY AFFINITY COLUMN CHROMATOGRAPHY. Susan M. Monroe, Gareth R. Eaton, and Sandra S. Eaton, Department of Chemistry and Biochemistry, University of Denver, Denver, CO 80208.

Purification of cytochrome c oxidase using a sepharose 4B-cytochrome c affinity column results in a type-2 Cu(II) EPR signal that is superimposed on the characteristic signal for CuI. The intensity of the type-2 signal corresponds to about 20% of the enzyme. The type-2 signal is attributed to damage to the dimeric CuI site that causes a substantial change in coordination of the Cu(II) at that site and/or release of Cu(II) from the CuI site and coordination to another site on the enzyme. Enzyme isolated by affinity chromatography did not contain summit III. Loss of this subunit has been linked to damage at the CuI site. The heme a and heme sites in the affinity column-isolated enzyme appear to be normal.


Partitioning of small piperidine-based nitroxides (2,2,6,6-tetramethyl-piperidine-N-oxyl-4-R) into lipid bilayers followed by examination of these systems through electron paramagnetic resonance (EPR) spectroscopy have provided useful information concerning the structure and function of the cell membrane. However, there are classes of membranes which do not readily lend themselves to partitioning studies by these nitroxides (for example, the red blood cell membrane). Additionally, piperidine-based nitroxides are typically spherically symmetric and do not provide much information about directional anisotropy in the lipid regions of membranes. Therefore we have developed a panel of oxazolidine-derived nitroxides of increasing chain length to both permit partitioning studies in formerly inaccessible membrane systems and to provide structural and hence motional anisotropy. We will describe the synthesis, derived from the method of Keana et al., of this series of nitroxide spin label probes and their characterization by IR, NMR, and mass spectrometry. Experimental results on partitioning and motion by X- and W-band EPR of these nitroxides in lipid bilayers (liposomes) of dipalmitoylphosphatidylcholine and phospholipid mixtures will also be presented and discussed.
MAGNETIC INTERACTIONS AND AROMATIC RING STACKING: AN EPR STUDY WITH THE TWO SYSTEMS
dichlorobis AND dibromobis-l-phenyl-3,5-dimethylpyrazole.
Otaciro R Nascimento, Antonio J.Costa-Filho, Claudia Munte, Pedrina Mattioli* and Rafael Calvo+
Instituto de Fisica de Sao Carlos-USP-Brazil, 'institute de Quimica de Araraquara-UNESP-Brazil, INTEC-CONICET-UNL-Santa Fe-Argentina

We report the synthesis and the structural and magnetic characterization of two new compounds, dibromobis(pdmp)copper(II) [CuBr2C22H24N4] (1) and dichlorobis(pdmp)copper(II) [CuCl2C22H24N4] (2), where pdmp=l-phenyl-3,5-dimethylpyrazole. Their structures were solved by the standard Patterson method followed by normal difference Fourier techniques. They were refined by full matrix least squares to R=0.095 and R=0.055, respectively. Compound (1) belongs to the space group P21/n with a=16.165(5)A, b=10.432(3)A, c=13.385(4)A, and Z=2. Compound (2) belongs to the space group P21/c with a=8.379(2)A, b=22.630(2)A, c=12.256(2)A, and Z=4. Detailed single crystal EPR measurements have been performed in single crystal samples of (1) and (2) at 9.4 and 34 GHz, at room temperature. The variation of the position and linewidth of the EPR lines were measured as a function of the magnetic field orientation. The data were used to study the electronic properties of the copper ions and to evaluate the exchange interactions between them, which are transmitted through the stacking of aromatic rings. Our results are discussed in terms of the electronic pathways provided by the stacking of pyrazole and phenyl rings of neighbor molecules in the structures of the compounds (1) and (2).

SPIN LABELLED TAXOL ANALOGUES REVEAL MICROTUBULE ASSEMBLY
Rina Nicholov, Winnie Y. Ho, Frank DiCosmo, Institute of Biomedical Engineering, University of Toronto, Ontario, MSS 1A4

Taxol is important natural anticancer agent. It binds to cellular microtubules and stabilizes microtubule assembly. Here we use three novel taxol analogues, containing nitroxyl free radicals to study the effect of microtubule assembly on the molecular mobility of taxol after binding to its tubulin target site. Taxol was modified at the carbon 2 or 7, of the taxane ring, and at C2' and 3'N of the side chain to yield a taxol biradical. All three analogues have tubulin polymerization activities. The spin labels C7 and C2 are sensitive to the process of tubulin polymerisation. They indicate significant restrictions on the mobility of the nitroxyl moiety after microtubule assembly, initiated by increased temperature. We assume taxane ring where the nitroxyl moieties attached is localized to a segment of tubulin that becomes more ordered after microtubule assembly, apparently due to adjacent protofilament interaction. In contrast, ESR spectra of biradical-taxol-spin probe SP-2'3' show no significant alteration during the process of tubulin polymerisation. The energy exchange between the two nitroxyls varied with temperature, however no drastic change was recorded associated with the microtubule assembly.

TWO-DIMENSIONAL IN-VIVO IMAGING USING RADIOFREQUENCY LONGITUDINALLY-DETECTED ESR (LODESIR IMAGING). Jan Nicholson, Margaret A. Foster, Fraser J.L. Robb, James M.S. Hutchison and David J. Lurie. Dept. of Bio-Medical Physics, University of Aberdeen, Foresterhill, Aberdeen, AB9 2ZD, UK.

In this work we have imaged the distribution of an injected nitrooxide free radical in the rat using LODESR imaging (Nicholson, I. et al. J. Magn. Reson. B104, 284-288, 1994). Longitudinal detection involves amplitude modulating the ESR irradiation and observing the oscillations in the spin magnetisation parallel to the main field. The LODESR coil assembly consists of a birdcage resonator (length 3.0 cm, diameter 7.5 cm) tuned to 300 MHz, for excitation of the ESR resonance. The signal is detected with a continuously wound solenoid (length 4.5 cm, diameter 6.5 cm) placed inside the birdcage resonator and tuned to 200 kHz. Two magnetic field gradients, transverse to the main field, were generated with D coils placed at the ends of the RF coil assembly. Sprague Dawley rats (~200g b.w.) were anaesthetised with i/p ketamine/xylazine. A cannula was surgically implanted into the left external jugular vein so that further anaesthetic and the free radical could be delivered without disturbing the animal in the imager. Rats were positioned in the detection coil so that either the heart, kidneys or bladder were approximately in the centre. The relatively short length of the birdcage resonator gave some degree of selection along the coil axis. Animals were given a dose of 2mmol/kg b.w. of bicarbonate buffered proxyl carboxylic acid (PCA) via the cannula. Within one minute after injection a LODESR signal was observed from the abdominal region. Sequential images showed the clearance of PCA through the kidneys and bladder. Animal motion did not affect the noise level in the images since the performance of the low frequency detection coil is not significantly affected by electrically conductive samples.
LOW-MAGNETIC-FIELD PULSED DNP RELAXOMETRY. B. Odintsov * R L. Belford,* 135 and R.B. Clarkson,** Illinois EPR Research Center and Departments of Veterinary Clinical Medicine and •Chemistry, University of Illinois, 190 MSB, 506 S. Mathews, Urbana, IL 61801, USA; also Zavoisky Institute, Kazan State University, Kazan, Tatarstan, Russia.

Dynamic nuclear polarization between unpaired electrons and magnetic nuclei can be induced instrumentally by pumping the electronic Zeeman transitions and observing intensity changes in the NMR signal. Both scalar and dipolar coupling between I and S can provide pathways for polarization. The pathways associated with dipolar coupling include spin transitions described by operators S1+ and S1-, which become more forbidden as B increases. Therefore, in many systems, low magnetic fields are most useful in achieving strong DNP effects. Keeping this in mind, we have developed a DNP spectrometer operating at about 100 G. It utilizes pulsed rf at 280 MHz, amplified by a Henry Radio 2 kW amplifier, as the electronic Zeeman pumping source, and observes spin echoes at a nuclear (proton) Larmor frequency of 425 kHz. Two concentric helical coils are tuned for the electron magnetic and nuclear magnetic resonance frequencies. Signals are averaged on a digital oscilloscope and read into a computer for analysis.

We will discuss the design of the DNP spectrometer, as well as report on a variety of experiments currently under way in our laboratory that make use of it. In particular, we shall describe how the instrument can be used to measure T2 and T1, in fast-relaxing metal ion systems (T2 < 10-5 sec) in aqueous solution, as well as to probe mechanisms of electron-nuclear relaxation and investigate I.S coupling at liquid-solid interfaces.

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EPR SPIN TRAPPING OF AMMONIUM DINITRAMIDE (ADN) RADICALS FROM
AQUEOUS PHASE DECOMPOSITION AND LIVER ENZYME METABOLISM,
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Ammonium dinitramide (ADN) (NH4N(NO2)2-) is an oxidizer for potential replacement of ammonium perchlorate in solid rocket fuels. Free radicals generated by ADN were detected by N-tert-buty1-a-phenylnitrone (PBN) spin trapping of liver enzyme metabolites and by PBN and ad-nitromethane (NM) aqueous phase decomposition of ADN using electron paramagnetic resonance (EPR). Within 5 minutes, in the presence of 10 mM PBN, ADN hydrolysis (pH 7) yielded a 1:2:2:1 quartet EPR spectrum having hyperfine couplings (hfcs) of a(14N) = a(H) = 1.42 mT. Further hydrolysis produced a second radical species with hfcs of a(14N) = 1.65 mT and a(H) = 0.4 mT. In basic aqueous solution (pH 12), quantitative NM trapping of N02 from photodecomposition of ADN indicated accelerated ADN decomposition with TiO2, catalysts. Incubation of ADN with lyophilized liver gave a 75% reduction of free radical concentration after one hour exposure to 10 mM ADN as compared to only 5 minutes of ADN exposure. A continuous increase of free radical concentration was observed in liver without ADN incubation. Because ADN solubility in water is very high (500 g/L), our studies indicate that ADN free radical chemistry must be considered in risk assessment.
DIRECT MEASUREMENT OF ZERO FIELD SPLITTING OF DIVALENT NICKEL IN A ONE-DIMENSIONAL SYSTEM BY HIGH FREQUENCY - EPR SPECTROSCOPY.

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The studies of divalent nickel linear chain compounds have a vast audience as the simplest practical realization of Haldane systems. The Ni(II) ion is well known to have a single ion anisotropy in many of its octahedral complexes, which is larger than the quantum of the microwave radiation at X- and Q-band. In this case the new High Frequency EPR techniques, allowing quanta from 3 to 20 cm\(^{-1}\) (95 - 600 GHz) are a valuable tool. The series of linear chain compounds Ni(ox)L\(_2\) (ox = oxalate, L = imidazole) are prone to doping with Zn(II) in any possible Ni/Zn ratio. Spectra of polycrystalline powder of Ni\(_{0.7}\)Zn\(_{0.3}\)(ox)(1-2-DMZ)\(_2\) in the 110 to 330 GHz frequency range are presented. From the spectra the sign and size of the ZFS parameter of Ni(II) are extracted.

PULSED EPR STUDIES OF PHOTOSYSTEM II SEMIQULNONE RADICALS

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The Q\(^\Lambda\) radical of PS II complexes isolated from spinach and Synechocystis has been studied using two and three pulse ESEEM spectroscopy in order to characterize the quinone binding site. These experiments reveal that in both the magnetically coupled iron-quinone system of spinach PSII complexes as well as the magnetically uncoupled iron-quinone system of cyanide treated PS II complexes the Q\(^\Lambda\) radical is coupled to at least two different nitrogen nuclei, one of which can be assigned to a peptide nitrogen based upon its quadrupole parameters. Complementary studies of cyanide treated, isotopically labeled PS II complexes from Synechocystis show that neither of these two nitrogens are from a histidine residue as would be predicted from the crystal structure of bacterial photosynthetic reaction centers. Interestingly, Fe-depletion and Zn-reconstitution of the spinach PS II complexes leads to the coupling of the Q\(^\Lambda\) radical to a new nitrogen nuclei, which can be assigned to a histidine residue based upon its quadrupole parameters. The appearance of this new coupling suggests that the Fe-depletion and Zn-reconstitution method of decoupling the iron and quinone spins results in a strong perturbation of the quinone pocket whereas the cyanide treatment methods leaves the quinone pocket relatively unperturbed.

LOW TEMPERATURE INTEGER SPIN Q-BAND SPECTROMETER FOR METALLOPROTEIN STUDIES, D. T. Petasis, M. P. Hendrich, Department of Chemistry, Carnegie Mellon University, Pittsburgh, PA 15213.

Most of the existing Q-band spectrometers employ cylindrical cavities for more intense microwave magnetic fields Bi but are so constructed that only one orientation between the external field B and Bi is allowed, namely the BJJBi orientation, thus limiting the use of the spectrometer for measurements on non-Kramers systems. We have designed and built epoxy resin microwave cavities to use as part of an integer spin Q-band (34 GHz) spectrometer operating in the range 1.2K<T<100K and geared toward studies on metalloprotein and metalloenzyme samples. The cylindrical cavities operate in the TE\(_{0n}\) mode with a side wall coupling to the waveguide probe which allows orientation of the cavity where the external field B can be parallel to the microwave field Bi. Such orientation allows observation of EPR transitions in non-Kramers ions. Rotation of the external magnetic field also permits a B1B\(_1\) orientation for observation of half-integer spin signals without disturbing the sample. The main body of the cavity consists of a metallic helix (silver, brass or aluminum) which suppresses unwanted extraneous modes (such as TM\(_m\)) and eddy currents. End walls with thin metallic annulli are used instead of solid metal walls, which adequately support the TE\(_{0n}\) mode but also allow excellent penetration of the modulation field and reduction of eddy currents. Reduction of eddy currents is important for improved sensitivity at low temperatures, especially in metalloprotein applications where signals are weak and improvements in signal-to-noise ratio are essential. The performance characteristics of our spectrometer will be discussed and measurements on samples of hemerythrin, ribonucleotide reductase and methane monoxygenase will be presented.
We have applied our dielectric-resonator-based stopped-flow EPR system [Sienkiewicz et al., RSI 65 (1994) 68] to chemical kinetics of spin labeled biomolecules in the subsecond regime. Folding/unfolding kinetics were observed where guanidine hydrochloride (GuHCl) was the denaturant. As brought on by 4 M GuHCl mixed with a total of 0.12 mL of spin labeled 100 μM protein, a 20 ms unfolding time could be resolved from two shots. Generally the GuHCl concentration was appropriately brought to the midpoint of the folding/unfolding transition (~0.9 M GuHCl) to initiate either folding or unfolding, and measurements were carried out at pH 6.5 or at pH 5.0. At pH 6.5, the unfolding curves fit to single exponential with unfolding time constant T» = 0.7 s, whereas the refolding curves showed two-phase behavior: t1ref = 80 ms, t2ref = 0.8 s. At neutral pH 6.5 inappropriate histidine ligation of the heme often leads to biphasic refolding. At pH 5.0, the unfolding and refolding were single-phase transitions with unfolding time constant T, = 70 ms and refolding time constant t = 160 ms. With the exception of the refolding kinetics at pH 6.5, there was approximate agreement in subsecond unfolding times as measured by EPR at the spin probe and by optical stopped-flow at the heme. Study is underway to determine under what conditions folding/unfolding kinetics arise from a 2-state equilibrium.

Multifrequency ESEEM and ENDOR investigation of chicken liver sulfite oxidase in phosphate buffer. P. Basu, P. Borbat, J.H. Enemark, R. LoBrutto*, A. Pacheco, and A. Raitsimring, University of Arizona, Department of Chemistry, Tucson, AZ, 85741; * Arizona State University, Department of Botany, Tempe, AZ, 85287.

Multifrequency ESEEM spectroscopy (8.6-15.6 GHz) has been applied for investigation of the Mo(V)-phosphate group hyperfine interaction in sulfite oxidase (SO). Through all operational frequencies an FT of the primary echo shows only one P-related line in the vicinity of twice the Larmor P frequency. The dependence of the maximal intensity of this line on the operational frequency has been investigated. Rather than attributing this dependence to a unique set of hyperfine parameters, we explain it in terms of a distribution of sets, with the isotropic constant varying in the range of 0-15 MHz, and an anisotropic constant of 0.8-1.0 MHz. This corresponds to a Mo-P distance of 3.3-3.5 Å. ENDOR measurements clearly show Mo(V) interaction with pterin protons (5.2-5.3 Å), and do not show interaction with closer protons. Implicitly the lack of close protons is confirmed by ESEEM. Based on these results, a tentative structure of the SO active site is suggested.

Determination of high-spin iron(III)-nitroxy1 distances in spin-labeled porphyrins. Margaret H. Rakowsky, Sandra S. Eaton, and Gareth R. Eaton, Departments of Chemistry, University of Denver, Denver, CO 80208 and Regis University, Denver, CO 80221.

The impact of the rapidly-relaxing low-spin Fe(III) center on the relaxation rate of a nitroxyl radical measured by saturation recovery (SR) has been used to determine the iron-nitroxyl distance in spin-labeled complexes (J. Am. Chem. Soc. 1995, 117, 2049). The same series of spin-labeled iron porphyrins has now been examined with axial ligands that cause the Fe(III) to be high spin: F-, Cl-, Br-. The zero-field splitting increases in the order F- < Cl- < Br-. The iron relaxation rates were determined by electron spin echo and SR at 4 to 6 K, by continuous wave power saturation between 4 and 10 K, and by analysis of the temperature-dependent contribution to linewidths above about 15 K. The SR curves for the nitroxyl in the spin-labeled complexes were analyzed to determine the inter-spin distance, using the independently determined iron relaxation rates and literature values of the zero-field splitting. Distances obtained for three iron-nitroxyl linkages will be compared with those for the low-spin analogs.
PULSED EPR, ENDOR, AND ESEEM OF MIXED VALENCE MN MODEL COM-
POUNDS AND THE PS II OXYGEN EVOLVING COMPLEX David W. Randall, 
R. David Britt, Department of Chemistry, University of California, Davis, CA 95616.

The pulsed EPR techniques of ESEEM and electron spin echo ENDOR are being used 
to characterize the oxygen evolving complex (OEC) of photosystem II (PS II). Experiments 
performed on the symmetry related tyrosine radicals of PS H, Yz, and Yz', allowed us to 
resolve a conflict regarding the molecular origin of an EPR signal by isotopically labeling all 
tyrosine residues in the PS II proteins. These experiments prove that this signal results from a 
tyrosine radical. This result suggests Yz is involved in water splitting chemistry and emphasizes 
that metallo-radical mechanisms for the OEC need to be considered for oxygen production by 
the OEC. Water directly ligated to a Mn(IH)Mn(IV) mixed valence Mn cluster constitutes an 
ideal model compound for substrate water binding to the OEC. ESEEM and ENDOR results 
indicate that the Mn water bond is shorter in this system than in [Mn(H2O)6]2+. Continuing 
55Mn ESE-ENDOR experiments on Mn(ni)Mn(rV) model compounds reveal new information 
about this biologically important moiety.

ELECTRON PARAMAGNETIC RESONANCE STUDY OF AN ELECTRIDE; 
144 Li [CRYPT AND [2.1.1]] ELECTRIDE. Kerry A. Reidv-Cedergren, James L. Dye, and John 
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Electrides are unique materials. They are a class of compounds in which an alkali metal is encapsulated by a 
complexant, usually a crown ether or a cryptand, in stoichiometric amounts, leaving the unpaired electron to 
occupy the anionic site in a well defined structural arrangement. The nature of the electron locales is important 
to the magnetic properties of electrides and can be studied by using EPR methods. Crystalline samples of 
Li+(C211)e- were carefully synthesized and were studied via EPR spectroscopy. EPR lineshape changes were 
observed as the temperature was changed. A picture of the channels and cavities in this electrde was derived 
from the crystal structure to help aid in understanding the electron trapping sites. This view shows that the 
cavities where the electrons are presumably located, are arranged in a zig-zag conformation. These views and 
the EPR data, help to understand better the sites in which the electrons primarily reside.

A "HYSCORE" INVESTIGATION OF THE (V0)(SALICYLALDOXIME), COM-
PLEX. CHARACTERIZATION OF NITROGEN COORDINATION AND IN-
TRAMOLECULAR HYDROGEN-BONDING. 
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Electron Spin Echo Envelope Modulation (ESEEM) is a powerful technique for the study of small hyperfine 
interactions occurring in biologically interesting metal complexes. Coupling of electron with surrounding nuclei 
gives information about the structure and activity of such compounds. However, it is usually difficult to 
get single crystals of these complexes. Interpretation of ESEEM spectra from polydomain (powder) samples is 
difficult because of superposition of signals corresponding to all possible orientations as well as of the modulation 
intensity anisotropy. Multifrequency and 2D-ESEEM allows to overcome some of these difficulties.

We will present a multifrequency and 2-D ESEEM (HYSCORE) study of a model oxovanadium complex 
(VO)(Salox). Our one and two dimensional ESEEM measurements cover the range of C- and X-band fre-
quencies. We take advantage of the possibility of measuring either polydomain or orientation-selective spectra.
From that we obtain information about the distance of intramolecular protons (hydrogen bonds) to the metal 
and about the value of the nitrogen spin coupling parameters. Furthermore, we demonstrate the possibility 
of utilizing the proton-nitrogen cross-correlation features in 2D-ESEEM to determine the relative signs of the 
hyperfine interactions.
A SYSTEMATIC ANALYSIS OF 1D AND 2D ‘N-ESEEM SPECTRA: APPLICATION TO A NITROGEN COORDINATED OXO-VANADIUM COMPLEX.
Edward J. Reijerse, Alexei M. Tyryshkin and Sergei A. Dikanov

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A ‘N-ESEEM simulation strategy based on first and second order perturbation analysis of peakpositions is presented and applied to the ESEEM data of the complex: Oxobis(2-methylquinolin-8-olato) Vanadium(IV) (VO(meox)). Making use of the information in the orientation selection ESEEM and HYSCORE spectra the number of free fitting tensor parameters can be reduced from 9 to 4 (i.e. the a and 3 Euler angles of both HFI and NQI interaction matrices). Further constraints based on local symmetry of the complex enable to reduce the number of free parameters to 2. It turns out that the best fit parameter space for this complex is consistent with its crystal structure data. The NQI tensor is near axial and pointing in the ligand plane. The hyperfine interaction is weakly anisotropic and one axis is oriented perpendicular to the ligand plane.

CROSSED-LOOP RESONATOR STRUCTURE FOR SPECTROSCOPY, A NEW TYPE BI-MODAL RESONATOR. George A. Rinard, Richard W. Quine Department of Engineering, Gareth R. Eaton, Department of Chemistry, University of Denver, Denver, CO 80208.

The crossed-loop resonator structure (CLRS) uses two orthogonal resonators and the circularly polarized nature of electron spins to isolate the EPR signal from the source. The first resonator excites the spins, and the second resonator detects the EPR signal. This very efficiently separates the EPR signal from phase noise and reflections. The circulator is eliminated, the spectrometer circuit is simplified, and phase noise is virtually eliminated (enabling dispersion measurements). Isolation of 70 db between the source and the signal was consistently obtained, even when both resonators were tuned to the same frequency. For samples with long relaxation times, dispersion could be measured at orders of magnitude higher power man absorption, resulting in high S/N. The high source isolation allows direct superheterodyne detection eliminating the need for field modulation and, thus, eliminating passage effects. For pulse work, the CLRS greatly decreases the dead time of the instrument, from 220 ns to 70 ns at S-band, and allows measurement of a portion of the signal previously impossible with a conventional pulsed spectrometer at this frequency. ELDOR is facilitated by the CLRS because the separation between the pump and observe frequencies is no longer limited by the bandwidth of the resonator. The CLRS is rugged, easy to tune, does not have to be critically coupled, and is easily adjusted to maintain source isolation with sample change. In addition to conventional applications, the CLRS could stimulate a new genre of EPR measurement techniques.


Recently, a new imaging technique called PEDRI, which is based upon the Dynamic Nuclear Polarization experiment, has shown good potential for imaging oxygen concentrations (1). In the PEDRI oximetry experiment, the enhancement of the nuclear signal, E, is dependent on many factors including the concentration of the ‘N nitroxide free radical [C] and the concentration of dissolved oxygen [O₂]. A model, developed by Bates (1), demonstrated the dependence of the DNP enhancement on [C] by consideration of spin-exchange interactions between nitroxide molecules. We have developed Bates's model further to include the effects of relaxation of the nitrogen nucleus and the presence of dissolved oxygen. This was done with reference to the work of Yin et al (2) and results in an analytical expression for E as a function of [C], [O₂] and all other relevant relaxation pathways. Unlike the previous model of PEDRI oximetry (1), saturation transfer between the hyperfine lines can now be included, which has been shown to be significant in some experimental circumstances (3). Importantly, we can now also model the dual and triple EPR iradiation of the hyperfine lines and compare it against recent experimental results (4).

A SMALL-BORE FC-PEDRI IMAGING SYSTEM by F. T. L. Robb, J. M. S. Hutchison, I. Nicholson and D. J. Lurie, Department of Bio-Medical Physics, University of Aberdeen, U.K.

Field-Cycled Proton Electron Double Resonance Imaging (or FC-PEDRI) has been shown to be a highly sensitive tool for imaging free radicals in-vivo. The technique of field-cycling is used to boost the Signal-to-Noise ratio of the experiment, to reduce the overall level of power deposition within the sample and allows collection of EPR based spectra. During FC-PEDRI the main $B_0$-field is changed rapidly between the polarization field (where the nuclear magnetisation is built up), the evolution field (during which EPR irradiation is applied) and the detection field (where image collection takes place). A flexible FC-PEDRI system therefore requires to satisfy two conflicting requirements. Firstly, fast field changes must be possible (< 100ms), as any delay between evolution and detection reduces the PEDRI enhancement. In our system this is achieved by rapid switching of magnet current power supply. Secondly, the detection field must have excellent DC stability to allow NMR image collection. Unfortunately, during field-cycling, eddy-currents are set up in the magnet windings creating small fluctuations in $B_0$ which makes image collection more difficult. This abstract details a novel circuit for automatic eddy-current compensation based upon an inductive feedback technique. A new design of FC magnet power supply will also be discussed. These two developments have significantly improved the performance of our FC-PEDRI system.

COMPLEXATION OF COPPER(II) WITH CARBONATE LIGANDS IN FROZEN AQUEOUS SOLUTION AS STUDIED BY CW AND PULSED EPR

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In this study CW and pulsed EPR methods have been used to investigate the complexation of Cu(II) with $^{13}$C labelled bicarbonate and carbonate ligands in aqueous solution. These complexes serve as model compounds for the investigation of the adsorption of Cu(II) on the calcite crystal surface, an important mineral phase in sediments. The structural characterization of surface complexes is expected to give insight on a molecular level into the mechanisms and kinetics of crystal growth and growth inhibition.

As expected from chemical speciation calculations, different carbonate species are found depending on the pH and the composition of the solution. The hyperfine couplings between the unpaired electron of the Cu(II) ion and the surrounding $^{13}$C and proton nuclei provide structural and electronic information about the complexes: monodentate bonding with the bicarbonate ligands shows only weak isotropic and dipolar coupling to the $^{13}$C nuclei and can take place both at equatorial and axial sites of the Jahn-Teller distorted octahedral coordination structure. The carbonate ions are able to form bidentate complexes in the equatorial plane; the larger couplings reflect the delocalization of spin density from the Cu(II) ion over the $a$ and $\%$ bonds to the $^{13}$C nucleus.

NUTATION-FREQUENCY-CORRELATED ESR SPECTROSCOPY, Stefan Stoll, Gunnar Jeschke, Zoltan Madi, and Arthur Schweiger, Laboratory of Physical Chemistry, Swiss Federal Institute of Technology, 8092 Zurich, Switzerland

The frequency of the transient electron spin nutation is a measure for the ESR transition probability, which in turn is a function of the parameters of the spin Hamiltonian. Depending on the system, transition probabilities may provide information on the g-factor anisotropy, on zero-field splittings, on hyperfine couplings and even on large nuclear quadrupole interactions. In addition, it is possible to use differences in nutation frequencies to separate contributions to an ESR spectrum. The primary-electron-spin-echo-detected rotary echo is introduced as a new approach to the measurement of nutation frequencies. By observing an electron spin echo one can separate the microwave irradiation from the detection, so that the measurement of nutation frequencies with high resolution and sensitivity becomes possible with standard pulse-ESR instrumentation. In addition, the formation of a rotary echo leads to refocusing of broad nutation frequency distributions. Since the resolution of the method depends on the microwave field homogeneity, we have measured the field distribution for dielectric and bridged-loop-gap resonators. The high potential of the measurement of the nutation frequency vs. the static field is demonstrated by simulations and experimental examples.

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DARK MAGNETIC RESONANCE

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Since a couple of years, the coherent optics community pays much attention to some new and fascinating phenomena like dark resonance (coherent population trapping), lasing without inversion, and the behavior of phase-soniums, which all are based on the concept of coherence. In optics the basic principles of these phenomena are usually discussed by means of a three-level system of A-configuration consisting of an upper level, and a low-frequency coherent superposition of two lower sublevels. Translated to magnetic resonance, the two optical transitions correspond to EPR transitions and the sublevel splitting to an NMR transition. In this contribution we describe the corresponding phenomena 'dark magnetic resonance' and 'masing without inversion' by using the product operator formalism commonly applied in pulsed EPR. We develop the theory for an $S=V_{1/2}$, $I=V_{1/2}$ spin system using semi-selective microwave pulses and demonstrate that similar phenomena as in coherent optics can also be observed with a specially prepared electron-nuclear spin system. Furthermore we discuss how the various standard pulsed EPR experiments will be affected by the dark magnetic resonance phenomenon.

DOUBLE-STACKED DIELECTRIC RING RESONATOR FOR SENSITIVE EPR MEASUREMENTS OF BIOLOGICAL SAMPLES - THEORY AND PRAXIS.
Marek Jaworski*, Andrzej Sienkiewicz*, and Charles P. Scholes*; Institute of Physics, PAS, Al. Lotnikow 32/46, 02-668 Warsaw, Poland, Chemistry Department, SUNYA, Albany, NY 12222.

We present a new theoretical approach for calculating the resonant frequency and for solving the field distribution problem of the cylindrical dielectric ring resonator (DR). The proposed model bridges the gap between rigorous and accurate finite-element - or Green function-based numerical procedures and approximate solutions in which the field distribution can be described analytically. With the latter approach the resulting resonance frequency is accurate within a few per cent. In our approach we modify the approximate solution for the microwave field distribution by substituting different values of the radial separation constants within the disk-shaped DR and outside of it. The model also takes into account the double-stacked structure of the resonator, the influence of the shielding walls, and the vertical sample hole along the cylindrical axis of the DR. The comparison of the calculated and measured resonant frequencies for our typical X-Band experimental DR-based systems resonating in their lowest transverse electrical TE_{018} mode reveals an accuracy better than 1%. We present and discuss the calculated and measured values of the resonator filling factor ($r$) for the single and double-stacked resonant structures containing either point or longitudinal (capillary) samples. The comparison of the calculated quality factor ($Q$) values for both types of resonant structures will also be given.

RIGHT ANGLE SPINNING (RAS) EPR
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Right angle spinning EPR (RAS-EPR) where the sample is rotated around an axis perpendicular to the static magnetic field $B_0$, is introduced. The method can be applied in cw and pulse EPR to improve sensitivity and resolution and to simplify the interpretation of EPR, ESEEM and ENDOR spectra of disordered systems.

A) ANISOTROPY RESOLVED (AR) EPR: In 1D AR-EPR the field-swept EPR spectrum is measured under RAS, leading to considerably increased spectral resolution. In 2D AR-EPR the first dimension is again represented by $B_0$. The second dimension which is achieved by Fourier transformation of the signal obtained by incrementing the speed of rotation of the sample, represents the anisotropy of the magnetic parameters of the spin system. The 2D approach allows one to separate overlapping spectra, to estimate small unresolved couplings, to determine angular variations of magnetic parameters (from a powder sample!) and to assigne transitions to particular magnetic quantum numbers.

B) IMPROVED SENSITIVITY: RAS can also be used to improve the sensitivity of two-pulse ESEEM and FT-EPR detected NMR experiments at field positions with weak spectral features (e.g. along $g\parallel$). The signal improvement in such an experiment may amount to more than one order of magnitude. The demanding instrumentation (rotation of the sample at a temperature of 10 K between 0 and 500 Hz incremented in steps of 5 Hz with a long-time frequency stability better than 0.1 %) will be discussed and experimental results will be presented.
THE FREE RADICAL METABOLISM OF PHENOLPHTHALEIN BY LACTOPEROXIDASE. Herbert J. Sipe, Jr., Jean T. Corbett, and Ronald P. Mason, Department of Chemistry, Hampden-Sydney College, Hampden-Sydney, VA 23943 and Laboratory of Molecular Biophysics, NIEHS/NIH, Research Triangle Park, NC 27709.

Phenolphthalein, a triphenylmethane derivative, is widely used as a laxative and is the active ingredient in more than a dozen and a half commercial products that are available for use (and possible abuse) as over-the-counter, non-prescription formulations. At ordinary dose levels, phenolphthalein appears to be metabolized to its glucuronide conjugate in the intestinal lumen and the liver, and excreted largely as the glucuronide. One recent study has demonstrated that phenolphthalein induces micronucleated erythrocytes in mice. The present study reports the results of EPR and oxygen uptake studies of the metabolism of phenolphthalein. EPR spin-trapping studies of incubations of phenolphthalein, lactoperoxidase, reduced glutathione, and hydrogen peroxide with DMPO demonstrate enhanced production of glutathionyl radical compared to an identical incubation lacking phenolphthalein. Similarly, enhanced production of superoxide trapped by DMPO is found in a system of phenolphthalein, NADH, and lactoperoxidase. Production of ascorbyl free radicals is also enhanced in a system of phenolphthalein, ascorbic acid, hydrogen peroxide and lactoperoxidase. Observation of enhanced radical production in these three systems, a consequence of redox cycling (or "futile metabolism"), suggests that phenolphthalein may be a significant source of oxidative stress in physiological systems.

A VISUAL USER INTERFACE USING THE ORIGIN® ENVIRONMENT FOR AN ESR SPECTROMETER. Ryan S. Henry and Herbert J. Sipe, Jr., Department of Chemistry, Hampden-Sydney College, Hampden-Sydney, VA 23943

A PC/AT-486 personal computer was used to create a data link with a JEOL JES-RE1X Electron Spin Resonance Spectrometer. The link was facilitated through the Origin® programming environment. The program created has all the capability to acquire spectral data, along with information concerning all experimental parameters of the spectrometer at the time the spectrum was obtained, and also to display that data in a plot window. All parameters of the spectrometer can be controlled via the personal computer. The spectral data and parameter information can then be saved into a file format that is immediately readable by the powerful spectra simulation and analysis software obtained from the laboratory of Molecular Biophysics at the National Institute of Environmental Health Sciences, Research Triangle Park, NC 27709.

[accessible on WWW as: http://alfred.niehs.nih.gov:80/LMB/pest/]

DOES EPR AT 95 GHz INDICATE THE DISTRIBUTION OF SMALL NITROXIDE PROBES IN A PHOSPHOLIPID BILAYER? A. I. Smirnov, R. B. Clarkson, and R. L. Belford, College of Medicine, Department of Chemistry, University of Illinois, Illinois EPR Research Center, Urbana, IL 61801.

Traditionally, X-band EPR spectroscopy of small nitrooxide radicals such as Tempo (2,2,6,6-tetramethylpiperedine-l-oxyl) or DTBN (di-tert-butyl nitroxide) has been employed to study partitioning in phospholipid membrane systems. Because of a lack of spectral resolution, these data provided no or very little information on molecular dynamics of the probe molecules in the membrane. It was shown recently that g-value resolution of W-band EPR substantially facilities such studies (Smirnov, Smirnova, and Morse II, P. D., Biophys. J. 68, 2350, 1995). However, the question remains whether dynamics behavior of the probe in the membrane still can be treated under a one compartment model, i.e., neglecting the membrane architecture. Improved sensitivity of the Illinois W-band EPR instrument and better handling of aqueous samples allowed us to measure high signal-to-noise spectra from Tempo/DPPC (1,2-dipalmitoyl-sn-glycero-3-phosphatidylcholine) system. Least-squares simulation analysis of these spectra shows that W-band EPR is sensitive to the statistical distribution of the probe within the membrane. We also demonstrate how this distribution becomes affected by anesthetics. This work was partly supported by NTH Grant RR01811.
HIGH-FREQUENCY (95 GHz) EPR SPECTROSCOPY TO CHARACTERIZE SPIN ADDUCTS. T. I. Smirnova, A. I. Smirnov, R. B. Clarkson, R. L. Belford, Y. Kotake, E. Janzen. Illinois EPR Research Center, University of Illinois, Urbana, IL 61801 Oklahoma Medical Research Foundation, Oklahoma, OK 73104.

Spin trapping experiments are usually carried out with continuous-wave (cw) X-band (9.5 GHz) EPR spectroscopy because of the good concentration sensitivity and ready availability of this method. Characterization of the spin adducts is usually based on analysis of isotropic hyperfine coupling and comparison of these coupling factors with those for the reference spin adducts. These experiments encounter two major challenges: (i) spin adducts from many carbon-centered free radicals have close g-values (resulting in strongly overlapping spectra), and (ii) measurable hyperfine couplings correspond to interactions of the electron spin with just the nearest nuclei. Therefore, very little or no information is obtained on the overall structure of the spin adduct molecule. In this presentation we demonstrate how high frequency EPR at 95 GHz (W-band) with enhanced g-value resolution and sensitivity to rotational motion can be applied to solve some of these problems. Ten-fold better g-value resolution allows us, e.g., to clearly separate methyl and trichloromethyl phenyl-tert-butyl nitronate (PBN) from a mixture at W-band while the presence of two species is practically unnoticeable in the corresponding X-band EPR spectra. Rotational dynamics parameters can be measured much more accurately at W-band, providing information on rotational radii which characterize the adduct molecule as a whole. This work used the resources of the IERC (NIH P41-RR01811). Y. K. and E. J. acknowledge support from NTH (Grant P41 RR05517)

CAN OVER-EXPRESSION OF GLUTATHIONE PEROXIDASE IN CELLS REGULATE PEROXIDE DERIVED RADICALS? A DMPO SPIN TRAPPING STUDY. Bradley E. Sturgeon, Eugene D. Barth, Alan M. Diamond and Howard J. Halpem University of Chicago Medical Center, Department of Radiation and Cellular Oncology, Chicago, Illinois 60637.

Reactive oxygen species are eliminated from intercellular membranes by an array of complex enzyme systems. The activity of these enzymes has been correlated with the onset of many degenerative diseases. Glutathione Peroxidase (GPx) is one such enzyme which catalyzes the breakdown of peroxide species. GPx is unique from the many catalase systems in that GPx can breakdown lipid peroxides as well as hydrogen peroxide. Hydrogen peroxide may undergo reduction via Fenton reactions to yield reactive hydroxyl radicals which will cause cellular damage. Furthermore, oxygen containing radicals are also thought to be involved in many signaling pathways. We have initiated a DMPO spin trapping study to determine if modulation of GPx expression in cells can alter the concentration of reactive species. Preliminary data indicates small but consistent effects on signals from DMPO spin trapping of menadione generated superoxide in MCF-7 cells with varied GPx levels. Our poster will present this and further results.

ELECTRON AND NUCLEAR RELAXATIONS IN PARAMAGNETIC METAL ION COMPLEXES Sandip K. Sur. 1647 Townwood Court, Charlottesville, VA 22901

The nuclear and electron spin relaxation mechanisms, especially in aqueous solutions of paramagnetic metal ion complexes are fundamental in our understanding of the role of paramagnetic contrast agents in medical Magnetic Resonance Imaging (MRI) and the functioning of many biological metalloproteins. We have measured electron and nuclear relaxations in paramagnetic metal ion complexes and analyzed them within the SBM framework. The relevant parameters contributing to the water proton relaxations by these complexes will be critically examined. Electron relaxations in metal ion complexes, particularly for S-state metal ions Mn(II), Fe(III) and Gd(III) cannot be understood in the light of the current theories of electron relaxation. A new magnetic relaxation mechanism in paramagnetic metal ion solutions will be proposed for the analysis of experimental EPR and NMR data.

Oxidation is widely assumed to play a causal role in the pathogenesis of atherosclerosis. Oxidative modification of low density lipoprotein (LDL) can be followed by analyzing the lag phase of the conjugated diene formation at 234 nm in LDL exposed to Cu⁺. This procedure is restricted to isolated LDL fractions. To make this assay applicable to different biological systems, we introduce a method to determine the lag phase by measuring the EPR signal intensity and thereby the concentration of the radicals formed. Stable radical spin adducts were generated using the spin trap PBN (N-tert-butyl-a-phenylnitrone) and could be detected by EPR spectroscopy. Comparing the specific formation of radicals and the generation of conjugated dienes as measured by UV absorbance revealed analogous lag-, propagation- and decomposition-phases. However, the EPR and UV measurements showed that the increasing amount of conjugated dienes is not directly correlated with an increase in the radical concentration.

Q-BAND ENDOR OF THE ELECTRONIC STRUCTURE FROM COPPER-CONTAINING NITRITE REDUCTASE.
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Nitrite reductase (NiR) catalyzes the reduction of nitrite (NO2⁻) to nitric oxide (NO). The enzyme contains a Type 2 catalytic copper (having three histidine ligands) where nitrite reduction occurs and a Type 1 blue-green copper (having two histidines, a cysteine, and a methionine ligand) which has a redox function. The enzyme is from a denitrifying variant of R. sphaeroides overexpressed in E. coli. Q-band (34 GHz) ENDOR, as opposed to X-band (9 GHz) ENDOR, removes spectral overlap of nitrogens and protons. Findings on the Type 2 catalytic center were: Histidine nitrogen couplings were in the 26-36 MHz range, and nitrite binding caused their features to sharpen and to become nearly electronically equivalent. 2) Exchangeable protons with couplings ~4.5 MHz were observed, their distance estimated at 3-4 Å from the Type-2 copper, and the detailed angle-selected ENDOR of one of these protons thought to be H-bonded to nitrite is underway. 3) As yet there is no evidence for direct hyperfine coupling to the nitrite nitrogen, implying that nitrite ligates to copper through its oxygen. Findings on the Type 1 redox center were: 1) Two markedly different histidine nitrogen couplings, one of 39 MHz, and the other of 15 MHz. 2) Non-exchangeable proton ENDOR features with couplings of 21 MHz and 9 MHz attributed to 8 protons of cysteine. A detailed overview of this blue-green Type 1 copper center's electronic structure will be presented. This work supported by NIH Grant GM 35103.


The complex [Rh(CN)]⁻ in a KCl host lattice is paramagnetic with a d,2 ground state and D₄h symmetry. Both g- and hyperfine tensors are anisotropic and depend on temperature due to the presence of localized anharmonic vibrations [N. V. Vugman and W. O. Franco, Physics Letters A 155, 516 (1991)]. The inversion recovery technique was used to measure spin-lattice relaxation times for this complex in the temperature range of 4.7 to 25 K. The experimental data fit very well to an Orbach resonant two-phonon relaxation process, with a low lying excited state, A = (36 ± 3) cm⁻¹. Since the first electronic excited state, dₓ²₋₂ y², should lie farther apart in energy than 36 cm⁻¹, this small energy is most probably associated with the localized Aₓ₂u vibration mode levels, in accordance with the literature (37 cm⁻¹ frequency, reference above). Angular variation experiments show that the spin lattice relaxation times are anisotropic, presenting axial symmetry. Relaxation rates fit very well to the axial nitrogens hyperfine interaction angular dependence, taking into account the g-value anisotropy. This strongly suggests that the main relaxation mechanism is the modulation of the axial nitrogens hf also as a consequence of the localized vibration modes. This work was supported by CNPq, FINEP and FUJB.
EXTRACTING MAGNETIC AND ELECTRIC DATA FROM DYSONIAN LINES.
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The general dysonian line is a function of two parameters \( X = d \nu_5 \) (\( d \) being the thickness of the sample and \( 5 \) the skin depth of the microwave field) and \( R = (T_D/T)^2 \) (\( T_\nu \) being the diffusion time of the spins across the skin depth and \( T \), the spin relaxation time). In the limit (\( d < \) or \( \sim \) 5) the line is a function of the \( X \) parameter only. In this case the line asymmetry (A/B) parameter can be related to only one \( X \) value, allowing to write microwave conductivity as \( c = X^2 (d^2 \pi \nu_0 u) \) where \( u \) is the vacuum permittivity and \( \nu_0 \) is the microwave frequency. This limit of Dyson's theory is easy to reach in low-dimensional synthetic metals. Although the line asymmetry is very useful to obtain conductivity, it introduces a problem in the determination of g values and linewidths. The dysonian line shows an apparent field for resonance and a peak-to-peak linewidth that are greater than the real ones. Area measurement are also more complicated. In this work we have fitted the dysonian line in the limit (\( d < \) or \( \sim \) 5) to a combination of absorption and dispersion lorentzian lines, allowing us to determine the true g value, linewidth, paramagnetic susceptibility and gigahertz conductivity from experimental parameters of the dysonian line.

OPTICALLY DETECTED ELECTRON SPIN ECHO ENVELOPE MODULATION IN ZERO MAGNETIC FIELD - A COMPARISON TO ESEEM IN THE HIGH FIELD LIMIT.
165 Volker Weis, Klaus Mobius and Thomas Prisner
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ESEEM in the electron spin high field limit is a widely used tool to detect nuclear transitions within an inhomogeneously broadened EPR line. For the low field limit only a few publications exist and no quantitative analysis is published for the zero field case. An ESEEM study in zero magnetic field was made on the photoexcited triplet state of acridine-d. Qualitative differences of the ESEEM effect as well as environmental effects on the echo decay under zero/low-field and high-field conditions are observed and discussed.

INTERMEDIATE X: LIGHTING THE PILOT LIGHT
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Proteins containing differerent clusters are capable of carrying out reactions with \( 0 \). In particular, the diiron center in ribonucleotide reductase (RNR) is important because its formation is accompanied by the oxidation of a tyrosine residue 122 to the tyrosyl radical that initiates the catalytic nucleotide reduction process. Several rapid-freeze-quench (RFQ), EPR and Mossbauer spectroscopic techniques have been used to investigate the mechanism by which the incubation of the apo R2 subunit of Escherichia coli RNR with Fe\(^{2+}\) and \( 0 \), leads to the self-assembly of its difererric cluster and the formation of the radical cofactor. These studies revealed the formation of a diiron intermediate (Intermediate X) that directly ignites the pilot light of RNR by oxidizing Y122-R2 to the tyrosyl radical. Here we present the use of RFQ Q-band \( ^1{O} \), \(^1{H} \) and \(^1{H} \) Electron Nuclear Double Resonance (ENDOR) spectroscopy to study the structure of Intermediate X.
Titanium-doped sapphire (Ti$^{3+}$: Al$^{2+}$), an important tunable solid state laser material for the near infrared spectral region, has already been investigated by EPR in 1960 by Kornienko et al. [1]. Although the spin system is quite simple ($S=1/2$), the exact determination of the $g$ values are to the best of our knowledge not known until now. The reason for this is that at X-band frequencies the standard CW experiment of this compound requires a static magnetic field $B_0$ of more than seven Tesla, because $g^\perp$ is estimated to be extraordinarily small ($g^\perp < 0.1$). This is caused by the orbital degeneracy of the ground state in a trigonal symmetry.

To evaluate such small $g$ values, we apply the electron spin echo detected rotary echo experiment [2], which allows one to measure the nutation frequency of the EPR signal observed with $B_0$ perpendicular to the $g$ value of interest. The transient nutation frequency, obtained with a very high turning angle pulse, is proportional to the transition moment and thus to the $g$ value along the direction of the pumping field. It is shown that in Tr$^+$: Al$^{2+}$, the measurement of the nutation frequency at the $g$ position of the spectrum ($g_n = 1.07, B_0 = 0.7$ Tesla) allows an exact indirect determination of the $g$ value. The accuracy of the method is also demonstrated on other compounds.


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We have built a novel reflection mode spectrometer based on quasioptical methods of radiation propagation and processing. The use of reflecting optics, wherever possible, ensures that the spectrometer is a broadband device. We present spectra of polyaniline taken with the reflection mode spectrometer at 170GHz and compare the sensitivity of the new device with our transmission mode spectrometer at 250GHz. We find that the reflection mode spectrometer is more sensitive than the transmission mode spectrometer. We attribute much of this improvement to the greater stability of operation in the reflection mode. The reflection mode spectrometer cannot use a conventional ferrite circulator; rather, it uses a polarization transforming reflector (PTR) to rotate the polarization state of the EPR signal. Exploiting the polarization state of the signal to separate it from the source radiation is known as polarization coding. We discuss other methods of polarization coding that may be used in conjunction with a bimodal Fabry-Perot resonator, which can duplex the millimeter wave source power and EPR signal without a PTR. Finally, we speculate on how our quasioptical techniques may be applied to the development of a broadband, pulsed, quasioptical, EPR spectrometer.

A new very high frequency/field EPR spectrometer is described. The spectrometer is based on a novel warm-bore superconducting magnet (Oxford Instruments Teslatron, maximum field 15/17.1 Tesla at 4.2/2.2 K). The sample is contained in a separate helium flow cryostat (Oxford Instruments CF1200) allowing temperature control from 1.8 to 300 K. The spectrometer contains a variety of microwave, millimeter and submillimeter wave sources. The high-frequency end of the spectrum (up to 3 THz) is supplied by a FIR laser pumped by a CO\textsubscript{2} laser (Edinburgh Instruments FIRL100). The submillimeter and millimeter waves are generated by a phase-locked Gunn diode operating at a fundamental frequency of 110 + 3 GHz multiplied upon demand up to 550 GHz, standard working frequency being 330 GHz. The low-end frequencies are supplied by a MVNA millimeter network vector analyzer (AB Millimetre, Paris) offering a continuous choice between Q and W bands. The spectrometer works in transmission mode. Currently a set of Fabry-Perot resonators is under construction to increase sensitivity at several discrete frequencies.


Typically, X-band (9.5 GHz) EPR spectra of Gd(III) chelates in aqueous solution exhibit a single, broad resonance line at \( g = 2, A_{Bpp} = 280 \) Gauss. The observable variations in linewidth with temperature and chelate structure are very small and difficult to model accurately. However, these same solutions at W-band (95 GHz) exhibit a much narrower \( g \approx 1.98-1.99 \) resonance line, with linewidths on the order of 25 Gauss. The order-of-magnitude narrowing of the Gd(III) resonance, together with the ten-fold increase in B, (hence, g-value dispersion), provides much higher resolution for this class of compounds; it has enabled us to look for partitioning of these compounds between aqueous and non-aqueous environments in proteins and membranes (both model and biological). Since the interest in Gd(III) chelates is due in part to their utility as MRI contrast agents, the ability of W-band measurements to resolve spectra of the agents in different environments is significant in our overall program to better understand mechanisms of targeting of the complexes in living systems.

We will discuss the multi-frequency EPR spectra of several Gd(III) complexes and consider how changes in the relative magnitudes of field-dependent and field-independent terms in the spin Hamiltonian can at least partially account for the observed B, dependence of the spectra. Applications of W-band spectroscopy to such topics as the measurement of \( T^2 \) in these solutions, and the relationship between chelate structure and biological targeting, also will be discussed.

Partial support was provided by the NIH (GM42208 and GM51630, RBC; RR01811, RLB) and by Sobering AG.

MODIFICATION AND USE OF A CW EPR SPECTROMETER FOR MEASURING RELAXATION TIMES IN THE LABORATORY AND ROTATING FRAME, C. S. Yannoni, R. D. Kendrick, H.-M. Vieth, J. Wegener, and D. Rugar, IBM Almaden Research Center, 650 Harry Road, San Jose, CA 95120. Permanent address: Department of Physics, Free University Berlin, Germany; Department of Physics, University at Dortmund, Germany.

A commercial X-band CW spectrometer has been modified to make rapid passage measurements of relaxation times in dilute electron spin systems in order to to establish excitation protocol for force detection of magnetic resonance. (J. A. Sidles et al, Rev. Mod. Phys. 67, 249-265 (1995)) Transient nutations have been observed and used to calibrate the B, field, while experiments designed to measure relaxation of field-modulated spin-locked magnetization have been performed. The effect of cross-relaxation in the rotating frame on these measurements will be discussed.
PROBE-PULSE DETECTION
Eric C. Hoffmann, Gunnar Jeschke, and Arthur Schweiger
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Standard continuous-wave (cw) EPR methodology uses magnetic field modulation followed by narrow-band phase-sensitive detection. Recently, a number of alternative detection schemes like echo-detected EPR, longitudinally-detected cw or pulsed EPR, field-swept FID-detected hole burning, and probe-pulse detection have been introduced. In this contribution we give a survey of the different experimental schemes based on probe-pulse detection, where a weak microwave field is used to probe a time-dependent electron or nuclear polarization or to detect evolving nuclear coherence. Probe-pulse detection, for example, is used to indirectly observe nuclear transient nutations, to monitor field-swept EPR spectra (inversion-recovery detected EPR) and electron transient nutations, and to measure nuclear frequencies in coherent Raman beat, generalized HYSCORE and primary nuclear spin echo experiments. The behavior of the spin system during probe-pulse irradiation in the linear regime approximation as well as far beyond the linear regime will be discussed and a number of experimental examples that demonstrate the advantages of probe-pulse detection will be presented.

PROGRESS AND PROSPECTS IN MAGNETIC RESONANCE FORCE MICROSCOPY,
C. S. Yannoni, IBM Almaden Research Center, 650 Harry Road, San Jose, CA 95120.

A variety of results obtained using force detection of magnetic resonance (J. A. Sidles et al, Rev.Mod.Phys.67, 249 (1995); C. S. Yannoni et al, Encyclopedia of Nuclear Magnetic Resonance, D. M. Grant and R. K. Harris, Eds., J. Wiley & Sons, 1996, Vol. 3, p. 2093) will be presented. In this talk, I will focus on the use of the magnetic resonance force microscope to detect EPR and to do EPR imaging. The goal of detecting small numbers of spins has motivated experiments at low temperature. (K. Wago et al, J. Vac. Sci. and Tech. (in press)) The long relaxation times found in the E. centers in y-irradiated silica facilitate force detection via cyclic adiabatic inversion (D. Rugar et al, Science 264, 1560 (1994)) and make it possible to measure a variety of relaxation times in the laboratory and rotating frames, to observe transient nutations, and to generate spin echoes. The implication of these results for doing EPR of single electron spins will be discussed.

INFRARED SPECTROSCOPIC, X-RAY AND NANOSCALE

Attenuated total reflectance (ATR) measurements were performed using Fourier transform infrared (FTIR) spectroscopy in the ATR mode with a thallium iodobromide (KRS-5) crystal to measure the frequencies of the V3 and V4 phonon absorption bands in thin strontium titanate films deposited on single-crystal yttrium-barium copper oxide (YBCO), lanthanum aluminate, magnesium oxide, and strontium titanate substrates. The KRS-S crystal enabled FTIR-ATR measurements to be made at frequencies above 400 cm\(^{-1}\). Atomic force microscopy (AFM) and X-ray diffraction (XRD) measurements were also made to further characterize the films. The measurements were repeated on single-crystal specimens of strontium titanate and the substrates for comparison. Softening in the frequency of the V4 transverse optical phonon in the lattice-mismatched films below the established value of 544 cm\(^{-1}\) is indicative of the highly textured, polycrystalline ceramic nature of the films and is consistent with the XRD and AFM results.
ON-LINE MONITORING AND CONTROL OF BATCH AND FED-BATCH BIOREACTORS USING MID-IR SPECTROSCOPY. Janice A. Phillips, Department of Chemical Engineering, Lehigh University, 111 Research Drive, Bethlehem, PA 18015

The inability to directly measure concentrations of substrates and products has been a longstanding limitation in the ability to appropriately and accurately control bioreactors. Over a decade ago, research proved that mid-IR spectroscopy would provide a solution if suitable instrumentation were available for in-situ analysis. Recent developments in the construction of sampling systems and the spectrophotometer now make this a reality. Results obtained on a 13 liter bench-scale bioreactor using the Applied Systems' ReactIR 1000 and DiComp probe will be presented for the E. coli batch and fed-batch fermentation. A series of fermentations were conducted to assess the probe and spectrometer performance characteristics (S/N, stability, fouling, etc.). These runs were also designed to understand the approach to calibration, with particular emphasis on dilute species measurement. Additional information was obtained on the changing characteristics of the medium during sterilization. This information was integrated with the computer control module associated with the fermentor in a set of fed-batch fermentations to effectively monitor and control substrate addition.

SIMPLIFICATION OF FTIR SPECTRA BY ROTATIONAL COOLING OF MOLECULES ENTRAINED IN A SUPersonic MOLECULAR BEAM EXPANSION. Steven W. Sharpe. Robin McDowell and Thomas Blake, Battelle, Pacific Northwest National Laboratory, Richland, Washington 99352

Supersonic molecular beam expansions provide a unique environment in which to acquire the infrared spectra of many molecular systems. Molecular beams combined with Fourier transform infrared spectroscopy represents a powerful tool for reducing or removing spectral congestion arising from both rotational and vibrational excitation that plagues room temperature techniques. FTIRS offers unparalleled spectral coverage in the infrared, from 5000 to 500 cm\(^{-1}\). Depending on expansion conditions, we routinely realize rotational temperatures on the order of 15 K. With the appropriate slit nozzle (12 cm x 50 microns), Doppler broadening is reduced six-fold or more over that of room temperature, static cells. A description of the PNNL FTIR-beam spectrometer will be given along with recent results for studies involving the fully rotationally resolved spectra of a number of compounds including perfluoroethane.

RECENT STUDIES OF BLACK CARBON (SOOT) SURFACE REACTIVITY. A. R. Chughtai, B. K. Konовалchuk, C. A. Sergides, M. M. O. Atteya, and D. M. Smith, Department of Chemistry, University of Denver, Denver CO 80208

In earlier studies of hexane soot structure, thermal desorption revealed the formation of C0, CO, H2O and H, as a function of temperature. More recent research, in which FTIR monitored the gaseous products of vacuum thermal decomposition of soot, has demonstrated also the formation of CH at temperatures above 450°C reaching a maximum in the 550-650°C range. A yellow condensate identified by FTIR as a mixture of quinone, carboxyls and phenols begins to form at 250°C and collects in the cooler regions of the reactor. These data further support a model of soot which is predominantly aromatic, although not graphitic, with a surface structure dominated by specific carbon-oxygen functionalities. The kinetics of the soot-ozone reaction, complex and involving three major stages, continues to be explored through the use of several techniques including FTIR. Of particular interest has been a catalytic decomposition of O, upon initial contact with soot which, at 0 concentration of 20 ppm or greater, represents as much as \(V^*\) dimunition of the 0 concentration in the first 2% of the reaction and is concentration dependent. Also important is the involvement of adsorbed molecular oxygen in reactions of, and adsorption on, the soot surface.
A DIFFUSE REFLECTANCE FTIR STUDY OF CO OXIDATION CATALYSTS IN STOICHIOMETRIC MIXTURES OF CARBON MONOXIDE AND OXYGEN. Kenneth G. Brown, Donna S. Duarte Department of Chemistry and Biochemistry, Old Dominion University, Norfolk, VA 23529 and Billy T. Upchurch and David R. Schryer, NASA-Langley Research Ctr., Hampton VA 23681

The reductive pretreatment of the catalyst material has been discussed in the previous paper. The catalyst is now exposed to a reaction gas mixture which for the purposes of this study consists of 0.5% oxygen and 1% CO with the catalyst being held at 55°C. We are able to monitor the reaction process as it is occurring. The interference from the rotational vibrational spectrum of gas-phase CO may be subtracted and the resultant adsorbed CO species can be identified. The process can be followed for an extended period of time yielding reaction curves that can be compared with those previously determined by gas chromatography. The only adsorbed species that we are able to identify on these particular materials is adsorbed CO whose vibration occurs in a region that has been assigned to a CO species that is bound in a linear geometry to a surface platinum atom. We have no evidence for a “bridged” species. The resultant relative intensity of the adsorbed CO species is sensitive to depend upon catalyst composition as well as the pretreatment conditions to which the catalyst was exposed.

A DIFFUSE REFLECTANCE FTIR STUDY OF THE REDUCTIVE PRETREATMENT OF CO OXIDATION CATALYSTS. Kenneth G. Brown, Donna S. Duarte Department of Chemistry and Biochemistry, Old Dominion University, Norfolk, VA 23529 and Billy T. Upchurch and David R Schryer, NASA-Langley Research Ctr., Hampton VA 23681

CO oxidation catalysts that are capable of operating at the temperature of the environment in which they are placed are beginning to find wide-spread appllication in a variety of products including CO₂ Lasers and face masks. These temperature conditions are much lower than those at which other catalysts developed for this purpose operate and range from room temperature to, at most 80°C. In order to prepare these catalysts they must first be activated with a reductive pretreatment. We have found that the conditions of that pretreatment are critical for the activity of the catalyst and determine whether or not they will be effective "low-temperature" catalysts. To determine the possible cause of the affect of pretreatment conditions on catalyst activity we undertook a diffuse reflectance study of the catalyst material. The particular advantage of the diffuse reflectance technique is that the actual pretreatment process may be followed under the same conditions that have occurred in the laboratory which have been monitored using Gas chromatography. We have managed to identify several adsorbed species the nature of which depend not only on pretreatment conditions and catalyst composition. These species include; formate, bicarbonate, hydroxyl, carbonate and surface adsorbed CO.

CHARACTERIZATION OF CATALYSTS AND POLYMERIC MATERIALS BY DIRECT DIAMOND ATR ANALYSIS. Steve Hill, ASI-Applied Systems, Millersville, MD 21108.

The demand by the industrial and consumer marketplace for consistent high quality product has placed a premium upon improved efficiency and accuracy of in-process verification methods for materials and reagents. However, the time and skill required to calibrate, validate, and facilitate an infrared quantitative method left little time to celebrate. Traditional quantitative techniques such as chromatography and visible/near infrared spectroscopy remain the preferred analytical method of choice. Recent technological advances have resulted in the development of an resilient diamond/Hastelloy C ATR sampling tool that provides an attractive alternative to many common infrared sampling techniques. Data will be presented for neat powders such as zeolites and polymer resins that benefit from improved measurement consistency with no sources of artifacts by specular reflectance, pressure, and salt diluent ion exchange. Routine applications for infrared solution analysis demonstrate benefits from the very small 50 microliter sample well, the full 6-reflection effective pathlength, and immunity to degradation by pH, corrosives, and insidious sample residues. Examples will be presented for latex paint, silicone, epoxy resin, bleach and detergent.
HIGH-TEMPERATURE RAMAN SPECTRA OF 9,10-DIHYDROANTHRACENE AND STILBENE VAPORS AND MELTS. Jaan Laane, Kevin Morris, Kristjan Haller, Whe-Yi Chiang, and Arnold del Rosario, Department of Chemistry, Texas A&M University, College Station, TX 77843-3255

The far-infrared spectra of 1,4-cyclohexadiene and 1,4-dioxacyclohexadiene-2,5 have shown these molecules to be planar in the vapor phase. An x-ray diffraction study of 9,10-dihydroanthracene, however, shows this analogous molecule to be bent in its crystalline form. Moreover, a recent dispersed fluorescence study has been interpreted to show the molecule to be non-planar in the vapor-phase. Various calculations (molecular mechanics, ab initio) are not in agreement on whether the molecule is planar or puckered in the vapor state. In order to help resolve the structure of this tricyclic molecule in the vapor, we have undertaken a high-temperature Raman investigation of this molecule in both vapor and liquid (melt) states. Of particular interest were the low-frequency modes which govern the conformational processes. The Raman data support the puckered structure for the vapor phase. trans-Stilbene and several of its derivatives as vapors or melts have also been studied by Raman spectroscopy at temperatures exceeding 300 C. Eight low-frequency modes, including the three torsional vibrations which govern the isomerization processes, were of special interest. Together with dispersed fluorescence spectra, the Raman data have made it possible to assign the low-frequency vibrations and to better understand the conformational dynamics.

APPLICATIONS OF POLARIZED FT-IR SPECTROSCOPY IN FERROELECTRIC LIQUID CRYSTALS, Cheol Soo Park, W. G. Jang, and N. A. Clark, Department of Physics, University of Colorado, Boulder, CO 80309-390

Polarized FT-IR spectroscopy has been used to study the Zig-Zag shape of molecular structure, the orientational behavior of carbonyls during chiral Sm C* switching, and the polarization direction change due to hydrogen bonding in Ferroelectric Liquid Crystal (FLC) phases. The polarized absorption profile of C=0 stretching peak is asymmetric with respect to the phenyl ring stretching direction with the electric field. This result suggests that there is the hindered rotation of the carbonyl group in the chiral part around the molecular long axis. The distribution function of the carbonyl group around molecular long axis is being calculated based on the addition of Fourier expanded distributions. We also report direct evidence of Zig-Zag shape of molecular structure in the chiral Sm C* phase. Polar plots of the absorption profile of phenyl groups and alkyl tails clearly show that some PLCs have structures in which the tails tilt 10° degrees less than the cores from the layer normal at temperatures far below the Sm A to Sm C phase transition. Finally, we will present changes in IR transition moment direction of carbonyls due to hydrogen-bonded interaction, for example as found in C=0—H-O and C=0—H-N. Not only is the maximum peak position of C=0 in the polar absorption profile changed from in the layer to normal to the layer but also the dichroic ratio is changed. These results will be interpreted by conformational change and transition moment direction calculations using ab initio electronic structure method.

INFRARED STUDIES OF CONFORMATIONAL ISOMERISM IN SOME ACRYLATES AND ACRYLIC ACIDS. MaryKay Orgill, Scott P. Leary, and Noel L. Owen. Department of Chemistry and Biochemistry, Brigham Young University, Provo. UT 84602

a-fi unsaturated carbonyl compounds are used extensively in industry as reagents for common polymers and in biochemical laboratories as model compounds for enzyme-substrate complexes within the active sites of the enzymes. These compounds have the possibility of existing in two heavy-atom planar structures (cis and trans) that research studies have shown to be of similar conformational energies. We have studied the infrared spectra for the gaseous, liquid and solid phases of acrylic acid, methacrylic acid and methyl methacrylate and have shown that for the acids, uv light brings about interconversion of the rotamers in the solid matrix-isolated phase, whereas this is not so for the ester. The conventional mechanism for rotational isomerism is through internal rotation, but in the solid matrix it probably occurs via hydrogen transfer.
RAMAN AND PHOTOACOUSTIC FTIR STUDIES OF POLYMERS SYNTHESIZED IN MICROGRAVITY. Kenneth G. Brown Karen S. Burns Department of Chemistry and Biochemistry, Old Dominion University, Norfolk, VA 23529 and Billy T. Upchurch, NASA-Langley Research Ctr., Hampton VA 23681

A module has been designed which enables the synthesis of polymers under microgravity conditions aboard the space shuttle. This unit has flown twice aboard STS-57 and STS-63 and will fly in May 1996 aboard STS-77. The overall experiment and the package will be described. However, this paper will concentrate on the vibrational study of polymers prepared on STS-57 and STS-63. We are primarily concerned with determining the homogeneity, or lack thereof of these polymers and secondarily any conformational differences which may occur because of the microgravity environment. In particular we will be concentrating on polymers that are prepared from initially immiscible monomers since there is the possibility of preparing new polymer materials when gravity is not present to force separation. We will discuss apparent differences that occur for these polymers when we compare them to the identical polymers synthesized on the ground.

STUDY OF LIFETIME STABILITY OF THIOL COATED SERS SUBSTRATES
Timothy O. Deschaines, Keith T. Carron, P.O. Box 3838, Chemistry Department, University of Wyoming, Laramie, WY 82071

We are using thiol coated Surface-Enhanced Raman Spectroscopy (SERS) substrates to develop an analytical procedure for detection and monitoring of contaminants in groundwater. Three different thiol compounds, 1-propanethiol, 1-dodecanethiol, and p-cresolthiol, were used to coat Ag surfaces. The thiols form a monolayer on the silver surface that creates an affinity for select compounds. This study investigates the stability and lifetime of the thiol substrates. For this study a saturated solution of benzene in water was used as a standard. These surfaces were studied over a month long period to see if significant changes in surface stability resulted. The SERS surfaces demonstrate long-term stability with only minimal day-to-day deviation in signal response. A discussion of optimal SERS surface preparation and storage conditions that were investigated for maximizing surface lifetime and stability will be presented.

DEVELOPMENT OF A SELECTIVE SERS SUBSTRATE FOR THE DETECTION OF ILLICIT DRUGS Roberta A. Sulk, Robert C. Corcoran, Keith T. Carron, P.O. Box 3838, Chemistry Department, University of Wyoming, Laramie, WY 82071

A method for the detection of illicit drugs has been tested. An indicator dye was synthesized and examined for its ability to determine the presence of morphine, cocaine, and benzoylecgonine in solution at a surface. The xanthate containing dye forms a robust monolayer on silver substrates. The spectroscopic technique used to examine this method was Surface-Enhanced Raman Scattering (SERS). We determined that the dye possessed surface-enhanced Raman bands which are characteristic of the molecular structure associated with the indicator and its conjugate acid. Furthermore, these bands are significantly changed in the presence of morphine, cocaine, or benzoylecgonine in solution. We have proposed an ion pair interaction and a $\text{T}_\text{X}^\text{ie}$ interaction between the dye and drug. Time-dependent changes to the shape, peak location, and intensity of the Raman bands were measured. Relative spectral intensities of individual bands were used to determine the concentration of adsorbate molecules on the surface. Optimal experimental conditions for obtaining the SERS enhancement were investigated.
APPLICATIONS OF NEAR-INFRARED SPECTROSCOPY TO BREATH ANALYSIS: POTENTIAL USE IN THE DIAGNOSIS OF DISEASE. Steven W. Sharpe, Robert Sams, Karla Thrall and James Toth, Battelle, Pacific Northwest National Laboratory, Richland, Washington 99352

The goal of our work is two fold; 1) to develop a portable rapid laser based breath analyzer for monitoring metabolic processes and 2) model these metabolic processes by physiologically based pharmacokinetic (PBPK) modeling. Small infrared active molecules such as ammonia, carbon monoxide, carbon dioxide, methane and ethane are present in exhaled breath and can be readily detected by both mid- and near-infrared laser absorption spectroscopy. In addition, many of the stable isotopomers of these molecules can be accurately detected, making it possible to follow specific metabolic processes. Potential areas of applications for this technology include the diagnosis of certain diseases (e.g. H. Pylori), detection of trauma due to either physical or chemical causes and monitoring nutrient uptake (i.e., malnutrition). In order to understand the origin and elucidate the metabolic processes associated with these small molecules, we are employing physiologically based pharmacokinetic (PBPK) models. A PBPK model is founded on known physiological processes (i.e., blood flow rates, tissue volumes, breathing rate, etc.), chemical-specific processes (i.e., tissue solubility coefficients, molecular weight, chemical density, etc.), and on metabolic processes (tissue site and rate of metabolic biotransformation). Since many of these processes are well understood, a PBPK model can be developed and validated against the more readily available experimental animal data, and then by extrapolating the parameters to apply to man, the model can predict chemical behavior in humans.

MEASUREMENT OF BENZENE IN GASOLINE USING NEAR- OR MID-INFRARED SPECTRA. James E. Tackett, Marathon Oil Company, P.O. Box 269, Littleton CO 80160. (303) 347-5470

Measurement of benzene in gasoline has become more important in the last few years because of the Reformulated gasoline regulations. ASTM D 4053 specifies this be done using a linear calibration of the benzene band at 673 cm\(^{-1}\) after correcting for toluene interference. A proposed ASTM method specifies use of a multivariate calibration in the 686 cm\(^{-1}\) to 664 cm\(^{-1}\) region. Some have suggested that accurate benzene analyses can be done in the first and second overtone near infrared regions. We developed a limited data set of 12 blended gasolines and 10 gasoline blending components using gas chromatographic benzene values. These samples were run in the mid-IR and first and second overtone near-IR spectral regions. PLS was used to develop benzene prediction models for each region. The PLS results were compared to results obtained using a linear calibration of the 675 cm\(^{-1}\) peak. The linear results were the best, but PLS results that were nearly as good were obtained by selecting optimum wavelengths.
REAL TIME DETECTION OF VOC'S AT A WASTEWATER TREATMENT PLANT USING LONG PATH FTIR AND ULTRAVIOLET SPECTROSCOPY. Philip A. Russell. (L/E WWTP, Englewood, Colorado, 80110), Amber Hodgson, and Donald H. Stedman (Chemistry Department, University of Denver, Denver, Colorado, 80210).

Studies have measured Volatile Organic Compounds (VOC's) using open, long path Fourier Transform Infrared (FTIR) and ultraviolet spectroscopy with observed detection limits for organic compounds in the hundreds of ppb range. VOC's have also been identified and quantified in individual automobile emissions, in real time, on highways, using long path ultraviolet (LPUV) and long path infrared spectroscopy (LPIR). Because of (1) the concerns that wastewater treatment facilities, in general, may emit detectable concentrations of VOC's, (2) the potential need to have a real time detector to monitor for VOC's entering the wastewater treatment facilities, and (3) the potential need to identify VOC's associated with odor problems, a joint effort was made by the Littleton/Englewood Wastewater Treatment Plant (L/E WWTP) and Dr. Donald Stedman at the University of Denver to perform a joint study to determine the feasibility of using LPUV and LPIR on-site at a wastewater treatment plant. Tests were conducted during February 1993 at various sites within the plant. Detection limits for the LPIR and LPUV spectrophotometers were estimated using the variables of beam path length, daily averaged noise levels, and instrument detection limits calculated by comparison with a spectral library on each separate day. Open air path lengths ranged from 62 to 15 meters. Detection limits for compounds measured by LP-FTIR ranged from $10^{-0.2}$ ppm and ~1000-3ppb for compounds measured by LPUV. Our study concluded that the use of real time LPUV and LPIR spectrophotometry is potentially useful in detecting VOC's at a wastewater treatment plant; the sensitivity of these techniques is currently not adequate to detect airborne odor producing VOC's at typical expected concentrations.

THE DETERMINATION OF BROMATE IN THE PRESENCE OF HALOACETIC ACIDS BY ION CHROMATOGRAPHY-INDUCTIVELY COUPLED PLASMA MASS SPECTROMETRY. Carol A. Brockhoff, John T. Creed, and *Matthew L. Magnuson, United States Environmental Protection Agency, National Exposure Research Laboratory, Human Exposure Research Division, 26 W. Martin Luther King Drive, Cincinnati, Ohio 45268. *National Research Council Postdoctoral Associate

Disinfection-by-products (DBPs) are formed by chemical reactions between source water constituents and the disinfecting agent. Bromate is a DBP which is formed when the source water contains bromide which is oxidized by the disinfecting agent ozone. Brominated haloacetic acids are also DBPs from the ozonation of drinking water. The quantification of bromate in drinking waters requires a chromatographic separation of bromate from brominated haloacetic acids prior to detection by ICP-MS. Two brominated haloacetic acids produce most of the problems associated with the detection of bromate by ion chromatography with ICP-MS detection. Bromoacetic acid co-elutes with bromate while tribromoacetic is strongly retained on the column. The tribromoacetic acid leads to rising backgrounds on mass 79 and slowly changing chromatographic retention times.

Two approaches to resolving this problem will be presented. The first approach involves the separation of the bromate from the bromoacetic acid using a PA-100 column and then removing the tribromoacetic acid with acetonitrile. The second approach involves the extraction of the haloacetic acids prior to analysis of bromate using an AGIO. The analytical advantages presented will be in terms of: 1) detection limits 2) tolerance to chloride, sulfate and nitrate matrices 3) overall analysis time.

LOW ENERGY LAMP FOR GRO/DRO WITH A TANDEM PID/FID. Jessie Crockett Butler and Terry Rankin, Finnigan Corporation/ 2215 Grand Avenue Parkway, Austin, Texas 78728-3812.

Leaking underground storage tanks pose a risk to surrounding water tables and must be monitored on a routine basis. The analysis is simplified by incorporating a Tandem Photoionization Detector and Flame Ionization Detector (PID/FID). The specificity of the PID clearly confirmed the presence and concentration of the polyaromatics through benzo(g,h,i)perylene. The Tandem PID/FID provides the enhanced sensitivity and specificity for the more toxic analytes like benzene. The author will present the data generated using a low energy Xenon lamp of 9.6 electron volts on the PID, for the analysis of gasoline, diesel and mineral oil petroleum fuels. The low energy lamp gave greater specificity for the aromatics and reduced the response for the lower alkanes. Using two dissimilar detectors, the confirmational analysis was performed simultaneously with a single injection. Soil and water samples were extracted and injected on a splitless capillary injector with a Restek DB-TPH capillary column. The linearity and sensitivity of the analysis will be shown. A table of the minimum detection limits will be presented and the stability of both detectors evaluated.
MINKOWSKI DISTANCE METRIC PATTERN RECOGNITION TECHNIQUES APPLIED TO COUNTRY-OF-ORIGIN DETERMINATIONS OF EMBARGOED OILS Neal D. Byington, U.S. Customs Service Laboratory, 630 Sansome St., Rm. 1429, San Francisco, CA 94111

Crude oils, fuel oils, and many other imported items with an interesting history, from our perspective, are analyzed to determine their Country-Of-Origin. Minkowski distance metric pattern recognition techniques have been developed to assist in these determinations. These techniques provide a numerical measure of the similarity or dissimilarity between capillary gas chromatograms obtained on samples of crude oils or fuel oils subject to an import or export embargo and reference samples. Current applications, limitations, and our assessment of the validity of these techniques are presented.

EVALUATION OF SOLIDS PREPARED BY SOL-GEL PROCESSES AS MEDIA FOR ELECTROCHEMICAL ANALYSIS, James A. Cox, Kathryn S. Alber, and Mark E. Tess, Department of Chemistry, Miami University, Oxford, OH 45056.

Electrochemistry in solid states in the absence of a contacting liquid phase is projected to have merits for a variety of applications, most notably the development of sensors and detectors for gaseous analytes. Solids prepared by sol-gel processes have particular promise as solid-state electrolytes; among their merits are the potential for tolerance of humidity variation over wide ranges, high ionic conductivities, ability to incorporate buffers in residual pore water, and the opportunity to modify their structures to include redox-active sites. These and other factors will be evaluated using various alcohols, ammonia, and carbon monoxide as test compounds. The electrochemical cells will be thin films of these solids (primarily vanadia and silica systems) cast on interdigitated microelectrode arrays in which the indicator electrode is modified with a mixed-valence ruthenium oxide catalyst.

BROMATE IN DRINKING WATER: TRACE LEVEL DETERMINATION BY ION CHROMATOGRAPHY. B. LO AND k. Subramanian. Bureau of Chemical Hazards, Environmental Health Directorate, Ottawa, Canada

Ozonation has emerged as a viable alternative to chlorination, and many utilities are turning to ozone disinfection because of the trihalomethane problem with chlorine. It is now known that ozone oxidizes bromide, which occurs to a maximum level of 2.0 mg/L in groundwaters and 0.8 mg/L in surface waters, to bromate. Risk assessment data indicate bromate to be a carcinogen at low ng/mL levels. Accordingly, there is a need to develop a method to determine bromate at the low ng/mL levels. Bromate, at trace concentrations, has seldom been monitored in drinking water until recently. This presentation will describe the development of an ion chromatographic method for the trace level determination of bromate in potable water supplies. The method involved ion exchange separation of bromate from the interfering chloride and sulphate species, preconcentration, and conductivity detection. No interference from chloride occurred up to chloride/bromate ratios of 500; above this ratio, interference occurs, and it is necessary to remove chloride using the silver cartridge. Sulphate interfered only at sulphate/bromate ratios of 5000 and above, and higher levels of sulphate should be removed using the barium cartridge. Both were based on the bromate concentration of 10 ug/L solution. The method detection limit, based on 3 standard deviation of 10 runs of a 1 ng/mL solution of bromate, was 0.4 ng/mL. The precision, expressed as % coefficient variation, was 8.9 at 1 ng/ml and 3.5 at 10 ng/ml. The method, validated using some tap and well water samples supplemented with 2.5, 5 and 10 ng/mL bromate, gave recoveries in the range of 97-100%. The method could be used for the reliable determination of as low as 2 ng/mL bromate.
NOVEL BUFFER/ADDITIVE COMBINATIONS IN EKC AFFORDING FAST, HIGH RESOLUTION SEPARATIONS WITH IMPROVED DETECTABILITY

Jeffrey R. Mazzeo, Edward R. Grover and Michael E. Swartz, Waters Corporation, 34 Maple Street, Milford, MA 01757

EKC has greatly enhanced the ability of CE to separate analytes based on mechanisms other than differences in free solution mobility. Although the most common form of EKC uses micelles (MEKC), other additives continue to be investigated. The majority of EKC separations performed at neutral to basic pH have employed common inorganic salts as the buffering agents (i.e., sodium phosphate, sodium berate, etc). However, because these buffers are so conductive, high currents are generated. This results in band broadening due to joule heating at relatively low voltages. Furthermore, capillary i.d.s of 50 urn are commonly used to reduce the amount of heat generated, but this comes at the expense of detectability when using on-column UV detection. We have developed novel buffer/additive combinations for EKC which give a slow electroosmotic flow for good resolution, but generate very little current. Therefore, very high voltages can be applied with 100 um i.d. capillaries for fast separations with excellent detectability. Several examples of these combinations will be given, and the advantages vs. electrolytes made with inorganic salts as the buffering agents will be demonstrated.

ANALYSIS OF NITRAMINE AND NITROAROMATIC EXPLOSIVES BY CAPILLARY ELECTROPHORESIS.

Stuart A. Oehrle, Waters Corporation, 34 Maple St., Milford, MA 01757

Analysis of nitramine and nitroaromatic explosives is of interest for both environmental and forensic applications. Analysis of 14 nitramine and nitroaromatic explosives was accomplished by micellar electrokinetic capillary chromatography, MECC. Analysis times under 11 minutes were possible employing a phosphate-SDS electrolyte. Detection limits for each explosive at different wavelengths (185 nm, 214 nm, 229 nm, and 254 nm) were calculated. Analysis of various extracts of high explosives such as composition C-4, tetrytol, and detonating cord was performed. Detection limits less than 1 mg/L were possible using a hydrostatic injection and direct UV detection at 214 nm.

DISCOVERING PRINCIPLES OF CHEMISTRY BY COMPUTER


Encouraging a sense of discovery in students is an important part of building enthusiasm for learning. To beginning students, Chemistry may seem to be only a "body of knowledge to be learned by rote. Dynamic computer-based tools such as widely available computerized periodic tables can be used by students as a means to discover relationships, patterns and principles. This talk will discuss the use of a periodic table program which is available on the Internet. It features six periodic table styles, 98 properties on five screens, logical searching of property values and comparative property graphing. Examples are given of students using the program as a research tool to find their own answers to questions such as: "Why do elements have different physical densities?" and "Why do some property values increase and decrease in regular patterns as atomic number increases?" Students learn to discover the answers using a professional research tool.
SPECIATION OF ARSENIC AND SELENIUM BY CAPILLARY ELECTROPHORESIS HYDRIDE GENERATION-INDUCTIVELY COUPLED PLASMA-MASS SPECTROMETRY DETECTION.

Matthew L. Magnuson, John T. Creed, and Carol A. Brockhoff United States Environmental Protection Agency National Exposure Research Laboratory, Human Exposure Research Division, 26 W. Martin Luther King Drive, Cincinnati, Ohio 45268. *National Research Council Postdoctoral Associate

An element's chemical form can dramatically affect its toxicity, and speciation allows the environmental levels of discrete chemical forms to be quantified. This leads to a more accurate risk assessment, because the use of total concentration can greatly over-estimate the risk if the less toxic species are present in higher amounts. Recently, we developed an ion chromatographic separation of arsenic species detected through hydride generation (HG) inductively coupled plasma-mass spectrometry (ICP-MS). The gas-liquid separator for the hydride generation unit is based on microporous polytetrafluoroethylene tubing. The excellent sensitivity and peak shapes possible with this HG-ICP-MS system led to the investigation of capillary electrophoresis to speciate several hydride forming elements, namely arsenic and selenium. The combination of hydride generation and on-column preconcentration through sample stacking allows for the analysis of solutions with analyte concentrations in the parts-per-trillion range. The design of this system will be described, and experimental results for several analytes in a variety of matrices will be presented.

ENVIRONMENTAL AND BIOLOGICAL MONITORING USING A UV LASER ABLATION ICP-MS. Rob Henry, Angelica Raith, Fisons Instruments, 1812 Mapleton Avenue, Boulder, CO 80304, USA, Bob Brown, Sam Wang, Elemental Research Inc., 309 –267 West Esplanade, North Vancouver, BC V7M 1A5, Canada

Ultraviolet Laser Ablation ICP-MS has been used for the analysis of Ferromanganese crusts in order to track sources of pollution and metal migration into the Baltic Sea. It has also been shown to be effective in the rapid analysis of biological materials to track the migration patterns of fish with a view to effectively managing fishing resources in the seas around North America. Data will be presented to illustrate the accuracy, speed of analysis and precision of the technique.

TECHNOLOGY ADVANCES IN THE APPLICATION OF QUADRUPOLE ICP-MS TO THE ROUTINE ANALYSIS OF SEMICONDUCTOR MATERIALS. Rob Henry, Paul Sigsworth, Tom Retberg, Fisons Instruments, 1812 Mapleton Avenue, Boulder, CO 80304, USA.

ICP-MS has been used for the analysis of process chemicals, gases and silicon wafers in the Semiconductor Industry for many years. As the levels of contamination required to be measured decreased with the advent of smaller geometry devices the limitations of the Quadrupole Mass Spectrometer were reached. With the advent of new hardware and software technology many of these limitations can now be overcome for the chemicals used in this industry.
The analysis of dissolved trace metals by ICP-MS is complicated by the fact that doubly-charged atoms and oxide- and argon-molecules form in the plasma and create spectral interferences. Although the frequency of formation of these species is dependent (to a degree) upon the instrument operating conditions, the problem cannot be avoided by modifying these conditions: it must be corrected post-analysis using information collected during the analysis run. The following is a list of trace metal isotopes which usually have interferences needing correction at typical natural water concentrations: $^{47}$Ti, $^{49}$Ti, $^{51}$V, $^{52}$Cr, $^{53}$Cr, $^{58}$Ni, $^{59}$Co, $^{60}$Ni, $^{63}$Cu, $^{64}$Zn, $^{65}$Cu, $^{66}$Zn, $^{68}$Zn, $^{75}$As, $^{77}$Se, $^{82}$Se, $^{110}$Cd, $^{112}$Cd, $^{112}$Cd, $^{112}$Cd, $^{151}$Eu, $^{153}$Eu, Gd, Tb, Gd, Dy, Yb, Yb and Lu. In general, correction of these interferences requires knowledge of the concentrations of sulfate, chloride, calcium, sodium, silica, magnesium, bromide, molybdenum, barium, neodymium, cerium, samarium, gadolinium and terbium. This paper will discuss the concentration levels at which each of these isotopes is likely to be impacted, along with strategies for effectively correcting for the interferences and checking to insure that the corrections are valid.

A STATISTICAL ANALYSIS OF ICP-MS METHODS DEVELOPMENT DATA.  

Greg W. Johnson and Virginia H. Houlding, Matheson Gas Products, 1861 Leit hand Circle, Longmont, CO 80501.

Matheson Gas Products is a world leader in supplying high quality gases for industrial and academic use. Residue and hydrolysis sampling for elemental content are the two most often used procedures used to sample gases prior to elemental concentration determinations. Residue sampling is currently being used for routine quality assurance testing of some of our gas products, and is being considered for application to some others because of several advantages offered by the residue method. Residue sampling techniques will be described. Cylinders of HCl, HBr, Cl$_2$, and BC$_3$ were sampled repetitively. Multi-element spikes were added to some sample containers and dried prior to the sampling step. Solutions were prepared by dissolving residue samples in HCl and/or HNO$_3$ diluent. Elemental concentrations were determined using ICP/MS, Graphite Furnace AA (GFAA), flame atomic emission, and ICP/AES spectroscopic techniques. Elemental composition of the residues, sample to sample variability, and spike recoveries were characterized. Our presentation will discuss analytical results in terms of standard statistical procedures and interpretation of results of the statistical tests performed. The work represents an initial phase of development for residue sampling protocol. Possible directions for further development of the residue sampling method will be discussed.


*On leave from the Geological Survey of Israel, Jerusalem.

A USN-membrane desolvation interface is characterized for trace element determinations using solvent extraction. As a result of chloroform rejection, the deleterious results of overloading are minimized; i.e., carbon formation on torch tubes and sampler cone, plasma instability, and formation of molecular ions. For the nebulization of APDC-NaDDC metal chelates in chloroform, 20 ml/min of oxygen were introduced into the plasma to avoid C build up on the cones. The role of membrane desolvation temperature on recovery and molecular ion intensity was evaluated. Due to chelate volatilization, it was concluded that the boiling temperature of the extraction solvent should be as low as possible to avoid analyte loss by volatilization. The use of a chloroform solution of metals in oil for universal calibration was not possible due to the removal of volatile metal species in the thermal stages of the interface. Advantages of the technique include enhanced LODs and reduced plasma and spectral interferences.
CHARACTERIZATION OF BENZO[a]PYRENE-DNA ADDUCTS VIA SOLID-MATRIX LUMINESCENCE AND SOLUTION FLUORESCENCE. R. J. Hurtubise and S. W. Tjoe, Department of Chemistry, University of Wyoming, Laramie, WY 82071.

It is well known that benzo(a)pyrene (B[a]P) is involved in chemical carcinogenesis by covalently binding to DNA to form DNA adducts. It is important to have very selective and sensitive analytical methods for the characterization of the adducts. Room-temperature solid-matrix luminescence (RTSML), especially from the DNA adducts adsorbed on filter paper, offers both high sensitivity and selectivity. Both Whatman No. 1 and Whatman 1PS filter papers are very good solid matrices to acquire room-temperature solid-matrix fluorescence (RTSMF) and room-temperature solid-matrix phosphorescence (RTSMP) from the adducts. For example, RTSMP excitation and emission spectra, and RTSMP lifetimes are readily obtained with samples at nanogram levels. RTSML methods were developed for the characterization of the two major forms of the B[a]P-DNA adducts, namely, the "external" and the "intercalated" species. Both RTSMF and RTSMP with Whatman No. 1 and Whatman 1PS filter papers were used. Selective RTSMP excitation of the adducts on Whatman No. 1 filter paper showed at least two populations of adducts, and RTSMF on Whatman 1PS paper indicated that the "external" form of the adducts interacted selectively with the silicone in the Whatman 1PS paper. The RTSML data were compared with solution fluorescence results for the adducts, and the comparison revealed how RTSML data complements solution fluorescence data for the adducts.

DETECTION OF POLYCYCLIC AROMATIC HYDROCARBON-HEMOGLOBIN ADDUCTS FOR HUMAN EXPOSURE MONITORING. Christian Hackl¹, Ainsley Weston¹, Jutta Lintelmann¹ and Antonius Kettrup¹. GSF-Forschungszentrum fuer Umwelt und Gesundheit, Institut fuer Oekologische Chemie, Postfach 1129, D-85758 Oberschleissheim, Germany, Environmental Health Sciences Center, Mount Sinai Medical Center, New York, NY 10029 USA.

PAHs (e.g. benzo[a]pyrene, chrysene and benz[a]anthracene) are carcinogenic environmental contaminants. Humans are exposed to these chemicals daily. Development of dosimetric methods for human exposure and biomonitoring have been hampered by exposure to complex mixtures and analytic sensitivity. PAH-hemoglobin adducts represent an important potential dosimeter because hemoglobin is a relatively accessible and abundant sample source, and adducts accumulate over the life-time of the erythrocytes. We have developed a novel method for the detection of hemoglobin adducts formed through the covalent binding of metabolically activated PAHs. The method comprises of an HPLC coupled-column switching technique that simultaneously enhances selectivity and provides good analytical resolution. Packed red cells (equivalent to 5 mL whole blood) are lysed and the globin is extracted. Adducts are acid hydrolyzed to their corresponding tetrahydrotetrols. Separation of these analytes from the hydrolysate is achieved by use of two pre-columns, the first contains a restricted access packing material and the second a copper phthalocyanine modified polymer. System integrated sample of processing allows for the direct introduction of the analytes of interest to the analytical column by back-flushing of the second pre-column with solvent delivered via a heated capillary. PAH residues are detected and identified by fluorescence spectroscopy.
METAL–LIGAND COMPLEXES AS A NEW CLASS OF LONG–LIVED FLUOROPHORES FOR 
PROTEIN HYDRODYNAMICS. Ewald Terpetschnig, Henryk Szmacinski, Henryk Malak, and Joseph R.
Lakowicz, Center for Fluorescence Spectroscopy, Department of Biological Chemistry, University of Maryland 
at Baltimore, 108 N. Greene Street, Baltimore, MD 21201.

We describe the use of asymmetric Ru-ligand complexes as a new class of luminescent probes. These 
complexes are known to display luminescent lifetimes ranging for 10 to 4000 ns. We show that the asymmetric 
complex Ru(bpy)(dcbpy) (PF$_6$)$_2$ displays an intensity decay time near 400 ns and a high anisotropy value near 0.26 
when excited in the long wavelength absorption band. For covalent linkage to proteins, we synthesized the N-hydroxy 
succimide ester. We measured the intensity and anisotropy decays of [Ru(bpy)(dcbpy)] when covalently linked to 
proteins and in solutions of increased viscosity. These data demonstrate that the probes can be used to measure 
rotational motions on the us timescale, which so far has been inaccessible using fluorescence methods. We also used 
this probe in a fluorescence polarization immunoassay (FPI) of HSA. We found that the steady-state polarization of 
labeled HSA was sensitive to binding of anti-HSA, resulting in a 200% increase in polarization. The labeled HSA was 
also used in a competitive format with unlabeled HSA as the antigen. The time-resolved anisotropy decays demonstrate 
increased correlation times for labeled HSA in the presence of anti-HSA, an effect which was partially reversed in the 
presence of unlabeled HSA. These results demonstrate the potential of the metal-ligand complexes to be used in the 
fluorescence polarization immunoassay of high molecular weight analytes. The use of such metal-ligand complexes 
enable fluorescence polarization immunoassays which bypass the usual limitation to low molecular weight antigens.

LIFETIME-BASED SENSING IN HIGHLY SCATTERING MEDIA. Henryk Szmacinski and Joseph 
R. Lakowicz, Center for Fluorescence Spectroscopy, Department of Biological Chemistry, University of 
Maryland at Baltimore, 108 N. Greene Street, Baltimore, MD 21201.

Fluorescence lifetime-based sensing is now recognized as a valuable methodology in clinical and analytical 
chemistry. For clinical chemistry, or for non-invasive sensing through skin, it is often necessary to obtain 
quantitative information in highly scattering media. Lifetime-based sensing can be used to obtain quantitative 
measurements in turbid media. We describe frequency-domain lifetime measurements in intralipid suspension, 
and present a reliable technique which allows phase-modulation lifetime measurements of fluorophores dispersed 
within or localized within intralipid. Lifetimes can be measured using an intensity decay law which accounts for 
the time delay, decay time, and pulse-broadening effects due to multiple light scattering events occurring in the 
intralipid suspension. Alternatively, the phase and modulation measurements can be performed relative to a 
reference fluorophore of known lifetime. This approach provided reliable lifetime data for fluorophore with 
double-exponential intensity decay for a fluorophore localized up to 4 mm under the surface of an intralipid 
suspension. Additionally, reference fluorophore allows chemical sensing based on phase and modulation 
measurements in turbid media with a single modulation frequency regardless of the heterogeneity of the sensor 
intensity decay.

INTERACTIONS OF POLYMERS WITH LUMINESCENT METAL COMPLEXES AND 
ORGANIC DYES. DESIGN OF USEFUL ANALYTICAL SYSTEMS. J. N. Demas, Wenying Xu, 
Kristi Kneas, and Sari Benmeir, Department of Chemistry, University of Virginia, Charlottesville, VA 
22901; B. A. DeGraff, Department of Chemistry, James Madison University, Harrisonburg, VA 22807. 
Ming Wu, Peter M. Goodwin, Rhett L. Affleck Richard A. Keller, Chemical Science and Technology 
Division, Los Alamos National Laboratory, Los Alamos, NM 87545

A variety of inorganic complexes show great promise as molecular probes and luminescence-based 
sensors. The majority of work uses d$^6$ systems Ru(II), Re(I), and Os(II) with a-diimine ligands (e.g., 2,2’-
bipyridine, 1,10-phenanthroline, and analogues). Central to the rational design of practical systems is an intimate 
understanding of the interactions between the probe or sensor molecule and the polymer based support or the 
target. Advances in understanding the interactions of metal complexes and polymeric supports will be discussed. 
A related area is the influence of binding luminescent dyes to polymers in solutions. Applications of this binding 
to ultra-low level detection, including single molecule detection, will be discussed. We conclude by pointing out 
that these areas are still in their infancy and that the ultimate goal of a totally rational design of probes, 
luminescence enhancers, and polymer-supported sensors is as yet an imperfectly realized goal.
OXYGEN SENSOR BASED ON THE QUENCHING OF ROOM-TEMPERATURE PHOSPHORESCENCE INTENSITY OF PHENANTHRENE (D₁₀) ADSORBED ON WHATMAN IPS FILTER PAPER. S.M. Ramasamy and R. J. Hurtubise, Department of Chemistry, University of Wyoming, Laramie, WY 82071-3838.

Phenanthrene (D₁₀) exhibits strong room-temperature phosphorescence (RTP) when adsorbed on Whatman IPS filter paper. An oxygen sensor was developed using the quenching of RTP intensity of adsorbed phenanthrene (D₁₀) by oxygen. The system was characterized by using a continuous nitrogen/nitrogen-air flow on the adsorbed phosphor. The sensor is simple to prepare and needs no elaborate fabrication procedure, but was found to show a somewhat drifting baseline for successive determinations of oxygen. Nevertheless, very good reproducibility was achieved with the RTP quenching data by obtaining the RTP intensities just before and at the end of each oxygen determination. The calibration plots showed a nonlinear relationship over the entire range of oxygen in air. However, a linear range was obtained up to 3% of oxygen. A detection limit of 0.2% of oxygen in dry nitrogen was obtained. Carbon dioxide was found to have a minimum effect on the RTP quenching of oxygen. Additional information on the quenching phenomena for this system was obtained from the RTP lifetime data acquired at various oxygen contents. The performance of the oxygen sensor was evaluated by comparing it to a commercial electrochemical trace oxygen analyzer.

DEVELOPMENT OF NEAR-INFRARED FLUORESCENT TRACERS FOR IMMUNOASSAYS. Anand Swamy, Abraham George and Gabor Patonay, Department of Chemistry, Georgia State University, University Plaza, Atlanta, GA 30303.

Development of near-infrared (NIR) fluorophores as tracers for immunoassay will be presented. Optimization and development of assay conditions and instrumentation will be discussed. The NIR region is relatively free of background interference and thereby detection is improved. The instrumentation used for imaging involves a near-infrared laser scanner with a 30 mW laser diode for excitation and a thermoelectrically cooled avalanche photodiode capable of measuring very low level signals for detection. A detailed description of the setup with the application of NIR immunoassay to clinical diagnostics and environmental applications will be discussed. The data obtained by this method will be compared with those obtained by other conventional methods.

STOCHASTIC ADSORPTION KINETICS AT LIQUID/SOLID INTERFACES: MEASURING RATE PROCESSES NEAR THE SINGLE-MOLECULE LIMIT. Richard L. Hansen and Joel M. Harris, Department of Chemistry, University of Utah, Salt Lake City, Utah 84112.

The adsorption of molecules at liquid/solid interfaces involves challenging questions about the kinetics of transport and adsorption. In this talk, a novel approach to probe reversible adsorption kinetics is described, based on fluctuations of numbers of molecules in a small volume at the interface defined by internal reflection excitation of fluorescence. When the number of fluorescing molecules in the probe volume is small, fluctuations in the population will dominate the noise in the signal. The kinetics of the population fluctuations, determined by autocorrelating the fluorescence transients, depend on mass transport to the interface, photostability of the fluorophore, and adsorption/desorption kinetics. Since the number of molecules observed is small, fluctuations are characterized by Poisson statistics where the ratio of the signal variance to its mean is used to determine the number of molecules at the interface without the need for calibration. Adsorption of rhodamine 6G at a C-18 derivatized silica slide is investigated. By counting the number of molecules at the interface based on their fluctuations, adsorption to a planar interface can be quantitatively compared with adsorption equilibria obtained chromatographically.

Recently developed optical techniques permit near-real-time imaging of pressure and temperature fields in studies of wind tunnel models and turbomachinery. By affixing luminescent molecules to a test article and monitoring dynamic quenching, oxygen concentrations and local pressures can be accurately determined over a surface of interest based on Stern-Volmer kinetics. Similarly, the luminescence from temperature-sensitive molecules can be employed to map temperature fields. Extending this technology to the study of unsteady aerodynamic phenomena places new demands on paint performance. Time-resolved and steady-state spectroscopic techniques have been employed to evaluate candidate lumophores and new paint formulations.

HEAVY-ATOMEFFECT AND TEMPERATURE DEPENDENCE OF PHOSPHORESCENCE LIFETIMES OF ORGANIC COMPOUNDS IN GLUCOSE GLASSES. Jiangshan Wang and Robert J. Hurtubise, Department of Chemistry, University of Wyoming, Laramie, WY 82071.

Phosphorescence lifetimes of benzo[f]quinoline (B[f]Q), 2-amino-l-methyl-6-phenylimidazo[4, 5-b]pyridine (PhIP), and 4-phenylphenol (4-PP) in glucose glasses were obtained at room temperature. By adding 10% NaI as a heavy-atom salt to the glucose glasses, the lifetimes measured were much shorter compared to the glasses without NaI. Also, the lifetime decay curves fit a double exponential equation with 10% NaI present which indicated there were at least two components in the system. The phosphorescence lifetimes without a heavy-atom salt for B[f]Q and PhIP in glucose glasses, at temperatures ranging from 296 to 93 K, were studied in detail. When the temperature decreased, the phosphorescence lifetimes of B[f]Q and PhIP increased. However, the lifetime and temperature relationships did not obey vigorously previous basic equations as in the case with most solid matrices investigated. The phosphorescence lifetimes of B[f]Q and PhIP in glucose glasses with 10% NaI at different temperatures were also obtained. In addition, the temperature dependence of phosphorescence intensities for B[f]Q and PhIP in glucose glasses with and without heavy-atom salt were compared. With the parameters calculated from the lifetime data, it was possible to elucidate some of the physicochemical interactions between phosphors and glucose glasses.

BREWSTER ANGLE AND FLUORESCENCE MICROSCOPY OF ELECTRIC-FIELD-PERTURBED LANGMUIR FILMS. Matthew A. Jones and Paul W. Bohn, Department of Chemistry, University of Illinois, Urbana, IL 61801.

Our laboratory has a long-standing interest in the active control of molecular transport. Past and present efforts have focused on the use of electric fields to alter the permeability state of an ultra-thin organic film barrier layer. This talk describes the use of Brewster angle microscopy and fluorescence measurements to characterize these fields and their interactions with organized monolayer films. Brewster angle microscopy exploits differences in refractive index between the film and its adjacent environments to allow imaging of film morphology. We’ve employed this technique to monitor the interaction of an inhomogeneous electric field with a cadmium stearate monolayer at the air-water interface. Application of dc fields on the order of 105 V/cm (nominal) results in an observable in the BAM image which has been attributed to interfacial instability. Characterization of the trans-membrane potential experienced by these systems is also of interest. Measurement requires a method which is: (1) accurate, (2) fast, (3) local, and (4) applicable over a wide range of experimental conditions. We are currently exploring the use of an in situ optical probe to meet these requirements. An electrochromic styryl dye is incorporated into the monolayer as an impurity. The monolayer is formed and transferred onto a semi-transparent indium-tin-oxide electrode by the Langmuir-Blodgett method. An electric field is then applied between the ITO electrode and an electrolytic solution. These systems are being evaluated for an electrochromic response of the fluorescence spectrum.
Novel Luminophores for Cation Sensing Based on Re(I) 2,2-Bipyridine and 1,10-Phenanthroline MLCT Excited States. Yibing Shen, B. Patrick Sullivan, Department of Chemistry, University of Wyoming, Laramie, WY 82071.

Derivatives of 2,2'-bipyridine and 1,10-phenanthroline have played a major role in the development of the chemistry of a-diimine metal complexes. The photochemical and photophysical properties of the complexes have been utilized in a wide range of probes. We now demonstrate that with a modest synthetic design a sensing luminophore based on the MLCT excited states of the fac-Re(CO)₃(a-diimine) unit can be made to be discriminate for metal ions, or for the proton in aqueous solution. The a-diimines in our studies are either 2,2'-bipyridine or 1,10-phenanthroline bearing appended aza-18-crown-6 or amine groups as the binding sites. Our aqueous rhenium-based luminophores overcome a major drawback of most sensing materials derived from organic fluorophores, in that they are freely soluble in aqueous solution.

STEADY-STATE FLUORESCENCE OF POLYSTYRENE IN SUPERCRITICAL CARBON DIOXIDE. Ming Li and Frank V. Bright, Department of Chemistry, State University of New York at Buffalo, Buffalo, NY 14260-3000.

A steady-state fluorescence study of low molecular weight polystyrene (MW=1,060 g/mol and 13,000 g/mol) in supercritical CO₂, is reported. In addition to excitation wavelength, molecular weight and polystyrene concentration dependencies, CO₂ density also strongly affects the emission spectral contours. A major increase in the steady-state fluorescence intensity and a significant decrease in the polystyrene 320 to 365 nm fluorescence intensity ratio are observed when CO₂ density is increased. Concentration and conformational changes in the polystyrene molecules are used to explain the observations and these results are proposed to arise from changes in the plasticization power of supercritical CO₂, over the density range studied. A theoretical model is proposed based on the assumption that at low CO₂ densities and low polymer concentrations, polystyrene intermolecular interactions are negligible. The proposed model is able to fit our observed fluorescence data from a CO₂ reduced density of 0.3 to 1.4.

No Abstract Available

Artemisinin or Qinghaosu (QHS) is an potent antimalarial agent isolated from Artemisia annua which is effective against chloroquine resistant strains of Plasmodium falciparum. Previously reported techniques used to quantify QHS have employed HPLC methods with UV (216 nm), electrochemical and thermospray - mass spectrometric detection. These methods suffer from a lack of simplicity or sensitivity. This report describes a simple, sensitive, selective and accurate method based on electrospay ionization - HPLC - mass spectrometry with a QHS analog as an internal quantitative standard. Deoxy-QHS is a synthetic analog which is not found naturally in Artemisia annua but which has HPLC and mass spectrometric properties similar to QHS, properties that are ideal for use as an internal quantitative standard. With a 5 pi C18 column (4.6 X 250 mm), isocratic elution in 85% acetonitrile in water, and selective ion monitoring acquisition, linear standard curves were established with ratios of QHS (m/z 283) to deoxy-QHS (m/z 267) over the QHS concentration range of 0.005 to 0.050 mg/ml. The minimum detection level was determined to be 25 ng QHS injected on column. A biomass source of Artemisia annua was ground, extracted with hexane (fast soxhlet), spiked with deoxy-QHS and analyzed by ESI-LCMS. The QHS content was determined to be 0.16% ± 0.02 % (wt/dry), a value comparable with that determined by the HPLC-ECD method. Specific mass selective searching routines also determined the presence of other QHS-type compounds in this biomass.

PROTEIN SEQUENCING USING MALDI IN-SOURCE METASTABLE DECAY IONS


Matrix-assisted laser desorption/ionization (MALDI) has evolved into an important tool for the biochemical researcher. Although initially employed as a means for accurately characterizing the molecular weights of very small quantities of analytes, the metastable ion decay which occurs in MALDI can also be employed to obtain information on the primary sequence of peptides and some small proteins. The utilization of delayed extraction (DE) of MALDI generated ions in a linear time-of-flight (TOF) mass spectrometry allows the observation of in-source decay (ISD) metastable ions. These metastable ions typically provide overlapping C and N terminal sequence specific fragments for peptides.

This presentation will detail initial attempts to exploit the MALDI ISD of peptide samples which have been isolated and purified by HPLC for the determination of primary sequence. Several purified peptide samples have been examined in a single blind study to test the utility of the ISD data for determining unknown peptide sequences. Results of these studies will be presented and the potential of the ISD data for sequencing unknowns will be discussed. Preliminary results on attempts to combine enzymatic cleavage of larger proteins followed by HPLC isolation of individual cleavage fragments with ISD sequencing will also be presented.

HIGH MASS RESOLUTION MALDI TIME-OF-FLIGHT MASS SPECTROMETRY

Robert S. Brown, Duane C. Reiber, Edward E. Durrant and Jinhua Feng, Department of Chemistry and Biochemistry, Utah State University, Logan, UT 84322-0300.

Delayed extraction (DE) when combined with time-of-flight (TOF) mass spectrometry of MALDI generated ions has resulted in greatly enhanced performance for this technique. One of the most dramatic improvements has been in the area of the mass resolution that is obtainable with TOF mass spectrometry. TOF mass spectrometers incorporating DE and MALDI now are available that routinely provide mass resolution of 10,000 or more (sufficient to easily resolve the isotopic multiplet of moderate sized biomolecules).

In this presentation, the instrumental limitations to high mass resolution with MALDI and DE-TOF mass spectrometry will be examined. These will include the effects of laser pulse width, matrix, extraction delay period, digitizer time resolution and total ion flight times on the obtainable mass resolution. Limitations to the improvement in mass resolution for larger (m/z>20,000) MALDI generated ions will also be examined. This will include the effect of increased metastable ion decay associated with larger m/z ions and current ion detector limitations associated with larger m/z ions.
THE EFFECTS OF ETHANOL ON THE METABOLISM OF PROSTAGLANDIN E2, IN RAT HEPATOCYTES

Joseph A. Hankin, Pat Wheelan, and Robert C. Murphy, National Jewish Center for Immunology and Respiratory Medicine, 1400 Jackson St., Denver, CO 80206

Prostaglandin E2 (PGE2) is one of the eicosanoid series of chemical mediators produced in the body. The physiological role of PGE2 is diverse and depends largely on the tissue type where the chemical is released. The efficient cellular metabolism of PGE2 is important in order to avoid subsequent responses from nearby tissues that might be incompatible with the primary response. The principal pathway for metabolism of PGE2 in most cell types appears to be P-oxidation, and several metabolites have been identified including the dinor- and tetranor-PGE2. The addition of small amounts of ethanol to isolated rat hepatocytes has been shown to alter the predominant metabolic pathway of leukotriene B4, P-oxidation. To better understand this observation, the effects of ethanol on the metabolism of PGE2 were studied using radiolabeled tracers, electrospray mass spectrometry, and chemical ionization mass spectrometry. Baseline measurements of the metabolism of PGE2 without ethanol yielded the dinor- and tetranor-PGE2, as well as several metabolites not previously identified including a second dinor-PGE2 with an additional unsaturation site and a taurine conjugate of the dinor-PGE2. Ethanol was found to inhibit P-oxidation of PGE2 and increase the dinor-PGE2 relative to the tetranor-PGE2.

NONENZYMATIC FORMATION OF BIOLOGICALLY ACTIVE EICOSANOIDS DURING LIPID PEROXIDATION

Lisa M. Hall and Robert C. Murphy, National Jewish Center for Immunology and Respiratory Medicine, 1400 Jackson St., Denver, CO 80206

Enzymatic oxidation of arachidonic acid leads to the formation of various products such as prostaglandins, leukotrienes, and hydroxyeicosatetraenoic acids which play important roles as lipid mediators. Recently, nonenzymatically formed compounds isomeric to prostaglandins and leukotrienes, termed F,-isoprostanes and B2-isoleukotrienes respectively, have been identified in models of lipid peroxidation. We have now expanded the investigation of free radical generated eicosanoids with the t-butylhydroperoxide treatment of red blood cell ghosts to initiate lipid peroxidation. Using HPLC, electrospray ionization mass spectrometry (ESI/MS) and a biological assay specific for Ca++ release from PMNs, 5-hydroxyeicosatetraenoic acid and 5-oxoeicosatetraenoic acid (5-oxoETE) were determined to be the two most abundant, biologically active compounds present. Determination of the phospholipid class containing 5-oxoETE as well as its formation was also investigated using ESI/MS. This is the first characterization of 5-oxoETE formed in a lipid peroxidation model system. We suggest that this eicosanoid may be important from the standpoint of its biological activity as well as being a novel marker of lipid peroxidation and free radical injury.
**XE AND XE AS PROBES OF VOID SPACE IN SOLIDS. Igor L. Moudrakovsky, Christopher I. Ratcliffe and John A. Ripmeester, Steacie Institute for Molecular Sciences, National Research Council of Canada, Ottawa, Ontario K1A0R6, Canada.**

Clathrates were some of the first model systems used to demonstrate the utility of xenon NMR spectroscopy in defining guest space in guest-host materials. Recent modelling studies (Jameson et. al.) have shown that the empirical cage size-shift relationships in fact have a sound theoretical basis, and give some confidence that xenon results can be used in a practical way to predict the way that cages will behave as sites toward specific guests. Carbon dioxide hydrates are used to test this idea, and results indicate that the NMR data give a better picture of subtle differences in cage geometry than structural data based on X-ray diffraction. We also have explored the use of Xe (I = 3/2) NMR as a probe of void space in solid lattices. Again a number of clathrates provide cages of different wall compositions and geometries. Xe spectra obtained at 7.0 and 14.1 T for xenon in non-spherical cages show only the central transition broadened by the 2nd order quadrupole interaction. Simulated spectra indicate quadrupole couplings up to 2 MHz, suggesting that Xe NMR has potential as a probe of longer-range interactions in the solid state.

**SURFACE BONDING, CHAIN DYNAMICS AND ORDER IN SELF-ASSEMBLED MONOLAYERS: SOLID-STATE NMR STUDIES. Linda Reven, Wei Gao, Antonella Badia, and Lucy Dickenson, Department of Chemistry, 801 Sherbrooke St W., McGill University, Montreal, Quebec, Canada H3A 2K6**

Self-Assembled Monolayers (SAMs), which form highly ordered, tightly bonded films on metal and metal oxide surfaces, are currently being developed as model organic surfaces, protective coatings, optoelectronic devices and modified electrodes. The three main systems: alkylsilanes, alkanethiols and metal alklyphosphonates SAMs, have been studied by solid-state NMR, yielding valuable information in regards to surface bonding, submonolayer structure, dynamics and conformational defects. (Langmuir 1995, 11, 1860.) Alkanethiol SAMs on gold colloids display chain-length dependent, reversible order/disorder transitions of the all-trans chains, which are shown to be undergoing large amplitude motions about the chain axes. (Langmuir, 1996, 12, 1262.) A sample which was isotopically labeled at the carbon next to the sulfur displays a broad resonance close to the shift of a model gold alkanethiolate complex. Alkylphosphonic acids bind to a range of metal oxides, forming dense, conformationally ordered monolayers. ^31^P solid-state NMR reveals the variation in surface bonding, which in turn influences the chain packing, characterized by 2D WISE experiments.

**SOLID STATE NMR INVESTIGATIONS OF THE THREE DIMENSIONAL STRUCTURES OF ZEOLITE-SORBATE COMPLEXES. Hiltrud Grondev, Colin Fyfe, Andrew Lewis, and Anix Diaz, Department of Chemistry, University of British Columbia, 2036 Main Mall, Vancouver, B.C., Canada V6T 1Z1.**

The determination of the structures of zeolite-sorbate complexes by solid-state NMR techniques, involves several distinct steps: Firstly, highly siliceous, highly ordered materials must be investigated. In these systems, narrow resonances are observed whose numbers and relative intensities reflect the numbers and relative intensities reflect the numbers and occupancies of the inequivalent sites in the asymmetric unit of the framework structure. Secondly, these resonances must be assigned to specific sites by using COSY or INADEQUATE experiments to delineate the bonding connectivity patterns. Thirdly, distances between relatively isolated nuclei on organic guest molecules to the ^29^Si nuclei at the (known) framework sites are determined by heteronuclear experiments based on dipolar interactions such as CP, REDOR and TEDOR. The results from a number of experiments of this type will be described using ^1^H, ^1^F, ^1^C and ^1^N as probe nuclei on the organic sorbates. The reliability of these experiments is established from the few known structures and they can be subsequently used to predict unknown structures.
STUDIES ON POROUS SILICON SURFACE BY Si CPMAS NMR. W.K. Chang, M.Y. Liao, K.K. Gleason, Department of Chemical Engineering, M.I.T., Cambridge, Massachusetts 02139.

Porous silicon (PS) has attractive optoelectronic properties. However, to our knowledge, the PS surface passivation and stability has not previously been characterized by NMR. PS was prepared by electrochemically etching single crystal silicon in hydrofluoric acid. In freshly made PS, nearly monolayer hydrogen passivation ($10^{15}/cm^2$) was measured by $^1$H NMR and no fluorine was detected by $^{19}$F NMR. The hydrogen content increased with exposure to room temperature air, probably as a result of water and/or hydrocarbon absorption. $^{29}$Si cross polarization-magic angle spinning (CPMAS) was used to selectively study the silicon near the PS surface. Polarization inversion, in addition to sample oxidization and reduction, facilitated the assignment of these spectra. The pore surface of the reduced PS is mainly composed of Si-H or Si-H$_2$ species (chemical shift ~ -100 ppm). After oxidation, the pore surface is mostly covered by Si-H species with either two or three backbonded oxygen atoms (chemical shift ~ -84 and -50 ppm respectively). Thus, at relatively low temperature, oxidation of PS in humid air appears to be taking place through the attack of the Si-Si backbonds, rather than the Si-H bonds. NMR surface characterization of a series of PS samples which vary only in thickness but have very different photoluminescence efficiency will be discussed in terms of proposed quantum confinement and chemical passivation theories of optoelectronic behavior.

TWO-DIMENSIONAL $^{29}$Si NUCLEAR MAGNETIC RESONANCE INVESTIGATIONS OF THE STRUCTURE OF ALKALI-SILICATE GLASSES. P. J. Grandinetti, P. Florian, P. Zhang, and J. F. Stebbins, department of Chemistry, Ohio State University, Columbus, OH, Department of Geology, Stanford University, Stanford, CA.

A common approach to quantify $Q_i^{(n)}$ species in silicate glasses is to use $^{29}$Si magic-angle spinning (MAS) nuclear magnetic resonance (NMR) and assume that the overlapping isotropic chemical shift distributions of $Q_i^{(n)}$ species are Gaussian. We have shown that a two-dimensional isotropic/anisotropic $^{29}$Si NMR experiment can not only determine the distributions of $Q_i^{(n)}$ species without any a priori assumptions about the distribution, but can also provide over an order of magnitude improvement in the precision of $Q_i^{(n)}$ species quantification in silicate glasses. Using this approach we have investigated an alkali silicate glass of composition 2 Na$_2$O • 3 SiO$_2$ and have observed a small concentration of in a sample mainly having $Q_i^{(2)}$ and $Q_i^{(3)}$. We have found that the distribution of isotropic chemical shifts for each of the $Q_i^{(n)}$ species is approximately Gaussian. The relative populations of $Q_i^{(1)}$, $Q_i^{(2)}$, and $Q_i^{(3)}$ obtained from these separated distributions give an equilibrium constant of 0.0129 ± 0.0001 for the disproportionation reaction 2 $Q_i^{(3)}$ $\rightarrow$ 3 $Q_i^{(1)}$.

CHARACTERISATION OF DISORDERED MATERIALS BY A COMBINED QUADRUPOLE NMR METHODOLOGY. Mark E. Smith, Department of Physics, University of Kent, Canterbury, Kent, U.K. CT2 7NR.

Several techniques are now available for deducing the NMR interaction parameters from quadrupole nuclei in solid materials. A methodology combining magic angle spinning at several applied magnetic fields (here 5), satellite transitions, off-resonance nutation and two-dimensional multiple quantum (MQ) experiments is applied. This combination of techniques is used to examine the important process of water dissolution in albite (NaAlSi$_3$O$_8$) glasses and the atmospheric decomposition of Na,HfO,. In albite glasses it is shown for the sodium sites that whilst there is very little change in the quadrupole coupling constant both the isotropic chemical shift and chemical shift dispersion vary markedly with water content. It is also emphasised that it is only by using a combined methodology that the conclusions can be unambiguously reached. Off-resonance quadrupole nutation is shown to be very sensitive to the mean quadrupole interaction but gives little information about the distribution of parameters. For Na,HfO, both direct $^{23}$Na and $^{19}$O MAS NMR are used to reveal the reaction with the atmosphere to form a sodium carbonate and a hafnia-related material. The sensitivity of the MQ experiment as a result of the enhanced resolution to very minor changes in the secondary phase that contain sodium is clearly demonstrated.
INVESTIGATION OF CESIUM PROMOTED CATALYSTS BY LOW TEMPERATURE SOLID STATE NMR. Paul D. Ellis*, Eric Hughes**, and Jeff M. Koons**

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Cesium is used in industry to enhance selective epoxidation of ethylene on supported silver catalysts. The exact mechanism of the role of cesium is unknown. We have observed changes in the $^{13}$C static lineshapes of chemisorbed mono- and di-labeled ethylene at 70 Kelvin as a function of cesium concentration. The resultant lineshapes have been analyzed by non-linear least squares techniques to extract the principal components of the chemical shift tensor, the dipolar tensor, and their relative orientation. The results indicate an increase in the carbon-carbon bond distance together with a discernable change in the orientation of the chemical shift tensor.

CADMIUM COMPLEXATION BY SUWANNEE RIVER FULVIC ACIDS

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The binding of cadmium to the Suwannee River fulvic acid standard has been studied using $^{113}$Cd NMR spectroscopy. The observed $^{113}$Cd NMR chemical shift changes with constant Cd$^{2+}$ concentration and varying fulvic acid concentration at pH 6.4 are consistent with the fast exchange model. Analysis of the $^{113}$Cd chemical shift data using a Scatchard plot yields a conditional binding constant of 6.7 x 10$^{2}$ mL/mg with about 90% of the carboxylate sites participating in the binding. Measurement of $^{113}$Cd Ti values and MOP AC calculations have been used to better understand these complexes at the molecular level. Experiments are underway to evaluate the fulvic acid aggregation state, especially as influenced by metal ion complexation. PFG NMR is used to measure apparent diffusion coefficients for the fulvic acid as a function of concentration and to detect changes in the aggregation state induced by cadmium binding.

PROBING DYNAMICS IN A NOVEL POLYMER ELECTROLYTE

David B. Zax, Shan Wong, and Hansjeorg Hegemann,

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Novel nanocomposite polymer intercalates have been synthesized by intercalation of polyethylene oxide into various layered silicates. In this work we use solid state NMR to probe dynamics associated with both the cations and the polymer over a broad temperature range. Spin-lattice relaxation studies reveal the influence of the polymer backbone dynamics on the Li$^+$ T$_1$, and we discuss why such measurements need to be interpreted with care. Cation dynamics are separated from that of the polymer by an analysis of the temperature dependence of the $^1$Li spectrum in the presence of paramagnetic impurities fixed in the silicate lattice. The intercalated polymer shows no evidence for either glass or melt transitions, and over the same temperature range exhibits thermally-activated polymer reorientation. Over the same broad temperature range, Li$^+$ cations prove to be mobile with the same activation energy. Such measurements appear to indicate that cation diffusion is much slower than polymer reorientation in these systems.
The adsorption of nitric oxide (NO) by ammonia over a series of V_2O_5/TiO_2 catalysts used for selective catalytic reduction (SCR) has been investigated by solid-state 'N NMR. The chemistry and the surface acidity are found to vary dramatically as the weight loading of vanadia is increased from 0 to 10%. NO reacts over evacuated TiO_2 and V_2O_5/TiO_2 at room temperature to form nitrous oxide (N_2O). The chemical shift of the terminal nitrogen of N_2O adsorbed on the catalyst is an indicator of the Lewis acid character of the surface. Ammonia adsorbs in two forms which differ in their surface mobility. The reaction of NO with NH_3 at room temperature produces N_2 and N_2O. The central nitrogen of N_2O derives from NO while the terminal nitrogen is from ammonia. Following pre-adsorption of ammonia, the chemical shift of the terminal nitrogen of N_2O indicates that ammonia is adsorbed predominantly on the Lewis acid sites of the catalyst, blocking the access of N_2O to these sites.

We have developed approaches for observing extremely broad 'N NMR powder patterns (I=1) with improved sensitivity, and for efficiently obtaining dynamical information. By selectively exciting the fundamental transitions (0→+1 or 0→-1), and using echo trains for improved detection sensitivity of only a small portion of the entire powder pattern, we have obtained a stepped-frequency spectrum of KN_0 (NQCC = 751 kHz). We also demonstrate a reorientation-induced redistribution of isochromats. A 30mm o.d. vial of KN_0 is slowly rotated at 16 mHz (!) about an axis perpendicular to the magnetic field. New crystallites in the sample are thus continually brought into resonance, thereby permitting more rapid pulsing without overheating the spins (hence the name RotIsseRIe). The sensitivity advantages of this technique have been modelled and compare well with experimental results. Dynamical information can be obtained, when the reorientation motion is not externally-imposed but rather intrinsic, by variants of hole-burning experiments. For the spherical molecule hexamethylenetetramine (HMT), whose 'N NQCC is 4.414 MHz, we obtain a correlation time for jumps between equivalent tetrahedral sites at 295K of 103 ms, in good agreement with other studies. Results may also be presented for nitric acid hydrates, which occur in polar stratospheric clouds and play a catalytic role in forming the ozone hole, including surface experiments with laser-polarized 'Xe.

We demonstrate a novel method of multiple-quantum (MQ) coherence excitation for half-integer quadrupolar nuclei in polycrystalline solids under the magic-angle-spinning (MAS) condition. The method utilizes the adiabatic coherence transfer process that occurs between the central transition and the largest symmetric MQ coherence during a spin-locking RF pulse (A. J. Vega, J. Magn. Reson. 96, (1992) 50). For the S=3/2 case, a detailed set of calculations and experimental results will be presented which reveal unique properties of the coherence transfer process. In particular, we examine the efficiency of the coherence transfer as a function of the magnitude of the quadrupole coupling constant and the resonance offset of the spin-locking pulse. We find that this method provides an excellent route to obtaining isotropic NMR spectra for half-integer quadrupolar nuclei via the MQMAS method (L. Frydman, and J. S. Harwood, J. Am. Chem. Soc. 117, (1995) 5367).
Polarized NMR signals result from electron transfer in photosynthetic reaction centers

Chemically Induced Dynamic Nuclear Polarization (CIDNP) SSNMR spectra of N-labeled photosynthetic reaction centers have emissive and enhanced absorptive lines associated with nitrogens in the tetapyrroles of the bacteriochlorophyll special pair (P*), associated imidazoles and the primary acceptor pheophytin (I*). The signals are from samples of Q-blocked N and excited in-situ by CW illumination from a Xenon arc lamp; they are observed with solid state NMR techniques. We presume the polarization results from a radical pair mechanism involving mixing of the electronic triplet and singlet radical pair spin states of P*. Selective labeling and comparison with chemical shifts of model compounds were used to assign the signals and were also used to distinguish directly and indirectly polarized signals. Signals at isotropic shifts of 163, 173, 232 and 236 ppm (relative to 1M NH4Cl in 2N HCl) were assigned as directly polarized signals. Signals at 147 and 201 ppm arise from the 8 and e nitrogens of bacteriopheophytin acceptor (I*), and some of these signals are sensitive to the lifetime of P, consistent with a RPM mechanism in which P acts as the nuclear relaxant for I. Chemical shift values generally correspond closely to those of related model compounds, although modest deviations are seen for a few, we intend to interpret in terms of local electrostatic perturbations.

Molecular conformation and phase structure of solid polymers and polypeptides investigated by 2D NMR.

The determination of the conformational structure of polymers and peptides in the unoriented solid state is a challenging problem. Novel two-dimensional (2D) solid-state NMR techniques make it possible to measure torsion angles in molecules that are isotopically labeled with dilute (1 % - 30 %) 13C or 15N spin pairs. Experiments with double-quantum excitation and evolution, providing intrinsic homonuclear dipolar decoupling in the evolution period and removing the natural-abundance background signal, yield 2D NMR spectra in which the first dimension displays the sum of the anisotropic background chemical shifts. Thus, the 2D spectral patterns depend on the torsion angle between the coupled sites. By exploiting C-H couplings in the double-quantum dimension, peptide conformations can be determined particularly well (SELF-TOQ experiment). The spectral patterns can be simplified by multiple-pulse homo- and heteronuclear decoupling during detection. Measurements of backbone torsion angles in semicrystalline and amorphous polymers as well as polypeptides with these new 2D NMR techniques will be presented. Structure and mobility on a larger length scale in semicrystalline polymers as well as the phase composition in phase-separating polymer blends have been investigated by spin diffusion and 2D WISE NMR.
The structural investigation of peptides, polypeptides, proteins and other biopolymers in the solid state is being pursued increasing by means of high resolution solid state NMR. Most of biopolymers considered here consist of repeating sequences of peptide bonds with twenty different types of substituents at the C(alpha) carbon. The secondary structures of these biopolymers are classified as alpha-helix, beta-sheet, omega-helix and so on, by a set of the dihedral angles (phi, psi). In the solution state, the NMR chemical shifts of biopolymers with internal rotations are often the average values for all internal rotation about the peptide bonds. In the solid state, however, chemical shifts are often characteristic of specified conformations because of highly restricted rotation about the peptide bonds. The NMR chemical shift is directly affected by a change in electronic state arising from the conformational change. NMR chemical shifts in the solid state, therefore, provide useful information about the electronic state and conformation of a biopolymer with fixed conformation. In this presentation we aim to introduce a series of our research works on structure of solid polypeptides as studied by high resolution solid state NMR and to demonstrate that high resolution solid state NMR is a very powerful means for determining of solid polypeptides.

MORPHOLOGICAL STUDY OF A SULFONATED POLY(STYRENE)/POLY(AMIDE) BLEND

Phase separation that would normally occur when one mixed poly(styrene), PS, with poly(amide), PA, can be overcome by attaching sulfonate groups on the PS residues since these groups interact strongly with the amide moieties on the PA. In this exploratory study, a low MW (=4000) PS, sulfonated in the ring para position at levels of 2.3, 7.0 and 11.9 mole% and having either Zn or Cu as associated metal cations, were mixed with a 10,2 nylon, fully methylated at the amide positions. These MSPS(n)/PA blends were investigated by both $^1$H and proton techniques. $^{13}$C CP MAS spectra were used to characterize crystallinity of the PA component. From energetic considerations, crystalline PA is the preferred state for the PA chains. Sufficiently strong heteropolymer interactions can prevent PA crystallization. Nevertheless, PA crystallinity appears as the sulfonation level or the stoichiometries reduce the density of heteropolymer interactions. The implications of crystallization for morphology and the distribution of components is studied by proton spin diffusion methods. Morphological changes with aging and exposure to humidity are also investigated briefly. Most studies are carried out using the diamagnetic Zn cation. Paramagnetic Cu ions strongly influence proton T,’s; hence, Cu-containing blends are used to test for homogeneity of cation distribution in the pure ionomers and for large regions of pure PA or undecorated PS molecules.

SPATIALLY RESOLVED NMR OF POLYMER MATERIALS

Different developments and applications of NMR with spatial resolution are reported. NMR imaging methods have been optimized with respect to maximum contrast in rubbery and rigid polymer materials. Good contrast for a manifold of material properties is obtained by $T_s$ and $T_e$ weights of the spin density and even relaxation by $T_2^*$ in inhomogeneous fields can be employed. In this way previously invisible inhomogeneities and dynamic parameters of material change can be detected. Examples are an interfacial layer in rubber covulcanisates, the effect of aging protectants, and the spatial and temporal progress of thermal aging and vulcanization. By spectroscopic and double-quantum imaging of deuterated spy oligomers in strained rubber bands local stress was analyzed. Spin diffusion has been exploited for image contrast for the first time to image local morphology changes in polyethylene cable insulation material from electrical aging by the formation of discharge trees. For investigations of large objects an NMR mouse (movable universal surface experiment) has been developed, which consists of a PC spectrometer and a palm size BJB probe for investigations of relaxation and molecular transport in surface regions of large objects from soft and glassy matter. An example are relaxation curves from the tread and the sidewall of an in-tact steel-belted car tire.
Polyaniline (PANI) is a member of the class of conducting organic polymers, whose conductivity increases by 10 orders of magnitude upon doping with protic acids. There is currently a lack of correlation between the electronic state of the doped polymer and its structure as both parameters are generally measured at the macroscopic level. With solid-state NMR this correlation can be established. In the HF doped polymer, both the 19F and 15N NMR spectra show that protonation of the imine nitrogen upon doping generates sites where the cation is localized to a single nitrogen and sites where the charge is distributed over several nitrogens. In addition, the 19F spectrum of the doped polymer also shows the presence of two structural conformers for the regions of localized cations. The regions of delocalized cations have a structure that is an average of the two conformers and arises from regions with more extended short range order. With 15N 19F REDOR the fluorine-nitrogen distances have been investigated for all three environments and the structures identified.
OBTAINING CONNECTIVITY AND DISTANCE INFORMATION BETWEEN SPIN-1/2 AND QUADRUPOLAR NUCLEI. Yong Ba, Faiza I. Poshni, Clare P. Grey and *Terry Gullion, Department of Chemistry, State University of New York at Stony Brook, Stony Brook, NY 11794-3400, * Department of Chemistry, Florida State University, Tallahassee, FL 32306.

It has been known that the dipolar interaction of coupled spins in rotating solids can be used to obtain connectivity and internuclear distance information. This has been explored in the REDOR[1], TEDOR[2] and TRAPDOR[3] NMR experiments. The combination of REDOR and TRAPDOR, i.e., REAPDOR[4], has been shown to have an advantage over TRAPDOR experiment for obtaining internuclear distances between spin-1/2 and quadrupolar nuclei. The pulse train can be imposed on the spin-1/2 nuclei during the dipolar dephasing time and only a short 'adiabatic pulse' of less than one rotor period needs to be applied to the quadrupolar nuclei for the population transfer. We will present our recent REAPDOR results. Theoretical analysis of the REAPDOR signal, along with the parameters required to obtain $^{13}$C/$^{14}$N distance, are discussed and compared with the experimental data. The REAPDOR experiment is also applied to probe the $^{29}$Si/$^{27}$Al connectivity in zeolites and to obtain the adsorption information of hydrofluorocarbon molecules on zeolite NaY.


HOW TO CALCULATE THE EVOLUTION OF LARGE SYSTEMS OF COUPLED SPINS-1/2. Alex D. Bain and Randall S. Dumont, Department of Chemistry, McMaster University, Hamilton, Ontario, CANADA, L8S 4M1.

In principle, all of spin dynamics of a spin system can be described by equation (1).

$$p(r) = \exp(-i L t) \ p(0) \ (1)$$

This is fine as a formal solution, but for the interesting large spin systems ( >6 spins 1/2 ) the matrices are forbiddingly large (792 x 792 for 6 spins). However, the matrices are also very sparse (contain mostly zeros), so that instead of using the exponential directly, we use a polynomial expansion. This permits the use of sparse matrix multiplication, in which only the non-zero elements need be considered. The best expansion of (3) is in terms of Chebyshev polynomials, since this is "guaranteed" to converge in a quick and predictable way. Combined with split operator methods, this allows us, for instance, to work with chemical exchange in systems with more than 6 coupled spins.

NMR STUDIES OF YTTRIUM TRIHYDRIDE. J. J. Balbach and Mark S. Conradi, Department of Physics, Washington University, St. Louis, Missouri 63130, T. J. Udovic, National Institute of Science and Technology, React E151, Gaithersburg, Maryland 20899.

Deuteron Magnetic resonance techniques were used to probe the structure and motional behavior of yttrium trideuteride, between 150 K and 400 K. The spectrum shows sharp features beginning at 300 K and is composed of three Pake doublets, indicating that there are three inequivalent species of deuterium. Ti studies show Arrhenius behavior above 300 K, but the field dependence is not $H^2$. T studies indicate a fluctuating quadrupolar interaction and that the motions of the three species are different; one Pake doublet relaxes much more quickly than the other two. Three-pulse echo studies confirm that motion of the deuterium atoms is responsible for the relaxation behavior, and that most of the relaxation is due to the one species.
Chemical-Shift Selective Imaging of Molecular Probes Used in Porosity Determinations* Robert E. Botto and Rex E. Gerald, Chemistry Division, Argonne National Laboratory, Argonne, IL 60439

A new, selective chemical-shift imaging pulse technique has been developed that incorporates several distinct advantages over conventional approaches that differentiate components solely on the basis of spin-lattice relaxation. The method was developed for use in investigations involving binary mixtures and is simple to implement. The methodology has been used in competitive solvent swelling measurements, and to study properties of gaseous diffusion, including physical and chemical adsorption processes of microporous materials that are potential candidates for fuel storage devices.

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

RELATIVE CSA ORIENTATION DETERMINATION IN PEPTIDES USING SOLID STATE \(^{13}\)C DOUBLE QUANTUM NMR SPECTROSCOPY.

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Several peptides of known and unknown structures structure have been investigated. \(^{13}\)C labels are incorporated at the carbonyl position in two adjacent peptide bonds. The mutual orientation between these two tensors can in a good approximation be said to depend only on the Ramachandran angles (\(\phi, \psi\)).

In our solid state CP-MAS experiment Double Quantum (DQ) coherence is created in one dimension of a two dimensional experiment. The coherence is then turned back into detectable single quantum coherence in the second dimension. The resulting 2-D spectrum is projected onto the DQ axis. This DQ spectrum shows strong dependence on the mutual CSA orientation and consequently on the Ramachandran angles.

19-F NMR INVESTIGATIONS OF GLASS CERAMICS CONTAINING FLUOROAPATITITES.

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Glass ceramics that include calcium apatite crystals are used as implant materials in medicine. Because most of these glass ceramics are comprised of fluoride-containing glass compositions, the included apatites could be fluoride-containing apatites. However, the fluorine content of these apatites is important for medical applications. The purpose of the current study was to determine the possibilities of measuring the fluorine content of these apatites. High resolution solid state MAS NMR spectra of apatite-containing glass ceramics have been obtained. The spectra of the samples confirm the assumption that all glass ceramics contain fluorapatite. Using the correlation between the isotropic \(^{19}\)F chemical shift and the fluorine content it was possible to determine the fluorine content of the apatites.

Independent from the phase separation behaviour of the base glasses, only in fluoride-containing glasses it was possible to precipitate apatite (in phosphate glasses as well as in silicate glasses). So it could be assumed, that a fluoride-containing glass composition is a prerequisite for the preparation of an apatite-containing glass ceramic.

Interestingly, in all samples the fluoride content is about 90 %. Reduction of the fluorine content of a glass composition led to the decrease of the portion of fluorapatite, but the fluorine content of the apatite was constant.
AUTOMATED ANALYSIS OF COMPLEX HYDROCARBONS USING NMR

Lawrence W. Dennis, Exxon Chemical Company, P.O.Box 4004, Baytown, Texas, 77522^004

When the first commercial NMR Spectrometer was installed in the Baytown Lab in 1953, one of its major justifications was the characterization of petroleum derived liquids, and this has always been a focus of NMR work in Baytown. The advent of C-13 NMR opened up a new realm of spectral detail, but the high information content made the analysis a time intensive task. Using NMR in rapid turnaround applications such as pilot plant support, requires automation of the analysis of C-13 NMR spectra. Modern NMR spectrometers have greatly enhanced macro capability which allows the total analysis to be performed on the host computer. A spectrum is acquired, phased and baseline corrected, then a single command plots the data, prints out a complete analysis, and stores the output integrals and analysis to disk. Samples ranging from crude oils and shale oils, to many commercial fuels and lubes products have now been characterized using this set of routines for rapid analysis of complex spectra. The programs are customizeable for specific research programs and pilot plant runs. Since such automated analysis involves various levels of assumptions, and these assumptions vary for different types of samples, this ability to change the foundation assumptions and reanalyze a spectrum without major effort is a big advantage of this automated analysis. This research program is an example of the benefits brought about by a marriage of analytical technique and modern computing hardware and software.

CROSS POLARIZATION FROM QUADRUPOLAR NUCLEI UNDER MAS.


Cross polarization from quadrupolar nuclei under Magic Angle Spinning (MAS) depends strongly upon the interplay between the rotor spinning speed, the spin-lock field strength, and the quadrupolar coupling constant. We have investigated the dynamics of cross polarization from 27Al-to-29Si and from 23Na-to-29Si at slow spinning speeds and at low radiofrequency field strengths and have used the improvement in the signal-to-noise ratio per unit time to perform two-dimensional experiments on minerals. We also have combined cross polarization of quadrupolar nuclei with the Multiple-Quantum MAS experiment (L. Frydman and J. S. Harwood, J. Am. Chem. Soc. 117, 5367 (1995)) to create a high-resolution heteronuclear correlation technique for the investigation of connectivities in inorganic samples.

SOLID-STATE NMR STUDIES OF BISMUTH MOLYBDATES

CATALYSTS, Michelle C. Douskey, Eric J. Munson, Department of Chemistry, University of Minnesota, Minneapolis, MN 55455.

Bismuth molybdates are used as partial oxidation catalysts for many industrial processes. Three phases of bismuth molybdates are known to catalyze the conversion of propene to acrolein. Solid-state NMR spectroscopy has been applied to the study of these catalysts as well as the catalytic process. Through solid-state NMR spectroscopy, we have the unique ability to observe both the catalyst and the reactant/product mixture before, during, and after the reaction takes place. 95Mo NMR spectroscopy has been used to help characterize the catalytically active sites of the bismuth molybdate structures. Both one and two-dimensional NMR spectroscopy has been used to follow the reaction of 13C-labeled propene to form acrolein. Spectra will be shown to illustrate the progression of the catalytic reactions from reactants to products as well as from the perspective of the catalyst itself. These solid-state NMR studies have given much insight into the mechanism of the catalytic partial oxidation of propene to form acrolein.
SOLID-STATE $^{13}$C NMR SPECTROSCOPY OF CELLULOSES AND MUSHROOM PARTS, E. A. Kegerise, E. J. Gaffney and C. Dybowski, Department of Chemistry, University of Delaware, Newark, DE 19716 USA.

We report $^{13}$C NMR spectroscopic results for chemically pure HVE cotton cellulose, PHV wood pulp cellulose and dried parts of mushrooms, using cross polarization, magic-angle spinning, and high-power proton decoupling. Spectra of celluloses are relatively well resolved, while the spectra of the mushroom parts are more complex. Various functional groups can be distinguished. By examining the spectra of plant parts, one can determine the location of certain materials.

THE CORRELATION OF NMR, MECHANICAL AND THERMAL ANALYSIS OF A NOVEL CLASS OF CARBOSILOXANE NETWORKS. Thomas A. Early, Slawomir Rubinsztajn, Judith Stein and Elizabeth A. Williams, General Electric Corporate Research & Development, Schenectady, NY 12301 and General Electric Silicones, Waterford, NY 12188

A series of novel carbosiloxane networks made by the hydrosilation of cyclic D$_n$ and linear N-mer divinylsiloxanes where N is 0, 1, 2, 3 and 6, have been characterized by cross polarization magic angle spinning nuclear magnetic resonance (CPMAS NMR) and dynamic mechanical analysis (DMA). The length of the divinylsiloxane has a dramatic effect on the mechanical and thermodynamic properties of the resulting network in a predictable way. For the CPMAS NMR analysis, all $^{29}$Si resonances can be resolved from one another. A comparison of the cross polarization behavior of the cyclic D resonance from each of the samples shows an interesting and predictable cross polarization trend, while analysis of the linear siloxane resonances shows more complex, unexpected behavior.

BROADBAND CROSS POLARIZATION AT HIGH SPEED MAGIC ANGLE SPINNING BY USING PHASE MODULATED "MEANDERING" SPIN-LOCK. Riqiang Fu, Philippe Pelupessy, and Geoffrey Bodenhausen, Center for Interdisciplinary Magnetic Resonance, National High Magnetic Field Laboratory, 1800 East Paul Dirac Drive, Tallahassee, Florida 32310

Cross polarization (CP) and its combination with magic angle spinning (CPMAS) have been widely used in solid state nuclear magnetic resonance (NMR). However, cross polarization is difficult at high spinning speed because the conventional Hartmann-Hahn condition $\omega_k = (\omega_h - \omega_0)$ becomes critical. This is because the dipolar interactions which provide a pathway for cross polarization are greatly reduced by sample spinning at very high speeds. Several methods have been developed to broaden the cross polarization matching condition at high spinning speed. In this contribution, we propose a new scheme in which the phase of the $^1$H radiofrequency (RF) during the spin-lock period is modulated. In effect, the $^1$H carrier frequency is modulated in the manner of a cosine wave about the on-resonance condition, while the $^1$H RF amplitude is kept constant. It is shown by experiment that this scheme dramatically broadens the matching condition. Matching profiles of $^1$C resonances in Alanine were obtained at 12 and 15 kHz spinning speeds to illustrate the advantages of this scheme.
**SOLID-STATE 13C NMR INVESTIGATION OF SUGAR RING CONFORMATIONS IN THE DICKERSON SEQUENCE, [d(CGCGAATTCGCG)]2 Karen B. Geahigan, John A. Stringer, Julie M. Miller, Gary P. Drobny, University of Washington, Department of Chemistry, Seattle, WA 98195**

Solid-state 13C NMR is being used to probe the conformation of the C9 sugar ring in the Dickerson sequence, [d(CGCGAATTCGCG)]2. This oligonucleotide contains the EcoRI restriction endonuclease binding site, 5'-d(GAATTC). Previous research has revealed the region about the C9-G4 base pair to be the most interesting from the point of view of dynamics and structure. C9 lies directly across from the enzyme cutting site. Solid-state deuterium NMR has detected large amplitude motion for the C9 sugar ring at increased hydration levels. It is thought that the specificity for binding and cutting may be attributed to the presence of this unusually mobile sugar ring. A series of CP-MAS experiments is being conducted on several biologically relevant forms of the synthetic DNA dodecamer containing a uniformly 13C labeled dC nucleotide incorporated at the C9 position. A parallel study of a sequence containing fully labeled dA at the A5 position will be used as a control. Deviations in chemical shifts between different forms of DNA are being monitored as a function of hydration level and ionic conditions. A chemical shift study of model nucleoside and nucleotide monomers, crystallized in particular sugar ring conformations, will complement the DNA results. The CP-MAS chemical shifts for each will be correlated with those seen for the various forms of DNA. Comparison of monomer and oligomer chemical shifts should provide insight into the conformation and dynamics of the C9 sugar ring in different forms of DNA.

**MOTIONALLY AVERAGED REDOR**

T. M. Goetz, J. Schaefer

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Dipole couplings between heteronuclear spin pairs are averaged if they undergo relative motion. Assuming that the spins move on timescales fast compared to the dipole-dipole interaction, an algorithm has been developed which describes how to simulate REDOR and TEDOR dephasing curves for the coupled spins. This algorithm is used to calculate the dephasing expected for a trifluoromethyl group, and the results are tested experimentally for natural abundance 13C in poly[trifluoroethyl methacrylate].

**COMPARISON OF TRAPDOR, REDOR, AND REAPDOR.** Lamy Chopin and Terry Gullion, Department of Chemistry, Florida State University, Tallahassee, FL 32306-3006

Dipolar interactions between spin-1/2 and quadrupolar nuclei can be detected by the MAS NMR experiments TRAPDOR, REDOR, and REAPDOR. These experiments differ substantially in their respective implementations. TRAPDOR is based on the application of log, intense rf pulses, REDOR recovers the dipolar interaction with simple 7t-pulse trains, and REAPDOR combines a pulse train with a single, short adiabatic-passage pulse to recover the dipolar interaction. We will present experimental results that compare the performance of these experiments.
During conditioning of glass electrodes in aqueous solutions a hydrated layer is formed, which is responsible for the functionality of such an electrode. For a detailed understanding of the formation of the „swelling layer” the structure of the untreated glasses as well as of the hydrated glasses are of importance. $^{27}$Al and $^{11}$B MAS NMR were used to investigate glasses of the systems Na$_2$O-Al$_2$O$_3$-SiO$_2$ and Na$_2$O-B$_2$O$_3$-SiO$_2$. Comparing the NMR lineshapes of the various glasses carefully the broad and featureless $^{27}$Al MAS spectra can be interpreted in terms of two different structural units. We are able to distinguish between AlO$_4$ tetrahedra connected to Q$^4$ groups only and AlO$_4$ tetrahedra linked to Q$^3m$ groups which differ in only about 7 ppm. In a similar way multiple BO$_4$ units can be detected (comparison of the spectra of the central transition). In both cases only one of the two structural units is removed during the reaction in hydrous solution which can easily be concluded from the changes of the $^{11}$B and $^{27}$Al MAS lineshape. The interpretation of two different AlO$_4$ units and two different BO$_4$ units are supported by REDOR and $^{29}$Si MAS NMR.

**Solid-State NMR Studies of Membrane-Bound Peptides**

We are investigating the secondary structure, orientation, and dynamics of magainins using REDOR, Rotational-Echo Double-Resonance and TEDOR, Transferred-Echo Double-Resonance. The magainins and their analogues are a group of cationic, amphipathic, peptides which kill pathogens by making their cell membranes permeable to ions. The precise mechanism is not known. To determine the orientation of magainin analogues in synthetic phospholipid bilayers we are using peptides with a single $^{13}$C label and phospholipids with a single $^{19}$F label at the acyl chain terminus. Preliminary results show observable $^{13}$C-$^{19}$F dipolar couplings which should arise only from peptides which traverse the bilayer. Some fraction of the magainins remain associated with the bilayer surface since intermolecular $^{13}$C-$^{19}$F dipolar couplings (peptide-phospholipid head group) are also observed.

Most solid-state double resonance experiments require simultaneous irradiation at two or more frequencies. It is impractical or impossible to achieve high rf magnetic fields in a single coil circuit when two of the frequencies (such as 65Cu and 27Al) are close; the resonant modes act as a mutual trap. We have circumvented this difficulty of designing and building a single-input double-tuned probe. The probe circuit and representative $^{59}$Cu($^{27}$Al) SEDOR experiments in Cu-ZSM5 catalysts will be discussed.

Dynamic Nuclear Polarization (DNP) transfers the high polarization of unpaired electrons to nuclei, giving rise to NMR signal enhancements of up to two orders of magnitude. The polarization transfer proceeds through a combination of three pathways: the direct and indirect thermal mixing effects, and the solid effect. These polarization transfer mechanisms differ in their dependence on the nuclear and electronic relaxation rates, the microwave power, the magnetic field, the temperature and the concentration of paramagnetic centers.

Experiments were performed on frozen water-glycerol solutions containing the free radical TEMPO at 5 Tesla (140 GHz EPR). The temperature and concentration dependence of electronic spin-lattice and spin-spin relaxation rates and nuclear spin-lattice relaxation rates were studied.

NMR signal enhancements were studied as functions of magnetic field, microwave power, and temperature to gauge the relative efficiencies of the three pathways.


Across a broad field of applications, there is a constant evolution occurring in order to produce higher quality product at a lower cost. Irrespective of the application, there is a need to understand how uncharacterized new materials will behave when standard processing approaches are utilized during manufacturing, or the behavior of well known materials when subjected to new processing approaches, or when new materials are subjected to new processing approaches. In the area of energetic materials manufacturing, there is a demand to reduce the amount of waste generated. To achieve this objective, we have been applying mri techniques to understand what phenomena are occurring during the injection processing of highly filled materials. In this paper, we will discuss the fabrication of a nonmagnetic injection loader capable of withstanding internal pressure of 1000 psi, review the mri techniques that we have used to explore the phenomena that occur during the processing of highly filled materials, and present our preliminary findings.

MULTIDIMENSIONAL $^{31}$P NMR INVESTIGATIONS OF SOLIDS. Christian Jager, Peter Hartmann, Martin Feike, Hans-Wolfgang Spiess, Friedrich Schiller University, PATF, Max Wien Platz 1, 07743 Jena, Germany, Max Planck Institute for Polymer Research, P.O. 3148, 55021 Mainz, Germany

A detailed investigation of the microstructure of glasses requires first of all the application of NMR techniques which have important advantages over traditional optical spectroscopy and diffraction techniques. The occurrence of the various $Q^n$ units can easily be determined quantitatively using $^{29}$Si and $^{31}$P MAS NMR for phosphate and silicate glasses. This result is important but by no means sufficient in order to determine the connectivities of these units in the amorphous state and therefore the medium range order. We have developed a new strategy to achieve this goal using multidimensional NMR. Connectivities between like units are probed by homonuclear polarization transfer despite high-speed MAS using rotorsynchronized r.f. irradiation and/or double quantum filtering (e.g. C7-sequence, Levitt). The basic idea of our approach is discussed in detail starting from 1D NMR to determine the $Q^n$ units, 2D NMR to probe connectivities between adjacent groups and finally the extension to 3D NMR to measure the connectivities of up to three combined units. Examples for polycrystalline phosphates and various phosphate containing glasses are shown, including bioactive glass ceramics serving as bone replacements.

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CHARACTERIZATION OF THE LEWIS ACID SITES IN ZEOLITE HY, WITH PROBE MOLECULE TRIMETHYLPHOSPHINE AND 31P/27Al DOUBLE RESONANCE NMR

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31P/27Al TRAPDOR NMR is used to probe the binding of trimethylphosphine (TMP) in dehydroxylated Zeolite Y. Three binding sites are observed with 31P isotropic chemical shifts of -32, -46 and -60 ppm at -150°C. The resonance at -46 ppm shows the largest TRAPDOR effects and can be assigned to the phosphine molecule directly bound to an aluminum atom. The TMP molecule is, however, the most mobile at the site resulting in the -60 ppm resonance.

All six peaks of the 31P-27Al sextet can be detected in the 31P INEPT spectrum of the TMP-AlCl3 complex. The intensities of these peaks are a function of the evolution time of the experiment, the length of the 27Al pulses used for the coherence transfers, and whether these pulses are rotor synchronized. A 31P INEPT spectrum has been observed, at room temperature, for the TMP bound to the Lewis acid which results in the resonance at -49 ppm. Only the peaks resulting from the 27Al I=±1/2 Zeeman levels are observed in the 31P spectrum, due to the large 27Al quadrupole coupling constant of this complex. The P-Al J-coupling has been measured from the variation of the INEPT signal with 27Al evolution time.

THE USE OF GRADIENTS IN MAGIC ANGLE SPINNING SPECTROSCOPY.

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Recently a number of studies have been reported in which magic angle spinning is applied to non-solid samples. Examples include polymer gels, lipids, tissue samples and the swollen resins used in combinatorial chemistry. Magic angle spinning removes part of the susceptibility broadening and results in a higher resolution than achieved in a typical solution spectroscopy set-up. We have developed a gradient set, which creates a field which is oriented along the magic angle spinner axis. The gradient field is therefore not modulated or averaged by the sample rotation. The application of this gradient field results in improved multidimensional spectra. We will show a number of MAS gradient experiments and the results from these experiments on a variety of samples.

HIGH RESOLUTION MULTIPLE QUANTUM MAGIC ANGLE SPINNING NMR OF QUADRUPOLAR SPINS

Laura Marinelli, Ales Medek, John Harwood and Lucio Frydman, Department of Chemistry (M/Cl 11), University of Illinois at Chicago, 845 W. Taylor St., Chicago, IL 60607-7601

The line broadening generated by second order quadrupolar effects in the NMR spectra of half integer spins introduces serious limitations in the resolution of chemically inequivalent sites. These second order anisotropics can be removed from the powder spectra of quadrupolar nuclei by combining Magic Angle Spinning (MAS) and bidimensional Multiple Quantum (MQ) spectroscopy. We discuss here basic aspect of the resulting MQMAS technique. It is shown that by using this technique, a simple visual inspection allows one to discriminate among the isotropic chemical and quadrupolar shifts of the various inequivalent sites without having to carry out a series of variable field measurements. The values of quadrupolar constants (e\(|Q|/h)) and asymmetry parameters (\(T\)) can also be obtained from these spectra with the aid of numerical simulations. Extensive analytical and numerical calculations were carried out in order to find the pulse sequence that can maximize the multiple quantum excitation process under different conditions. The results of these calculations will be reported, paying special attention to the effects introduced by chemical shift anisotropics.
RESOURCE FOR SOLID-STATE NMR OF PROTEINS. Ronald McNamara, Kathleen G. Valentine, Tai V. Le, and Stanley J. Opella, Department of Chemistry, University of Pennsylvania, Philadelphia, Pennsylvania 19104

A new NIH sponsored Resource is being established at the University of Pennsylvania for the development and application of high field solid-state NMR spectroscopy for the study of proteins. The instrumentation of the Resource includes two home-built NMR spectrometers capable of the full range of multiple-pulse, multiple-resonance, and sample spinning experiments that constitute high-resolution NMR spectroscopy. One spectrometer has a wide-bore (89mm) 12.9T Magnex magnet with a $^1$H resonance frequency of 550 MHz. The second spectrometer has a mid-bore (62 mm) 17.6T Magnex magnet with a $^1$H resonance frequency of 750 MHz. The high resonance frequencies give substantial enhancement in sensitivity and resolution, and are having their greatest impact by making $^1$H chemical shifts available for resolution and spectroscopic analysis. The main area of applications is membrane proteins. The instrumentation will be described in detail and representative results on biopolymers will be presented. A staff member will be present to discuss opportunities for service, collaborative, and core research at the Resource.

HIGH FIELD SOLID-STATE NMR SPECTROSCOPIC STUDIES OF ORIENTED BIOLOGICAL SYSTEMS. Ronald McNamara, Kathleen G. Valentine, Martine Monette, Kathleen P. Howard, Francesca M. Marassi, Tai V. Le, and Stanley J. Opella, Department of Chemistry, University of Pennsylvania, Philadelphia, Pennsylvania 19104

Solid-State NMR studies of proteins benefit greatly from the use of high magnetic fields. This will be demonstrated with comparisons among spectral results obtained on spectrometers with magnets between 8.4T and 16.5T. These experiments utilize oriented samples such as mechanically oriented membrane proteins in lipid bilayers, magnetically oriented membrane proteins in bicelles, and magnetically oriented fd bacteriophage. The 12.9T and 16.5T spectrometers are home-built spectrometers and are the major instrumentation of the Resource for Solid-State NMR of Proteins at the University of Pennsylvania. The experiments were performed with home built probes designed at the Resource equipped with round, square, and flat coils.

$^{59}$Co MAGIC-ANGLE SPINNING NMR STUDIES OF HEXACOORDINATED PORPHYRIN COMPLEXES. Ales Medek, Veronica Frydman and Lucio Frydman, Department of Chemistry (M/C111), University of Illinois at Chicago, 845 W. Taylor St., Chicago, IL 60607-7061

$^{59}$Co MAS NMR methods were applied to the investigation of hexacoordinated Co(III) complexes bound to a variety of porphyrin and nitrogenated axial ligands. By controlling the rf irradiation power, spin excitations were confined to the -1/2 $\rightarrow$ +1/2 transition from within the eight levels of the Zeeman manifold. The resulting spectra showed extensive spinning sidebands patterns originating from the cobalt shielding anisotropy, and peak linewidths dominated by second-order quadrupolar effects. Variable-magnetic field and variable-spinning speed experiments were carried out on all samples in order to quantify the isotropic chemical shifts, isotropic quadrupolar shifts and shielding anisotropics characterizing the various cobalt environments. These studies revealed that by contrast to what was previously reported on the basis of solution relaxation observations, $^{59}$Co shielding anisotropics in porphyrin complexes are substantially large (>1500 ppm). The observed shielding and quadrupolar parameters could also be used to obtain insight into the changes in the electronic structure that occur throughout the series of analyzed compounds.
SOLID-STATE DIPOLAR-DEPHASING NMR EXPERIMENTS: ISOTROPIC TRANSFORMS AND PURE DIPOLAR SPECTRA Karl T. Mueller and David J. Aurentz, Department of Chemistry, The Pennsylvania State University, 152 Davey Laboratory, University Park, PA 16802-6300; and Thomas P. Jarvie, CuraGen Corporation, 322 E. Main Street, Branford, CT 06405.

We have found analytic solutions for the time-evolution of dipolar-dephasing NMR signals obtained from rotational-echo double-resonance (REDOR), transferred-echo double-resonance (TEDOR), and related homonuclear experiments. With simple functional forms available for the evolution, we have been able to calculate general inverse functions for these time-domain signals and formulate pure dipolar transforms. Since these transforms are linear, direct dipolar spectra are obtained. In many situations it is also possible to use fast time-domain nonnegative least-squares analysis to produce optimized dipolar spectra.

We present both theoretical and experimental findings, the latter including the simultaneous measurement of multiple internuclear distances in biomolecules using a REDOR transform. Extensions to two-dimensional experiments are also shown, allowing measurements of multiple internuclear distances as a function of chemical shift.


Solid-state NMR correlation experiments provide direct spectroscopic evidence of atomic connectivities in complex solids including zeolites and glasses. One-dimensional cross-polarization/magic-angle spinning (CPMAS) and transferred-echo double-resonance (TEDOR) experiments yield heteronuclear connectivities between nuclei through the distance-dependent dipole coupling. With the results of these experiments we can, for example, determine the composition of the second coordination spheres of phosphorus network formers in phosphate and aluminophosphate glasses. Two-dimensional versions of these experiments also offer increased resolution through spectral editing. In systems where two-dimensional CPMAS and TEDOR experiments reveal a non-trivial spectrum for quadrupolar species, dynamic-angle spinning/cross-polarization/magic-angle spinning (DAS/CP/MAS) heteronuclear correlation experiments are also useful. Improved resolution is achieved in both spectral dimensions by correlation of the DAS NMR spectrum of quadrupolar spins (such as $^{23}$Na) in one dimension with the MAS spectrum of nearby spin-1/2 (or quadrupolar nuclei) in the second dimension.

UNDERSTANDING POLYMORPHISM IN PHARMACEUTICALS USING SOLID-STATE NMR, POWDER X-RAY DIFFRACTION, AND COMPUTER SIMULATION. Haijian Zhu, Z. Jane Li, David J. W. Grant, Brian E. Padden, Mark T. Zell, and Eric J. Munson. Departments of Pharmaceutics and Chemistry, University of Minnesota, Minneapolis, MN 55455.

Polymorphism is commonly defined as the ability of a substance to exist in two or more crystalline phases that differ in the arrangement or conformation of the molecules in the crystal lattice. The polymorphic form of a drug may significantly change its physical and thermodynamic properties. For many drugs, multiple crystalline polymorphs exist whose crystal structures are not known. Solid-state $^{13}$C magic-angle spinning (MAS) NMR spectroscopy is a powerful technique for studying these structures. It can be used to determine the degree of crystallinity, to identify the number of crystallographically inequivalent sites in the unit cell, to study the dynamics of molecules via relaxation measurements, and to understand the molecular structure based on the chemical shift of the individual resonances. We have been using solid-state NMR spectroscopy in conjunction with powder X-ray diffraction and computer simulation to predict the crystalline structure of polymorphs for which no single-crystal X-ray diffraction data is available. The ultimate goal of this research is to be able to determine the conformation of pharmaceutical solids based solely on their solid-state NMR spectrum.
AN 19F AND 13C NMR STUDY OF CF₃ PREPARED BY VARIABLE TEMPERATURE FLUORINATION OF CHARCOAL WITH ELEMENTAL FLUORINE. Edward W. Hagaman, David K. Murray, and G. D. Del Cul, Chemical & Analytical Sciences Division, Oak Ridge National Laboratory, Oak Ridge, TN 37831-6201.

The preparation of CF₃ by fluorination of charcoal is studied using 19F and 13C NMR spectroscopy. CP/MAS experiments are used to determine the extent of fluorination vs. temperature and is correlated to results from gravimetric and ESCA analyses. Four types of carbon species are observed over the temperature range 193 K to 623 K, assigned to graphitic carbon, CP, CF₂, and CF₃. These species are extensively characterized using dipolar dephasing and variable contact time experiments. The fluorinated carbons are fully polarized in tenths of milliseconds, while polarization transfer among graphitic carbon is slower and can only be explained by a two component model. One component cross-polarizes in less than 1 ms and is assigned to carbon adjacent to fluorinated carbon. The other component cross-polarizes on the order of milliseconds, and is assigned to more remote carbon species. CF₃ structure and the nature of fluorination in light of these results will be presented.

VARIABLE TEMPERATURE NMR RELAXATION STUDIES OF ASPHALTS. Daniel A. Netzel and Francis P. Miknis, Western Research Institute, 365 North 9th Street, Laramie, WY 82070; Jeni L. Soule and Arland E. Taylor, Chemical and Petroleum Engineering Department, University of Wyoming, Laramie, WY 82071

The relaxation times from variable contact time and dipolar dephasing experiments for aromatic and aliphatic components in several asphalts were obtained at six temperatures in the range +20°C to -45°C. This temperature range encompasses the glass transition temperature region for the asphalts. It was found that the methylene carbons in the solid state can be resolved into rigid and semi-rigid phases each with their own characteristic T₂, relaxation times. From the changes in relaxation times with temperature, the activation energies were obtained for the segmental and rotational motions of the methylene and methyl carbons, respectively.

FLUORINE NMR OF COLCHICINE AND PACLITAXEL COMPLEXES WITH TUBULIN. Mark D. Poliks, Barbara M. Poliks, Jennifer Pardes, Henry Eichelberger and Susan B. Hastie, State University of New York at Binghamton, New York, 13902-6000 and *IBM Corporation, T37/Materials Science, 1701 North Street, Endicott, NY 13760.

The cytoskeleton of eucaryotic cells is formed by few different types of filamentous assemblies. Microtubules belong to one class of them. Their cylindrical structure is built from two kinds of similar 50-kd protein subunits, α- and β-tubulin. Calf brain tubulin reconstituted in vitro by the modified method of Weisenberg et al. [Biochemistry 9, 4110 (1970)] was used in this paper to study the binding of two ligands: colchicine and paclitaxel. These ligands play opposite roles in tubulin polymerization: colchicine inhibits and paclitaxel promotes formation of microtubules. Little is known about the location of their respective binding sites and their conformation while bound to tubulin. In this poster we present the solution and solid-state high speed MAS 19F NMR results for fluorinated analogues of both ligands bound to tubulin. Solid NMR spectra were obtained for rapidly frozen and lyophilized samples. Using electron microscope we were able to prove that both assembled and non-assembled tubulin survives freezing in samples of 0.5 ml volumes in its native state. These results are the first step to ensure that future REDOR experiments on strategically labeled ligands will be feasible.
Study of structural units in glassy and crystalline $xNa_2S + (1-x)B_2S_3$ by MAS and 2D-MQ MAS $^1B$ NMR. S.-J. Hwang, C. Fernandez, J.P. Amoureux, D.P. Lang, J. Cho, S.W. Martin, and M. Pruski, Ames Laboratory, Ames, IA 50011, USA; Universite de Lille, Villeneuve d’Ascq F-59655, France; Iowa State University, Ames, IA 50011, USA

Two-dimensional multiple-quantum (2D-MQ) NMR of $B_2O_3$ in conjunction with traditional high speed magic angle spinning (MAS) at different magnetic fields was applied to elucidate the structure of $B_2O_3$ glass as well as glasses and polycrystals in the series $xNa_2S + (1-x)B_2S_3$. The computer simulation of the MAS spectra was used to augment the experimental data to provide the quadrupole and chemical shift parameters as well as quantitative information. The MAS NMR of $B_2O_3$ produced overlapping anisotropic lineshapes corresponding to $-1/2 \leftrightarrow 1/2$ transition in the ring and non-ring boron atoms. A combination of MAS with multiple-quantum method resulted in better resolved 'DAS-like' $B$ spectrum of $B_2O_3$. A remarkable enhancement of resolution of the 2D-MQ MAS NMR proved instrumental in finding and identifying various structural units in $xNa_2S + (1-x)B_2S_3$. In the low-alkali region ($0 \leq x < 0.33$), rapid structural change takes place from thioboroxyl rings to dithioborate units ($BS_4$), whereas metathioborate and orthothioborate units are formed in the high-alkali region ($0.5 \leq x < 0.8$). In addition, the fingerprints of $B_2OS_2$, $B_2O_2S$, and $B_2O_3$ structures were identified in the 2D-MQ MAS NMR spectra of glassy and crystalline samples.

MULTI-DIMENSIONAL SOLID-STATE NMR SPECTROSCOPY

**OF PEPTIDES, A. Ramamoorthy, L. M. Gierasch**, and S. J. Opella*,

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Multi-dimensional solid-state NMR methods that correlate and separate various spectral parameters are being experimentally demonstrated on $^{15}N$ and $^{13}C$ labeled peptides and proteins. These experiments are applicable to single crystals, powders under stationary and magic angle spinning conditions, and uniaxially oriented samples, including lipid bilayers. The basic three-dimensional experiment, correlating $^1H$ chemical shift, $^1H-^{15}N$ dipolar coupling, and $^{15}N$ (or $^{13}C$) chemical shift, is being used to describe the spin interaction tensors associated with the $^{15}N$ and $^{13}C$ sites in peptides and to resolve resonances from individual sites in oriented membrane proteins. Four-dimensional experiments that utilize dilute or abundant spin-exchange are being used for additional resolution in uniformly labeled proteins and the sequential assignment of amide residues in polypeptides.

SOLID-STATE NMR STRUCTURAL STUDIES OF ORIENTED AND UNORIENTED MEMBRANE PROTEINS,

A. Ramamoorthy, F. M. Marassi, and S. J. Opella, Department of Chemistry, University of Pennsylvania, Philadelphia, PA 19104

Solid-state NMR studies are being carried out on several $^{15}N$-labeled, oriented and unoriented, membrane peptides and proteins. Membrane associated proteins incorporated in lipid bilayers oriented between glass plates utilise a flat-coil probe, while those incorporated in lipid vesicles utilise a MAS probe for solid-state NMR experiments. High resolution spectra of uniformly $^{15}N$-labeled membrane proteins are obtained using multi-dimensional methods. The results demonstrate the ability to resolve resonances from individual sites and that structures can be determined from the spectral parameters measured from multi-dimensional spectra.
CONSTRUCTION OF BROADBAND HETERONUCLEAR CROSS POLARIZATION SEQUENCES VIA NUMERICAL OPTIMIZATION. SambasivaRao, Nanduri 1, NarSingh Ready, NMR Laboratory, Indian Institute of Chemical Technology, Hyderabad 500 007, India. (present address: NMR Centre, Dept of Medical Genetics, University of Toronto, Medical Sciences Buildings, Toronto M5S 1A8, ON, Canada.)

A set of new hetero_TOCSY composite pulse sequences, termed HOTSON (Hetero_TOCSY Sequences Obtained via Numerical Optimization) sequences, have been designed via the numerical optimization procedure by maximizing the heteronuclear coherence transfer efficiency. These sequences have much shorter super cycle lengths with better band widths, compared to most of the sequences that are now in routine use for executing this experiment in liquid state NMR spectroscopy (For example HOTSON-1 with 14(0) 295(180) 263(0) 27(180) 306(0) 253(180) 74(0) 231(180) 338(0) and HOTSON-2 with R = 315(0) 305(180) 66(0) 268(180) 366(0), have total supercycle (S = RRRR) lengths of 7200 and 5280 deg respectively, while DIPSI-2 has 10360 deg, WALTZ-16 has 8640 deg and a hetero TOCSY sequence recently constructed by Sunita Bai et al (J Magn Reson A 106, 248(1994)) has a supercycle length of 9408 deg). The performance characteristics of the HOTSON sequences have been evaluated and compared with the other mixing sequences.

SOLID STATE NMR OF TRANSITION METAL COMPLEXES SUPPORTED ON SILICA AND ALUMINA: ANALYTICAL TOOL IN ORGANOMETALLIC CHEMISTRY

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In the frame of systematic search of effective catalysts a number of transition metal complexes with monocyclic, polycyclic and heteroarenes as well as metal carbonyls were physisorbed on silica and alumina and investigated by means of solid state MAS NMR. High degree of mobility for such complexes adsorbed on inorganic oxides leads to "quasi solution spectra" with line widths in carbon spectra less than 15 Hz for the majority of the substances. This gives us possibility to investigate the structure, dynamic and relaxation properties, the nature of the binding with the surface and some reactions (ligand exchange in metal coordinational sphere, "hot particles" recombination and complex decomposition etc.) on it for these substances without separation from silica or alumina after column or thin layer chromatography. This could be treated as a new and convenient analytical tool in organometallic, coordination chemistry and catalysis. For most of the substances supported on silica and some on alumina 2D spectroscopy (HETCOR) was successfully used and full assignments in proton and carbon spectra were attained.

NMR IMAGING OF LIQUID CRYSTALLINE POLYMER FLUID FLOW THROUGH A 4-TO-1 CONTRACTION. Yiqiao Song, Kurt Scheinpflug, Susan J. Muller, and Jeffrey A. Reimer, Center for Advanced Materials, Materials Sciences Division, Lawrence Berkeley National Laboratory and Department of Chemical Engineering, University of California, Berkeley, Berkeley, CA 94720

Velocity profiles for a solution of HPC, a lyotropic liquid crystalline polymer, have been obtained combining MRI and pulsed field gradient techniques. The results to date, on a 4-to-1 axially symmetric contraction flow, indicate anomalously large upstream vortices which presumably affect both the pressure required for flow and the downstream orientation of the polymer chains. These results, though preliminary, may have profound implications for extrusion processing of liquid crystalline polymers.
SOLID-STATE C-13 NMR ANALYSIS OF CROSS-LINKED POLYETHYLENE.


Process of cross-linking in polyethylene is not very well understood. Depending on the degree of cross linking, it can be very difficult to dissolve or melt the sample without some degradation of the polymer. This limits the number analytical methods which can be used to obtain structural information on cross-linked polyethylene. In this work we have used the traditional CPMAS C-13 NMR techniques to measure the relaxation times (T1p) of the crystalline and amorphous regions of polyethylene, before and after cross-linking. Also, a variation of the Torchia sequence has been used to obtain individual chemical shift anisotropy (CSA) patterns for the amorphous and crystalline regions. The before and after CSA's provide some indications about where the cross linking may be occurring.

DESIGN AND CHARACTERIZATION OF A LOW-FIELD NMR SYSTEM FOR INSPECTION OF SOLID ROCKET MOTORS. Steve W. Sinton and Joseph H. Iwamiya, Lockheed Martin Missiles and Space, Advanced Technology Center, Mail Stop O/93-50 B/204, 3251 Hanover St., Palo Alto, CA 94034 (415) 424-2532, Charles Moeller and Peter Czipott, Quantum Magnetics, 11558 Serrento Valley Road, San Diego CA 92121, E. J. VanderHeiden, Affiant TechSystems, Magna, UT 84044

The design and performance of a NMR spectrometer intended for the nondestructive inspection of propellant relaxation times in solid rocket motors will be presented. The system utilizes a custom C dipole magnet configuration to produce a static magnetic field inside the rocket motor with a well-defined gradient to allow selective inspections of a thin volume of propellant near the motor case bond. A surface coil produces the necessary radio frequency fields and acts as the detector coil. The system operates at sufficiently low frequency (~ 1MHz) to allow penetration of the rf fields through motors with graphite composite cases. The signal-to-noise performance of the system will be described along with strategies for obtaining usable relaxation data by pulsed rf methods in the inhomogeneous fields.

STRUCTURES OF CYCLOOLEFINIC COPOLYMERS STUDIED BY NMR SPECTROSCOPY. Bernd Sperlich.

Juhana Ruotoistenmaki and Maija Mikola-Santala, Technical Research Center of Finland (Chemical Technology). Biologinkuja 7, PL 1401, 02044 VTT. Finland

Homogenous Ziegler-Natta catalysts based on group IV metalloccenes are known to be capable of polymerizing cyclic olefins like norbornene. In our studies, we prepared several copolymers of ethene and norbornene with different mole ratios and in the presence of two different catalysts. The assignment of "C- and ^H-NMR spectra was done by four methods: a) 2DNMR correlation and indirect detection experiments, b) preparation of low molecular model compounds, which represent structural units of norbornene ethene copolymers c) copolymerization of norbornene and deuterated ethylene and investigation by NMR d) molecular modelling calculations. The NMR-signals of isolated norbornene units, alternating sequences as well as norbornene diads could be assigned in the carbon spectra with regard to the configuration of the enchained norbornene units. There is no evidence of longer norbornene sequences than diads in copolymers up to 50 mole-% norbornene content. In the case of higher norbornene content, side-reactions take place, which lead to new signals in the carbon spectrum. We suggest a mechanism in order to explain these signals. The used principles and results are shown to be useful tools for the structure determination of polymers of norbornene derivatives as well.
MULTIDIMENSIONAL CORRELATION SPECTROSCOPY IN ROTATING SOLIDS VIA DIPOLAR RECOUPLING. B.-Q. Sun, P.R. Costa, C. M. Rienstra, J.-G. Hu, P. T. Lansbury, Jr., J. Herzfield, and R.G. Griffin, Chemistry Department, Brandeis University, Waltham, & Francis Bitter Magnet Laboratory and Chemistry Department, MIT, Cambridge MA 02139

Recent developments in high-resolution solid-state NMR have made it possible to study the molecular structure of amorphous or polycrystalline solid samples in a manner similar to that routinely used in solution NMR. These techniques require high spectral resolution, so that individual spectral lines can be identified and associated with specific nuclei and their local environment in the system under study, and some method of inducing observable interactions between nearby nuclei. Quantitation of these interactions provides information about internuclear distances, and hence molecular conformation. In solid-state NMR, these techniques have traditionally focused on low-y nuclei (e.g. $^1$C, $^1$N, $^{31}$p) in isotopically-enriched samples. Spectral resolution is increased by dispersing the signal over two or more dimensions; nuclear spin connectivities between resolved resonances are then observed as cross-peaks in the multidimensional correlation spectrum, arising from dipolar recoupling in the MAS framework. We demonstrate the feasibility of these techniques by application to a series of biological molecules.

SOLID-STATE NMR STUDIES OF THE STRUCTURE AND DYNAMICS OF FUNCTIONAL MOLECULES IN POROUS CERAMICS. Li-Oiong Wang, Jun Liu, WD Samuels, and GJ Exarhos, Pacific Northwest National Laboratories, Richland, WA 99352

Multinuclear solid-state magic-angle spinning (MAS) nuclear magnetic resonance (NMR) spectroscopy has been used to characterize the structure and dynamics of surfactants in the synthesis of advanced porous ceramic composites. NMR measurements provide direct information on the local environment of all NMR active nuclei in ceramic composites through chemical shifts, coupling between different nuclear spins, and electric field gradients. The dynamics of the system can be probed by measuring spin lattice relaxation times as well as measurements and interpretations of dynamic lineshapes. Variable-temperature $^{13}$C solid-state MAS NMR was used to investigate the structure and dynamics of surfactant molecules in mesophasic silicates. Functional groups and side groups in the surfactant were identified from high resolution spectra, while information on how surfactants organized onto silicates and their relaxation behavior were obtained using a combination of NMR line-shape and relaxation-time analyses with variable temperature NMR. Due to the high sensitivity of $^{31}$P nucleus, phosphate containing surfactants were also used to synthesize the advanced porous materials and were investigated by $^{31}$P solid-state MAS NMR.


The proton NMR lineshape of water in the zeolitic isomorphs clinoptilolite and heulandite approximate a Gaussian and (reduced splitting) Pake doublet respectively*. Different cations are the distinguishing chemical characteristic of the two isomorphs. Clinoptilolite has Na and K as the most prevalent cations, whereas heulandite has Ca. Nearly homoionic Na-, K-, and Ca- clinoptilolite have been prepared by ion-exchange methods in order to investigate the effects of the cation on the proton spectrum of clinoptilolite. Each sample has been studied by proton NMR at 300 MHz using single-pulse Bloch and quadecho acquisitions both as a function of NMR parameters and heat treatment. Each homoionic form of clinoptilolite reveals structure in the proton spectrum that is not observed in the naturally occurring zeolite. In addition, the log of the amplitude of the quadecho response is a linear function of the pulse spacing rather than quadratic as observed for common dipolar echoes of spin 1/2 pairs such as CaS0$_2$•2H$_2$O. This data will also be discussed in terms of cation water interactions.


This work was performed under the auspices of the U.S. Department of Energy under contract W-7405-ENG-48 and the U.S. Nuclear Regulatory Research Commission, Division of Regulatory Applications under Contract No. NRC-02-88-005.
Applications of incoherent (noise) spectroscopy have reappeared at infrequent intervals for some 30 years in NMR, and have more recently made their way into optical experiments. Despite this extensive history, relatively few NMR spectroscopists have exploited the advantages of incoherent, weak-field excitation. We have recently explored how noise excitation sequences might be applied to a variety of problems in solid state NMR, and present our applications to accurate and reliable measurements of quadrupolar lineshapes and intensities, to dynamically averaged systems, and to low-power low-temperature NMR studies. These experiments are easy to implement on our spectrometer and provide significant technical and/or theoretical advantages over more traditional coherent single-pulse methods in a wide range of applications. We also attempt to explain the theoretical basis for understanding the experiments, and the dependence of signal intensities on experimental parameters.

Natural abundance NMR methods were employed to investigate the phase transition properties of two lyotropic liquid-crystalline polymers, poly(p-phenylene terephthalamide) (PPTA) and poly(β-benzamide) (PBA), at a molecular level. $^{13}$C and $^1$H NMR spectra were recorded on solutions of PPTA and PBA in absolute sulfuric acid as a function of temperature, concentration, and molecular weight. Transitions from an isotropic to a nematic phase and on to a solid-like aggregate phase could be detected in both the solute and solvent NMR spectra. The temperature-dependent $^{13}$C NMR spectra of the dissolved polymers at the nematic/isotropic interphase could be successfully simulated using tensor parameters measured on the solid using bidimensional isotropic-anisotropic correlation NMR. These simulations suggest that the structures of the aromatic polymer molecules in the nematic phase are not linear, in agreement with results observed in the solid by X-ray diffraction. The thermodynamic parameters involved in the isotropic ↔ anisotropic equilibria as well as kinetic information about rates of molecular migration between the two phases, will also be presented and discussed.

NMR spectra based on magic-angle spinning (MAS) and on direct polarization (DP) or cross polarization (CP) signals have been obtained on a variety of organic and inorganic pollutants adsorbed on soil and soil components, e.g., silica, clays and humics. $^{13}$C labeled species are used for the industrial solvents studies, e.g. Cl₂C=CHCl, CC₄, CH₃COCH₃, C₆H₆, HOCH₂CH₂OH and pesticides. For some organic pollutants (e.g., organophosphate pesticides), nearly the same isotropic chemical shifts are observed as for the pure materials, but dramatic differences in molecular mobilities are observed in some cases in terms of variations in spinning sideband patterns, relaxation times and/or CP-vs-DP characteristics. Much greater pesticide hydrolysis activity is noted in pesticide/clay samples than in pesticide/humic samples. The adsorbed acetone spectrum displays hydrogen-bonding shifts. Patterns of relaxation times are useful in characterizing the state of a pollutant in these systems. NMR phenomena based on the dipole-dipole interaction (e.g., CP) are useful for examining sites and/or dynamics of interaction of a pollutant with a soil component (e.g., $^{113}$Cd and a humic; or $^{13}$C-labeled ethylene glycol and a clay). NMR shows excellent promise for providing valuable new information on pollutant/soil systems at a molecular level of detail.
SMALL STEPS IN SOLID-STATE NMR, EXPERIMENTAL AND COMPUTATIONAL. John S. Waugh. M.I.T., Room 6-235, Cambridge, Massachusetts 02139

There are times when ideas for new experiments in pulsed NMR are too complicated to be analyzed by approximate theory or to be explored entirely by experiment. ANTIOPE, a general purpose computer program for simulation of spin dynamics, has sometimes been found useful for preliminary testing. An example is provided by the development of improved CRAMPS sequences (P. Kuhns and J. Waugh, to be published) where a new 24-pulse sequence has been found which gives greatly improved resistance to the degradation in resolution caused by sample spinning. Some purely educational applications of computer simulations will also be mentioned.

SIMPLE NMR EXPERIMENTS ON COMPLEX SYSTEMS. Joseph J.H. Ackerman. Department of Chemistry, Campus Box 1134, Washington University, One Brookings Drive, St. Louis, MO 63130-4899.

Intact functioning biological tissues represent an extreme in complexity when considered as an "NMR sample". Additionally, many (most) of the sample manipulation strategies that can be used with inert systems are untenable with functioning biological systems. Nevertheless, very simple NMR experiments can be used to great advantage in posing focused biophysical questions of considerable importance with living systems. This presentation will describe "simple" NMR experiments yielding exceedingly "simple" spectra of only a few lines but which provide considerable insight into fundamental biophysical processes. Questions of both a static ("how much?") and dynamic ("how fast?") nature will be addressed. The usual (1H, 19F) and unusual (133Cs) suspects will be interrogated.

DETERMINATION OF THE NITROGEN COMPOSITION IN COAL: BACK TO DYNAMIC NUCLEAR POLARIZATION. Robert A. Wind', Ronald J. Pugmire', Paul D. Ellis', and David M. Grant'; Environmental Molecular Sciences Laboratory', Battelle/Pacific Northwest National Laboratory, Richland, WA 99352. Departments of Chemical and Fuels Engineering' and Chemistry', University of Utah, Salt Lake City, UT 84112.

The standards mandated by the clean air act require increasing progress in reducing NO\textsubscript{x} emissions from coal combustion systems. Although several empirical relationships for nitrogen evolution from coal during devolatilization and char oxidation have been developed, the fundamental chemistry of coal nitrogen evolution is still not known and is a weak link in any NO\textsubscript{x} mitigation approach. In the seminar a joint research effort between the University of Utah and the Pacific Northwest National Laboratory (PNNL) will be discussed. The objective is to study the nitrogen forms in coal and the transformation processes of nitrogen prior to their release into the gas phase, using NMR combined with dynamic nuclear polarization (DNP) to enhance the sensitivity of nitrogen NMR spectroscopy at the natural abundance level by two to three orders of magnitude. Such sensitivity enhancement will permit experiments that can provide new information on the chemical structures in coals and the dynamics of electron-nuclear and nuclear-nuclear interactions. Both the sensitivity enhancement due to DNP and the quantitative character of the measurements will be discussed.
NMR STUDIES OF STRUCTURE AND DYNAMICS IN UREA INCLUSION

Inclusion compounds exhibit interesting combinations and variations of disorder, conformational preference, and molecular dynamics. This talk will focus on a simple example; urea inclusion compounds (UICs). The urea host forms a hexagonal crystal lattice with long, narrow channels occupied by guest molecules, such as n-alkanes or n-alkanoic acids. Carbon and deuteron magnetic resonance spectroscopies have been used to investigate structure and dynamics in these materials. Selective deuteration allows the host and guest to be studied independently. The host urea molecules rotate about both C=O and CN bonds; with rates that depend on the guest. Temperature dependent lineshapes, selective inversion and relaxation times provide information about activation energies and mechanisms of rotational motion, which occur on time scales from picoseconds to milliseconds. For comparable chain length, alkanoic acids rotate more slowly than alkanes, presumably due to hydrogen bond interactions with host molecules. An unusual variation of quadrupole splittings with alkyl chain length is observed for alkanoic acid UICs. Molecular dynamic simulations, which included explicit hydrogen atoms and nine adjacent host channels, agree with the observed quadrupole splittings for alkanes but not alkanoic acid guests.

SOLID STATE NMR OF LIGAND BINDING TO ELECTROCATALYST SURFACES AND TO HEME PROTEINS.

We have recently investigated the binding of several small ligand molecules to metal atoms in a variety of environments: in organometallics and metal clusters, at the surface of bulk metal electrocatalysts, as well as in heme proteins.

For the organometallics and heme proteins, chemical shift tensors can be deduced via using solid state techniques, and analyzed by using density functional theory. Results on CO, RNC, O2 and RNO binding will be outlined.

NMR spectra can also now be readily obtained from species (CO, CN) adsorbed onto large metal particle electrocatalysts, in an electrochemical environment. Variable temperature Ti and T2 results will be presented, and the effects of surface diffusion and applied potentials will be discussed.

UNDERSTANDING NMR OF REACTIVE SPECIES USING CALCULATIONS OF STRUCTURES, ENERGIES AND CHEMICAL SHIFTS.

Ab initio calculations are very useful in the design and interpretation of NMR studies of carbenium ions and carbanion-like organometallic intermediates on metal oxide surfaces. The properties of adsorption complexes in zeolites and other catalytic intermediates challenges one's intuition, and calculation provides the means to more exactly test spectral assignments.

This talk will focus on practical considerations in the choice of methodology, selection of basis sets and treatment of correlation in such problems.
Investigations of self-diffusion of guest molecules in zeolites requires experimental techniques that distinguish among the different time and length scales of adsorbate mobility. First-time applications of solid-state exchange $^{13}$C NMR techniques to the study of the reorientation dynamics of molecular hydrocarbon species in porous solids have allowed the geometry and time scales of molecular hopping processes in faujasite-type zeolites to be characterized directly and model-free on a nanometer length scale. Specifically, two-dimensional (2D) exchange NMR on static samples and one-dimensional (1D) magic-angle spinning (MAS) exchange-induced-sidebands (EIS) methods allow motional correlation times on the order of milliseconds to seconds to be extracted directly from the experimental data. The advantages and limitations of the 2D exchange and 1D EIS techniques will be discussed in light of the complementary information they provide for characterizing local transport processes. Exchange intensity contributions in the spectra arising from spin diffusion among different benzene molecules (99% $^{13}$C-enriched at a single site) were identified through exchange spectra acquired with high-power proton decoupling during the mixing time and are found to be temperature-independent. In this way, contributions from spin diffusion and molecular reorientation have been separated to yield molecular measurements of discrete transport events in heterogeneous microporous solids.

LIMITS OF HIGH RESOLUTION PROTON NMR IN SOLIDS. B.C. Gerstein. Iowa State University, Ames, Iowa, 50011-3111, Toshihiko Taki, Faculty of Engineering, Tokushima University, Tokushima, Japan, David Grant, Ronald Pugmire, and Mark Solum, Department of Chemistry, The University of Utah, Salt Lake City, Utah 84112.

The recently reported use of delayed acquisition to achieve high resolution NMR of protons in strongly homonuclear dipolar coupled solids is discussed. Utility and limitations of the technique are delineated, and compared with the more technically demanding procedures of HETCOR and CRAMPS. The sources of residual broadening in high resolution solid state NMR of protons in solids is considered.


HETERONUCLEAR DECOUPLING AND SPIN COHERENCE LIFETIMES IN ROTATING SOLIDS. Chad M. Rienstra, Andrew E. Bennett, Boqin Sun and Robert G. Griffin. Francis Bitter Magnet Laboratory and Department of Chemistry, MIT, Cambridge, MA 02139, and Laboratory of Chemical Physics, NIH, Bethesda, MD 20892

Two-pulse phase-modulated (TPPM) decoupling has been shown to be an effective general technique for line narrowing in strongly coupled spin systems under magic-angle-spinning. Under typical experimental conditions, the homogeneous contribution to the linewidth (in nuclei such as $^{13}$C or $^{15}$N) is dominated by residual dipolar coupling to H nuclei. However, with strong (> 100-125 kHz) phase-modulated decoupling fields, this contribution may be almost completely eliminated, so that other contributions to the linewidth — such as scalar couplings to low-y nuclei, and the effects of quadrupolar nuclei such as $^3$N—become limiting. These effects are explored as a function of magnetic field, magic-angle-spinning speed, and decoupling conditions. Beyond the advantages of improved sensitivity and resolution in solid state NMR, the implications for polarization transfer and dephasing via weak homo- and heteronuclear couplings will be discussed. In particular, the effects of coherence relaxation upon the measurement of weak dipolar couplings will be critically examined.
We have recently developed a new NMR technique for determining heteronuclear distances in solids that requires irradiation on only one of the nuclear species of a spin pair. The resulting Dipolar Exchange-Assisted Recoupling (DEAR) experiment is particularly well suited to the analysis of systems where at least one of the spins is quadrupolar. The 2D DEAR spectrum on the right correlates the IS dipolar interaction with the sum of the dipolar and the CSA interactions, thus allowing the orientation of this tensor with respect to the internuclear vector. A 3D version of DEAR combines such separated-local-field information with the high resolution of MAS. The theory and quantitative application of these techniques to the analysis of solids will be presented.

DEUTERIUM NMR OF PARAMAGNETIC MATERIALS AND MAGNETICALLY ORDERED BILAYERS. Regitze R. Vold, R. Scott Prosser, John A. DiNatale and Jimmy S. Hwang, Department of Chemistry and Biochemistry, University of California, San Diego, La Jolla, California, 92093-0359

During the last few years our research has been focused on 2H magnetic resonance of paramagnetic solids, and the use of transition metal ions for macroscopic re-alignment of nematic, discoidal phospholipid bilayers. Lineshape analysis of deuterium quadrupole powder spectra has been used to study molecular reorientation in solid transition metal chelates, and we are exploring how static and MAS 2H NMR can be used to characterize the environment of transition metal ions, including ion-nuclear distances. Examples include glycinate complexes of Ni(II) and Cu(II) where α-methylene group deuterons can be distinguished, and hydrated lanthanide complexes, where D0 ligands have been found to be located in different magnetic environments.

Recently, we have explored to which extent deuterium and proton NMR can be used to determine the structure and dynamics of membrane associated peptides. In the course of this work, we discovered that lanthanide ions with positive magnetic susceptibility (Eu**, Er**, Tm** and Yb**) can be used to induce positive alignment (n || B0) of phospholipid bilayers, which normally align with n⊥ B0. This is potentially very useful for structural and dynamic studies of membrane spanning peptides and proteins.


- Natural-abundance double-quantum 13C NMR in a liquid crystal – determination of molecular conformation without isotope labelling.
- A theoretical model for explaining anomalous rotational resonance lineshapes.
- Implications for molecular structural studies.
- A 7-fold symmetric pulse sequence for efficient double-quantum excitation and dipolar recoupling in rotating solids (collaboration with N.C. Nielsen, Aarhus).
- A new computer algorithm for simulating dynamics under periodic spin Hamiltonians.
- Rotational resonance estimations of molecular geometry in the retinal chromophore of the visual pigment rhodopsin (collaboration with group of J. Lugtenburg, Leiden).
- Rotational resonance estimations of molecular geometry for a small inhibitor molecule bound to a 200kD membrane protein (collaboration with group of A. Watts, Oxford).
- Study of phosphate group orientations in DNA fibres: Implications for the structure of the C form of DNA (collaboration with A. Rupprecht, Stockholm).
NEW SOLID STATE NMR TECHNIQUES FOR THE STUDY OF THE STRUCTURE
AND DYNAMICS OF BIOPOLYMERS. G. Drobny, D.M. Gregory, M. A. Hatcher,
K. Geahigan, J. Stringer, S. Kihne, and M. Mehta, Departments of Chemistry and Physics,
University of Washington, Seattle, WA 98195.

The application of windowless dipolar recoupling (DRAWS) pulse sequences to the study of
the structure and dynamics of biopolymers will be discussed. The theoretical basis for dipolar
recoupling by DRAWS will be introduced using Floquet theory. The ability of DRAWS to define
internuclear distances to high accuracy will be described. In particular the measurement of \(^{19}\text{F}-^{19}\text{F}\) distances with DRAWS will be described and applications to the measurement of distances in
selectively fluorinated RNA oligomers will be described.

The use of DRAWS in multiple quantum experiments will also be described and the
information content of double quantum spectra obtained using DRAWS will be discussed in detail.
As an application of double quantum DRAWS (DQDRAWS) spectroscopy, the first, direct
measurement of the relative orientation of pyrimidine bases in a hydrated, nucleic acid by solid state
NMR will be reported.

Prospects for using DRAWS to define the internal dynamics of biopolymers in amorphous,
hydrated powders and in crystalline form will be discussed.

SEPARATING QUADRUPOLAR-BROADENED LINES IN POWDER
SOLIDS: MULTIPLE-QUANTUM NMR SPECTROSCOPY FOR SPIN-
1 AND SPIN-3/2. Melinda J. Duer and Clare Stourton, Department of
Chemistry, University of Cambridge, Lensfield Road, Cambridge, CB2, 1EW,
Great Britain.

A method is proposed for resolving quadrupolar-broadened NMR lines from powder
samples according to multiple-quantum frequency shifts. It is applied here to spin-3/2
systems which suffer significant second-order quadrupolar broadening, and spin-1
systems which only suffer first-order broadening. The method is applicable to all
quadrupolar spins with small or large quadrupole coupling constants. It offers a real and
significant improvement in resolution for NMR spectra of quadrupolar nuclei, whilst still
allowing the quadrupole parameters to be determined. The success of any technique
employing multiple-quantum coherences in powder solid samples depends on being able
to excite multiple-quantum coherences evenly over all molecular orientations in the
sample. This is a well-known problem which is addressed and solved in this work.

HIGH FIELD CPMAS NMR: PROBLEMS AND PROSPECTS. Anil Mehta, Brett Tounge,
Sean Burns, Xiaoling Wu, Iwen Wu and Kurt W. Zilm, Department of Chemistry,
Yale University, 225 Prospect Street, New Haven, CT. 06511.

In this talk we will discuss progress in the development of CPMAS methods suitable for high resolution NMR
of organic solids at fields greater than 18.8 T. Problems with decoupling and CP transfer, especially at MAS
rates over 25 kHz will be described, and solutions to these difficulties presented. Operation at high fields is
especially attractive for samples uniformly labeled with \(^{13}\text{C}\) and \(^{15}\text{N}\). Limitations to the resolution attainable in
such systems will be investigated, especially in the context of measuring small J couplings between \(^{13}\text{C}\) nuclei
in the solid state. 2D and 3D NMR techniques using dipolar recoupling and/or evolution under J couplings
for structure elucidation of uniformly labeled macromolecules will be presented in applications to uniformly
labeled nucleotides and sugars.
Two dimensional 3 and 5Q-MAS-NMR spectroscopies have been applied to the discrimination of the different $^{27}$Al sites in several compounds of industrial interest. It is shown that the new quintuple quantum method which gives an extraordinary resolution can be applied to any spectrometer with wide or narrow bore, low or high-field magnet. For example, on a high field spectrometer (18T), the virtual Larmor frequency along Fl is 1GHz for $^{27}$Al !!.

The pure-absorption 2D spectra allow the direct determination of different species, the correct and direct determination (without simulation) of both actual chemical shifts and quadrupolar parameters. In addition, the method gives incomparable information about the distributions of both the chemical shifts and quadrupolar coupling constants. The quantitative analysis is also demonstrated.

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FDA undertook the revision of the current good manufacturing practice (cGMP) regulation for devices (aka quality system regulation or QSR) in part to add the design controls authorized by the Safe Medical Device Act of 1990 to the cGMP regulation. This presentation will examine design control as specified by the new cGMP regulation with emphasis on the software validation aspect of design control. In particular, it will examine the following questions:

- What is Design Control?
- Why is Design Control necessary?
- Who must do Design Control?
- What are the elements of Design Control?
- What is software, and what is software validation?
- Why is software validation necessary?
- What are some keys to software validation?

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Phospholipids (PL) are being used in many new controlled release pharmaceutical preparations. Therefore, we have developed an HPLC/MS method for the quantitation of phospholipid classes (phosphatidylcholine-PC and phosphatidylethanolamine-PE, primarily) and their degradants and contaminants. Highly dilute samples of the PL and the pharmaceutical product containing the PL were analyzed using a Rainin Microsorb-MV silica column, 5µm, 100A pore diameter, and mobile phase consisting of 1600mL acetonitrile, 360mL methanol, and 200mL 0.01 M ammonium acetate with reserpine as the internal standard. For routine analyses of PE and PC, the Perkin-Elmer SciEx API-III+ mass spectrometer was operated in the positive ion ESI mode. In three periods, the reserpine molecular ion (609.2amu) was monitored, then the range 710-830amu to detect the PE envelope, and the 730-850amu range to detect the PC envelope.
A t-butyl ether extract of charcoal stripped human plasma spiked with estradiol, estrone, norethindrone and equilin (as the internal standard) was injected on a 2.1mm x 10cm C18 reverse phase HPLC column. The extracts were separated and eluted using a methanokwater gradient program. Since the optimal collision energy to produce the most sensitive response for each of the molecular reaction monitoring (MRM) transitions differed, it was necessary to utilize the ability of the SciEx API 300 triple stage quadrupole mass spectrometer to change the collision cell energy during each MRM experiment. The changing of the collision energy with each ion pair dwell also required the ability to regulate the ion transmission parameters through the collision cell. These concomitant analyses resulted in a 5pg/mL limit of quantitation for estrone using the dehydrated M+H protonated molecular ion in an MRM positive ion mode triple stage quadrupole experiment. The MRM experiments used to detect norethindrone and estradiol produced limits of quantitation at 25pg/mL and 10pg/mL of human plasma, respectively.

THE ROLE OF AMINO ACIDS IN FETAL GROWTH. Michelle Timmerman, Adrian W. Pike, Paul V. Fennessey, and Giacamo Meschia, Department of Pediatrics and Physiology, University of Colorado Health Sciences Center, Denver, Colorado 80262.

Proper nutrition is an important consideration for optimal growth of the developing fetus. Chronic reduction of essential nutrition during intrauterine life can result in premature birth, coupled with a marked reduction of placental size and fetal weight. Our knowledge of the transport of important nutrients by the placenta (glucose, fats and amino acids), is limited. Of the three important food groups, glucose has been studied the most, both in vivo and in vitro. Relationships between maternal plasma levels of amino acids, transport across the placenta, fetal plasma levels, and fetal utilization for both growth and energy, are the focus of this research.

The compartments outlined above were studied in pregnant ewes during acute and chronic conditions. Specifically, amino acids (both essential and nonessential), isotopically labeled with [13C], [15N], or [2H] were infused into the fetal and/or maternal circulation. Gas chromatography-mass spectrometry was used to measure uptake, turnover, utilization and oxidation products of these components. The data provided detailed examination of each compartment. Results from these studies will be presented.

DETECTION OF ARTEMISININ BY DERIVATIZATION WITH DIAZO DYES. Michael D. Green, Nisha B. Gandhi, G. Daniel Todd, and Dwight L. Mount, Centers for Disease Control and Prevention, 1600 Clifton Rd., Atlanta, GA 30333. Emory University, Atlanta, GA 30322.

Artemisinin or qinghaosu is a naturally occurring sesquiterpene endoperoxide that is receiving considerable attention in the treatment of malaria. Detection of artemisinin has proven to be a challenge as it does not possess any sensitive or specific spectrophotometric characteristics. Although artemisinin does absorb ultraviolet radiation between 210 and 220 nm, the extinction coefficient is relatively small and detection at the lower wavelengths usually results in poor selectivity and increased baseline noise when high-performance (HPLC) methods are used. Therefore, a procedure has been developed for the derivatization of artemisinin to compounds that absorb light at longer wavelengths (330-500 nm). Artemisinin is initially converted to an enolate that reacts with diazonium salts to produce the derivatives. The diazonium salt reagents used for derivatization include fast black K, diazo red RC, fast red TR, varamine blue RT, fast corinth V, fast violet B, fast yellow GC, and fast blue B. The artemisinin derivatives were separated from the derivatizing reagents by reverse-phase high-performance liquid chromatography (HPLC), detected by ultraviolet (UV) or visible light absorbance, and evaluated against a known pre-column derivatizing technique. Among the diazonium salts tested, the coupling of diazo red RC with the artemisinin enolate showed the best improvement in sensitivity.
An Investigator’s Point of View: Significant Good Manufacturing Practice Deviations. Terri L. Dodds, DHHS/PHS/FDA, Denver Federal Center, Building 20, 6th Avenue and Kipling Street, Denver, CO 80225-0087

An FDA investigator discusses Good Manufacturing Practice deviations which may be considered significant enough to warrant regulatory or administrative action or withholding of a drug application. The investigator’s perspective is primarily from a manufacturing process point of view.

Aseptic Drug Production Quality Control and Its Effect on Good Manufacturing Practice During Audits of Pharmaceutical Industries. Steven C. Madzo, US Food and Drug Administration, Denver Federal Center, Building 20, PO Box 25087, Denver, CO 80225-0087

The manufacturing process for products which require a sterile drug formulation are strictly controlled throughout the production cycle to maintain a high degree of confidence that the end product will be rendered sterile and remain in this condition until administered by the end user. FDA investigators and regulatory scientists frequently audit the firm's production facilities and note deviations from accepted good manufacturing practices which may affect the aseptic quality control necessary for production of sterile pharmaceutical products. Significant deviations which may warrant either regulatory or administrative actions or affect NDA/ANDA approvals are discussed.


Human corticotropin releasing factor (hCRF) is a 41 amino acid peptide currently being investigated for a number of therapeutic applications. The solution behavior of hCRF has been investigated at near neutral pH under a variety of conditions. At low peptide concentration, hCRF adopts a largely random structure. However, as the peptide concentration is increased, the amount of a-helix increases dramatically. Increases in a-helical secondary structure appears to be due to the formation of a compact tetramer, similar to the peptide, melittin. Populations of both monomer and tetramer can be seen by dynamic light scattering. The effect of additives has been investigated on the secondary structure and thermostability of hCRF. Furthermore, there seems to be a sizable kinetic barrier to dissociation of the tetramer upon dilution of the peptide. Future studies will include a more detailed characterization of the aggregation state of hCRF.
A NOVEL MICROWAVE AUTOCLAVE FOR AUTOMATION OF PHARMACEUTICAL RESEARCH APPLICATIONS. W. Gary Engelhart, Werner Lautenschlager, Martin Metzger, Milestone MLS, 7289 Garden Road # 219, Riviera Beach, Florida 33404.

Hundreds of laboratories currently utilize microwave systems to accelerate the preparation of samples for research purposes, quality control and process control analyses. Conventional microwave systems with multi-mode cavities and doors are designed for manual operation. A new microwave autoclave eliminates the impediments to automating microwave chemistry procedures. The ultraCLAVE™ system combines microwave heating and high pressure vessel technology allowing chemical reactions to be conducted at pressures and temperatures up to 200 Bar (2,900 psig) and 350°C. The system is specifically designed for semi-automated batch processing of multiple samples. Full automation is achieved by interfacing a laboratory robot arm to load/unload sample racks. Fundamental design and operating principles of the system will be presented along with examples of pharmaceutical research applications performed in the system, (e.g.; synthesis reactions, solvent extractions, peptide/protein hydrolyses, acid digestion of implant materials, etc.).

A NEW APPROACH TO GROSS ALPHA MEASUREMENTS IN LIQUID SAMPLES USING EXTRACTION CHROMATOGRAPHY AND LSC, Michael Fern, Anil Thakkar, Thomas Kupka, James Harvey, Eichrom Industries, Inc., 8205 S. Cass Avenue, Suite 107, Darien, IL 60561; Charles Passo, James Thomson, Canberra Packard Instrument Co, Meriden, CT.

The traditional method of gross alpha measurements for liquid samples using gas flow proportional counting suffers from a number of limitations. In order to minimize the problem of self absorption, the volume of sample which can be analyzed is limited by the amount of dissolved solids found in the liquid. Counting efficiency of alpha particles by GPC is 35-40% at best and declines to as low as 10% when 100 mg of solids are left on the counting planchet. Counting time in excess of 1000 minutes are typically required to reach a detection limit of 0.1 Bq/L. Samples containing extremely high levels of dissolved solids may require even longer counting times to achieve the desired detection limit since an even smaller sample size must be used.

Alpha liquid scintillation counting has been proposed as an alternate to GPC for gross alpha measurements. The inherent counting efficiency for alpha particles by LSC is in excess of 90% solids. However, the sample size is limited by what can be put into an LSC vial, and so for samples larger than 10 mL, some form of sample concentration must be performed.

Eichrom Industries' Actinide Resin show excellent uptake for all the actinides and for radium under neutral to slightly acidic conditions. Because of these characteristics it is a good candidate to preconcentrate samples prior to alpha LSC. A method had been developed which combines this resin and alpha liquid scintillation counting to measure total alpha activity in water samples. The method is fast and simple. As many as 20 samples can be processed in 24 hours, requiring only 1 or 2 hours of hands-on time. Using a 500 mL sample, a detection limit of 0.1 Bq/L and be reached with only 30 minutes counting time.
MICROWAVE DISSOLUTION OF SOILS FOR RADIOCHEMICAL ANALYSIS, Richard Robinson

Richard Peters, Joseph Rodriguez, Yassar Ebaid, Catherine Hensley, Alice Slemmons, Claudine Amenta, Edward Gonzales, Steve Goldstein, Los Alamos National Laboratory, P.O. Box 1663, MS K-484, Los Alamos, NM 87545.

We have improved our recently developed ten gram microwave oven matrix destruction procedure for the radiochemical analysis of soils for plutonium, and americium. A new step, a high temperature furnace step to decompose complex organic materials was added to our microwave oven dissolution procedure. Those organic substances were not decomposing in either our open beaker hot plate or previous microwave digestion methods. The new step was not required to improve recoveries for the QC/QA samples but rather to reduce the variability of the tracer recoveries for some of our routine samples. Some of our regular environmental surveillance samples have complex organic substances (from pine needles?) that require decomposition in order to improve the variability of the tracer recoveries.

Programmable ramping of the pressure and temperature result in repeatable and defined dissolution conditions. Results for quality control samples indicate that equivalent accuracy and better precision are obtained relative to hot plate digestions. Open beaker hot plate dissolution procedures require large volumes of acids, numerous hot plates, and extensive hood space. The microwave oven dissolution procedure had reduced the volume of both nitric and hydrofluoric acids required by approximately an order of magnitude. Use of this procedure results in a major reduction in the volume of hazardous/corrosive reagents used, a reduction in the workspace requirements, a doubling in sample throughput, and improved data quality.

Our 10 gram procedure which allows for the venting of gases, has enabled us to cross a 0.5 to 1 gram sample size barrier that had been previously considered the limit for standard microwave vessels. We have also incorporated a scaled down procedure for 2.0 gram soil samples which are analyzed for uranium.

WHO'S WATCHING THE FOXES AS THEY GUARD THE HENHOUSES? (THE STATE OF INDEPENDENT EVALUATION OF RADIOCHEMICAL DATA), Keith Wegner, QuantaLex, Inc., 300 Union Blvd., Suite 600, Lakewood, CO 80228

The federal facility sector of the environmental industry is being particularly impacted by government budget cutting and resulting uncertainties in project funding as well as the lack of a focused enforcement strategy by federal environmental regulators. One of the notable areas of reduction has occurred in third party evaluation of environmental measurement data. Fueled by the laboratory fraud scandals of the late 1980's and historical public mistrust of data supplied by federal facilities, third party verification, validation, and/or assessment of analytical data became a mainstay of the environmental quality assurance consulting until recently. Radiochemical data was particularly targeted for independent evaluation because of the nuclear facility sources of the data and because the data users, regulators, litigators, and the public seldom had a solid understanding of the nature of radiochemical measurements. Reduction or elimination of third party data evaluation has resulted in the data generators and data collectors evaluating the quality of their own data. The author will explore the propriety of this practice as well as the cost and value-added issues associated with third party evaluation of radiochemical data.
DISTRIBUTION OF STRONTIUM BETWEEN WATER AND GEOLOGIC MATERIALS AT THE
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IDAHO NATIONAL ENGINEERING LABORATORY, Michael J. Liszewski, U.S. Geological Survey,
INEL, MS-4148, P.O. Box 2230, Idaho Falls, ID  83403-2230.

The U.S. Geological Survey and Idaho State University, in cooperation with the U.S. Department of Energy, are
investigating the distribution of strontium between water and geologic media at the Idaho National Engineering
Laboratory. The objective of the investigation is to provide site-specific chemical solute transport parameters for
strontium which are suitable for use in solute transport modeling equations. Solute transport often is dependent on
various physical and chemical processes which govern solute distribution between the geologic media and the
aqueous phase. At thermodynamic equilibrium, this distribution is described by an empirically determined
parameter called the distribution coefficient (K).

Investigations have focused on strontium Kj's of surficial and interbedded sediments at the INEL, and were
determined using batch experimental techniques. Three areas of interest were investigated: 1) experimental method
development, 2) effects of solution chemistry on strontium K„'s, and 3) areal and vertical distribution of strontium
IC/s at the INEL.

Experimental method variables included the length of time and method of sample agitation, use of crushed or non-
crushed sediment, and the mass-to-volume ratio. The use of synthesized aqueous solutions in place of aquifer water
for these experiments also was investigated. The effects of solution chemistry on strontium Kj's were investigated
by determining K/s using variable dissolved concentrations of calcium, magnesium, potassium, sodium, and
hydrogen <pH). Areal and vertical strontium K distribution in surficial and interbedded sediments at the INEL was
investigated by sampling a diverse range of sediment textures.

The mass-to-volume ratio was the only experimental variable which appreciably affected strontium K/s.
Synthesized aqueous solutions generally were suitable for use in these Kj experiments. Variable concentrations of
dissolved calcium, magnesium, sodium, and pH affected strontium K„'s while variable concentrations of dissolved
potassium did not affect strontium Kj's within the concentration ranges investigated. Preliminary strontium Kj's
for a variety of collected surficial and interbedded sediment samples ranged from 36 to 447 milliliters per gram.

BENEFITS OF THE DEEMS DATA DELIVERABLE. Terry McKibbin, Dave Burns, Michael
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Sheetz, Paragon Analytics, Inc., 225 Commerce Drive, Fort Collins, CO 80524.

Paragon Analytics, Inc. (as Analytical Technologies, Inc.) participated in the pilot study of a
DOE specification for a standardized electronic deliverable of radiochemistry data. DEEMS
(Department of Energy Environmental Management Electronic Data Deliverable Master
Specification) was developed by the DOE to manage large amounts of analytical data in support
of environmental restoration and waste management activities at sites across the country. With
the development of a standardized EDD, radiological data can be transmitted, manipulated,
verified, and validated throughout the DOE complex without the intensive labor requirements of
translating data into various formats. This standardization holds the promise of reducing the time
and effort (thus the cost) of data handling within the DOE. Furthermore, DEEMS has the
potential of becoming an interagency standard that would allow a more global sharing of
analytical data. As the specification becomes the promulgated data deliverable for the DOE,
feedback from the data producers and users is essential. Some specifics of the DEEMS are
presented.
BLOOD ALCOHOL ANALYSIS BY STATIC HEADSPACE WITH DUAL FIDS/MEGABORE CAPILLARY COLUMNS. Jessie Crockett Butler and Terry Rankin, Finnigan Corporation, 2215 Grand Avenue Parkway, Austin, TX 78728-3812

Headspace analysis of blood alcohols with dual Flame Ionization Detectors (FIDs) has been performed with packed columns for many years. With the introduction of Megabore capillary columns, the analysis time may be shortened to only four minutes. The primary and confirmational analyses are now achieved in a single injection by incorporating a guard column and "Y" splitter with two dissimilar Megabore capillary columns and dual FIDs. The analysis is performed isothermally, eliminating the equilibration time required in a temperature programmed run. The sample is incubated for five minutes before injection into a standard heated inlet with a Megabore adapter. The headspace autosampler demonstrated in this publication features a heated gas tight syringe and incubator with a mixer to enhance the equilibration of the gases between the gas and liquid phases of the sample. Blood samples were prepared by adding saponin to increase the extraction efficiency. The linearity and sensitivity of the analysis will be shown in water and blood samples. A table of the minimum detection limits on both columns will be presented.

STATIC HEADSPACE ANALYSIS OF RESIDUAL SOLVENTS IN PHARMACEUTICALS USING FID AND TANDEM PID/FID. Jessie Crockett Butler and Terry Rankin, Finnigan Corporation, 2215 Grand Avenue Parkway, Austin, TX 78728-3812

The analysis of residual organic solvents in pharmaceuticals is performed by static headspace with a Flame Ionization Detector (FID). Solvents such as benzene and methylene chloride are easily separated on most Megabore capillary columns. By incorporating a Tandem Photoionization Detector and FID (PID/FID), both the primary and confirmational analyses are performed simultaneously with a single injection. The author will show the analysis of residual solvents using the Tandem PID/FID and a static headspace autosampler. The PID provides the enhanced sensitivity and specificity for the more toxic solvents, like benzene. The headspace autosampler features a heated gas tight syringe and incubator with a mixer to enhance the equilibration of the gases between the gas and liquid phases in the vial. The powder sample is dissolved in water and incubated before injection into a standard heated inlet with a Megabore adapter. The linearity and sensitivity of the analysis will be shown in various matrices. A table of the minimum detection limits on both columns will be presented.


Developing HPLC methods for basic drugs or mixtures of basic, acidic, and neutral drugs requires selecting a column with good silica and bonded phase properties. Ultra-pure, fully hydroxylated silicas are recommended to improve peak shapes for basic compounds. Although C18 bonded phases are the most popular, consideration should be given to other bonded phases, both aliphatic and non-aliphatic, especially with respect to the mobile phase conditions. Optimizing selectivity, column lifetime and method reproducibility will be discussed in relation to mobile phase pH and bonded phase. Selecting the best bonded phase includes evaluating chain length, bonded phase stability, and column endcapping. Choosing the best mobile phase includes evaluating the effects of organic modifier, buffer strength, pH, and other mobile phase modifiers on selectivity and peak shape.
CHOOSING THE OPTIMUM HPLC COLUMN CONFIGURATION FOR PHARMACEUTICAL ANALYSIS. Patrick W. Coleman, Maureen J. Joseph, and Marilyn A Stadalius, MAC-MOD Analytical, 127 Commons Court, Chadds Ford, PA 19317.

HPLC columns are manufactured in a variety of lengths and internal diameters, and are packed with particles of various sizes, pore diameters and bonded phases. Since there is no "universal" column dimension or bonded phase, chromatographers often make unnecessary compromises in method development projects and are left with methods that are more costly and less robust than desired. The discussion will focus on how current technology can be used to develop both new methods and to update existing methodology to be more efficient with respect to time and solvent savings. Selection of the appropriate column configuration based on sample characteristics will be discussed. Discussion will also center on the use of proper pore size, optimum particle size and the benefits of short chain bonded phases. The relative benefits of each column configuration along with possible problems will be discussed.

WHEN ALL ELSE FAILS-SPECIAL SEPARATION TECHNIQUES. Maureen J. Joseph and Marilyn A. Stadalius, MAC-MOD Analytical, 127 Commons Court, Chadds Ford, PA 19317.

The techniques of gradient elution, ion-pair chromatography and normal phase chromatography will be discussed. Although gradient elution is optional in most pharmaceutical analysis, it is required where high molecular weight samples such as peptides and proteins are being analyzed. Gradient theory will be reviewed along with the appropriate parameters to change when optimizing a gradient separation with regard to resolution and analysis time. For samples not retained or poorly resolved on reversed phase chromatography, normal phase or ion-pair chromatography is recommended. These techniques will be discussed along with ways of improving method robustness and reproducibility.

CHARACTERIZATION OF SEVERAL NEW SUBSTITUTED CINNAMIC ACIDS AS MATRICES FOR MALDI. Tinhua Feng and Robert S. Brown, Department of Chemistry and Biochemistry, Utah State University, Logan, UT 84322-0300.

Substituted cinnamic acids are one of the most important classes of matrices currently employed in MALDI for protein and peptide characterization. In earlier studies utilizing a limited number of commercially available alpha substituted cinnamic acids, it was shown that the extent of higher order charge states observed in the MALDI spectra of proteins correlated well with the expected acidity of the matrix based upon the relative electron withdrawing strength of the alpha substituent. No similar correlation with the extent of matrix adducting was apparent.

In the present studies, several new MALDI matrices with a wider variety of alpha substituents (phenyl, mercapto, hydroxy, cyano, methyl and acetylamino) and aromatic ring substituents have been synthesized by using the Knoevenagel reaction and azalactone synthesis. They have been purified by sublimation and recrystallization. We have undertaken a much more extensive investigation of the role of the alpha substituent on the MALDI process. The performances of these synthesized compounds as MALDI matrices will be discussed with respect to the extent of matrix adducting, the generation of higher order charge states of analytes, and the observed metastable ion fragmentation of analytes.
Society for Applied Spectroscopy

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Please list completed courses (by title) in the chemical sciences. (Attach separate sheet or transcript if more space is needed).

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There are four start dates for membership: 1 January, 1 April, 1 July, and 1 October. We are anxious to begin your membership as soon as possible and will therefore enroll you immediately upon approval of your application by the ACS Admissions Committee. Dues for 1994 are $96.00. Your membership will begin at the nearest quarter and you will be billed accordingly. Those entering 1 October will be billed for the three remaining months of the year plus the full dues for the following year (or 15 months dues) or the new member may pay for the final three months of the current year only. Former members who did not resign will be assessed a $110.00 reinstatement fee. Please send no money now.

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