

## Rocky Mountain Conference on Magnetic Resonance

Volume 37 37th Rocky Mountain Conference on  
Analytical Chemistry

Article 1

July 1995

# 37th Rocky Mountain Conference on Analytical Chemistry

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(1995) "37th Rocky Mountain Conference on Analytical Chemistry," *Rocky Mountain Conference on Magnetic Resonance*: Vol. 37 , Article 1.

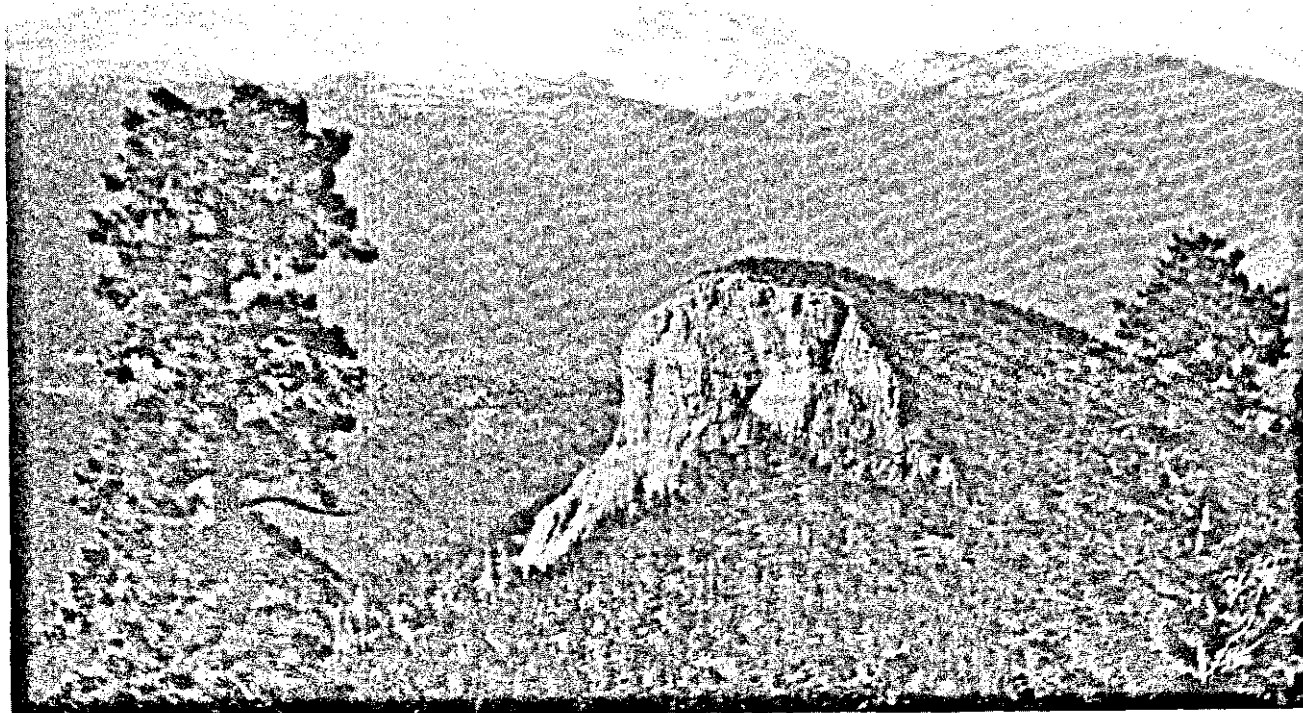
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# 37TH ROCKY MOUNTAIN CONFERENCE ON ANALYTICAL CHEMISTRY



## FINAL PROGRAM AND ABSTRACTS

**JULY 23-27, 1995**

**HYATT REGENCY DENVER  
1750 WELTON STREET  
DENVER, COLORADO**

SPONSORED BY:

ROCKY MOUNTAIN SECTION  
SOCIETY FOR APPLIED SPECTROSCOPY  
&  
COLORADO SECTION  
AMERICAN CHEMICAL SOCIETY

## TABLE OF CONTENTS

Conference Organizers.....	2
Symposia Organizers.....	3
Registration and Event Information.....	5
Exhibitor List.....	8
Hotel and Visitor Information.....	9
Employment Clearing House and Professional Memberships.....	9
Short Courses.....	10
Vendor Workshops.....	12
Symposia Schedule:	
Atomic Spectroscopy.....	17
Chromatography.....	18
Compost (Biogeochemistry of).....	19
Electrochemistry.....	20
Environmental Chemistry.....	22
EPR.....	25
FTIR/NIR/RAMAN Spectroscopy.....	37
General Posters.....	37
ICP-MS.....	39
Laboratory Safety.....	41
Luminescence.....	42
Mass Spectrometry.....	44
NMR.....	47
Pharmaceutical Analysis.....	59
Quality Assurance.....	60
Downtown Denver Street Map.....	Inside back cover

Abstracts start after page 61. They are listed in numerical order and correspond to number listed with titles and authors in the Symposia Schedule section.

Applications for membership in the American Chemical Society and the Society for Applied Spectroscopy can be found in the back of this program.

## VENDOR WORKSHOP SCHEDULE

	Sun. 7/23/95		Weds. 7/26/95		Thurs. 7/27/95	
	AM	PM	AM	PM	AM	PM
Bruker	x	x				
Varian	x	x				
Waters				x		
Jones Chromatography			x	x		
Western Analytical Products J&W Scientific				x		
CEM					x	
Thermo Jarrell Ash					x	x

O C Z Z O

Room	Sunday 6/23/95		Monday 6/24/95		Tuesday 6/25/95		Wednesday 6/26/95		Thursday 6/27/95	
	am	pm	am	pm	am	pm	am	pm	am	pm
Grand Ballroom			EPR	EPR	EPR	EPR	EPR	EPR	EPR	
Moulin Rouge			NMR	NMR	NMR	NMR	NMR	NMR	NMR	
Far East			Atomic Spec.	Atomic Spec.	Environ. Chem.	Environ. Chem.	Environ. Chem.	Western-J&W Sci.		
Royal			Lumin.	Lumin.	Electro. Chem.	Electro. Chem.	Quality Assurance	Waters	CEM	
Gold		Speaker Prep.	Speaker Prep.	Speaker Prep.	Speaker Prep.	Speaker Prep.	Speaker Prep.	Speaker Prep.	Speaker Prep.	
Florentine	Bruker	Bruker	Compost	Compost	Pharm.	Pharm.	Jones Chrom.	Jones Chrom.		
Parisienne		Varian	Mass Spec.	Mass Spec.	Mass Spec.	Mass Spec.	Lab Safety			
Vista			FTIR		ICP/MS	ICP/MS	Chrom.			
Board Room			MS Posters	MS Posters	MS Posters	MS Posters	MS Posters	MS Posters		
Imperial Ballroom			Exhibits	Exhibits	Exhibits	Exhibits	Exhibits			
Imperial Foyer			General Posters	General Posters	General Posters	General Posters	General Posters	General Posters		
Conference Center Room 210									Thermo Jarrell Ash	Thermo Jarrell Ash

O O S O C Z O E V O O O V G Z O E O g i •

## **Organizers of the 37th Rocky Mountain Conference**

**Conference Chair - Jeffery L. Cornell**, Quanterra Environmental Services, Inc.  
4955 Yarrow Street, Arvada, CO 80002; (303) 421-1025, ext. 206; fax (303) 431-7171

**Exhibits and Vendor Workshops - Sue Zeller**, Huffman Laboratories, Inc.  
4630 Indiana Street, Golden, CO 80403; (303) 278-4455; fax (303) 278-7012

**Registration Chair - Barbara Coles**, Hauser Chemical Research, Inc.  
5555 Airport Blvd., Boulder, CO 80301; (303) 443-4662; fax (303) 441-5803

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

**Treasurer - Glenda Brown**, U. S. Geological Survey  
MS407, 5293 Ward Road, Arvada, CO 80002; (303) 467-8122; fax (303) 431-8331

**Mailing Database - Carol Gies**, Rocky Flats  
General Lab Building 881, P.O. Box 464, Golden, CO 80402-0464; (303) 966-7380; fax (303) 966-4365

**Audio Visual Chair - Ted Struzeski**, U. S. Geological Survey  
MS407, 5293 Ward Road, Arvada, CO 80002; (303) 467-8147; fax (303) 431-8331

**Social Chair - Chuck Bates**, Geneva Pharmaceuticals, Inc.  
2555 West Midway Blvd., Box 446, Broomfield, CO 80038-0446; (303) 438-4469;  
fax (303) 466-7935

## **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**

**Denise Kent**  
11671 Baca Road  
Conifer, CO 80433  
1-800-252-4752 ext. 6987

### **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  
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### **ELECTROCHEMISTRY**

**C. Michael Elliott**  
Colorado State University  
Department of Chemistry  
Ft. Collins, CO 80523  
(303)491-5204 fax:(303)491-1801

### **ENVIRONMENTAL CHEMISTRY**

**Maria Tikkanen**  
Assoc. of California Water Agencies  
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### **EPR**

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**Sandra Eaton**  
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Denver, CO 80208  
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### **FT1R / NIR / RAMAN SPECTROSCOPY**

**Abdul Chughtai**  
University of Denver  
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(303)871-4404 fax:(303)871-2932

### **GENERAL POSTERS**

**Mary Cast**  
National Water Quality Lab  
U.S.G.S. 5293 Ward Road  
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(303)467-8135 fax:(303)431-8331

### **ICP/MS**

**Howard Taylor**  
3215 Marine Street  
Boulder, CO 80303  
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## **SYMPOSIA ORGANIZERS**

### **LABORATORY SAFETY**

**Victoria Swancutt**  
Geneva Pharmaceuticals, Inc.  
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(303)438-4469 fax:(303)466-7935

### **LUMINESCENCE**

**DeLyle Eastwood**  
Lockheed Environmental Systems  
and Technologies Company  
980 Kelly Johnson Drive  
Las Vegas, NV 89119  
(702)897-3287 fax:(702)897-6641

**Robert Hurtubise**  
University of Wyoming  
Department of Chemistry  
Box 3838 University Station  
Laramie, WY 82071  
(307) 766-6241 fax: (307) 766-2807

### **MASS SPECTROMETRY**

**Joseph Zirrolli**  
National Jewish Center  
Department of Pediatrics  
K923  
Denver, CO 80206  
(303)398-1853 fax:(303)398-1694

### **NMR**

**Alexander J. Vega**  
Dupont Central Research and  
Development  
P. O. Box 80356  
Wilmington, Delaware 19880-0356  
(302)695-2404 fax:(302)695-1664

### **PHARMACEUTICAL ANALYSIS**

**Mike Cutrera**  
Integra Life Sciences Corp.  
105 Morgan Lane  
Plainsboro, NJ 08536  
(609) 683-0900 fax (609) 799-3297

**Robert Lantz**  
Rocky Mountain Instrumental Labs  
456 South Link Lane  
Ft. Collins, CO 80524  
(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**

**William Shampine**  
U.S. Geological Survey  
P.O. Box 25046 MS414  
Denver, CO 80225  
(303) 236-4932 fax: (303) 236-4937

### **RADIOCHEMISTRY**

**Canceled this year due to concurrent  
annual meeting of the  
Health Physics Society in Boston.  
For more info, contact Ann Mullin  
(303) 467-8235 fax: (303) 467-8240**

### **ROBOTICS (canceled)**

**Jerry Hoffman**  
U.S. Geological Survey/NWQL  
5293 Ward Road  
Arvada, CO 80002  
(303) 467-8082 fax: (303) 467-8240

## CONFERENCE LOCATION

Technical sessions and the exhibition for the 37th Rocky Mountain Conference on Analytical Chemistry will be held in the Hyatt Regency Denver, 1750 Welton Street, Denver, Colorado 80202.

## REGISTRATION

Admission to all technical sessions, vendor sponsored users groups and the exhibition is by the name badge for the 37th Rocky Mountain Conference. Pre-registration, using the form at the back of this program, is encouraged. The deadline for the receipt of the pre-registration form and full remittance of the conference fees is July 7, 1995. Conference fees are payable by check (denominated in \$US, only) made payable to the Rocky Mountain Conference. Visa and Mastercard are accepted, as well.

## REGISTRATION FEES -1995

	Preregistration (recvd. by 7/7/95)	<u>On Site</u>
Regular (entire conference and exhibitions)	\$75.00	\$90.00
One Day (specify day: M, T, W, R) includes exhibitions	\$40.00	\$50.00
Retired / Unemployed	\$25.00	\$35.00
Full Time Student - Regular (student ID required)	\$25.00	\$35.00
Student - One Day (specify day: M, T, W, R)	\$10.00	\$15.00
Additional Vendor (beyond 3)	\$45.00	\$45.00
Exhibition Only (non-vendor)	\$15.00	\$15.00
Black Hawk Casino Trip: to be the evening of July 25 includes transportation, dinner and more!	\$8.00	\$8.00

## REFUNDS

Requests for refunds of conference fees must be received by July 10, 1995.



### **REGISTRATION TIMES**

On-site registration for the 37th Rocky Mountain Conference will be held in the Imperial Ballroom Foyer of the Hyatt Regency Denver during the following hours:

Sunday, July 23	5:00 p.m.	9:00 p.m.
Monday, July 24	7:30 a.m.	3:30 p.m.
Tuesday, July 25	7:30 a.m.	3:30 p.m.
Wednesday, July 26	7:30 a.m.	3:30 p.m.
Thursday, July 27	8:00 a.m.	2:30 p.m.

### **SPEAKER PREPARATION ROOM**

The conference will be providing a speaker preparation room from Sunday noon, July 23 through Thursday noon, July 27. The Gold Room will have an overhead projector and a slide projector available for authors to prepare for their talks. Please be considerate of others when using the room as it will be available on a first come, first served basis.

### **SCHEDULE OF EVENTS**

Sunday, July 23	Registration Mixer	5:00 p.m. - 9:00 p.m.
Monday, July 24	Exhibition	10:00 a.m. - 5:00 p.m.
Monday, July 24	General Posters	3:00 p.m. - 5:00 p.m.
Monday, July 24	Conference Reception	5:00 p.m. - 7:30 p.m.
Tuesday, July 25	Exhibition	10:00 a.m. - 5:00 p.m.
Tuesday, July 25	Black Hawk Casino Trip	6:00 p.m. - 11:00 p.m.
Wednesday, July 26	Exhibition	10:00 a.m. - 12:00 p.m.
Wednesday, July 26	Social Hour	5:00 p.m. - 7:00 p.m.

## **SOCIAL PROGRAM AT THE HYATT REGENCY DENVER**

### **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 5:00 - 9:00 p.m. Plan to meet other conference attendees and beat the Monday rush to pick up your conference badge and final program.

### **GENERAL POSTER SESSION AND CONTEST**

This will be the second year that the conference will sponsor a poster contest to acknowledge outstanding submissions to the General Poster Symposium. Since these posters cover a wide range of subjects, they will be judged by attendees on clarity of written presentation, display of information (including use of graphics and illustrations), and visual appeal. Come participate in the voting on Monday between 3 and 5 p.m. in the Imperial Ballroom Foyer. Prizes will be awarded to the top three presenters.

### **CONFERENCE RECEPTION**

On Monday evening, July 24, from 5:00 to 7:30 p.m., all attendees are cordially invited to join us for a 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*.

### **BLACK HAWK / CENTRAL CITY CASINO TRIP**

Head for the hills on Tuesday night! Transportation will be provided from the Hyatt Regency to the historic mining town of Black Hawk where you will enjoy dinner and experience the night life in these revitalized mountain towns. Your \$8.00 includes: transportation each way, a *prime rib* buffet and two drinks. In addition, get \$20.00 in quarters or tokens when you purchase \$15.00 at the casino. The bus will leave the hotel at approximately 6 pm and return by midnight.

### **WEDNESDAY EVENING SOCIAL HOUR**

Join friends and colleagues for a drink before dinner at the cash bar in the Imperial Ballroom Foyer from 5 to 7 p.m.

## 1995 EXHIBITORS

The Rocky Mountain Conference exhibition provides an opportunity to see and discuss the latest in analytical instrumentation, supplies and services. Vender representatives will be on hand to display and demonstrate their latest products. Stop by the exhibit area to see what's new and register to win a bottle of wine from your favorite vender.

Allen Scientific Glass, Inc.  
American Chemical Society, Colorado Section  
APD Cryogenics, Inc.  
Bruker Instruments, Inc.  
CEM Corporation  
Continental Water Systems, Inc.  
Directed Energy, Inc.  
Doty Scientific  
Finnegan MAT  
Fisons Instruments  
Hewlett Packard Company  
High-Purity Standards  
JEOL USA, Inc.  
Jones Chromatography USA, Inc.  
Leeman Labs, Inc.  
Micro-Now Instrument Co., Inc.  
Otsuka Electronics USA, Inc.  
Oxford Instruments, Inc.  
Perkin Elmer Corporation  
Rainin Instrument Company, Inc.  
Resonance Technologies, Inc.  
Rosemount Analytical  
Society of Applied Spectroscopy, Rocky Mountain Section  
Star Scientific, Inc.  
Supelco, Inc.  
Teledyne Electronic Technologies  
Thermo Jarrell Ash Corporation  
Update Instrument, Inc.  
Varian Associates, Inc.  
Waters  
Webster Associates, Inc.  
Western Analytical Products Company, Inc.  
Wilmad Glass

**Exhibit Hours:**

Monday, July 24	10:00 a.m. to 5:00 p.m. *
Tuesday, July 25	10:00 a.m. to 5:00 p.m.
Wednesday, July 26	10:00 a.m. to 12:00 noon

**The Conference Reception will be held in the exhibit area from 5:00 p.m. until 7:30 p.m. on Monday night.**

## **HOTEL ACCOMMODATIONS**

Hotel rooms at the Hyatt Regency Denver, 1750 Welton Street, Denver, Colorado 80202, (303) 295-1234, are available at the **special discounted conference rate of \$95 per night (single or double), plus applicable fa\***, Please identify yourself as a Rocky Mountain Conference attendant when making reservations to receive this discounted rate. Please see the Hyatt hotel reservation form in the back of this program for more information. This form must be returned directly to the hotel. **The conference location and all associated social functions for the conference will be held at the Hyatt Regency Denver.**

## **VISITOR INFORMATION**

Contact the Guest Services in the main lobby of the Hyatt Regency Denver for suggestions on the large number of activities that are enjoyable in Denver and the surrounding area. For information about statewide attractions contact the Colorado Tourism Board, 1625 Broadway, Suite 1700, Denver, CO 80202, (303) 592-5510.

## **MESSAGE CENTER**

Incoming telephone messages for conferees will be posted 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.

## **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.

## **PROFESSIONAL MEMBERSHIPS AND EMPLOYMENT CLEARING HOUSE**

Inquiries about membership to the American Chemical Society and the Society for Applied Spectroscopy can be addressed to the ACS/SAS booth in the exhibition hall.

The Employment Committee of the Colorado Section of the American Chemical Society will conduct an employment clearing house at a booth in the exhibition hall. Resumes will be accepted during the meeting for review by perspective employers.

## **SHORT COURSES**

(Sponsored by the Colorado Section of the ACS)  
to be held in conjunction with the 37th Rocky Mountain Conference

### **Basic Principles of Gas Chromatography/Mass Spectrometry and Interpretation of Organic Mass Spectra**

**July 26-28, 1995 Fee:** \$400 member; \$450 non-member **Faculty:** Dr. Joe Zirrolli

This course will describe the principles of gas chromatography/mass spectrometry and apply them to the identification of organic compounds. Gas chromatography (sample preparation and derivatization, injectors, column selection), ionization process (positive, negative, chemical, electronic modes), mass analysis and detection will be discussed with emphasis on molecular ion analysis and understanding simple fragmentation processes. The course will develop an approach to the determination of elemental composition and diagnostic fragmentation patterns, and the student will become familiar with mass spectra of pesticides and pollutants. The interpretation approach is based upon, and uses as a reference, the Interpretation of Organic Mass Spectra, Fourth Edition by F.W. McLafferty, and F. Turecek, University Science Books, 1993.

### **Quality Assurance Practices for the Environmental Laboratory**

**July 27-28, 1995 Fee:** \$400 member; \$450 non-member **Faculty:** Steve Callio

This course is designed for laboratory analysts, engineers, project managers and others who require an introduction to quality assurance and quality control practices as applied to environmental measurements. The course will begin with a brief discussion of some of the basic statistical concepts (i.e. mean, standard deviation, confidence intervals, detection limits, etc.). This is followed by in-depth discussions of the principles and practices of important quality control operations. These range from the preparation of duplicate and spiked samples use internal standards and standard reference materials to instrument calibration, the role of the QA manager, training requirements and record documentation. The emphasis of this class is on real applications and problem solving.

### **Laboratory Waste Management**

**July 27-28, 1995 Fee:** \$550 member; \$600 non-member **Faculty:** Cindy Salisbury  
& Russell Phifer

If you are a lab manager, researcher or technician responsible for management of laboratory waste, you should attend this course. Participants will learn which environmental regulations apply to management of your laboratory's waste and how to classify laboratory waste in accordance with RCRA regulations. You will learn how to manage discarded samples, standards and QA solutions, and the components necessary for an effective laboratory waste management program. You will receive up-to-the-minute regulatory information and citations. You will learn how to implement a comprehensive environmental compliance program at your laboratory.

**For short Course Registration, no later than July 14, 1995 contact:**

Gary Clapp, PhD  
Hauser Laboratories  
5555 Airport Blvd.  
Boulder, CO 890301  
Tel: (303) 443-4662; ext. 1107  
Fax: (303) 443-5803

Richard Graham, PhD  
U.S. EPA-Region VIII  
999 18th Street, Ste. 500 (ART-RTI)  
Denver, CO 80202  
Tel: (303) 391-6938  
FAX: (303) 293-0988

## SHORT COURSE REGISTRATION

Courses sponsored by the Colorado Section of the American Chemical Society  
at the 37th Rocky Mountain Conference.  
Denver, Colorado

	Member (ACS or SAS)	Non-Member
<b>Basic Principles of Mass Spectrometry &amp; Interpretation of Organic Mass Spectra</b>		
July 26-28, 1995	[ ] \$400	[ ] \$450
<b>Laboratory Waste Management</b>		
July 27-28, 1995	[ ] \$550	[ ] \$600
<b>Quality Assurance Practices for the Environmental Laboratory</b>		
July 27-28, 1995	[ ] \$400	[ ] \$450

Member: ACS [ ] SAS [ ] Member\*

Name: \_\_\_\_\_

Organization: \_\_\_\_\_

Address:

City, State Zip:

Phone:

Fax:

Pre-registration is encouraged as class space is limited.

**Refund Policy:** Full refunds will be made if requests are received on or before July 14, 1995. Make checks payable to **Colorado Section ACS** and send payment with this form by July 14, 1995 to:

Gary Clapp, PhD  
ACS Short Course Registration  
c/o Hauser Laboratories  
5555 Airport Blvd.  
Boulder, CO 80301  
Tel: (303) 443-4662; ext. 1107  
FAX: (303) 441-5803

## **VENDORWORKSHOPS**

*Bruker Instruments, Inc.*

### **Third Annual Rocky Mountain Conference Workshop on Solid State NMR**

Bruker Instruments will host a workshop dedicated to solid state NMR on Sunday, July 23, 1995 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 contact Doug Burum at (508) 667-9580 ext. 120.

*Marian Associates*

### **Varian NMR Instruments 4th Conference for Solids System Owners and Users**

Varian Solids Systems' Owners and Users are invited to a half day conference with Varian Application Scientists, R&D Engineers, and Product Managers on Sunday, July 23, 1995. There will be lectures on emerging applications and specific topics contributed by users. This is an excellent opportunity for long-term Varian customers and newcomers to gather for an afternoon of stimulating scientific interaction which will then adjourn for an evening of dining as guests of Varian.

For registration material, please call Ms. Bee Sehrt in Palo Alto, CA at (415) 424-4526. Please indicate if you wish to make a presentation. For other information regarding this conference, please contact Iain Green at (708) 945-3757.

## VENDOR WORKSHOPS

*Otsuka Electronics USA Inc. - Chemagnetics® Instruments*  
**6th Annual Solid State NMR Spectroscopy Workshop**

**Dates:** Friday, July 28th and Saturday, July 29th

**Location:** Otsuka Electronics  
2607 Midpoint Dr.  
Ft. Collins, CO 80525

### ***Friday, July 28 Solid State NMR Techniques and Applications***

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

### ***Saturday, July 29 Hands-on "New Techniques" Workshop***

Spinsight Software and new hardware will be discussed and demonstrated on the CMX Spectrometers. Small groups of attendees will work with several experiments and are encouraged to bring several of their own samples to run.

For further information contact: Dr. JimFrye      Tel: (970)484-0428  
Fax: (970) 484-0487  
E-mail: [jimf@otsuka.com](mailto:jimf@otsuka.com)

**To register:** Complete the form below and return it to the following address prior to June 30th:

Pam Jarrett  
Otsuka Electronics USA Inc.  
2607 Midpoint Dr.  
Ft. Collins, CO 80525

There is no fee to attend the workshops, however local accommodations and meals are at the attendees expense.

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

**Name:**

**Phone:**

**P a x :**

**Organization:**

**Address:**



## VENDORWORKSHOPS

### *Thermo Jarrell Ash Corporation* ThermoSPEC User's Seminar

Thermo Jarrell Ash will be holding its annual user's seminar on Thursday, July 27, 1995. The format will be two half-day seminars for interested AA and ICAP users. Both seminars will provide new and exciting updates. Come meet the other users. The seminar is free and will include lunch. See you there!

To make reservations, please contact Loretta Beauvais at (303) 972-9814.

### *Jones Chromatography* Solids State Extract Method Development

Jones Chromatography is pleased to announce a Vendor Workshop entitled "Solid Phase Extraction Method Development" at the Rocky Mountain Conference on Wednesday, July 26, 1995. This all-day course will consist of a three hour morning session and a three hour afternoon session. Complimentary break refreshments will be provided.

This workshop will give attendees a broad overview of SPE and demonstrate specific examples of how SPE can be utilized in various laboratory applications. The benefits of sample preparation and SPE will also be discussed. Seminar topics include the following:

- **A Review of the Principles of SPE**
- **Chemical Foundations for the Effective Use of Bonded Silica Sorbents**
- **Optimizing SPE Procedures for the Extraction of Ionizable Species from Aqueous Matrices**
- **Recent Developments in the Extraction of Basic Drugs from Biological Fluids**
- **Advances in Application of SPE to Waste water**
- **Sample Preparation Open Forum**

The open forum will present an opportunity for seminar attendees to raise questions about individual sample preparation problems and to obtain advice on troubleshooting of attendees' current SPE procedures can be discussed. Attendees are encouraged to bring structural and other analytical information concerning their analytes of interest. For additional information or to register for the seminar, please contact Jennifer Minear of Jones Chromatography at (303) 989-9200.

## VENDOR WORKSHOPS

*Waters Chromatography*

### **A WORKSHOP TO EXPLORE WHY CIA IS USEFUL**

Water CAPILLARY ION ANALYSIS - Why are those guys analyzing ions **by** capillary electrophoresis rather than ion chromatography?

- \* **Because it's faster.**
- \* **Because it's simpler**
- \* **Because it generates 250,000-500,000 theoretical plates rather than the 5000-10,000 plates that IC does and peak capacity (36 peaks in 89 sec) is phenomenal.**
- \* **Because it's matrix independent.**

This seminar will be held Wednesday afternoon, July 26, 1995. To make reservations, contact Denise Kent at (800) 252-4752 ext. 6987.

*CEM Corporation*

### **Microwave Digestion and It's Application for EPA Methods, Industrial Hygiene and Difficult Organic Samples**

Preparation of a sample prior to elemental analysis is typically the time consuming factor in analyzing samples. Laboratories spend many hours getting their samples prepared so that they can be analyzed by today's sophisticated instruments such as graphite furnace, atomic absorption or inductively coupled plasma mass spectrometry. Industry today is placing more emphasis on ways to reduce the time consuming steps of sample preparation with the use of microwave technology.

This workshop is designed for the inorganic chemist who wants to improve their acid digestion process. It will focus on the use of CEM Corporation's closed vessel Microwave Digestion Systems for the preparation of:

- \* **Water, soil and sediment samples using EPA methods 3015 and 3051.**
- s **A difficult organic with the use of a 600 psi heavy duty vessel.**
- S **Industrial Hygiene samples (paint chips, wipes, air filters) for Pb analysis.**

The workshop will be held on July 27, 1995 form 8:30 a.m. to 12:00 p.m. For more information, contact Jay Leazer at 1-800-726-3331.

## **VENDOR WORKSHOPS**

*Western Analytical Products Co., Inc. - J. W. Scientific*

### **A QUICK OVERVIEW OF PRACTICALITIES IN GAS CHROMATOGRAPHY**

Dr. Walter Jennings will speak on considerations of basic GC principles and interrelationships; the relationship of column selection to elementary GC theory; application of GC theory to practical laboratory problems; column care and maintenance; prolonging column life; newer practical development in columns and accessories.

Dr. Walter Jennings is an Emeritus Professor of the University of California, having served thirty-five years on the Davis Campus. Recipient of several awards and honors, Professor Jennings frequently serves as a national and international Plenary Lecturer and/or Keynote Speaker. He is a Past Chair of the American Chemical Society's Subdivision of Flavor Chemistry and the Subdivision of Chromatography and Separations Chemistry and has always been an active supporter of chromatography discussion groups. Since the early 1970's, he has each year instructed some thirty extra curricular courses in gas chromatography, from Caracas to Osaka, from Munich to Sydney... points all over the world. It has been estimated that over 30,000 chromatographers from all walks of life have attended these courses to which Professor Jennings, now fully retired from the University, but still functioning as a consultant, intends to remain heavily committed.

This workshop will be held on Wednesday, July 26 in the afternoon.

## **SYMPOSIUM ON ATOMTC SPECTROSCOPY**

Organized by Gary Rayson

Monday, July 24, 1995

8:30 Opening Remarks

Keynote Speaker

8:40 *New Sources for Atomic Mass Spectrometry.* Gary M. Hiefije, Thomas W. Burgoyne, Giangqiang Li, Patrick P. Mahoney, and Steven J. Ray, Department of Chemistry, Indiana University, Bloomington, IN 47405 (1)

9:20 *High Resolution ICP-MS for Accurate Determination of Elemental and Isotopic Composition of Trace and Ultratrace Elements.* M. J. Allen, C. B. Douthitt, M. P. Schmidt, Finnigan MAT, 355 River Oaks Parkway, San Jose, CA 95134 (2)

9:40 *The Use of ICP-AES and ICP-MS in One Instrument: POEMS (Plasma Optical Emission and Mass Spectrometer).* John Schmelzel, A. van der Hoeff, Ke Hu, G. Knuselman, and J. Sotera, Thermo Jarrell Ash, Franklin, MA 02038 (3)

10:00 Break

10:30 *The Use of Dual Axial and Radial View ICP-OES Spectrometer for the Analysis of Environmental Samples.* Randy L. Hergenreder and Mark A. Paustian, Perkin-Elmer Corp., Norwalk, CT 06859 (4)

10:50 *Optimization of Operating Conditions for an Axially-viewed ICP Torch.* Geoffrey N. Coleman, G. H. Gower, C. J. Harris, M. O'Boyle, and R. Starek, Fisons Instruments Elemental Analysis, Beverly, MA 01915 (5)

11:10 *Inductively Coupled Argon Plasma Axial Viewing Absorption with Electrothermal Vaporization Sample Introduction.* Gary D. Rayson and C. A. Hensman, Department of Chemistry and Biochemistry, New Mexico State University, Las Cruces, NM. (6)

11:30 Lunch

Invited Speaker

1:30 *Radio Frequency Powered Glow Discharges: Whose Problems Can They Solve.* R. Kenneth Marcus, Department of Chemistry, Howard L. Hunter Chemical Laboratories, Clemson University, Clemson, SC 29634-1905 (7)

- 2:10 ***Elemental Analysis of Soil Samples by Laser Induced Breakdown Spectroscopy.*** Terry L. Thiem. S. Dementiev, H. Melville, J. H. S. Melville, Technical Assistance International, El Paso, TX; A. F. Kotyuk, and M. Ulanovskiy, MelAOK, Inc., Moscow, Russia.(8)
- 2:30 Break
- 3:00 ***Improved Thermal Stability from Composite Materials Enhances Reliability of Sequential ICP Measurements.*** Geoffrey N. Coleman. G. H. Gower, C. J. Harris, Fisons Instruments Elemental Analysis, Beverly, MA. (9)
- 3:20 ***Depth Resolved Analysis of Metallic and Insulating Layers by RF Glow Discharge Atomic Emission Spectrometry.*** Mark Parker and R. Kenneth Marcus. Department of Chemistry, Howard L. Hunter Chemical Laboratories, Clemson University, Clemson, SC 29634-1905.(10)
- 3:40 ***Local Thermodynamic Equilibrium Simulation of Chemical Processes Within a Graphite Furnace Atomizer.*** Gary D. Rayson and Kowit Saeteung, Department of Chemistry and Biochemistry, New Mexico State University, Las Cruces, NM. (11)
- 4:00 ***Reducing Organic Solvents in Wear Metals in Oil Analysis Using Emulsions and Inductively Coupled Plasma Spectroscopy.*** Terry L. Thiem and Jeff Watson, Department of Chemistry, HQ USAFA/DFC, USAF Academy, CO. (12)

## **SYMPOSIUM ON CHROMATOGRAPHY**

Organized by Denise Kent

Wednesday, July 26, 1995

- 8:25 Opening Remarks.
- 8:30 ***Liquid Chromatographic Separation and Characterization of Inorganic Colloids.*** J.P. Wilcoxon. S. Craft, Sandia National Laboratories, Mail Stop 1421, P.O. Box 5800, Albuquerque, NM, 87185-142L (13)
- 9:00 ***Capillary Ion Analysis of Anions, Organic Acids and Cations in Circuit Board Extracts.*** Stuart Oehrle. Waters Corporation, 34 Maple Street, Milford, MA, 01757.(14)

- 9:30 ***Solving Common HPLC Detector Problems with the Evaporative Light Scattering Detector.*** Tnga Henderson. Donna Young, Alltech Assoc. Inc., 2051 Waukegan Road, Deerfield, Illinois, 60015. (15)
- 10:00 ***Determination of Drug-Protein Interactions by HPLC,*** Philip B. Graham. Metasyn Inc., 71 Rogers St., Cambridge, MA 02142. (16)

## **SYMPOSIUM ON THE BIOGEOCHEMISTRY OF COMPOST**

Organized by Cal Kuska and Robert L. Wershaw

Monday, July 24, 1995

- 8:25 Opening Remarks
- 8:30 ***Overview of Composting Problems.*** G. B. Willson. George B. Willson Associates, Loveland, CO. (17)
- 9:00 ***Placement and Seasonal Effects on Performance of Degradable Plastic Bags in Yard Waste Compost.*** P. E. Aeschleman and M. A. Cole. Department of Agronomy, University of Illinois, Urbana, IL. (18)
- 9:30 ***How to Investigate and Evaluate Composting Systems.*** Antje Rieger and Werner Bidlingmaier, University GH Essen, Essen, Germany. (19)
- 10:00 BREAK
- 10:30 ***Less Well-Known Fundamentals of the Composting Process.*** G. B. Willson. George B. Willson Associates, Loveland, CO. (20)
- 11:00 ***Comparison of Biodegradability and Microbial Activity During Composting of Solid Wastes.*** C. E. Atkinson, D. D. Jones, and J. J. Gauthier, Department of Biology, University of Alabama at Birmingham, Birmingham, AL. (21)
- 11:30 LUNCH

- 1:00 *A postulated Reaction Sequence for Deriving Aquatic Humic Structures From Lignin and Lipid Structures.* J. A. Leenheer and R.L. Wershaw, U.S. Geological Survey, Arvada, CO. (22)
- 1:30 *Application of Nuclear Magnetic Resonance Spectroscopy to Elucidating the Composting Process.* R. L. Wershaw and J. A. Leenheer, U.S. Geological Survey, Arvada, CO. (23)
- 2:00 *Analysis of Compost—Results from a Parallel Interlaboratory Test with 95 Laboratories.* Andreas Maile and Werner Bidlingmaier, Universitat GH Essen, Essen, Germany. (24)
- 2:30 BREAK
- 3:00 *Natural Organic Matter (NOM) and Compost Bulletin Board on the Internet.* Discussion group open to all participants.

## SYMPOSIUM ON ELECTROCHEMISTRY

Organized by C. Michael Elliott

Tuesday, July 25, 1995

- 8:55 Opening Remarks
- 9:00 *Synthesis and Electrochemical Oxidation of This Film  $La_2CuO_4$ .* William J. Donahue, Bruce A. Parkinson, Michael K. Crawford, Jay A. Switzer. (25)
- 9:25 *Preparation and Photoelectrochemical Characterization of II-IV-V<sub>2</sub> Calcopyrite Semiconductors.* Y. C. Wen, Bruce A. Parkinson. (26)
- 9:50 *Studies of Electrochemical Deposition of Metal Adlayers on Diamond Thin Film Electrodes.* Greg M. Swain, Shokoofeh Alehashem, Michael Granger. (27)
- 10:15 BREAK
- 10:30 *Fabrication and Characterization of Gold Nanotubule Arrays.* Kshama B. Jirage, Charles R. Martin. (28)

- 10:55 *Rutheniumtrisbipyridine-type Monomers in Current Rectifying Polymer Films.*  
Daniel Derr, C. Michael Elliott. (29)
- 11:20 *Redox Dependent Interactions of the Metal Sites in Carbon Monoxide Bound Cytochrome c Oxidase Monitored by Infrared and UV/Visible Spectroelectrochemical Methods.* Eric D. Dodson, C. Michael Elliott, W. S. Caughey. (30)
- 11:45 LUNCH
- 1:30 *Electrochemical Studies of Electroactive and Non-electroactive Monolayers: Factors Affecting the Electron Transfer Kinetics and Adsorbate Interactions.*  
James W. Walker, Daniel A. Buttry. (31)
- 1:55 *Anomalous Electrolyte Effect on Electrochemical Kinetics at Nanoelectrode Ensembles.* Vinod P. Menon, Charles R. Martin. (32)
- 2:20 *Mechanistic Studies of Advanced Oxidation Processes on Titanium Dioxide Using Surface Enhanced Raman Spectroscopy.* Karen L. Norrod, Kathy L. Rowlen, Carl A. Koval. (33)
- 2:45 BREAK
- 3:00 *Continuing Investigations of the Changes in Redox Behavior of Conducting Polymers in the Presence of Neutral Organics.* Susan M. Hendrickson, C. Michael Elliott. (34)
- 3:25 *Enzyme Facilitated Transport of Ethanol* Brinda B. Lakshmi, Charles R. Martin. (35)
- 3:50 *Separation of Butadiene Using Copper (I) / Copper (II) Electrochemistry.*  
Takavuki Suzuki, David K. Watts, Carl A. Koval. (36)



## **SYMPOSIUM ON ENVIRONMENTAL CHEMISTRY**

Organized by Maria W. Tikkanen

Tuesday, July 25, 1995

Maria W. Tikkanen, Presiding

8:30 Opening Remarks

8:35 *Use of Statistical Sampling Design and Analysis to Determine Geological Background Concentrations and Threshold Values of Selected Inorganic Constituents in Soil and Groundwater at F. E. Warren Air Force Base, Wyoming.* Robert A. Boyd, Kent D. Becher, Richard Daddow, and Randal K. Lambrecht, U. S. Geological Survey, 2617 E. Lincoln Way, Cheyenne, Wyoming, 82001. (40)

8:55 *Arsenic Detection Limits in Environmental Samples Using a Simultaneous Graphite Furnace AA: Investigation of Parameters that Effect Signal to Noise Ratio.* Randy L. Hergenreder, John C. Latino, and Douglas C. Sears, Perkin-Elmer Corp., 761 Main Ave. M/S 695,079,648, Norwalk, CT 06859. (41)

9:15 *Analysis of Uranium in Environmental Samples by ICP-MS.* William R. Varnon, USX Texas Uranium, George West, Texas 78022 and Rob Henry, Fisons Instruments, P.O. Box 20460, Boulder, CO 80304. (42)

9:35 *Arsenic Speciation in Soil Using High Performance Liquid Chromatography-Inductively Coupled Plasma-Mass Spectrometry (HPLC-ICP-MS).* Dean A. Bass, Judith S. Yaeger, Kathleen J. Parish, Jeffrey S. Crain, James T. Kiely, and Mark Gowdy, Argonne National Laboratory, Argonne, IL 60439-4831; and Greg Mohrman, Rocky Mountain Arsenal, Commerce City, CO 80022-2180. (43)

9:55 *Using Polymeric Microencapsulation Arrays to Concentrate Trace Metal Ions from Dilute Aqueous Solutions.* Veronica M. Cepak, Ranjani Parthasarathy, and Charles R. Martin, Colorado State University, Department of Chemistry, Fort Collins, CO 80523.(44)

10:15 Break

Invited Speaker

- 10:35 ***Trends in USEPA Methodology for the Determination of Trace Elements in Environmental Samples.*** Theodore D. Martin and John T. Creed, U. S. Environmental Protection Agency, National Exposure Research Laboratory, Aquatic Research Division, 26 W. Martin Luther King Dr., Cincinnati, OH 45268. (45)
- 11:15 ***Method Evaluation with Round Robin Techniques Using Arsenic Determination by SPE-AA, HG-AA and HG-ICPMS.*** Andrew Eaton. Montgomery Laboratories, 555 E. Walnut, Pasadena, CA 91101, and Maria Tikkanen, Association of California Water Agencies, 910 K Street, Suite 250, Sacramento, CA 95814. (46)
- 11:35 ***Improving Drinking Water Analysis Productivity by EPA Method 200.8.*** Rob Henry. Chris Tye, Paul Sigsworth, Tom Rettberg, Fisons Instruments, P.O. Box 20460, Boulder, CO 20460-3460. (47)
- 12:00 Lunch
- 1:30 ***Evaluation of Geologic and Land-Use Factors that Produce Uraniferous Waters, Arkansas River Valley, Southeastern Colorado.*** Robert A. Zielinski. Sigrid Asher-Bolinder, Allen L. Meier, Craig A. Johnson, Barney J. Szabo, U. S. Geological Survey, MS 974, Denver Federal Center, Denver, CO 80255. (48)
- 1:55 ***Microwave Assisted Digestion of Paint Chips and Air Filters for Lead Analysis.*** Sara Littau and Robert Revesz, CEM Corp. 3100 Smith Farm Road, Matthews, NC 28105. (49)
- 2:15 ***Preparation of Free Available Bromine Species and Measurement of Molar Absorptivities Using UV-Visible Spectrophotometry and Iodometric Analysis.*** Gary L. Emmert. Renee D. Gauw and Gilbert Gordan, Department of Chemistry, Miami University, Oxford, OH 45056. (50)
- 2:35 Break
- 3:00 ***Glycine as a Quenching Agent for Ozone in Bromate Ion Formation Studies.*** Gary L. Emmert and Gilbert Gordan, Department of Chemistry, Miami University, Oxford, OH 45056. (51)
- 3:20 ***Circular Dichroism for Detecting Microorganisms Modeled with Light Scattering Theory.*** David L. Rosen and David Pendleton, U.S. Army Research Laboratory, Battlefield Environment Directorate, ATTN: AMSRL-BE-S, WSMR, NM 88002. (52)
- 3:40 ***The Analysis of Cyanobacterial Toxins in Freshwaters.*** Kevin J. James and Ian R. Sherlock, Ecotoxicology Research Unit, Chemistry Department, Cork RTC, Bishopstown, Cork, Ireland. (53)

**Wednesday, July 26, 1995**

Maria W. Tikkanen, Presiding

8:30 Opening Remarks

**Invited Speaker in Environmental Mass Spectrometry**

8:35 *Membrane Introduction and Ion Trap Mass Spectrometry.* R. Graham Cooks.  
Department of Chemistry, Purdue University, West Lafayette, IN 47907. (54)

9:15 *Development of an Improved, Direct Method for the Determination of Haloacetic Acids.* Viorica Lopez-Avila, Yan Liu, Midwest Research Institute, 625-B Clyde Ave. Mountain View, CA 94043, and Ruth Hund. AWWA Research Foundation, 6666 W. Quincy Avenue, Denver, CO 80235. (55)

9:35 *Characterization of Iodination Disinfection Byproducts by Solid-Phase Microextraction.* Paul A. Frazey, Robert M. Barkley, and Robert E. Sievers, NASA Specialized Center for Research and Training (NSCORT) in Space Environmental Health, Global Change and Environment Quality Program, Cooperative Institute for Research in Environmental Studies, Department of Chemistry and Biochemistry, University of Colorado, Boulder, CO 80309-0216. (56)

9:55 *Microwave Solvent Extraction of Chlorinated Pesticides from Soil.* Jamie Fish. FAS Analytical Services, P.O. Box 533, Monroe, NC 28111, and Robert Revesz, CEM Corporation, P.O. Box 200, Matthews, NC 28106-0200. (57)

10:15 Break

10:35 *Residual Polymer Analysis by Immunoassay.* Andrew J. Dunham and Robert Wetegrove, Nalco Chemical Company, One Nalco Center, Naperville, IL, 60563-1198 (58)

10:55 *A Comparison of Rural and Urban Carbonyl Concentrations.* Mary Ann Magoun, Larry G. Anderson, and Randolph Eisenhardt, C.U.-Denver, Chemistry Department, Campus Box 194, P.O. Box 173364, Denver, CO 80217-3364. (59)

11:15 *Analysis of Environmental Samples for Explosives and Explosives Degradation Products by Thermospray Liquid Chromatography - Mass Spectrometry.* Paul M. Gates, Edward T. Furlong, Christopher E. Lindley and Mark R. Burkhardt, U.S. Geological Survey, National Water Quality Laboratory, 5293 Ward Road, Arvada, CO 80002. (60)

## **18th International EPR Symposium**

Organized by Sandra S. Eaton and Gareth R. Eaton

Sunday, July 23, 1995

6:00 Meet in Hyatt lobby for bus transportation to an open house at the University of Denver.

Monday, July 24, 1995

Session I, Gold Medal Award Session

James R. Norris, presiding

8:30 Opening Remarks and Welcome, Gareth R. Eaton

8:35 **Presentation of International EPR Society Gold Award to Professor Samuel I. Weissman**

Comments on Contributions of Prof. Weissman summarized by Prof. Norris.

8:45 **Award Address, S.I. Weissman**, Washington University. (61)

9:20 ***Microwave Frequency Dependence of CIDEP.*** J. Hirota. Kyoto University, Japan. (62)

9:55 Break

10:25 ***Angle Selected ENDOR Spectroscopy; EPR Spectra as 3-Dimensional Energy Surfaces.*** R. Kreilick. University of Rochester. (63)

10:55 ***Application of FT-EPR in the Study of Mechanisms of Photochemical Reactions.*** H. van Willigen. University of Massachusetts - Boston. (64)

11:30 ***Probing Electron Transfer with Low and High Field EPR*** J. Norris. University of Chicago. (65)

12:00 Lunch

Session II, Gold Medal Award Session

James R. Norris, presiding

1:30 ***EPR and DNP at High Magnetic Field.*** R. Griffin. MIT. (66)

- 2:05 ***ESR of Photoexcited Alkali-Metal Solutions. The Way It Is.*** H. Levanon. Hebrew University, Israel. (67)
- 2:40 ***Light-Induced Nuclear Coherences in Photosynthetic Reaction Centers*** G. Kothe. University of Freiburg, Germany. (68)
- 3:15 Break
- 3:45 ***From Conventional to Echo-Detected Transient Nutation of the Photo-Excited Triplet State.*** T. Lin. Washington University. (69)
- 4:20 ***Transient EPR with No RF Pulse -A Fast Switching Experiment.*** D. Sloop. Washington University. (70)
- 5:00 Conference Reception and Instrument Exhibits

Tuesday, July 25, 1995

Session III, H van Willigen presiding

- 8:30 ***Doublet and Triplet ESR Above and Below  $T_c$  in (BED!) $3Ta_2F_{11}$ .*** J. V. Acrivos and L. Chen, San Jose State University. (71)
- 8:50 ***Two-Center Model for Radiation-induced Aluminum Hole Center in Stishovite: High Pressure Phase  $SiO_2$ .*** K. Ogoh, C. Yamanaka, M. Ikeya, and E. Ito, Osaka University and Okayama University, Japan. (72)
- 9:10 ***Electron Paramagnetic Resonance Study of Transition Ion Dimers Formed in  $CeC_{2-}$ .*** E. Abi-Aad, A. Bennani, A. Aboukais. Universite des Sciences et Technologies de Lille and Universite du Littoral, France. (73)
- 9:30 ***Recent Developments of the Dynamic Imaging of Diffusion ESR Technique in the Application of Polydispersed Polymer Samples.*** D. Xu, J. K. Moscicki, J. H. Freed, E. Hall, and C. K. Ober, Cornell University. (74)
- 9:50 Break

- 10:20 *An ESR and ENDOR Study of Radical Cations Generated from Arylsilanes and -Germanes.* M. Lehnig, H. Klaukien, S. Reib and P. Such, Universitat Dortmund and Bruker Instruments. (75)
- 10:40 *A Study of the Structure of Surface Bound Surfactant Aggregates: Application to Shear Flocculation.* M. G. Bakker and D. D. Murphy, University of Alabama. (76)
- 11:00 *Combined Time-Resolved Fluorescence Quenching and EPR to Study Statistical Distributions and Collision Rates of Additive Molecules in Micelles.* B. L. Bales, C. Stenland and M. Almgren, California State University at Northridge and University of Uppsala, Sweden. (77)
- 11:20 *Biological Effects of the Nitrogen Dioxide Releasing-Agent Dinitramide. An EPR/Spin-Labeling Study.* A- J- Carmichael, J. Armengol, A. Young, K. Dean, M. D. Pace, and L. Steel-Goodwin, Armed Forces Radiobiology and Naval Research Institutes. (78)
- 11:40 *The Fast Reaction Stopped Flow EPR Technique As Applied to the Unfolding of Proteins: Limitations and Potential Remedy.* R. E. Hansen. Update Instruments, Inc. (79)
- 12:00 Lunch
- Session IV, R. LoBrutto presiding
- 1:30 **Presentation of International EPR Society Silver Medal in Biology/Medicine to Professor Lev Blumenfeld.**
- 1:35 **Award Address:** Professor Lev Blumenfeld, Russian Academy of Science, Moscow.
- 2:10 *When is a g-value not a g-value and a Symmetry not a Symmetry in EPR of Proteins with High Spin Ferric Iron?* B. J. Gaffhey. Johns Hopkins University. (80)
- 2:30 *Application of Angle Selected ENDOR for Structure Determination.* D. Mustafi. University of Chicago. (81)
- 2:55 Coffee Break

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

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

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

(Posters are listed alphabetically by presenting author)

A ***Saturation Recovery EPR of Cu(catechol)<sub>2</sub>***- W. Froncisz, W. E. Antholine, C. C. Felix, and J. S. Hyde, Jagiellonian University, Poland, and Medical College of Wisconsin. (82)

B ***EPR Study of Extrinsic Defects in Amorphous Silica***. W. R. Austin and R. G. Leisure, Colorado State University. (83)

A ***Is a Second Radical Involved in the Hemoglobin Autoxidation under Hypoxia?*** C. Balagopalakrishna, O. O. Abugo, and J. M. Rifkind, National Institute of Aging. (84)

B ***<sup>51</sup>VESE-ENDOR Studies of Vanadium Complexes***. J. A. Ball and R. D. Britt, University of California - Davis. (85)

A ***The Design of Mints-Style Transmission Cavities for Pulsed EPR***. C. Bender, Albert Einstein College of Medicine. (86)

B ***Experimental Investigations of the Linear Electric Field Effect***. C. Bender, Albert Einstein College of Medicine. (87)

A ***Pulsed EPR Studies of the Type I Copper Center of Rusty Iron***. C. Bender, D. Casimiro, and H. J. Dyson, Albert Einstein College of Medicine and The Scripps Institute. (88)

B ***Pulsed EPR Studies of 'Engineered' Yeast Superoxide Dismutase***. C. Bender, Y. Lu, J. Goto, J. Valentine, and J. Peisach, Albert Einstein College of Medicine and University of California, Los Angeles. (89)

A ***Unpaired Electron Delocalization in Acceptor-Bridge-Donor Molecular Structures***. R. Krzyminiwski, A. Bielewicz, J. Kudynska, and H. A. Buckmaster, Adam Mickiewicz University, Poland and University of Victoria, Canada. (90)

B ***Continuing Oxidation Studies of Motor Oils at Typical Crankcase Temperatures***. J. Kudynska and H. A. Buckmaster, University of Victoria, Canada. (91)

- A *Anisotropic Rotational Dynamics of MRI Paramagnetic Contrast Agents.* J. W. Chen, R. B. Clarkson, and R. L. Belford, University of Illinois. (92)
- B *PEN Spin Trap Inhibits Kupffer Cell Phagocytosis and Liver Nitric-Oxide Synthase.* J. Z. Chen, L. A. Reinke, S. Yamashiro, G. Chen, B. A. Quinn, T. Hayes, and E. G. Janzen, University of Guelph and University of Oklahoma. (93)
- A *Pulsed ENDOR at 35 Ghz.* C. E. Davoust, B. M. Hoffman, P. E. Doan, and V. J. DeRose, Northwestern University. (94)
- B *Investigation of the Dinuclear Fe Center of Methane Monooxygenase by Advanced Paramagnetic Resonance Techniques: On the Geometry of DMSO Binding.* V. J. DeRose, K. E. Liu, S. J. Lippard, and B. M. Hoffman, Northwestern University and Massachusetts Institute of Technology. (95)
- A *Electron Spin Echo Envelope Modulation Spectroscopic Analysis of Altered Nitrogenase MoFe Proteins from Azotobacter vinelandii.* V. J. DeRose, C.-H. Kim, J. Peters, W. E. Newton, D. R. Dean, and B. M. Hoffman, Northwestern University and Virginia Polytechnic Institute and State University. (96)
- B *The Contour Lineshape of Cross-Peaks in Two-Dimensional ESEEM Spectra of Orientationally-Disordered Spin Systems  $S=1/2$  and  $I=1/2$ .* S. A. Dikanov and M. K. Bowman, Pacific Northwest Laboratory. (97)
- A *Orientation Selection in ENDOR and ESEEM: Towards a Set of Guidelines for Interpreting Complex ENDOR and ESEEM Patterns.* P. E. Doan and B. M. Hoffman, Northwestern University. (98)
- B *Mass Spectrometric Study of PBN Spin Trapping Products from Hydroxyl Radical Generating Sources.* C. M. DuBose, E. G. Janzen, and H. Sang, Oklahoma Medical Research Foundation. (99)
- A *250 GHz EPR Studies of Solvent Cage Structure in o-terphenyl (OTP).* K. A. Earle, N. Polimeno, J. Moscicki, and J. H. Freed, Cornell University. (100)
- B *Silicon Graphics Implementation of Programs for Spectral Simulation in Metal Ion EPR.* K. S. Doctor, B. C. Maguire, and B. J. Gaffney, Johns Hopkins University. (101)
- A *A High Frequency EPR Study of the Radical Formed Upon Inhibition of E. coli Ribonucleotide Reductase with a Substituted Deoxynucleotide.* G. J. Geifsn, B. F. Bellew, W. van der Donk, D. J. Singel, R. G. Griffin, and J. Stubbe, MIT and Montana State University. (102)



- B ***S-Band Stepped-Field Electron Electron Double Resonance Spectroscopy.*** B. T. Ghim, R. W. Quine, G. A. Rinard, S. S. Eaton, and G. R. Eaton, University of Denver. (103)
- A ***Spin Labeling of Unsaturated Lipids with Nitroso-Compounds.*** T. Guiberteau and L. J. Berliner, Ohio State University. (104)
- B ***Viscosity Measured in Animals with Deuterated Spin Labels and Very Low Frequency EPR: Significance and Limits.*** H. J. Halpern, G. V. R. Chandramouli, and E. D. Barth, University of Chicago. (105)
- A ***Primary Nuclear Spin Echoes in EPR Induced by Microwave Pulses.*** M. Hubrich, E. C. Hoffmann, and A. Schweiger, Swiss Federal Institute of Technology, Zurich. (106)
- B ***Pulse Train-Detected Electron Spin Envelope Modulation.*** E. C. Hoffmann, M. Hubrich, and A. Schweiger, Swiss Federal Institute of Technology, Zurich. (107)
- A ***Advanced EPR, CW and Pulsed ENDOR, and ESEEM, Studies of Bis(maleonitrile-dithiolato)Ni(III) Complexes.*** J. E. Huyett, S. B. Choudhury, M. J. Maroney, and B. M. Hoffman, Northwestern University and University of Massachusetts Amherst. (108)
- B ***Multi-Frequency EPR Measurement of the Zero-Field Splitting of MRI Paramagnetic Contrast Agents.*** H. Kang, J.-H. Hwang, R. B. Clarkson, and R. L. Belford, University of Illinois. (109)
- A ***A Time-Resolved EPR (35 GHz) Study of Carotenoid Cation Radicals.*** A. S. Jeevarajan, N. I. Avdievich, M. D. E. Forbes, and L. D. Kispert, University of Alabama and University of North Carolina. (110)
- B ***Decay Rates of Nitroxide Radicals in the Presence of Biological Reducing Agents.*** Y. Kotake, Z. Yu, and E. G. Janzen, Oklahoma Medical Research Foundation. (111)
- A ***Electron Nuclear Double Resonance (ENDOR) Studies of the Carbon Monoxide Inhibited MoFe Protein of Nitrogenase.*** H. I. Lee, R. C. Pollock, L. M. Cameron, V. J. DeRose, B. J. Hales, W. H. Orme-Johnson, and B. M. Hoffman, Northwestern University, MIT, and Louisiana State University. (112)
- B ***Far-infrared ESR of Some Distorted Tetrahedral Manganese (II) Complexes.*** W. B. Lynch, R. M. Wood, D. M. Stucker, and J. H. Freed, University of Evansville, Gettysburg College, and Cornell University. (113)

Tuesday evening - Dinner to recognize recipients of International EPR Society Gold and Silver Medals: Samuel I. Weissman, Lev Blumenfeld, and recipients of Silver Medals in Chemistry and Physics/Instrumentation. All attendees are invited, contact G.R. or S.S. Eaton for details.

Wednesday, July 26, 1995

Session VI, B. Gaffney presiding

- 8:30 *ESE-ENDOR Studies of Paramagnetic Centers of Photosystem II.* R. D. Britt.  
D. W. Randall, M. L. Gilchrist, Jr., and J. A. Ball, University of California Davis. (114)
- 8:55 *Investigation of the Electronic Structure of the Primary Electron Donor in Bacterial Photosynthesis by High-Frequency (95 GHz)/High-Field EPR.* M. Huber.  
J. T. Topping, U. Fink, R. Feick, C. C. Schenck, W. Lubitz, and K. Mobius, Free University of Berlin, Technical University of Berlin, University of Munich, and Colorado State University. (115)
- 9:20 *ENDOR and ESEEM Experiments on the Radical Cation of the Primary Donor, P700<sup>+</sup> in Photosystem I.* H. Kafil.  
P. Fromme, L. E. Andreasson, F. Lendzian, H. T. Witt, and W. Lubitz, Technical University of Berlin and University of Goteborg, Sweden. (116)
- 9:50 *EPR and ESEEM Determination of the Structure of a Free Radical Intermediate in the Reaction of Lysine 2,3-aminomutase.* M. D. Ballinger, P. A. Frey, G. H. Reed, and R. LoBrutto.  
University of Wisconsin at Madison and Arizona State University. (117)
- 10:15 Break
- 10:45 *Analysis of Static Conformational Distributions in the Solid State by <sup>1</sup>H ESEEM Spectroscopy: Angular Dispersion in Side Chain Orientations in Amino Acid Tyrosine Radicals.* K. Warncke.  
G. T. Babcock, and J. McCracken, Michigan State University. (118)
- 11:10 *The Nature of the Cu<sup>2+</sup> Site in Nitrous Oxide Reductase from Pseudomonas Stutzeri.* F. Neese.  
W. G. Zumft, W. E. Antholine, and P. M. Kroneck, University of Konstanz, University of Karlsruhe, and Medical College of Wisconsin. (119)
- 11:35 *Time-Domain EPR Determination of Interspin Distances in Spin-Labeled Hemoglobins.* V. Budker, M. Seiter, J.-L. Du, S. S. Eaton, and G. R. Eaton,  
University of Denver. (120)

12:00 Lunch

Session VII, H. Halpern presiding

1:30 ***Time-Resolved Electron Spin Resonance Studies of Spin Trapping: Quantitative Aspects of Nitrene Spin-Trapping.*** K. P. Madden and H. Taniguchi, University of Notre Dame. (121)

1:50 ***Quantitative EPR Spin Trapping I. Nitrite Ions in Alkaline Solution.*** M. D. Pace and A. J. Carmichael, Naval Research Laboratory and Armed Forces Radiobiology Research Institute. (122)

2:10 ***Could Nitrosyl Chloride (ClNO) be Produced by Human Skin Keratinocytes and Sulfur Mustard (HD)? A Magnetic Resonance Study.*** C. M. Arroyo and C. A. Broomfield, U. S. Army Medical Research Institute of Chemical Defense. (123)

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 ***ESEEM Studies of  $^6\text{Mg}$  Coupling in Photosystem I: Electronic Structure Determination of P700'*** M. Mac. X. Tang, B. Diner, G. T. Babcock, and J. McCracken, Michigan State University and E.I. DuPont de Nemours Co. (124)

D ***Multifrequency 2-Dimensional ESEEM of VO(Salicylaldoxime) Model Complexes.*** E. J. Reijerse, J. I. Martinez, and D. Collison, University of Nijmegen, Universidad de Zaragoza, and University of Manchester. (125)

C ***Comparative Analysis of Configuration-Related Radiation-Induced Defects in Amorphous Silicon Dioxide and Silicon Nitride.*** V. A. Mashkov and R. G. Leisure, Colorado State University. (126)

D ***PBNSpin Trap Inhibits LPS-Induced Nitric Oxide Generation in Mice. A Spin Trapping Study.*** T. Miyajima and Y. Kotake, Oklahoma Medical Research Foundation. (127)

- C ***Photo-Enhanced Production of the Spin-Adduct DMPO-OH in Aqueous Menadione Solution.*** S. Monroe and S. S. Eaton, University of Denver. (128)
- D ***Development of an Educational EPR Module for Teaching the Principles of MRJ.*** A. I. Smirnov, P. D. Morse, and R. L. Belford, Illinois State University and University of Illinois. (129)
- C ***Simultaneous EPR Measurements of Kinetics of Oxygen and Spin Label Consumption by Baby Hamster Kidney Cells.*** P. D. Morse and A. I. Smirnov, Illinois State University and University of Illinois. (130)
- D ***Current Status of High-Frequency (95 GHz) EPR Methods for Measuring Nitroxide Reduction by a Single Mammalian Cell.*** A. I. Smirnov and P. D. Morse. University of Illinois and Illinois State University. (131)
- C ***Choosing Standards for EPR Concentration Measurements: Effect of Spin Hamiltonian Parameters on Line Intensities.*** V. Yu. Nagv and D. P. Sokolov, Russian Academy of Sciences, Moscow. (132)
- D ***Electron and Light Microscopy Studies on Particulate Probes Lithium Phthalocyanine, Fusinite, and Synthetic Chars.*** S. W. Norby, H. M. Swartz, and R. B. Clarkson, University of Illinois and Dartmouth Medical School. (133)
- C ***In Vitro Spin Trapping of Nitric Oxide in Activated Nerve Cells and Macrophages.*** S. W. Norby and R. B. Clarkson, University of Illinois. (134)
- D ***Electron Trapping Oxygen Vacancy Centers in Coesite and Stishovite: High Pressure Phase SiO<sub>2</sub>.*** K. Ogoh, C. Yamanaka, M. Ikeya, and E. Ito, Osaka University and Okayama University. (135)
- C ***Pulsed EPR Studies of Photosystem II Semiquinone Radicals.*** J. Peloquin, and R. D. Britt, University of California Davis. (136)
- D ***Bimodal S-Band Loop-Gap Resonator.*** W. Piasecki, W. Froncisz, and J. S. Hyde, Medical College of Wisconsin. (137)
- C ***Folding of iso-1 Cytochrome c Probed at Site-Specifically Spin Labeled Cys<sup>2</sup> - Equilibrium and EPR Stopped-Flow Kinetics.*** K. Qu, J. Vaughn, J. Fetrow, A. Sienkiewicz, and C. P. Scholes, SUNY at Albany. (138)
- D ***ESEEM Studies of Oxo-Mo(V) Centers in Model Compounds and Sulfite Oxidase.*** P. Basu, A. M. Raitsimring, P. Borbat, A. Pacheco, N. V. Shokhirev, and J. H. Enemark, University of Arizona. (139)

- C *"I+2 " Train - A New Variety of Pulse Adjustable ESEEM Spectroscopy.*  
A. Raitsimring and P. Borbat, University of Arizona. (140)
- D *ESEEM and ESE-ENDOR Studies of Manganese Clusters.* P. W. Randall and  
R. D. Britt, University of California Davis. (141)
- C *Copper Re-Entrant Style Loop-Gap Resonators for Multi-Frequency EPR.*  
G. A. Rinard, B. T. Ghim, M. Sueki, and G. R. Eaton, University of Denver. (142)
- D *EPR Investigation of the Effect of Ultrasonification on the Penetration of  
Model Spin Probes and Spin-Labeled Antibiotics Through Bacterial Cell Walls.*  
R. W. Pope and N. Y. Rapoport, University of Utah. (143)
- C *Spontaneous Radical Formation from 1,3-Dipolar Molecular Addition of  
Halocarbons to C-Phenyl N-tert-Butyl Nitron (PBN).* H. Sang, E. G. Janzen,  
and J. L. Poyer, Oklahoma Medical Research Foundation. (144)
- D *Nuclear and Electron Spin Relaxation in Paramagnetic Solutions containing  
Transition Metal and Lanthanide Ions with Spin > 1/2.* R. P. Sharp, University of  
Michigan. (145)
- C *Simple Analytical Model for the Description of CIDN(E)P Formation in  
Radical (-ion) Pairs.* N. V. Shokhirev, M. B. Taraban, and T. V. Leshina,  
University of Arizona and Institute of Chemical Kinetics and Combustion, Russia. (146)
- D *Tunable Q-band Cavity for EPR and ENDOR Experiments -Application to  
Oxygen Bound to Activated Bleomycin.* A. Sienkiewicz, A. Veselov, B.  
Smith, H. Taylor, R. Burger, and C. P. Scholes, SUNY at Albany. (147)
- C *ESR Spectroscopic Studies of Phenolic Antioxidant Food Additives. Physical-  
Biochemical Experiment for Advanced Undergraduate Laboratories.*  
H. J. Sipe, Jr., R. J. Geiger, Jr., T. W. Johnson, D. M. Goldin, and C. St. John,  
Hampden-Sydney College. (148)
- D *Effect of Ethanol on Oxygen Permeability of Model Phospholipid Bilayer.*  
A. I. Smirnov and R. L. Belford, University of Illinois. (149)
- C *Accuracy of Oxygen Measurements in T2 (Linewidth) EPR Oximetry.*  
T. I. Smirnova, A. I. Smirnov, R. B. Clarkson, and R. L. Belford, University of  
Illinois. (150)

- D *ESEEM and ENDOR Studies of Non-Kramers Spin Systems Near Zero Field.* P. R. Sturgeon, J. M. Nocek, B. M. Hoffman, K. E. Liu, S. J. Lippard, D. Burdi, W. H. Tong, J. Stubbe, N. Gupta, and D. M. Kurtz, Jr., Northwestern University, MIT, and University of Georgia. (151)
- C *Computer Programs for Analysis of EPR and ENDOR Spectra of General Spin Systems Using Methods of Exact Calculation.* J. Telser. Roosevelt University. (152)
- D *Evidence of Non-Curie Law EPR Behavior in Samples Obtained from Illinois No. 6 Coal.* R. L. Thompson, K. S. Rothenberger, and H. L. Retcofsky, Pittsburgh Energy Technology Center. (153)
- C *The New Low-Potential c-Type Cytochrome from Shewanella Putrefaciens.* A. Tsapin, and H. Nealson, University of Wisconsin Milwaukee. (154)
- D *Reconstruction of the 2Fe-2S Center and g=1.90 EPR Signal into Overproduced Wild-Type and Mutant Forms of the Rieske Protein.* A. Tsapin, T. Kallas, Y. S. Cho, X. Wu, and B. Holton, University of Wisconsin Milwaukee. (155)
- C *EPR Studies Related to Arsenate Binding in Zeolite/Cement Composites.* G. L. Turner, M. G. Bakker, and P. M. Brown, University of Alabama and U. S. Bureau of Mines. (156)
- D *Magnetic Field (g-value) Dependence of Proton Hyperfine Couplings Obtained from ESEEM Measurements: Determination of Axial Ligand Orientation in Glassy Samples of Low-Spin Iron(III) Porphyrins.* F. A. Walker, T. Kh. Shokhireva, P. Borbat and A. M. Raitsimring, University of Arizona. (157)
- C *Microelectrode-Detected ESR Signals of Free Radicals in Electrolyte Solutions.* H. Yokoyama, T. Satoh, H. Ohya-Nishiguchi, and H. Kamada, Yamagata Technopolis Foundation, Japan. (158)
- D *Mobile Oxygen in Highly-irradiated Oxygen-Deficient  $\alpha$ -SiO<sub>2</sub>.* L. Zhang and R. G. Leisure, Colorado State University. (159)
- C *Anomeric Conformations of Six-Membered Cyclic Aminoxyls with a  $\beta$ -alkoxyl Substituent.* Y.-K. Zhang, Oklahoma Medical Research Foundation. (160)
- D *Resonant Enhancement in FID-Detected EPR Beats.* Y. C. Zhong, Monash University, Australia. (161)

- C ***The SGI Defect: A Ge Dangling Bond in Oxygen Impanted SiGe.*** M. E. Zvanut, P. J. Macfarlane and W. E. Carlos, University of Alabama at Birmingham and Naval Research Laboratory. (162)

Wednesday evening - Chinese dinner, see poster area for details.

Thursday, July 27, 1995

Session IX, B. Bales presiding

- 8:30 ***A Novel Reflection Mode Spectrometer for 250 GHz.*** K. A. Earle and J. H. Freed, Cornell University. (163)
- 9:00 ***Multifrequency and High-Frequency (95 GHz) EPR in Studies of Fast Molecular Dynamics in Liquids.*** A.I. Smirnov, T. I. Smirnova, R. B. Clarkson, P. D. Morse, and R. L. Belford, University of Illinois and Illinois State University. (164)
- 9:30 ***Novel Effects in Pulsed ENDOR.*** P. E. Doan and B. M. Hoffman, Northwestern University. (165)
- 10:00 Break
- 10:30 ***SEDOR-ENDOR: A New Pulsed Electron Nuclear Nuclear Triple Resonance Technique.*** M. Bernardo and H. Thomann, Exxon Research. (166)
- 11:00 ***Increasing the Sensitivity of Measurements of Radiation Induced Hydroxyl Radicals in Living Animals with Novel Spin Trapping Systems and Very Low Frequency EPR.*** H. J. Halpern, G. V. R. Chandramouli, E. D. Barth, S. Pou, and G. M. Rosen, University of Chicago and University of Maryland. (167)
- 11:30 ***A New Millimeter-Wave EPR Spectrometer and its CW and Pulsed Operation.*** G. G. Maresch, P. Hofer, K. Holczer, and D. Schmalbein, Bruker Instruments and University of California, Los Angeles. (168)

12:00 Lunch

Thursday lunch and afternoon: Bruker User's Group. Please contact Dr. Arthur Heiss for information.

## SYMPOSIUM ON FTTR/NTR/RAMAN SPECTROSCOPY

Organized by Abdul R. Chughtai

Monday, July 24, 1995

8:55 Opening Remarks

9:00 *Spectroscopy of Various Black Carbons (Soots)*. Abdul R. Chughtai, Brian Konowalchuck, and Dwight M. Smith, Department of Chemistry, University of Denver, Denver, CO 80208. (169)

9:30 *Diamond ATR: The Universal Approach for FT-IR Analysis*. Steve Hill, ASI-Applied Systems Analysis, Annapolis, Maryland, 21401. (170)

10:00 *Measurement of Wax Cloud in Live Crude Oils by Infrared Spectroscopy*. James Tackett, Marathon Oil, 7400 S. Broadway, Littleton, CO 80122. (171)

10:30 *Fourier Transform Infrared Spectroscopy of 5,8-Dihydroquinoline*. Fedri M. Marrugo, Stephen D. Wathen, and Donald C. Zapien, Department of Chemistry, University of Colorado at Denver, Denver, CO 80217-3364. (172)

## GENERAL POSTER SYMPOSIUM

Organized by Mary E. Cast

*Improved Determination of Barium by Flame AES*. John Schmelzel, Susan Manabe, Gerald Dulude, and David Pfeil, Thermo Jarrell Ash, Franklin, MA 02038. (175)

*A Minaturized, Automated DOC Fractionation Procedure*. Charles F. Tabor, and Larry B. Barber, II, U.S. Geological Survey, Boulder, CO 80303. (176)

*Neural Network Pattern Recognition of Photoacoustic FTIR Spectra and Knowledge-Based Techniques for Detection of Toxigenic Fungi in Corn*. Sherald H. Gordon, Donald T. Wicklow, Bruce C. Wheeler, Robert B. Schudy, and Richard V. Greene, U.S. Department of Agriculture, ARS, National Center for Agricultural Utilization Research, Peoria, IL 61604. (177)



***Determination of Residues of Chloransulam-methyl in Soybean Grain, Forage, and Hay by Capillary Gas Chromatography of Mass Selective Detection.*** D. D. Shackelford, D. O. Duebelbeis, and B. E. Snell, DowElanco, Indianapolis, IN 46268-1054. (178-withdrawn)

***Silica Gel, Tenax, and Carbon Media Adsorption Tube for the Sampling of a Wide Variety of Organic Compounds in Air.*** Steven F. Baugh, Havelick & Associates, Ltd., Broomfield, CO 80020. (179)

***Determination of Methanol and Ethanol in Ambient Air by Gas Chromatography with Flame Ionization Detector.*** Debra L. Kirschenman, Larry G. Anderson, and John L. Lanning, University of Colorado, Denver, CO 80217. (180)

***Sulfuric Acid/Charring Clean-up Method for PCBs in Gas Condensate.*** Sandy K. Brown, Public Service Company of Colorado, Englewood, CO 80110. (181)

***Analysis of Low-level Anions in Power Generation Systems.*** Cheryl A. Quinlin, and Becki L. Sheridan, Public Service Company of Colorado, Englewood, CO 80110. (182)

***Impurity Detection of GC-FT-IR Data Employing the Assessment of Singular Value Evolving Profiles.*** Nickey J. Messick, Gregory A. Bakken, and John H. Kalivas, Department of Chemistry, Idaho State University, Pocatello, ID 83209. (183)

***Sample Dependent Principal Component Regression.*** Dixie R. Long-Reitzel and John H. Kalivas, Department of Chemistry, Idaho State University, Pocatello, ID 83209. (184)

***A Comparison of the Detection of Decoquinone Using HPLC/UV and HPLC/EC.*** Jeffrey A. Hurlbut, David H. Desandre, and Patrick B. Cooper, Chemistry Dept., Metropolitan State College of Denver, Denver, CO 80217, and Joseph M. Storey and Carolyn A. Geisler, U.S. Food and Drug Administration, Denver Federal Center, Denver, CO 80225. (185)

***Analytical Comparison of Ephedrine in Nutritional Supplements and Herbal Preparations by CE, HPLC, GC/FID and GC/MS.*** Barbara S. Portz, Kent C. Faul, Terri L. Thomas, Jeffrey H. Cutting, Jennifer C. Pensoneau and Jeffrey A. Hurlbut, Food and Drug Administration, General Chemistry Section, Denver Federal Center, Denver, CO 80225-0087. (186)

***Analysis of Methylene Blue in Catfish Tissue.*** Sherri B. Turnipseed, Jose E. Roybal, Allen P. Pfenning, Jeffrey A. Hurlbut, and Austin R. Long, Food and Drug Administration, Animal Drugs Research Center, Denver Federal Center, Denver, CO 80225-0087. (187)

***Determination of Oxolinic Acid Residues in Shrimp by High Performance Liquid Chromatography-Fluorescence/UV Detection.*** Allen P. Pfenning, Robert K. Munns, Sherri B. Turnipseed, Jose E. Roybal, and Austin R. Long, Food and Drug Administration, Animal Drugs Research Center, Denver Federal Center, Denver, CO 80225-0087. (188)

***Liquid Chromatographic Separation and Analysis of Inorganic Colloids Synthesized in Inverse Micelles.*** S. Craft and J. P. Wilcoxon, Sandia National Laboratories, Albuquerque, NM 87185-1421. (189)

***Use of Response Surface Methodology in Optimization of Reversed-Phase HPLC Chiral Separation of Amino Acid and Amino Acid Analogs.*** John A. Blackwell and William L. Champion. The DuPont Merck Pharmaceutical Co., DuPont Chambers Works/PRF (S-1), Deepwater, NJ 08023. (190)

***A Blind Assessment Study of the Branch of Geochemistry.*** Belinda Arbogast. U. S. Geological Survey, MS 973, Box 25046, Denver, CO 80225. (191)

***A Comparison of Fluorimetric Derivatisation Methods for the HPLC Analysis of Diarrhetic Shellfish Toxins.*** K. J. James. E. P. Carmody and S. S. Kelly, Ecotoxicology Research Unit, Chemistry Department, Cork RTC, Bishopstown, Cork, Ireland. (192)

***The Analysis of Volatile Organic Compounds in Soil Using Solid Phase Microextraction for Headspace Gas Chromatography.*** Kevin J. James and Mary A. Stack. Ecotoxicology Research Unit, Chemistry Department, Cork RTC, Bishopstown, Cork, Ireland. (193)

***Fourier Transform Infrared Spectroscopy of 5,8-Dihydroxyquinoline.*** Fedri M. Marrugo, Stephen D. Wathen, and Donald C. Zapien. Department of Chemistry, University of Colorado at Denver, Denver, CO 80217. (172)

***Structure Analysis of Two Novel Alkaloids from *Speranskia Tuberculata* Baill,*** Hanging Wang and Jiangong Shi, Lanzhou Institute of Chemical Physics, Lanzhou, P.R.China. (194)

## **SYMPOSIUM ON TCP-MS**

Organized by Howard E. Taylor

Tuesday, July 25, 1995

9:25 Opening Remarks

9:30 ***Laser Ablation ICP/MS Analysis of Low Level Hanford Tank Waste and Simulants: Optimizing Experimental Parameters.*** Michael L. Alexander. Monty R. Smith, David W. Koppenaal, and John S. Hartman, Battelle, Pacific Northwest Laboratories, Richland, WA. (195)

9:50 ***Analysis of Rocks, Soil and Sediment for the Chalcophilic Elements by Laser Ablation ICP-MS.*** Xun Guo and Fred E. Lichte. U.S. Geological Survey, Denver, CO. (196)

- 10:10 ***Geological and Environmental Analysis using a New UV Laser Ablation Microprobe Coupled to an ICP-MS.*** Rob Henry, Angelica Raith, Fisons Instruments, Boulder, CO., William T. Perkins, Institute of Earth Studies, University of Wales, Aberystwyth, Wales, UK. (197)
- 10:30 Break
- 11:00 ***Techniques for Validating Trace Element Determinations in Environmentally Related Materials by ICP-MS.*** Ron C. Antweiler and Howard E. Taylor, U.S. Geological Survey, Boulder, CO. (198)
- 11:20 ***Trace Analysis of Corrosive Gas Products by ICP/MS.*** Greg W. Johnson, and Jude Proctor, Matheson Gas Products, Longmont, CO (199)
- 11:40 ***Analysis of Snow Core Samples from Alaska's North Slope using Sub-Boiling Evaporative Concentration and ICP-MS.*** John R. Garbarino and Gerald L. Hoffman, U.S. Geological Survey, Denver, CO., Elaine Snyder-Conn, U.S. Fish and Wildlife, Service, Fairbanks, AK. (200)
- 12:00 Lunch
- 1:30 ***Use of Stable Isotope Dilution ICP-MS Techniques for the Determination of Mercury in Environmental Materials.*** David A. Roth and Howard E. Taylor, U.S. Geological Survey, Boulder, CO. (201)
- 1:50 ***Microwave Induced Plasma Time-of-Flight Mass Spectroscopy of Chlorinated VOCs.*** Alex F. Schreiner, Chung H. Sin, and Jon W. Carnahan, Department of Chemistry, Northern Illinois University, DeKalb, IL. (202)
- 2:40 ***Development of a Second Generation High Resolution ICP-MS and its Applicability to Trace Element Analysis in Real Sample Matrices.*** Rob Henry, Nicola Reed, Robert Hutton, Fisons Instruments, Boulder, CO. (203)
- 3:00 Break
- 3:30 ***Practical Experience with a DIN-HR-ICP/MS in the Semiconductor Industry.*** Barton D. Tillotson, Anthony J. Schleisman, Texas Instruments, Inc., Dallas, TX. (204)
- 3:50 ***Protocol Development for Quantitative Multi-element Analysis of Biological Samples by Inductively Coupled Plasma-Mass Spectrometry.*** Chiung-Sheng Hsiung, Joseph D. Andrade, and K. Owen Ash, ARUP, 500 Chipeta Way, Salt Lake City, UT. (205)

## **LABORATORY SAFETY**

Organized by Victoria Swancutt

37TH ROCKY MOUNTAIN CONFERENCE ON ANALYTICAL CHEMISTRY  
Laboratory Safety Symposium presents a seminar on

### **"How to Protect Yourself from Hazards in the Laboratory"**

**by Norman V. Steere**

When: 8:30am on Weds., July 26, 1995. Open to all Conference Attendees.

Where: Hyatt Regency Denver, 1750 Welton Street, Denver, Colorado

Topics and Who Should Attend: Chemists and others who are concerned about safety in their labs, or who have part-time responsibility for lab safety and health. The seminar will focus on practical measures for preventing incidents, fires, or exposure to minimize injury to lab employees. Brief discussions on regulations, standards and good practices will also be included.

**Key topics include:**

- o Lab Safety and Health & the OSHA Lab Standard
- o Effective Use of Lab Hoods
- o Hazards of Old Solvents, Peroxidizable Compounds
- o Fire & Explosion Hazards
- o Procedures for Clothing Fires, Spills and Splashes
- o Safe Storage of Chemicals

Norman V. Steere is a laboratory safety and design consultant who teaches the ACS short course on laboratory safety and health. His firm presents in-house courses for laboratories and consults on design of laboratory and storage facilities. Mr. Steere edited two editions of the "Handbook of Laboratory Safety" and three volumes of "Safety in the Chemical Laboratory". Recent activities include co-editing "Designing a Laboratory" (1989) writing a chapter in "Safe Storage of Laboratory Chemicals" (1991), and membership on the committee responsible for the NFPA "Standard on Laboratories Using Chemicals" (NFPA 45-1991).

## **LUMINESCENCE SYMPOSIUM**

Organized by DeLyle Eastwood and Robert J. Hurtubise

Monday, July 24, 1995

Robert J. Hurtubise, Presiding

8:30 *Opening Remarks*

8:35 *Characterization and Determination of Benzo(a)pyrene-DNA Adducts and Their Hydrolysis Products Via Solid-Matrix Luminescence.* R.J. Hurtubise, Y. Chu, and S.W. Tjioe, Department of Chemistry, University of Wyoming, Laramie, WY 82071. (206)

9:00 *Heavy-Atom Effect on the Room-Temperature Phosphorescence of 2-Amino-1-Methyl-6-Phenylimidazo[4,5-B]Pyridine in Glucose and Trehalose Glasses as Solid Matrices.* Jiangshan Wang and Robert J. Hurtubise, Department of Chemistry, University of Wyoming, Laramie, WY 82071. (207)

9:25 *Measuring the Texture of a Surface Using Excitation Energy Transport.* T. Gregory Dewey, Department of Chemistry, University of Denver, Denver, CO 80208. (208)

9:50 *Probing the Binding Properties of Aggregate Materials with the Tripositive Europium Ions.* Leo V. Azarraga, U.S. Environmental Protection Agency, Environmental Research Laboratory, 960 College Station Road, Athens, GA 30605-2700. (209)

10:15 Break

10:40 *An Organized Media Enhanced Fiber Optic Luminescence Sensor for Environmental Monitoring.* P.M. Hanlon, Seton Hall University, L.J. Cline Love, Chemistry Department, Seton Hall University, DeLyle Eastwood, Lockheed (LESAT), Las Vegas, NV 89119 and K. Rubelowsky, Spex Ind., Inc., Edison, NJ 08820. (210)

11:05 *Fluorescence Anisotropy Measurements in the Determination of Humic Acid Associations.* Reginald R. Engebretson and Ray von Wandruszka, Chemistry Department, University of Idaho, Moscow, ID 83844. (211)

11:30 *Luminescence and Photochemical Reaction Detection in Capillary Electrophoresis.* Rob Milofsky, Fort Lewis College, Durango, CO 81301. (212)

12:00 Lunch

DeLyle Eastwood, Presiding

- 1:30 Remarks, DeLyle Eastwood
- 1:35 ***Characterization of Polymeric Materials by Fluorescent Charge-Transfer Probes.*** J.W. Hofstraat, H.J. Verhey<sup>1</sup>, J.W. Verhoeven<sup>1</sup>, M. Kiimke<sup>2</sup> and L.B. McGown<sup>2</sup>, Akzo Nobel Central Research, Department RGL, P.O. Box 9300, NL-6800 SB Arnhem, The Netherlands, <sup>1</sup> University of Amsterdam, Department of Physical Organic Chemistry, Amsterdam, The Netherlands, <sup>2</sup> Duke University, Department of Chemistry, Durham, NC 27708.(213)
- 2:05 ***Diagnostics for Simultaneous Quantitation of Dissolved Oxygen Concentration, Particle Size, and Surface Mass Deposition Rate in Thermally Stressed Aviation Fuel.*** James R. Gord, Wright Laboratory, Aero Propulsion & Power Directorate, Wright-Patterson Air Force Base, OH 45433-7103; William L. Weaver and Viroj Vilimpoc, Systems Research Laboratories, Inc., 2800 Indian Ripple Road, Dayton, OH 45440-3696; and Steven W. Buckner, Department of Chemistry & Geology, Columbus College, Columbus, GA 31907-5645.(214)
- 2:30 ***Energy-Gap Law and Solid-Matrix Room Temperature Phosphorescence.*** S-M. Ramasamy and R.J. Hurtubise, Department of Chemistry, University of Wyoming, Laramie, WY 82071.(215)
- 2:55 ***The Study of the Moisture-Quenching of Solid-Matrix Room-Temperature Phosphorescence with Infrared Spectroscopy.*** Jie Chen and Robert J. Hurtubise, Department of Chemistry, University of Wyoming, Laramie, WY 82071. (216)
- 3:20 **Break**
- 3:45 ***Effect of Dissolved Oxygen and Soft Thermal Annealing on the X-Ray Induced Luminescence of Amorphous Silicon Dioxide.*** A.J. Miller, V.A. Mashkov, Lin Zhang and R.G. Leisure, Department of Physics, Colorado State University, Fort Collins, CO 80523. (217)
- 4:10 ***Effects of Stabilizers on Discoloration of EVA Encapsulant for PV Modules.*** S.H. Glick, and F.J. Pern, National Renewable Energy Laboratory, 1617 Cole Boulevard, Golden, CO 80401-3393.(218)
- 4:35 ***Stabilizing Effects of UV-Filtering Glass and Gas Permeable Polymer Superstrates on Discoloration of EVA Encapsulant for Photovoltaic Modules.*** F.J. Pern, National Renewable Energy Laboratory, 1617 Cole Boulevard, Golden, CO 80401-3393. (219)

## SYMPOSTTJM ON MASS SPECTROMETRY

Organized by Joseph A. Zirrolli

Research Symposium

Monday, July 24, 1995

8:55 Opening Remarks: Joseph Zirrolli

Keynote Speaker

9:00 *Flights of Fancy*. Chris Enke. Professor of Chemistry, Department of Chemistry, University of New Mexico, Albuquerque, New Mexico, (no abstract)

10:00 *F2-Isoprostane Analysis by Electrospray Mass Spectrometry*. Russell J. Waugh and Robert C. Murphy, Department of Pediatrics, National Jewish Center for Immunology and Respiratory Medicine, 1400 Jackson Street, Denver, Colorado 80206. (220)

10:20 *Pyrolysis-Quadrupole Trap Mass Spectrometry of Pathogenic Bacteria*. Franco Basile, Ted L. Hadfield' and Kent J. Voorhees, Department of Chemistry, Colorado School of Mines, Golden, Colorado 80401 and 'Armed Forces Institute of Pathology, Washington, D.C. 20306. (221)

10:40 Break & Exhibition

11:00 *Fast Metastable Ion Decay Processes in Matrix-Assisted Laser Desorption/Ionization*. Robert S. Brown and Duane Reiber, Department of Chemistry and Biochemistry, Utah State University, Logan, Utah 84322-0330. (222)

11:20 *Reactivity and Secondary Kinetic Isotope Effects in some S<sub>2</sub> Reactions of Oxygen and Sulfur Containing Nucleophiles*. Gustavo E. Davico, Charles H. DePuy and Veronica M. Bierbaum, Department of Chemistry and Biochemistry, University of Colorado at Boulder, Campus Box 215, Boulder, Colorado 80309-0215. (223)

11:40 *Pyrolysis Mass Spectrometry of Oligopeptides Ranging from Six to Fifty Amino Acids Units in Length*. Alan Hendricker and Kent J. Voorhees, Department of Chemistry, Colorado School of Mines, Golden, Colorado 80401. (224)

12:00 Lunch & Exhibition

- 1:30 ***Electrospray Ionization LC/MS Characterization of Oxidized Phospholipids.*** Kathleen A. Harrison and Robert C. Murphy, Department of Pediatrics, National Jewish Center for Immunology and Respiratory Medicine, 1400 Jackson Street, Denver, Colorado 80206. (225)
- 1:50 ***Identification of Proteins Using Data Dependent LC/MS/MS and Protein Database Searching.*** Iain Mylchreest. Adrain Land and Kevin Wheeler, Finnigan MAT, 355 River Oaks Parkway, San Jose, California 95134. (no abstract)
- 2:10 ***Gas Phase Chemistry of Methy Cation (CH<sub>3</sub><sup>+</sup>) and Boron Cation (BH<sub>2</sub><sup>+</sup>).*** Joseph A. Hankin. Ed Motell, C.H. DePuy and Robert Damrauer, Department of Chemistry and Biochemistry, University of Colorado at Boulder, Campus Box 215, Boulder, Colorado 80309-0215. (227)
- 2:30 ***Use of Py MS/MS to Study Biomarker Mechanisms in Whole Cells.*** Christy Abbas-Hawks. Dave Sickenberger' and Kent J. Voorhees, Department of Chemistry, Colorado School of Mines, Golden, Colorado 80401 and 'U.S. Army ERDEC, Aberdeen Proving Ground, Maryland, 21010. (228)
- 2:50 Break & Exhibition
- 3:20 ***Evidence for Nonenzymatic Metabolism of PAF via Free Radical Oxidation.*** Lisa M. Nickelson and Robert C. Murphy, Department of Pediatrics, National Jewish Center for Immunology and Respiratory Medicine, 1400 Jackson Street, Denver, Colorado 80206. (229)
- 3:40 ***Confirmatory Analysis by on-line Photodegradation and Liquid Chromatography - Mass Spectrometry.*** Dietrich A. Volmer and Jon G. Wilkes, U.S. Food and Drug Administration/National Center for Toxicological Research, 3900 NCTR Drive, Jefferson, AR 72079. (230)
- 4:00 ***Enhancement of Electrospray Detectability for Nitrosamine by Photochemical Degradation.*** David L. Vollmer and Jack Lay, U.S. Food and Drug Administration/National Center for Toxicological Research, 3900 NCTR Drive, Jefferson, AR 72079. (231)
- 4:20 ***Ultra-Sensitive Detection in Complex Matrices by Quadrupole Ion Trap Mass Spectrometry.*** William Schnute. Finnigan MAT, 355 River Oaks Parkway, San Jose, California 95134.(232)



4:40 ***Collisional-Induced Dissociation of Eicosanoids: Bridging Fundamental Gas Phase Ion Chemistry to Biomedical Mass Spectrometry.*** Joseph A. Zirrolli. Pat Wheelan and Robert C. Murphy, Department of Pediatrics, National Jewish Center for Immunology and Respiratory Medicine, 1400 Jackson Street, Denver, Colorado 80206. (no abstract)

5:00 Exhibition

New Technology & Developments Symposium  
Tuesday, July 25, 1995

8:55 Opening Remarks: Joseph Zirrolli  
(Note: Abstracts not available for today's symposium.)

9:00 ***Recent Developments in Quadrupole and Ion Trap LC/MS/MS Technology.*** Iain Mylchreest. Adrain Land and Ian Jardine, Finnigan MAT, 355 River Oaks Parkway, San Jose, California 95134.

9:30 ***Improvements to Electrospray and APCI Ion Sources for CE/MS and LC/MS Applications with TOF, Quadrupoles, FTMS, Ion Traps and Magnetic Sector Spectrometers.*** Craig M. Whitehouse. Fred Banks, Erol Gulcicek, Thomas Dresch, Bruce Andrien and Shida Shen. Analytica of Branford, Inc., 29 Business Park Drive, Branford, Connecticut 06405.

10:00 ***Improvements to Electrospray and APCI Ion Sources for CE/MS and LC/MS Applications with TOF, Quadrupoles, FTMS, Ion Traps and Magnetic Sector Spectrometers.*** Craig M. Whitehouse, Fred Banks. Erol Gulcicek, Thomas Dresch, Bruce Andrien and Shida Shen. Analytica of Branford, Inc., 29 Business Park Drive, Branford, Connecticut 06405.

10:30 Coffee Break & Exhibition

11:00 ***Uses and Applications of LC Combined with a Mass Detector and Photodiode Array Detector for Component Identification and Quantitation.*** Ken Lykins. Waters Corporation, 34 Maple Street, Milford, Massachusetts, 01757-3696.

11:30 ***Recent Developments in Benchtop LC/MS and LC/MS/MS.*** Leo Raftogianis. PE Sciex Instruments, 850 Lincoln Centre Drive, Foster City, CA 94404.

12:00 ***TBA***, Perseptive Biosystems, Inc., 500 Old Connecticut Path, Framingham, Massachusetts 01710.

12:30 Lunch & Exhibition

- 2:00 *New Developments in Gas Chromatography/Mass Spectrometry.* Joseph Weitzel, Hewlett-Packard.
- 2:30 *GCQ: Breakthrough in GC/MS Technology.* William Schnute. Finnigan MAT, 355 River Oaks Parkway, San Jose, California 95134.
- 3:00 *OPEN ACCESS, A New Era in Mass Spectrometry.* Mark McDowell. Fisons Instruments, Inc., VG Organic, 55 Cherry Hill Drive, Beverly, Massachusetts, 01915-1068.
- 3:30 *A New Angle on Mass Spectrometry.* Mark McDowell. Fisons Instruments, Inc., VG Organic, 55 Cherry Hill Drive, Beverly, Massachusetts, 01915-1068.
- 4:00 Exhibition

### **SYMPOSIUM ON NMR**

Organized by L. Frydman, J. R. Garbow, B. C. Gerstein, J. A. Reimer, H. Thomann, A. J. Vega, R. A. Wind and J. P. Yesinowski

Sponsorship of this Symposium by:

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is gratefully acknowledged.

Monday Morning, July 24, 1995

#### **ORGANIC MATERIALS**

Jeffrey A. Reimer, Presiding

- 8:25 WELCOMING REMARKS. Alexander J. Vega
- 8:30 *New Approaches to Protein Structure Determination by Solid State NMR*, Robert Tycko and David P. Weliky, Laboratory of Chemical Physics, NIDDK, National Institute of Health, Bethesda, MD 20892. (244)

2:00 *NMR Study of the Behavior of Pesticides U*  
Mark Seger, and GarV E. Maciel. Departmer]  
Fort Collins, CO 80523. (251)

2:30 *CFCAlternatives: Characterization ofAdv*  
*Basic Zeolites*, Clare P. Grey. SUNY Stony  
NY 11794-3400. (252)

3:00 BREAK

### NEW PERSPECTIVES ON DATA ACQUISITH

Robert A. Wind, Presiding

3:30 *Noise Spectroscopy in Solid State NMR am*  
Benjamin G.M. Chew, Department of Chemi  
Ithaca, NY 14853. (253)

4:00 *Time-Domain Analysis of Solid-State NMR*  
*Fourier Transform*, Karl T. Mueller and Th<  
The Pennsylvania State University, Univers:'

4:30 *The Effect of Decoupling on Carbon-13 Lit*  
Sachleben. Stefano Caldarelli, and Lyndon F  
of Illinois, Chicago, IL 60607, Section de C  
Lausanne, Switzerland, and Ecole Normale :  
(255)

5.00 *<sup>13</sup>C NMR Relaxation via Paramagnetic Niti*  
Blane Baker and James P. Yesinowski. Nav  
20375-5342. (256)

Tuesday Morning. July 25. 1995

### QUADRUPOLEAR NUCLEI

Lucio Frydman, Presiding

8:30 *Adiabatic Passages for Sensitivity Enhance*  
and Mark S. Conradi. Department of Physic,  
and Department of Physics, Washington Uni  
abstract)

*Soil and Soil Components*, I-Ssuer Chuang,  
of Chemistry, Colorado State University,

*irption Sites for Hydrofluorocarbons in*  
Brook, Chemistry Department, Stony Brook,

#### •N AND ANALYSIS

*NQR*, David B. Zax, Ming-Yuan Liao, and  
Jtry, Baker Laboratory, Cornell University,

*Signals: Isotropic Alternatives to the*  
James P. Jarvie, Department of Chemistry,  
•y Park, PA 16802-6300. (254)

*eshapes in Solid-State NMR*, Joseph R.  
•msley, Department of Chemistry, University  
lime, Universite de Lausanne, CH-1005  
ieperieure de Lyon, 69364 Lyon, France.

*ogen Centers in Synthetic Diamond*, D.  
Research Laboratory, Washington, DC

*ment of Quadrupolar Nuclei*, Jiirgen Haase  
University of Leipzig, Leipzig, Germany,  
'ersity, St. Louis, MO 63130-4899. (no

- 9:00 ***Higher Resolution Through Higher Dimensional Solid-State NMR Experiments***, Ayyalusamy Ramamoorthy, Chin Hsiang Wu, and Stanley J. Opella, Department of Chemistry, University of Pennsylvania, Philadelphia, PA 19104. (245)
- 9:30 A ***CPMASNMR Characterization of the Conducting Polymer Polyaniline***, Matthew Espe, Ben Mattes, and Jacob Schaefer, Department of Chemistry, Washington University, St. Louis, MO 63130, and Los Alamos National Laboratory, Los Alamos, NM 87545. (246)

10:00 BREAK

## INTERFACES

Jeffrey A. Reimer, Presiding

- 10:30 ***NMR and the Overthrow of Zeolite Superacidity***, Japies F. Haw, Larry Beck, David Ferguson, Tom Krawietz, Teng Xu, and John Nicholas, Department of Chemistry, Texas A&M University, College Station, TX 77843, and Pacific Northwest Laboratories, Richland, WA 99352. (247)
- 11:00 ***<sup>29</sup>SUIH and <sup>15</sup>N-H CP/MAS REDOR in Zeolites: A New Way to Characterize Surface Active Sites***, Alexander L. Blumenfeld, Dominique J. Coster, and Jose J. Fripiat, Department of Chemistry and Laboratory for Surface Studies, University of Wisconsin-Milwaukee, Milwaukee, WI 53201.(248)
- 11:30 ***Applications of Xenon NMR in Solids: Chemical Shift Anisotropy***, Igor L. Moudrakovski, Hirokazu Nakayama, Chris. I. Ratcliffe, and John A. Ripmeester, Steacie Institute for Molecular Sciences, National Research Council of Canada, Ottawa, Ontario K1 A 0R6, Canada. (249)

12:00 LUNCH

Monday Afternoon, July 24, 1995

## ENVIRONMENTAL STUDIES

Robert A. Wind, Presiding

- 1:30 ***NMR Determination of Hydrogen Coordinates and Dynamics in Inorganic Solids***, Herman Cho, Robert Maxwell, Donald Stec, and Chaoying Rong, Environmental Molecular Sciences Laboratory, Pacific Northwest Laboratory, Richland, WA 99352. (250)

2:00 *NMR Study of the Behavior of Pesticides in Soil and Soil Components*, I-Ssuer Chuang, Mark Seger, and Gary E. Maciel. Department of Chemistry, Colorado State University, Fort Collins, CO 80523. (251)

2:30 *CFC Alternatives: Characterization of Adsorption Sites for Hydrofluorocarbons in Basic Zeolites*, Clare P. Grey, SUNY Stony Brook, Chemistry Department, Stony Brook, NY 11794-3400. (252)

3:00 BREAK

## NEW PERSPECTIVES ON DATA ACQUISITION AND ANALYSIS

Robert A. Wind, Presiding

3:30 *Noise Spectroscopy in Solid State NMR and NQR*, David B. Zax, Ming-Yuan Liao, and Benjamin G.M. Chew, Department of Chemistry, Baker Laboratory, Cornell University, Ithaca, NY 14853. (253)

4:00 *Time-Domain Analysis of Solid-State NMR Signals: Isotropic Alternatives to the Fourier Transform*, Karl T. Mueller and Thomas P. Jarvie, Department of Chemistry, The Pennsylvania State University, University Park, PA 16802-6300. (254)

4:30 *The Effect of Decoupling on Carbon-13 Lineshapes in Solid-State NMR*, Joseph R. Sachleben, Stefano Caldarelli, and Lyndon Emsley, Department of Chemistry, University of Illinois, Chicago, IL 60607, Section de Chimie, Universite de Lausanne, CH-1005 Lausanne, Switzerland, and Ecole Normale Superieure de Lyon, 69364 Lyon, France. (255)

5:00 *<sup>13</sup>C NMR Relaxation via Paramagnetic Nitrogen Centers in Synthetic Diamond*, D. Blane Baker and James P. Yesinowski. Naval Research Laboratory, Washington, DC 20375-5342. (256)

Tuesday Morning, July 25, 1995

## QUADRUPOLAR NUCLEI

Lucio Frydman, Presiding

8:30 *Adiabatic Passages for Sensitivity Enhancement of Quadrupolar Nuclei*, Jtirgen Haase and Mark S. Conradi. Department of Physics, University of Leipzig, Leipzig, Germany, and Department of Physics, Washington University, St. Louis, MO 63130-4899. (no abstract)

- 9:00 ***A Comparison between  $^{13}\text{C}$  CPMAS and  $^2\text{D}$  CPMAS Experiments***, Shimon Vega.  
Department of Chemical Physics, The Weizmann Institute of Science, Rehovot 76100,  
Israel. (258)
- 9:30 ***Multidimensional NMR Techniques Involving Quadrupolar Nuclei***, Jay Shore.  
Shuanhu Wang, Susan DePaul, Rebecca Taylor, Matthias Ernst, Alexis T. Bell, and  
Alexander Pines, Material Sciences and Chemical Sciences Divisions, Lawrence  
Berkeley Laboratory, and Departments of Chemistry and Chemical Engineering,  
University of California, Berkeley, CA 94720. (259)
- 10:00 BREAK
- GLASSES
- Lucio Frydman, Presiding
- 10:30 ***Investigation of the Mixed Alkali Effect in (Na, Li) Disilicate Glasses by NMR and Conductivity Measurements***, Mark C. Termy. Fatima Ali, A. V. Chadwick, G. N. Greaves, and Mark E. Smith, Physics Laboratory, University of Kent, Canterbury, Kent CT2 7NR, UK, Chemical Laboratory, University of Kent, Canterbury, Kent CT2 7NH, UK, and EPSRC Daresbury Laboratory, Warrington, Cheshire WA4 4AD, UK. (260)
- 11:00 ***Elucidating the Structure of Inorganic Materials: Progress by New and Old Concepts***, Christian Jager. Karin Herzog, Berthold Thomas, Martin Feike, and Hans-Wolfgang Spiess, Max Planck Institute for Polymer Research, D-55021 Mainz, Germany, and Freiberg University of Mining, Institute of Analytical Chemistry, D-09596 Freiberg/Sa., Germany. (261)
- <sup>17</sup>
- 11:30 ***O Dynamic-Angle Spinning NMR Studies of the Structure of Network-Modified Silicate Glasses***, P. J. Grandinetti. P. Florian, K. E. Vermillion, I. Farnan, and J. F. Stebbins, Department of Chemistry, Ohio State University, Columbus, OH 43210, CRPHT, CNRS, 45071 Orleans, CEDEX 2, France, and Department of Geology, Stanford University, Stanford, CA 94305-2115. (262)
- 12:00 LUNCH

Tuesday Afternoon. July 25, 1995

POSTER SESSION

Joel R. Garbow, Presiding

2:00 - 4:30

*Solid State<sup>13</sup>C and<sup>15</sup>N NMR Investigations of Novel Pyridines, Pyrimidines, and their N-Oxides*, Karen L. Altmann, Lawrence H. Merwin, Robin A. Nissan, and William S. Wilson, Chemistry & Materials Branch, Naval Air Warfare Center Weapons Division, China Lake, CA 93555.(263)

*Numerical Simulation of Pulse Sequences in Solid-State NMR*, J. P. Amoureux, C. Fernandez, and Y. Dumazy, Universite de Lille 1, F59655 Villeneuve d'Ascq, France. (264)

*Off-Resonance DOR Nutation Experiments*, J. P. Amoureux, C. Fernandez, and Y. Dumazy, Universite de Lille 1, F59655 Villeneuve d'Ascq, France. (265)

*New 1 and 2D Methods for Double Rotation Experiments*, J. P. Amoureux, C. Fernandez, and Y. Dumazy, Universite de Lille 1, F59655 Villeneuve d'Ascq, France.(266)

*MAS<sup>13</sup>C and DNP-NMR Study of High Temperature Crosslinking in PMR Polyimides*, April H. Baugher, Jon M. Goetz, Matt Espe, Jacob Schaefer, and Ruth H. Pater, NASA Langley Research Center, Hampton, VA 23681, and Department of Chemistry, Washington University, St. Louis, MO 63130.(267)

*NMR Imaging of Water Distributions and Diffusion in Engineered Fibrous Substrates*, Haskell W. Beckham, Wallace W. Carr, Carsten Ftilber, and H. W. Spiess, School of Textile and Fiber Engineering, Georgia Institute of Technology, Atlanta, GA 30332, and Max-Planck-Institut fur Polymerforschung, D-55021 Mainz, Germany. (268)

17

*O NMR Studies of Zeolites*, Ray Dupree, Jay Shore, Young K. Lee, Lucy M. Bull, Sheryl L. Gan, Anthony K. Cheetham, and Alex Pines, Materials Research Laboratory, University of California, Santa Barbara, CA 93106, Department of Physics, University of Warwick, Coventry, CV4 7A1, UK, and Department of Chemistry, University of California, Berkeley, CA 94720. (269)

*A Multiple-Quantum <sup>1</sup>H-NMR Study of Conformational Biasing of Biphenyl in a Nematic Liquid Crystal*, T. Chandrakumar, James M. Poison, and E. Elliot Burnell, Department of Chemistry, University of British Columbia, Vancouver, BC V6T 1Z1, Canada. (270)



***Multi-Nuclear NMR Studies on Biominerals***, B.A. Concannon, P. D. Ellis, A. S. Lipton, R. A. Santos, R. A. Wind, and R. E. Wuthier, Environmental and Molecular Sciences Laboratory, Battelle, Pacific Northwest Laboratories, Richland, WA 99352, and Department of Chemistry and Biochemistry, University of South Carolina, Columbia, SC 29208. (271)

***Sulfur-33 Solid-State NMR with MAS and Cross-Polarization at Low and High Magnetic Field Strengths***, William A. Paunch and Peter L. Rinaldi, Department of Chemistry, The University of Akron, Akron, OH 44325-3601. (272)

***Application of  $^{17}\text{O}$  MAS NMR to Mixed Oxide Gels, Glasses and Perovskite Type Materials***, Peter J. Dirken, Ray Dupree, Mark E. Smith, and Harold J. Whitfield, Physics Laboratory, University of Kent, Canterbury, Kent CT2 7NR, UK, Department of Physics, University of Warwick, Coventry CV4 7AL, UK, CSIRO Division of Materials Science and Technology, Clayton, Victoria 3169, Australia, and Department of Applied Physics, Royal Melbourne Institute of Technology, Melbourne, Victoria 3001, Australia. (273)

13 13

***Measurement of  $^{13}\text{C}$ - $^{13}\text{C}$  Distances in a Solid DNA Using Dipolar Recoupling with a Windowless Sequence (DRAWS)***, David Gregory, Dan Mitchell, Manish Mehta and Gary Drobny, Departments of Chemistry and Physics, University of Washington, Seattle, WA 98195. (274)

***NMR Study of a Thermotropic Liquid Crystalline Polyester and Blends at Elevated Temperatures and Pressures***, Michael B. Gertzler, Morton M. Denn, and Jeffrey A. Reimer, Department of Chemical Engineering, University of California, Berkeley, CA 94720-9989. (275)

***Radial Distributions of  $\text{Li}^+$  Ions in Polyethylene Oxide in a Cylindrical Cavity Imager***, Rex E. Gerald II, Jerome W. Rathke, and Robert J. Klinger, Argonne National Laboratory, Chemical Technology Division, Argonne, IL 60439. (276)

***High-Field Dynamic Nuclear Polarization: Polarization Transfer in a Frozen Aqueous Solution***, Dennis Hall, Gary Gerfen, Lino Becerra, Souheil Inati, Henry Spindler, David Singel, and Robert Griffin, Department of Chemistry and Francis Bitter National Magnet Laboratory, Massachusetts Institute of Technology, Cambridge, MA 02139. (277)

***Distribution of Cesium in Synroc. A Cesium-133 Magic Angle Spinning NMR Study***, J. S. Hartman and E. R. Vance, Department of Chemistry, Brock University, St. Catharines, Ontario L2S 3A1, Canada, and Australian Nuclear Science and Technology Organization, Menai, New South Wales 2234, Australia. (278)

***Structure of Alkali Thioborate  $MjS-Bft$  ( $M=Li, Na, Rb$ ) Glasses Studied by Multi-Nuclear MAS and DOR NMR***, Son-Jong Hwang. D. P. Lang, Jaephil Cho, S. W. Martin, C. Fernandez, J. P. Amoureux, and M. Pruski, Ames Laboratory, and Department of Material Science, Iowa State University, Ames, IA 50011, and Universite de Lille 1, F59655 Villurbanne d'Ascq, France. (279)

***Investigations of the Local Disorder in the AFIMicroporous Framework***, Michael Janicke. Dirk Demuth, Ferdi Schiith, Christian Jager, and Bradley F. Chmelka, Department of Chemical Engineering, University of California, Santa Barbara, CA 93106, Institut fur Anorganische Chemie, Johannes Gutenberg-Universitat, and Max-Planck-Institut fur Polymerforschung, Mainz, Germany. (280)

***A Low Temperature Probe for the Magic Angle Turning Experiment***, Yi Jin Jiang. Anit M. Orendt, Shi Bai, Mark S. Solum, Donald W. Alderman, Charles L. Mayne, Ronald J. Pugmire, and David M. Grant, Departments of Chemistry and Chemical and Fuels Engineering, University of Utah, Salt Lake City, UT 84112. (281)

***Use  $^{31}P$  Solid NMR for the Investigation of the Interfacial Structure of Polyphosphazene-Phosphate Molecular Composites***, William D. Samuels, Li-Qiong Wang, Gregory J. Exarhos, Jami K. Kimble, and Lawrence Carter, Pacific Northwest Laboratory, Richland, WA 99352, University of Colorado, and Xavier University of Louisiana. (282)

***Physico-Chemical Characterization of Creams and Ointments by Diffusion NMR***, W. Kuhn and M. Szayna, Fraunhofer Institute for Biomedical Engineering, Magnetic Resonance Department, D-66386 St. Ingbert, Germany. (283)

***$^{13}C$  NMR Study of Component Dynamics in Aroclor/Polyfvinylethylene) Mixtures***, Kenneth J. McGrath and C. Michael Roland, Naval Research Laboratory, Washington, DC 20375-5342. (284)

***Resource for Solid-State NMR of Proteins***, Ron McNamara. Kathy Valentine, Tai Le, and Stanley J. Opella, Department of Chemistry, University of Pennsylvania, Philadelphia, PA 19104.(285)

***Orientation and Rotation of Axial Ligands in (Porphyrinato)-Iron(III) Complexes***, Konstantin I. Momot. Nikolai V. Shokhirev, Tatjana Kh. Shokhireva, and F. Ann Walker, Chemistry Department, University of Arizona, Tucson, Arizona 85721. (286)

***Heteronuclear Correlation Experiments with High-Resolution for Quadrupolar Nuclei***, Karl T. Mueller. Robert M. Wenslow, and Thomas P. Jarvie, Department of Chemistry, The Pennsylvania State University, University Park, PA 16802-6300. (287)

***A Study of the Molecular Motions in Asphalts Using Variable Temperature Dipolar Dephasing<sup>13</sup>CNMR***, Daniel A. Netzel, Francis P. Miknis, J. Calhoun Wallace, Jr., Clinton H. Butcher, and Kenneth P. Thomas, Western Research Institute, Laramie, WY 82070-3380. (288)

***Transient Intermediates in Solid State Reactions. A Carbon-13 NMR Study of Monosubstituted Bullvalenes***, Raphy Poupko, Klaus Miiller, Herbert Zimmermann, and Zeev Luz, Weizmann Institute of Science, Rehovot 76100, Israel. (289)

***<sup>1</sup>H CRAMPS Spectroscopy of Rigid Solids, Polymers, Transition Metal Complexes, and Clusters***, A. I. Rebrov, S. V. Rykov, and M. P. Filatova, Institute of Petrochemical Synthesis, Russian Academy of Sciences, 117912 Moscow, Russia. (290)

***Study of<sup>69</sup>Ga Overhauser Effect by Direct NMR Detection in Optically Pumped GaAs***, H Room, E. L. Hahn, T. PietraB, Y.-Q. Song, and A. Pines, Departments of Physics and Chemistry, University of California, Berkeley, CA 94720. (291)

***Solid and Liquid State NMR Studies of the R3230AC Mammary Adenocarcinoma in Model Fischer Rats***, R.A. Santos, B. A. Concannon, K. M. Groch, D. N. Rommereim, and R. A. Wind, Pacific Northwest Laboratories, Richland, WA 99352. (292)

***Analysis of the Temperature Dependence of the <sup>1</sup>H Contact Shifts in Model Hemes and Heme Proteins: Explanation of "Curie" and "Anti-Curie" Behavior within the Same Molecule***, Nikolai V. Shokhirev and F. Ann Walker, Chemistry Department, University of Arizona, Tucson, Arizona 85721. (293)

***Multiple-Quantum NMR of Methyl- and Chloro-Benzene in a Nematic Liquid Crystal***, Raymond T. Syvitski and Elliot Burnell, Department of Chemistry, University of British Columbia, Vancouver, B. C. V6T 1Z1, Canada. (294)

11 27

***B- Al Double Resonance NMR on Alumoborate Glasses***, Leo van Wiillen, Lars Ziichner, and Hellmut Eckert, Department of Chemistry, University of California, Santa Barbara, CA 93106, and Institut fur Physikalische Chemie, Universitat Minister, Germany. (295)

***Spectral Editing of<sup>69</sup>F-<sup>13</sup>C CPMAS Spectra***, Stephanie A. Vierkotter and Edward W. Hagaman, Chemical and Analytical Science Division, Oak Ridge National Laboratory, Oak Ridge, TN 37831.(296)

***A High Resolution Solid State<sup>13</sup> C NMR Investigation of the Local Chain Dynamics of Compatible Blends of Polystyrene and Poly(vinylmethylether)***, Todd A. Wagler, Peter L. Rinaldi, and Chang D. Han, The University of Akron, Akron, OH 44325-3601. (297)

*Investigation of the Structure and Dynamics of Surfactant Molecules During Nucleation of Mesophase Silicates Using Solid-State NMR*, Li-Qiong Wang, Jun Liu, Rodolfo A. Santos, and Anthony Y. Kim, Pacific Northwest Laboratories, Richland, WA 99352. (298)

*<sup>7</sup>Li Solid State NMR Study of Nonlinear Optical Materials  $Lil-xNbl-xW_03$* , Yin Xia, Leo van Wiillen, Xuehua Wu, Charles Lakeman, Hellmut Eckert, Fred Lange, and Stan Anderson, Chemistry Department and Materials Department, University of California, Santa Barbara, CA 93106, and Westmont College. (299)

*Molecule Structure and Dynamics of Coal at High Temperature and under Solvent Saturation as Studied by <sup>1</sup>H CRAMPS*, Jincheng Xiong and Gary Maciel, Chemistry Department, Colorado State University, Fort Collins, CO 80523. (300)

*NQR, NMR and SQUID Detection of <sup>14</sup>N and <sup>35</sup>Cl Cocaine Base and Hydrochloride*, James P. Yesinowski, Michael L. Buess, Allen N. Garroway, Marcia Ziegeweid, and Alexander Pines, Chemistry Division, Naval Research Laboratory, Washington, DC 20375-5342, SFA, Inc., Landover, MD 20875, and Materials Sciences Division, Lawrence Berkeley Laboratory and Department of Chemistry, University of California, Berkeley, CA 94720. (301)

*<sup>13</sup>C Chemical Shift Principal Values in an Analogous Series of Heterocyclic Aromatic Compounds*, Wei Wang, D. W. Alderman, Mark S. Solum, Ronald J. Pugmire\* and David M. Grant, Department of Chemistry and Chemical and Fuel Engineering\*, University of Utah, Salt Lake City, UT 84112. (302)

*<sup>13</sup>C Dipolar Spectrum of Matrix Isolated Benzyne-1,2-<sup>13</sup>C*, Anita M. Orendt, J. G. Radziszewski, J. C. Facelli, J. Michl\* and D. M. Grant, Department of Chemistry, University of Utah, Salt Lake City, UT 84112 and \*Department of Chemistry and Biochemistry, University of Colorado, Boulder, CO 80309. (303)

Tuesday Evening, July 25, 1995

## VENDOR SESSION

Bernard C. Gerstein, Presiding

7:30 - 8:30

Posters presented by:

AMT, Jim Lukes and Lowell Beezlev, 3080 Enterprise Street, Brea, CA 92621

Bruker Instruments, Manning Park, 19 Fortune Drive, Billerica, MA 01821-3911.

Chemagnetics/Otsuka Electronics, Cindy Ridenour. 2555 Midpoint Drive, Fort Collins, CO 80525.

Doty Scientific, Bruce Scruggs. 700 Clemson Road, Columbia, SC 29223.

JEOL USA, William H. Bearden. 11 Dearborn Road, Peabody, MA 01960.

Oxford Instruments, Adrew J. Tucker. Scientific Research Division, 130a Baker Avenue Extension, Cocord, MA 01742.

Varian, Laima Baltusis. Nuclear Magnetic Resonance Instruments Division, 3120 Hansen Way, M/S D-300, Palo Alto, CA 94304-1030

Wednesday Morning, July 26, 1995

### **ROBERT W. VAUGHAN MEMORIAL SYMPOSIUM**

Alexander J. Vega, Presiding

8:30 **R. W. Vaughan Lecture - *Chemical Shift Tensor Measurements and their Utility in the Three Dimensional World of Chemistry***, David M. Grant. J. C. Facelli, D. W. Alderman, R. J. Iuliucci, W. Wang, M. S. Solum, F. Liu, and C. Phung, Department of Chemistry, University of Utah, Salt Lake City, UT 84112. (304)

9:30 ***Connectivities and Cation Distributions in Glasses: Solid State NMR Studies***, Hellmut Eckert. Becky Gee, Leo van Wiillen, Lars Ziichner, and Werner Muller-Warmuth, Institut fur Physikalische Chemie, Westfalische Wilhelms-Universitat Minister, D-48149 Miinster, Germany. (305)

10:10 BREAK

10:40 ***Solids NMR of Complex Mixtures and Macromolecules: Spectral Editing and 2D NMR of Uniformly Labeled Molecules***, Sean Burns, Anil Mehta, Xiaoling Wu, Matthew P. Augustine, Brett Tounge, Iwen Wu, and Kurt W. Zilm. Department of Chemistry, Yale University, New Haven, CT 06511. (306)

11:20 ***Chemical Shifts and Distributions of Rare Gas Clusters in Zeolites***, Cynthia J. Jameson. University of Illinois at Chicago, Chicago, IL 60607-7061. (307)

12:00 LUNCH

Wednesday Afternoon. July 26. 1995

## FLUID DYNAMICS

Hans Thomann, Presiding

- 1:30 *Study of Molecular Transport within Microporous Solids by MRM*, George D. Cody, Rex E. Gerald II, and Robert E. Botto. Chemistry Division, Argonne National Laboratory, Argonne, IL 60439. (308)
- 2:00 *NMR Imaging of Pore Structures and Liquid Flow Paths in Porous Media*, Donald E. Woessner. The University of Texas Southwestern Medical Center at Dallas, Rogers Magnetic Resonance Center, Dallas, TX 75235-9085. (309)
- 2:30 *High-Volume Fraction Suspension Flows Studied by NMR Imaging*, Steve W. Sinton, Andrea W. Chow, and Joseph H. Iwamiya, Lockheed, Palo Alto, CA 94304-1191. (310)
- 3:00 BREAK
- 3:30 *MR Imaging of the Heart: From Flow to Perfusion*. Michael Jerosch-Herold and Norbert Wilke, Department of Radiology, University of Minnesota, Minneapolis, MN 55455.(311)
- 4:00 *How are Molecules Displaced and Reoriented in Thin Surface Layers? A Field-Cycling Relaxometry and Field-Gradient Diffusometry Study*, Rainer Kimmich and Siegfried Stapf, Universitat Ulm, Sektion Kernresonanzspektroskopie, 89069 Ulm, Germany. (312)
- 4:30 *In Vivo and In Vitro Investigation of Human Skin by NMR Microscopy: Uptake of Different Ointments into the Skin*, M. Szayna and W. Kuhn, Fraunhofer Institut fur Biomedizinische Technik, D-66386 St. Ingbert, Germany. (313)

Thursday Morning. July 27. 1995

## NEW TECHNIQUES

James P. Yesinowski, Presiding

- 8:30 *Multidimensional NMR Correlations on Quadrupolar Nuclei*, Ales Medek, Joseph R. Sachleben, John S. Harwood, and Lucio Frydman. Department of Chemistry, University of Illinois at Chicago, Chicago, IL 60607. (314)

- 9:00 ***Molecular Dynamics in a <sup>19</sup>F-Labeled Polycarbonate***, J. M. Goetz, J. H. Wu, A. F. Yee, and J. Schaefer, Department of Chemistry, Washington University, St. Louis, MO 63130, and Materials Science and Engineering, University of Michigan, Ann Arbor, MI 48109. (315)
- 9:30 ***Measurement of <sup>13</sup>C-<sup>13</sup>CDipolar Couplings by MAS NMR***, Terry Gullion and Joel R. Garbow, Department of Chemistry, Florida State University, Tallahassee, FL 32306, and Monsanto Corporate Research, Monsanto Company, St. Louis, MO 63198. (316)
- 10:00 BREAK

## INORGANIC MATERIALS

James P. Yesinowski, Presiding

- 10:30 ***Xenon NMR in Pores: Observations on Chemical Shifts as a Function of Temperature***, Yong-Wah Kim, Douglas M. Smith, and William L. Earl. Quantum Magnetics, San Diego, CA 92121, Department of Chemical Engineering, University of New Mexico, Albuquerque, NM 87131, and Chemical Science and Technology Division, Los Alamos National Laboratory, Los Alamos, NM 87545. (317)
- 11:00 ***Inorganic Glass Structure from NMR Shifts and Lineshapes***, Josef W. Zwanziger. Department of Chemistry, Indiana University, Bloomington, IN 47405. (318)
- 11:30 ***NMR Measurement of Weak Homonuclear Indirect Couplings in GaAs***, Larry D. Potter and Yue Wu. Department of Physics and Astronomy, University of North Carolina, Chapel Hill, NC 27599-3255. (319)

**SYMPOSIUM ON PHARMACEUTICAL ANALYSTS**

Organized by Robert K. Lantz, Patricia L. Sulik and Michael Cutrera

Tuesday, July 25, 1995

8:25 Opening Remarks

8:30 ***Characterization of Protein Secondary Structures Using Fourier Transform Infrared Spectroscopy.*** Aichun Dong, Pin Huang, Winslow S. Caughey and John F. Carpenter, Department of Pharmaceutical Sciences, School of Pharmacy, University of Colorado Health Center, Denver, CO 80262 and Department of Biochemistry and Molecular Biology, Colorado State University, Fort Collins, CO 80523. (320)

8:50 ***Karl Fischer Moisture Analysis of Chemical and Pharmaceutical Product- Tips, Tricks and Techniques.*** Andreas Dietrich, Hoechst Celanese Corp., Bucks, AL. (321)

10:30 Break

10:50 ***In Vivo and in Vitro Investigation of Human Skin by NMR Microscopy: Uptake of Different Ointments into the Skin,*** M. Szayna and W. Kuhn, Fraunhofer-Institute fur Biomadizinische Technik, Ingbert, Germany. (322)

11:20 ***Physico-chemical Characterization of Emulsions by NMR Techniques.*** W. Kuhn and M. Szayna, Fraunhofer Institute fur Biomedizinische Technik, Ingbert, Germany. (323)

11:40 ***Analysis of AMT, a Toxic AZT metabolite, by HPLC/MS.*** Robert K. Lantz and Patricia L. Sulik, Rocky Mountain Instrumental Laboratory, Ft. Collins, CO. (324)

12:00 LUNCH

1:30 ***Stabilization of Proteins During Freezing and Drying.*** John Carpenter, School of Pharmacy, UCHSC, Denver, CO. (325)

2:15 ***Bile Acids and Steroid Hormones in Women with Cholestasis of Pregnancy.*** Adrian Pike, Paul Fennessy, Kim Leslie, Dept. of Pediatrics, UCHSC, Denver, CO. (333)

2:35 ***Sample Preparation for FTIR.*** Robert Dyce, Midac Corporation, Irvine, CA. (327)

3:30 Break

3:45 ***HPLC/MS/MS in Real World Pharmaceutical Analysis.*** Alan Breau, Perkin Elmer Sciex, Foster City, CA. (no abstract)



## **SYMPOSIUM ON QUALITY ASSURANCE**

Organized by William J. Shampine

Wednesday, July 26, 1995

- 8:55 Introduction, W. J. Shampine
- 9:00 ***Implementing a Quality Assurance Plan for the Ethanol Project at the National Renewable Energy Laboratory.*** D. W. Templeton, C. I. Ehrman, R. O. Ruiz, and J. S. Brigham, National Renewable Energy Laboratory, Golden, CO. (329)
- 9:25 ***A Quality Assurance Program for In-Situ Radiological Surveillance.*** P. D. Fledderman and M. M. Khalil, Westinghouse Savannah River Company, Aiken, SC. (330)
- 9:50 ***IPEP - The Integrated Performance Evaluation Program for the Department of Energy's Office of Environmental Management.*** P. C. Lindahl, W. E. Streets, D. A. Bass, P. L. Johnson, J. J. Marr, A. E. Scandora, Jr., J. E. Hensley, and K. J. Parish, Argonne National Laboratory, Argonne, IL. (331)
- 10:15 ***Common Noncompliance Issues Within Laboratories That Conduct Testing for National Pollutant Discharges Elimination System Permitted Parameters.*** Jimmy L. Seidel, U.S. EPA-NEIC, Denver, CO. (332)

**SYMPOSIUM ON RADIOCHEMISTRY**

This symposium has been canceled for 1995 due to the current annual meeting of the Health  
Physics Society in Boston.  
We regret any inconvenience this may have caused.

**SYMPOSTUM ON ROBOTICS**

This symposium will not be held in 1995 due to a lack of presenters.  
We regret any inconvenience this may have caused.

- 1 NEW SOURCES AND DETECTION SYSTEMS FOR ATOMIC MASS SPECTROMETRY.** Gary M. Hieftje, Thomas W. Burgoyne, Gangqiang Li, Patrick P. Mahoney, Steven J. Ray, Department of Chemistry, Indiana University, Bloomington, IN 47405.

Plasma source mass spectrometry, usually embodied as inductively coupled plasma-mass spectrometry (ICP-MS), still suffers from a number of shortcomings, the most prominent among which are limited precision, the existence of isobaric overlaps caused by polyatomic species, difficulty in handling transient samples, and high cost. In large part, these limitations can be overcome by new sources and mass-spectrometer designs. In this presentation, several such alternatives will be explored. Among the sources to be discussed are a novel tandem arrangement that couples an electrospray system with a microwave-induced plasma and another that utilizes a magnetic field in conjunction with a radiofrequency glow discharge. Applicable to liquid and solid samples, respectively, these two sources offer an abundance of features that are not available from an ICP. Greatest emphasis on mass-spectrometer design will be placed on the performance of a time-of-flight mass spectrometer. Such a device has already yielded detection limits, in a truly simultaneous multielement mode, that rival those of commercial instruments (parts per trillion), precision that is limited only by counting statistics and therefore by the patience of the operator, and resolution that cannot be attained by quadrupole-based mass spectrometers. Being inherently a high-speed form of mass spectrometry, the new device is especially attractive when coupled with flow injection, chromatographic elution, laser ablation, or electrothermal atomization.

- 2 HIGH RESOLUTION ICP-MS FOR ACCURATE DETERMINATION OF ELEMENTAL AND ISOTOPIC COMPOSITION OF TRACE AND ULTRATRACE ELEMENTS.** M.J. Allen, C.B. Pouthitt, M.P. Schmidt, Finnigan MAT, 355 River Oaks Parkway, San Jose, CA 95134

Despite the enthusiastic reception afforded quadrupole ICP-MS (Q-ICP-MS) by the analytical chemistry community, the advantageous characteristics of atmospheric plasma ionization with respect to quantitative multi-element or isotopic analysis are significantly deteriorated by the limited resolving power of quadrupole analyzers, -unit resolution across the mass range. Spectral Interferences from polyatomic or multiply-charged species pose major limitations to precise and accurate measurement of many elements. A novel high resolution ICP-MS mass spectrometer (HR-ICP-MS, Finnigan MAT model ELEMENT) overcomes many of the problems inherent in Q-ICP-MS by using a double focussing-magnetic sector analyzer which allows routine use of variable resolution (R=300,3000,7500). The system has found immediate applications for accurate analysis of the trace and ultratrace element composition of natural and industrial waters, and industrial chemicals. In conjunction with HPLC, the ELEMENT holds considerable promise for studying elemental speciation. UV laser ablation in conjunction with HR-ICP-MS allows *in situ* ppb level elemental and isotopic analysis of solids, it is expected that HR-ICP-MS will complement Q-ICP-MS as an analytical tool, and will find a place alongside the electron microprobe and the ion probe as an indispensable tool in materials characterization. Because the front end is at ground, it is relatively straightforward to port alternative ion sources onto the analyzer of the ELEMENT (e.g. GD, TIMS, MIP), it is envisioned that researchers will develop novel high resolution instruments based on the platform of the ELEMENT.

**3 THE USE OF ICP-AES AND ICP-MS IN ONE INSTRUMENT: POEMS (PLASMA OPTICAL EMISSION AND MASS SPECTROMETER). John Schmelzel, Ke Hu, Garry Kunselman, and John Sotera, Thermo Jarrell Ash, 8E Forge Pkwy., Franklin, MA 02038**

The objective of this work is the construction of an ICP sequential in which a detector for optical emission (ICP-AES) and a quadrupole for the detection of positive ions (ICP-MS) operate simultaneously. This paper will describe modifications to the plasma, the sampler cone and the structure of the software in order to take advantage of the dual detector type instrument. Environmental and biological reference materials will be analyzed as analytical models in order to prove the viability of the technique. In these real world samples, some elements may be found in high concentrations, requiring dilution prior to analysis on an ICP instrument employing a MS detection system only. This often requires the pre-screening and possibly the pretreatment of samples prior to introduction. By shielding the MS cones from the sample and performing an emission measurement of the sample, the POEMS instrument allows the software to determine the optimum analysis mode for the sample. For example:

1. Unknown concentrations: AES analysis, intelligent dilution, MS analysis.
2. High, medium and trace concentrations: AES analysis, preset dilution, MS analysis.
3. Medium and trace concentrations: simultaneous AES and MS analysis.
4. Low and trace concentrations: MS analysis only.
5. High and medium concentrations: AEA analysis only.

In this manner optimum sample throughput may be maintained without operator intervention.

**4 THE USE OF A DUAL AXIAL AND RADIAL VIEW ICP-OES SPECTROMETER FOR THE ANALYSIS OF ENVIRONMENTAL SAMPLES. Randy L. Hergenreder and Marc A. Paustian, Perkin-Elmer Corporation, 761 Main Ave M/S 695 & 200, Norwalk, CT 06859**

An ICP optical emission spectrometer which is capable of both radial and axial viewing of the plasma is used for the analysis of trace and major elements in environmental samples. Axial viewing improves detection limits by an order of magnitude over radial viewing. This allows the analysis of trace elements such as As, Se, TL and Pb at levels approaching graphite furnace detection limits. The radial view allows higher levels of major elements to be analyzed with minimal dilution's. The unique optical system and detector gives the analyst choices of less sensitive wavelengths to extend the upper working range to even higher concentrations. Detection limits, linearity and long term stability data will be presented.

**OPTIMIZATION OF OPERATING CONDITIONS FOR AN AXIALLY-VIEWED ICP TORCH; Geoffrey N. Coleman, G.H. Gower, C.J. Harris, M. O'Boyle, R. Starek; Fisons Instruments Elemental Analysis, 55 Cherry Hill Drive, Beverly MA 01915.**

Both published and anecdotal reports indicate that while axial viewing of an ICP torch offers improved limits-of-detection, interferences are more significant than when traditional radial viewing is employed. The use of an argon (or even air) "knife" or counter flow has been found to be effective in removing ground state atoms from the optical path, thereby minimizing non-linearity due to self-absorption. However, systematic studies of power, outer argon flow, and aerosol carrier velocity indicate that there are significant differences between conditions which provide low detection limits and those which offer the greatest immunity from matrix interferences: high power density and low injection velocity have been found to be most effective. Unfortunately, the resulting temperatures diminish the lifetime of typical quartz torches, but a silicon nitride outer (plasma containment) tube provides an exceptionally effective solution.

- 6           INDUCTIVELY COUPLED ARGON PLASMA AXIAL VIEWING ABSORPTION WITH ELECTROTHERMAL VAPORIZATION SAMPLE INTRODUCTION, **Gary D. Ravson** and **Carl A. Hensman**, Department of Chemistry and Biochemistry, New Mexico State University, Las Cruces, NM 88003

The inductively coupled argon plasma (ICAP) is an efficient source for the atomization and subsequent excitation of metals in a variety of samples. It is this same feature that results in one of the greatest difficulties in its application to the determination of trace components of a metal-rich sample, spectral interferences. One approach to the minimization of spectral interferences is to engage in often labor intensive procedures to physically separate the trace components from the bulk of the sample matrix (which is the source of the interfering emission lines). An alternate approach, which has been pursued in our laboratory, is the utilization of atomic absorption for the detection of the ground-state species generated within the plasma discharge. This involves the axial viewing of the sample introduction channel of the plasma while modulating the amplitude of the applied rf power. Through the use of time-gated acquisition, atomic absorption measurements can be made exhibiting maximum signal-to-noise and signal-to-background (emission). Recently, electrothermal vaporization has been investigated as a method of introduction of the sample vapor into the discharge. The progress of these efforts will be described and its implications for the development of this detection scheme for the analysis of complex samples will be discussed.

- 7           RADIO FREQUENCY POWERED GLOW DISCHARGES: WHOSE PROBLEMS CAN THEY SOLVE?. **R. Kenneth Marcus**, Department of Chemistry, Howard L. Hunter Chemical Laboratories, Clemson University, Clemson, SC 29634-1905 USA

The area of direct solids, spectrochemical analysis is receiving a great deal of interest. Of the commercially available options, the rf glow discharge has the fundamental advantage of permitting direct analysis of both conductive and nonconductive sample types, but this is not its sole redeeming point. In both AES and MS operation modes, substantial increases in analyte signal-to-background and temporal stability have led to better precision and lower detection limits than its d.c. counterpart as well as the historically accepted arc/spark emission methods. Given the long history of these more "conventional" sources, use of the rf-GD is not a matter of fad, but one of pragmatism. At the end of the day one must ask which problems have been solved and at what cost. This presentation focus on the pragmatic implementation of radio frequency powered glow discharges in atomic emission and mass spectrometry. Figures of merit for *real world* analyses and demonstration of the wide applicability of the devices will be described. Examples will include bulk and depth resolved analyses of high purity metals, glasses, and various other types of bulk samples. An additional application in the area of direct analysis of bulk and layered polymer materials will be presented. It is hoped that such examples will expand the listener's minds to include a much broader spectrum of solids analyses.

- 8           ELEMENTAL ANALYSIS OF SOIL SAMPLES BY LASER INDUCED BREAKDOWN SPECTROSCOPY, Terry L. Thiem, Slava Dementiev, James H.S. Melville, and Hayward S. Melville, *Technical Assistance International*, 1320 Loma Verde, El Paso, TX 79936; Andrei F. Kotyuk and Michael Ulanovskiy, *MeLAOK, Inc.*, Moscow, Russia.

Soil chemistry is very important in determining the environmental impact from contamination from a spill or underground storage tank. The usual analytical procedure for elemental analysis is acid digestion or acid leaching of the sample followed by elemental analysis by atomic absorption spectroscopy (AAS), either flame or graphite furnace, inductively coupled plasma (ICP), or inductively coupled plasma-mass spectroscopy (ICP-MS). In this study elemental analysis is performed on soil, soil/sand mixtures, and sand previously spiked with varying concentrations of aqueous and oil elemental standards using laser induced breakdown spectroscopy. The MA 5095 laser microanalyzer will be tested on its ability to perform elemental analysis of these samples. Spectra, detection limits, and the ability of the instrument to perform multi-element analysis will be discussed.

IMPROVED THERMAL STABILITY FROM COMPOSITE MATERIALS ENHANCES RELIABILITY OF SEQUENTIAL ICP MEASUREMENTS. Geoffrey N. Coleman, G.H. Gower, C.J. Harris, Fisons Instruments Elemental Analysis, 55 Cherry Hill Drive, Beverly MA 01915.

Thermal stability is one of the most emphatic determinants of analytical stability in ICP-AE spectrometry. The lowering of thermally-induced wavelength shifts can allow improved analytical accuracy to be achieved. Calibration drift can be significantly improved by sensible design, providing the analyst with higher sample throughput, and higher confidence in the results produced.

Our objective in this study was to retain the desirable optical and thermo-mechanical characteristics of a traditional Czerny-Turner spectrometer with a 1.0m focal length, while achieving a weight reduction of 85%. Tactics for the selection of high-tech composite materials are quite different from those inherited from traditional methods of spectrometer design and manufacture.

Our test program utilized a purpose-built environmental chamber in which a traditional ICP-AE spectrometer was used as a reference bench mark for optical and analytical stabilities. With this tool we were able to quickly establish the adequacy of alternate designs, and to speed the development of the final structure.

In this paper we will present the results of this study of optical and analytical stability of the new spectrometer, with comparison to those achieved with a spectrometer of a more traditional design.

10 DEPTH-RESOLVED ANALYSIS OF METALLIC AND INSULATING LAYERS BY RF GLOW DISCHARGE ATOMIC EMISSION SPECTROMETRY. Mark Parker and R. Kenneth Marcus. Department of Chemistry, Howard L. Hunter Chemical Laboratories, Clemson University, Clemson, SC 29634-1905 USA

The ability of the radio frequency glow discharge (rf-GD) to sputter-atomize insulating materials such as oxides and polymers is an important characteristic for depth-resolved analyses. Materials are often coated with thin films or contain distinct layers for a variety of reasons. These may be to resist corrosion, provide electrical isolation, reduce friction, or provide a protective optical layer. These layers may be dysfunctional if contaminated or improperly manufactured and thus their correct composition and structural determination are critical. The rf-GD-AES can meet these requirements as no sample dissolution, or loss of spatial integrity of the analyte, is required prior to analysis. In this presentation, preliminary evaluation of the operating characteristics of a new rf-GD-AES system employing a Jobin-Yvon (Longjumeau, France) J-Y 5000 RF polychromator will be described. The combination of the rf-GD source and a new high dynamic range detector (HDD) system permits the rapid analysis of almost any layered material regardless of the concentration range and distribution of the analytes. The data presented here will illustrate the effects of operating parameters on profile quality and the advantages of rf-GD-AES analysis for several layered systems.

- 11 LOCAL THERMODYNAMIC EQUILIBRIUM SIMULATION OF CHEMICAL PROCESSES WITHIN A GRAPHITE FURNACE ATOMIZER, Gary P. Rayson and Kowitz, Department of Chemistry and Biochemistry, New Mexico State University, Las Cruces, NM 88003

The graphite furnace atomizer used in atomic absorption spectrometry enables the determination of ultratrace concentrations of metals in micro-sized samples. However, the complex chemistry occurring within this semi-enclosed graphite tube often requires that the sample matrix be modified to enable the realization of minimal sample-dependent variations in the resulting analytical signal(s). The list of chemical modifiers reported in the literature is nearly as varied as samples analyzed and the metals determined. The present study attempts to understand the potentially complex gas-phase chemical environment within the graphite furnace during the thermal pretreatment (i.e., ash, char, or pyrolysis) stage of the furnace temperature program. This is being accomplished by applying the assumptions of local thermodynamic equilibrium and diffusion controlled mass transport within the atomizer during that relatively long-lived stage. Free energy minimization calculations of the gas-phase composition of separate segments of the furnace volume are undertaken. These calculations utilize a data base of possible species numbering more than 5000. The calculation of diffusion-controlled mass transport between adjacent segments followed by the recalculation of the "new" equilibrium composition enable the simulation of the environment within the graphite furnace atomizer. The mechanics of this simulation will be described and the implications of these investigations on the selection of chemical matrix modifier(s) for analyses will be discussed.

- 12 REDUCING ORGANIC SOLVENTS IN WEAR METALS IN OIL ANALYSIS USING EMULSIONS AND INDUCTIVELY COUPLED PLASMA SPECTROSCOPY, Terry L. Thiem, Jeff Watson, Department of Chemistry, HQ USAFA/DFC, 2354 Fairchild Dr. Suite 2A21, USAF Academy, CO 80840.

Wear metals, especially transition metals, are key indicators of the condition of specific components within an engine, whether it be a car, truck, or jet. Determination of these elements can greatly reduce the chance of engine failure. Traditionally this is done by atomic absorption spectroscopy (AAS) or inductively coupled plasma (ICP) with organic solvent dilution with MIBK, xylene, or kerosene. This, however, creates a large quantity of organic waste that is expensive to dispose. Several groups have used acid extraction with emulsions with great success. In the study, 21 elements are determined from a 300 µg/g base oil solution using ICP. Extraction efficiencies with HCl, HNO<sub>3</sub>, H<sub>2</sub>SO<sub>4</sub> will be discussed. Application of this method on "real world" samples will also be presented.

- 13 LIQUID CHROMATOGRAPHIC SEPARATION AND CHARACTERIZATION OF INORGANIC COLLOIDS. J.P. Wilcoxon, and S. Craft, Sandia National Laboratories, Mail Stop 1421, P.O. Box 5800, Albuquerque, NM 87185-1421.

Liquid Chromatographic methods have traditionally focused on separation and analysis of organic molecules, including polymers. Recently developed techniques for the controlled synthesis of inorganic colloids, both metals and semiconductors, using inverse micelles have created novel separation and characterization requirements. Inorganic colloids are tiny chunks of solid matter and have physical properties and dimensions which cannot be analyzed only using the techniques available to solid state physics (e.g. HRTEM, SAD, etc.). They range in size from a few atoms to many thousands of atoms. At the lower range of this size scale they behave much like big molecules. We show that LC separation of both metal and semiconductor colloids can be achieved using both traditional SEC columns and bonded phase columns. Size analysis using SEC can complement HRTEM and scattering methods of analysis as we demonstrate. The surface specific adhesion properties of various bonded phase columns are particularly useful in elucidating differences in colloid surface structure. We use PDA, conductivity, luminescence, and refractive index to characterize the properties of the purified colloids. Some of our most interesting findings include size quantization effects of the band-gap of nanosize FeS<sub>2</sub>, MoSe<sub>2</sub>, determination of colloid surface charge, and the effect of colloid size on the plasmon resonance in gold and silver colloids. An extremely novel luminescence is demonstrated for the smallest (molecular-size) noble metal colloids investigated.

## 14    **CAPILLARY ION ANALYSIS OF ANIONS, ORGANIC ACIDS AND CATIONS IN CIRCUIT BOARD EXTRACTS**

**STUART A. OEHRLE**  
Waters Corporation  
34 Maple St Milford, MA 01757

Analysis of ions (cations, anions and organic acids) in circuit board extracts is important in the electronics industry as far as overall board performance. Analysis of these ionic compounds was accomplished by capillary ion analysis (CIA) in less than 8 minutes. CIA is a capillary electrophoretic technique which is optimized for the rapid analysis of low-molecular weight inorganic and organic ions. Indirect UV detection at 254 nm or direct UV detection at 185 nm was used throughout. An electroosmotic flow modifier (OFM) was added to the electrolyte for anion and organic acid analysis. For anion analysis two different electrolytes were investigated, chromate and phosphate. Simultaneous analysis of organic acids and anions in a variety of circuit board extracts was investigated using both electrolytes. Cation analysis was done using a UV Cat-2 electrolyte with indirect UV detection at 185nm. Using a hydrostatic injection technique low part-per-million (ppm) to mid part-per-billion (ppb) levels could easily be detected for both anion and cation analysis.

- 15    **DETERMINATION OF DRUG-PROTEIN INTERACTIONS BY HPLC.** Philip B. Graham,  
Metasyn Inc., 71 Rogers Street, Cambridge MA 02142

The binding of pharmaceuticals to Human Serum Albumin was investigated using size-exclusion HPLC. The drug and protein of interest are injected into a mobile phase containing low levels of the drug. Results from this study, along with an example of how this technique can be used to measure drug-drug interactions, will be presented.

- 16    **SOLVING COMMON HPLC DETECTION PROBLEMS WITH THE EVAPORATIVE LIGHT  
SCATTERING DETECTOR.** Inga Henderson. Donna Young, Alltech Assoc. Inc., 2051  
Waukegan Road, Deerfield, Illinois, 60015.

Evaporative light scattering detection (ELSD) is gaining popularity for the HPLC detection of many difficult analytes. The versatile ELSD detects any sample less volatile than the mobile phase, eliminating common problems with RI and UV detection. The ELSD's response does not depend on the samples optical characteristics, detecting any compound in the sample, regardless of its functional groups. Non-chromophoric compounds are detected even at low concentrations, and nearly equivalent response factors for all sample types gives a closer representation of sample composition. Unlike RI and low-wavelength UV, the ELSD uses multisolvent gradients for improved resolution and faster separations. The ELSD produces a stable baseline signal and does not respond to ambient temperature changes. The ELSD provides a better signal to noise ratio and therefore greater sensitivity than an RI detector. The solvent front, which commonly interferes with RI detection is also eliminated with ELSD detection. The unique method of detection is the key to the ELSD's versatility and performance. The ELSD nebulizes the column effluent into a fine mist. The mist passes through a heated drift tube, where the mobile phase is evaporated. Laser light is scattered by the remaining sample particles in the flow cell. A wide range of applications including, surfactants, underivatized amino acids, phospholipids, pharmaceuticals, triglycerides, and carbohydrates will be shown demonstrating the utility of the ELSD. With the evaporative light scattering detector many common HPLC problems are solved.



- 17** AN OVERVIEW OF COMPOSTING PROBLEMS. George 3. Willson. George B. Willson Associates. 407 N. Lincoln Ave.. No. 103. Love I and. Colorado. 80537.

Although composting is widely perceived as an environmentally friendly activity, as soon as serious efforts get underway to site a project, the NIMBY's (Not In My Back Yard) get to work. Favorite concerns are odors, *Aspergillus Fumigatus*. truck traffic, and noise. Once a composting facility gets into operation, another set of problems are apt to plague the operator including: 1. Marketing 2 Problems with the initial mix. usually moisture content and porosity or nutrient balance. 3. Problems with the aeration system or its control system. 4. Meeting the requirements of the EPA's 503 regulations for pathogen survival and vector attraction reduction.

- 18** PLACEMENT AND SEASONAL EFFECTS ON PERFORMANCE OF DEGRADABLE PLASTIC BAGS IN YARD WASTE COMPOST. P.E. Aeschleman. M.A. Cole. Dept. of Agronomy, 1102 S. Goodwin, Univ. of Illinois, Urbana, IL 61801.

Previous work indicated that slow fragmentation of some bags interfered with timely composting because conditions within the compost were not conducive to plastic degradation. Circumstantial evidence suggested that the polyethylene bags—regardless of whether they were labeled as photo- or bio-degradable—would disintegrate only when exposed on the compost surface, but not when buried in the compost. The purpose of this work was to determine whether or not buried vs. surface exposure and climatic conditions affected degradation. An outdoor study with windrows 4.9 m long, 1.5 m high, and 2.5 m wide was conducted to determine the time required for fragmentation of 13 formulations of commercially available and experimental bags when they were buried or exposed on the compost surface. Experiments were begun in early April (Spring) or early June (Summer) to assess the impact of weather conditions on the time required for fragmentation. None of the bags fragmented when buried in compost, whereas most materials fragmented in 12 to 60 d when placed on the compost surface. Time required for fragmentation during the Spring was significantly longer for all materials than seen during the Summer. The results indicated that the primary degradation reactions are driven by a combination of light + heat, with a negligible contribution from thermal or biodegradation reactions for buried materials.

- 19** HOW TO INVESTIGATE AND EVALUATE COMPOSTING-SYSTEMS. Antie Rieeer. Werner Bidlingmaier, Universitat GH Essen, FB 10, Abfallwirtschaft, Universitätsstrafie 15, D-45141 Essen, Germany

In waste-management the biological treatment is becoming more and more important The offer of different kind of composting-systems of organic waste, such as static, semistatic or dynamic systems, is increasing. The difficulty for the general customer, in most cases for the municipals, is to choose a suitable system. Therefore investigations and evaluations have to be carried out concerning, besides the expenses, a big range of items eg. air-consumption, gas-development, emissions and characteristics of the material (water-content, loss of organic matter due to burning, temperature and quality). The problem will be shown with the extensive investigations and evaluations of two different composting systems. 1.) composting in containers 2.) composting in silos. Both were developped as self-controlled systems, eg.the automatic regulation of the dynamic process (moving bottom) by the continuous measurement of CO<sub>2</sub> and temperature. One special investigation was to proof the function of the moving bottom and the necessary homogeneous mix of the input material (organic household-waste). To show this, two different formed wood-pieces were added as tracer-material. In dependency of the amount of input-material and the time of the filling the round wooden pieces were sprinkled first and then the elongated pieces. After some time of composting the counting of the wood-pieces in the samples allowed an evaluating of the mix. Horizontal or vertical stackings, or even places which **Averen't** moved at all could be identified.

- 20** LESS WELL-KNOWN FUNDAMENTALS OF THE COMPOSTING PROCESS. George B. *Willson*. George B. Willson Associates. 407 N. Lincoln Ave.. No. 103. Loveland. Colorado. 80537.

Although the art of composting has a long and colorful history, some of the earliest references to compost are to be found, in the Bible, the systematic study of the practice and science of composting did not begin until early this century. Thus it is not surprising that several fundamental principles of the process are nearly unknown. Some of these include: 1. The prevalence of anaerobic microbial activity within aerobic processes (aerobic activity is a surface effect). 2. The role of fungi in the composting process and its effect on the optimum temperature. 3. The importance of *Aspergillus Fumigatus* to the process. 4. The role of the windrow turner in aeration- of windrows. 5. Risk of dust explosion. 6. Causes of fires in stored *compost*.

- 21** COMPARISON OF BIODEGRADABILITY AND MICROBIAL ACTIVITY DURING COMPOSTING OF SOLID WASTES. Cheryl F. Atkinson, Daniel D. Jones, and Joseph J. Gauthier, Biology Department, University of Alabama at Birmingham, Birmingham, AL 35294. (205) 934-5659.

Composting is a method for recycling the organic matter in solid wastes to produce a useful end-product. As volumes of material to be recycled increase, it is desirable to find ways to enhance the rate and extent of composting. A better understanding of the comparative microbial ecology of different compost mixes was therefore undertaken. In this study, the biodegradability of municipal solid waste, oxidation ditch sludge, poultry litter, supplemented and unsupplemented pulp and paper solids, and two bulking agents, pine sawdust and hardwood sawdust, were each investigated during four to six weeks of in-vessel composting. The levels of microorganisms detected throughout composting of these wastes changed significantly only in the supplemented pulp and paper solids. Activities of exoenzymes were different during composting of each waste. For example, pine and hardwood sawdusts exhibited the lowest levels of growth and exoenzyme production whereas municipal solid waste had the highest. Fiber analysis revealed significant amounts of cellulose degradation only in the municipal solid waste.

- 22** A POSTULATED REACTION SEQUENCE FOR DERIVING AQUATIC HUMIC STRUCTURES FROM LIGNIN AND LIPID STRUCTURES. Jerry A. Leenheer and Robert L. Wershaw, U.S. Geological Survey, 5293 Ward Road, Arvada, CO 80002

Spectrometric, titrimetric, and elemental analytical studies were used to construct structural models of aquatic humic substances isolated from a wide range of natural environments. These models revealed many common features that were indicative of a convergent decay process despite major differences in source materials and environments. Strong-acid functional groups in aquatic humic substances are predominately aliphatic carboxylic acids that are clustered on oxygen-heterocycle rings where oxygen is part of an ether or ester linkage. Weaker carboxylic acids are substituted succinic acids attached by carbon or oxygen cross-links to aromatic rings. A reaction sequence beginning with either unsaturated lipids or lignin that involves oxidative coupling at unsubstituted aromatic or olefinic carbons, p- and Q -oxidation- (coupled to respiration) of aliphatic hydrocarbon chains, and hydroxylation and cleavage of aromatic rings to produce substituted succinic acids at ring cross-links should produce materials with structure similar to humic substance models. The relative content of aromatic to aliphatic structures is dependent on the degree of degradation along the postulated reaction sequence and on the nature of the source material.

- 23 **APPLICATION OF NUCLEAR MAGNETIC RESONANCE SPECTROSCOPY TO ELUCIDATING THE COMPOSTING PROCESS.** Robert L. Wershaw, Jerry A. Leenheer, and Kay R. Kennedy, U.S. Geological Survey, 5293 Ward Road, Arvada, Colorado 80002.

Composting of plant wastes is widely used for the production of a valuable soil amendment. Nuclear magnetic resonance (NMR) spectroscopy allows one to follow the changes in chemical functionality that take place during composting. The solid-state  $^{13}\text{C}$  NMR spectra of composted and uncomposted leaves are composed of the same spectral bands; however, the relative ratios of the band intensities are different. In general, the relative intensities of the bands that represent lignin and hydrocarbons are markedly increased in the spectra of the composted leaves compared to the spectra of the uncomposted leaves. In addition, the carboxylate band is much stronger in the composted leaves. These results indicate that the carbohydrate components of plant tissue are more rapidly degraded than the lignin components, and that carboxylic acid groups are formed by the degradation reactions. During the composting process part of the plant tissue is transformed into water-soluble products. These water-soluble products have been fractionated by adsorption chromatography on macroreticular resins, and the fractions have been characterized by solid-state and liquid-state NMR spectroscopy. The NMR data from the water-soluble products support the conclusion that composting consists mainly of depolymerization and oxidation reactions, and that oxidative coupling reactions are probably not important.

- 24 ANALYSIS OF COMPOST - RESULTS FROM A PARALLEL INTERLABORATORY TEST WITH 95 LABORATORIES. Werner Bidlingmaier, Andreas Maile. Universitat GH Essen. FB 10 Abfallwirtschaft, Universitätsstr. 15, D-45141 Essen, Germany

A total of 95 laboratories took part in a parallel inter laboratory test in 1993. Each laboratory analysed for 31 parameters four compost samples - allotted to them at random - from homogenized fresh compost. Calculations have been carried out of total mean, median, standard deviation, coefficient of variation, range and percentil range for the datar cleared of the outliers, of the respective laboratory means, this representing essential statistical measures of location and dispersion. The assessment of the laboratories has been effected by the number of unsuccessful analyses which each laboratory has recorded. According to DIN 38 402 the total means  $M_{tot}$  - free of outliers - were used as measure for the "conventionally correct values" of each parameter. The outliers of the complete data of each laboratory mean were elihnated by the Grubbs test. Furthermore, all laboratory means showing more than a twofold standard deviation  $Stdv(M_{Lab})$  from the total mean  $M_{tot}$  were rated as unsuccessful analyses as per the data free of outliers. Even after having eliminated the outliers of the data and after having restricted the admissible range of analysis results to the twofold standard deviation of laboratory means, most of the parameters still show considerable variations in analysis among the different laboratories. Heavy metals, soluble nutrients and degree of composting are to be emphasized as particularly critical parameters. Deviations from the respective total mean could be found in heavy metal contents ranging between 26 % in zinc up to 76 % in chromium.

" The oxidation level (3) of  $\text{La}_2\text{CuO}_{4+x}$  has been recognized as the primary factor determining both superconductivity and the transition temperature in these and related materials. In  $\text{La}_2\text{CuO}_{4+x}$ , three or more superconducting phases have been discovered. Each of these phases have different oxygen stoichiometries and transition temperatures. We have developed a simple low temperature method to prepare thin film  $\text{La}_2\text{CuO}_4$  on ITO coated glass. Electrochemical oxidation of  $\text{La}_2\text{CuO}_4$  films at scan rates below 25 V/sec allows for the resolution of three oxidation waves previously not seen in the bulk materials. These waves may relate to the three superconducting phases. The first two oxidation peaks at 290 and 335 mV (vs. Ag/AgCl) are reversible while the third oxidation peak at 405 mV (vs. Ag/AgCl) is not. We have oxidized  $\text{La}_2\text{CuO}_4$  to different oxidation levels in order to investigate their phase behavior and related transition temperatures. The films have been analyzed by low angle x-ray powder diffraction, SQUID measurements, and SEM. Film preparation, oxidation and analysis will be discussed.

**26 PREPARATION AND PHOTOELECTROCHEMICAL CHARACTERIZATION OF H-IV-V<sub>2</sub> CHALCOPYRITE SEMICONDUCTORS.** Y. C. Wen, and Bruce A. Parkinson,

Department of Chemistry, Colorado State University, Fort Collins, CO 80523.

The chalcopyrite **II-IV-V<sub>2</sub>** semiconductors are isoelectronic with well known III-V materials, but have the advantage for solar cell and photovoltaic applications, of containing more abundant elements. We have synthesized **ZnSiAs<sub>2</sub>**, **CdSiAs<sub>2</sub>**, **CdSiP<sub>2</sub>**, and **ZnSiP<sub>2</sub>** single crystals by chemical vapor transport technique. The crystal structure and surface composition were verified by X-ray powder diffraction analysis and SEM. The basic electronic properties were investigated by photoelectrochemical techniques and compared with those from Hall effect measurement. Different buffers and redox electrolytes ( $\text{V}^{3+}/\text{V}^{2+}$ ,  $\text{S}^{2-}/\text{S}_2^{2-}$  and  $\text{Fe}(\text{CN})_6^{4-}/\text{Fe}(\text{CN})_6^{3-}$ ) have been used for Mott-Schottky measurement and photocurrent spectra. The pH dependence of flatband potential and the improvement of quantum yield by wet chemical etching will also be discussed.

- 27      **STUDIES OF THE ELECTROCHEMICAL DEPOSITION OF METAL ADLAYERS ON DIAMOND THIN FILM ELECTRODES.** Shokoofeh Alehashem, Michael Granger and Greg M. Swain. Department of Chemistry and Biochemistry, Utah State University, Logan, UT 84322-0300

The use of synthetic diamond thin films as electrodes is a relatively unexplored application of this advanced material. Diamond thin films possess several "electrochemical" attributes including high thermal conductivity, hardness, corrosion resistance, variable conductivity via doping, and optical transparency. Our laboratory is involved in studies directed towards understanding the structure-reactivity relationship of electrochemical interfaces formed at conductive and semiconductive diamond thin film electrodes. One important class of reactions under study is metal deposition. The goal of these efforts is to understand the factors which influence the nucleation and growth of metal deposits on diamond films. The presentation will discuss recent results from the in situ characterization of the electroreduction of Hg, Ag and Cu adlayers on the surface of conductive diamond thin film electrodes. The reactions have been examined as a function of the electrolyte composition and electrode surface pretreatment. Cyclic voltammetry, chronamperometry and ac impedance spectroscopy have all been used to electrochemically characterize the deposition reactions. Scanning electron microscopy and the in situ scanning probe microscopies, STM and AFM, have been used to study the structure and spatial distribution of the metal deposits. Results from similar experiments performed on highly ordered pyrolytic graphite and glassy carbon will also be presented.

- 28 **FABRICATION AND CHARACTERIZATION OF GOLD NANOTUBULE ARRAYS.** Kshama B. Jirage. Charles R. Martin, Colorado State University, Department of Chemistry, Fort Collins, Colorado, 80523, (970) 491-6160.

**Microporous membrane filters were used as templates to make arrays of gold nanotubules. Electroless deposition of gold on the the surface and the walls of the pores was carried out to make the nanotubules. Low temperature and maintaining a constant pH of the plating solution allows a slow controlled growth of the gold. The plating time can be varied to get pores of required diameter. Fluxes of various gases through the nanotubules of different diameters were studied. The fluxes of helium and hydrogen which show Knudsen flow were used to characterize the pore size.**

**The nanotubules arrays with such small diameters have a large number of applications which are being explored. Among them are to use them as filters, to fix carriers like hemoglobin and cobalt porphyrin on the pore walls to study the facilitated transport of oxygen.**

- 29 **STUDIES OF RUTHENIUMTRISBIPYRIDINE-TYPE POLYMERS SANDWICHED BETWEEN TWO ELECTRODES.** Daniel Derr and C. Michael Elliott, Department of Chemistry, Colorado State University, Fort Collins, CO 80523.

The conductivity of redox active polymer films can be studied by sandwiching the polymer between two electrodes, at least one of which is porous to solvent and ions. By setting the potential of one electrode positive of a redox couple of a polymer film, and the other electrode negative of the couple while the assembly is in contact with an electrolyte solution it is possible to establish concentration gradients of the oxidized and reduced species within the film. We are attempting to investigate polymers in which these types of gradients are 'locked' in place by making the counterions which are necessary for electroneutrality immobile. It is predicted the resulting film will be current rectifying. Two polymers have been investigated in this regard. Synthesis and characterization of their monomers, polymerization techniques, electrode construction, and electrochemical studies will be discussed. The most straight forward way to attempt 'locking' the gradient in place is to allow the film to dry while a potential is applied across it. Voltammetry of the dry film does not indicate the predicted current rectification. The response is also not easily rationalized and may indicate some residual counterion mobility. Other methods of 'locking' the concentration gradient will be discussed.

- 30 **REDOX DEPENDENT INTERACTIONS OF THE METAL SITES IN CARBON MONOXIDE BOUND CYTOCHROME c OXIDASE MONITORED BY INFRARED AND UV/VISIBLE SPECTROELECTROCHEMICAL METHODS.** Eric D. Dodson<sup>1</sup>, X.J. Zhao<sup>2</sup>, C. Michael Elliott<sup>1</sup>, and W. S. Caughey<sup>2</sup>, Departments of Chemistry<sup>1</sup> and Biochemistry<sup>2</sup>, Colorado State University, Fort Collins, Colorado 80523.

Spectroelectrochemical titration studies involving the binding of the infrared-active probe ligand carbon monoxide (CO) to the heme  $a^{\text{C}}$  site of beef heart cytochrome c oxidase (CcO) have been reexamined. The spectroelectrochemical cell employed was constructed to monitor both the infrared (IR) and visible/Soret spectra of the CcO-CO complex as a function of the overall oxidation state of the enzyme. The well documented shift in the CO *stretch horn* 1963.3  $\text{cm}^{-1}$  (CcO fully reduced) to 1965.5  $\text{cm}^{-1}$  (CcO partially oxidized) was carefully titrated electrochemically. Deconvolution of the asymmetric CO stretches indicates the existence of two different states of CO vibrators within the enzyme, presumably due to two conformers which are present in a ratio of approximately 5:1. Upon incrementally stepping the potential from the fully reduced state to the partially oxidized state, it is possible to follow the decrease in the intensity of the original pair of these conformers and the concomitant increase of a resultant pair while maintaining this 5:1 ratio between the conformers. By plotting the change in the deconvoluted CO peak intensities versus the redox potential as well as the absorbance changes in the visible/Soret spectra versus the redox potential, it was found that not only did both fit an  $n=1$  electron process but that the spectral changes track each other identically within experimental error. Furthermore, the second-derivative of the Soret spectra allowed for the qualitative monitoring of the oxidation state of the  $\text{Fe}_b$  site which again tracked identically to that of the CO shift in the IR region. As a consequence of the C-0 IR stretching frequency only changing by 2  $\text{cm}^{-1}$  with no corresponding change in the half bandwidth, we are suggesting that the change seen in the CO stretching frequency, ligated to reduced  $\text{Fe}_{b,1}$ , is caused by a conformational change induced by perturbing the oxidation state of  $\text{Fe}_b$ , and that  $\text{Cu}_a$  must remain reduced as long as CO is bound to the  $\text{Fe}_b$  site.

- 31 **ELECTROCHEMICAL STUDIES OF ELECTROACTIVE AND NON-ELECTROACTIVE MONOLAYERS: FACTORS AFFECTING ELECTRON TRANSFER KINETICS AND ADSORBATE INTERACTIONS.** Barnes W. talker, and Daniel A. Bur-try, Dept. of Chemistry, University of Wyoming Laramie, WY/ 8 & 0 7 1 T 3 8 3 S

Cyclic Voltammetry was used to study the electrochemical properties of mixed monolayer systems. These mixed monolayers consisted of analkanethiol as well as a lower surface coverage of a functionalized organothiol. The purpose of the functionalized molecule was to act as a gate (non-electroactive case) or as a mediator (electroactive case) for heterogeneous electron transfer. Interactions between electroactive adsorbates was also examined. This work builds on our previous electrochemical and Raman investigations involving viologen derivatives and includes some preliminary studies of isonicotinate bearing adsorbates.

- 32 **ANOMALOUS ELECTROLYTE EFFECT ON ELECTROCHEMICAL KINETICS AT NANO-ELECTRODE ENSEMBLES.** Vinod P. Menon, Charles R. Martin, Department of Chemistry, Colorado State University, Fort Collins, CO 80523.

Nanoelectrode ensembles have many advantages over conventional macro-size electrodes including higher sensitivity and freedom from spurious uncompensated solution resistance effects. Such ensembles are also capable of measuring extremely high electron transfer rate constants at moderate scan rates. Using a template synthetic method we have fabricated ensembles with individual electrode radii as small as 5 nm. These ensembles have been used to obtain rate constants as high as 70 cm/s. We have observed an unusual electrolyte dependence on the rate constants measured at these ensembles. In contradiction to electrochemical theory, the rate constant for heterogeneous electron transfer decreases with increasing electrolyte concentration. We have observed this effect for a number of redox couples in a large number of electrolytes. The effect is dependent on the charge of the redox species and is not observed for uncharged species. The effect is observed for both oxidations as well as reductions and on either side of the pzc. Furthermore, the effect is much more pronounced as the individual electrode radius in the ensemble decreases. We have tentatively attributed this effect to ion-pairing of the redox species in solution. Electrochemical simulations of ion-pairing seem to correlate well with experimental data. Some of the electrochemical data and simulations will be presented at this meeting.

- 33 **MECHANISTIC STUDIES OF ADVANCED OXIDATION PROCESSES ON TITANIUM DIOXIDE USING SURFACE ENHANCED RAMAN SPECTROSCOPY.** Karen L. Nnrrod, Kathy L. Rowien, Carl A. Koval. Department of Chemistry and Biochemistry, Campus Box 215, University of Colorado, Boulder, CO 80309.

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 (TiO<sub>2</sub>), with long-wavelength UV light, thus permitting the sun to be used as the light source. By using the TiO<sub>2</sub>/UV APO, the possibility exists of practical systems requiring only sunlight, air, and photocatalyst to treat waste streams that contain many harmful pollutants. The three most important questions to address with respect to understanding AOPs at TiO<sub>2</sub> are 1) is the reaction taking place at or near the surface, 2) what are the intermediate species, and 3) what is the rate of reaction for each intermediate. In order to address the questions an information-rich spectroscopic technique is required that is not hindered by the complex reaction environment. One technique that elegantly meets both of these requirements is surface enhanced Raman spectroscopy (SERS), which arises from molecules' interactions with roughened metal surfaces and results in a substantial increase in their Raman scattering signals. Another advantage of SERS is its distance dependency, which permits oily surface reactions to be monitored. Preliminary efforts have succeeded in establishing a reproducible method of depositing a photoactive layer of TiO<sub>2</sub> onto a SERS-active Ag electrode. The distance dependency of the SERS signal from benzoic acid on the TiO<sub>2</sub> overlayer has also been investigated.

- 34 CONTINUING INVESTIGATIONS OF THE CHANGES IN REDOX BEHAVIOR OF CONDUCTING POLYMERS IN THE PRESENCE OF NEUTRAL ORGANICS. Susan M. Hendrickson and C. Michael Elliott, Department of Chemistry, Colorado State University, Fort Collins, CO 80523

Our group observes large shifts in the cyclic voltammetry of certain conducting polymer films in aqueous solutions containing trace neutral organics. Polymers currently under investigation include poly(N-methylpyrrole), poly(3,4-diphenylpyrrole) and composite films of each of these with the polyelectrolyte anion, polystyrenesulfonate. These films, although different by only a ring substitution, exhibit drastically different voltammetry in aqueous solutions. The majority of these studies have focused on one and two carbon chlorinated compounds as the neutral organics. These systems are currently being developed for amperometric detection of neutral organics in waste water. In order to improve the detection systematically, we are also characterizing the interaction between the organics and the polymer films using cyclic voltammetry, electrochemical quartz crystal microgravimetry and flow injection analysis. By better understanding this interaction, we hope to modify the polymer such that better sensitivity and selectivity will be attained.

- 35 **ENZYME FACILITATED TRANSPORT OF ETHANOL.**  
Brinda. B. Lakshmi. Charles.RMartin, Colorado State University,  
Department of Chemistry, Fort Collins, CO80523.

Facilitated transport occurs when there is a chemical agent which can selectively interact with a solute in a feed mixture thus facilitating the transport of the solute through the membrane. Enzymes in the absence of the cofactor will still have the binding site for the substrate but will not convert it into product. Enzymes can thus act as a carrier to transport the substrate. Alcohol dehydrogenase (adh) entrapped in a microporous membrane filter plugged with polypyrrole on both sides was used to study the transport of ethanol. Polypyrrole was grown in aqueous medium first to plug the pores. The enzyme was filtered into it and polypyrrole was grown in nonaqueous medium on top. Since ADH is specific to ethanol it would transport ethanol faster through the membrane than phenol from a mixture of both. This aspect of facilitated transport is being explored.

- 36 SEPARATION OF BUTADIENE USING COPPER(I)/COPPER(II) ELECTROCHEMISTRY.  
Takayuki Suzuki, David K. Watts, and Carl A. Koval, Dept. of Chemistry and Biochemistry,  
Campus Box ? 15, University of Colorado, Boulder, CO 80309-0215

Separation and concentration of gases using complexing agents is one of the most promising areas for chemical and environmental industries. Copper(I) forms a Tt-complexes with diolefins or olefins, while copper(II) does not bind either effectively. An effective separation of butadiene from a C4-hydrocarbon mixtures by an electrochemically modulated complexation system in which copper(I) works as a butadiene carrier is expected. Olefin complexes of copper(I) salts as olefin carriers have been limited to copper(I) halides. Competition between halide ions and olefin or ligand sites on copper(I) is no doubt an important factor in determining the stability of these complexes. Copper(I) trifluoromethanesulfonate (CuOTf) bound to benzene which stabilizes the copper(I) cation with a weak *n-bond* was synthesized. CuOTf has been shown to bind butadiene in various solutions electrochemically and spectroscopically. From their cyclic voltammograms, potentials for Cu(I)/Cu(II) were measured. This is expected to develop into the electrochemically modulated complexation system.



- 40 USE OF STATISTICAL SAMPLING DESIGN AND ANALYSIS TO DETERMINE GEOCHEMICAL BACKGROUND CONCENTRATIONS AND THRESHOLD VALUES OF SELECTED INORGANIC CONSTITUENTS IN SOIL AND GROUND WATER AT EE. WARREN AIR FORCE BASE, WYOMING. Robert A. Boyd, Kent D. Becher, Richard L. Daddow, and Randall K. Lambrecht, U.S. Geological Survey, 2617 E. Lincolnway, Cheyenne, Wyoming, 82001.

Soil and ground water in areas of EE. Warren Air Force Base (Base) have been contaminated by past use, storage, and disposal of hazardous materials. Concentrations of selected inorganic constituents in soil and shallow ground water on the Base were evaluated to determine whether the constituents are naturally occurring or are a result of past handling of hazardous materials. The objective of the study was to determine statistically defensible background concentrations and threshold values for the constituents. An unbalanced nested analysis of variance (ANOVA) sampling design was applied to surface soil, subsurface soil, and shallow ground water. The ANOVA primarily evaluated the areal variation of concentration of each constituent; however, the ANOVA also addressed the variation of the concentration of each constituent with depth in the soil and with time in the ground water. The results obtained from the ANOVA were used to determine if the sampling densities were sufficient to calculate representative background concentrations and threshold values for each constituent. The mean and standard deviation of each constituent were calculated according to a method for singly censored data. The threshold value of each constituent was calculated with the above mentioned mean and standard deviation and a t-statistic at the 95-percent-confidence interval.

- 41 ARSENIC DETECTION LIMITS IN ENVIRONMENTAL SAMPLES USING A SIMULTANEOUS GRAPHITE FURNACE AA: INVESTIGATION OF PARAMETERS THAT EFFECT SIGNAL TO NOISE RATIO. Randy L. Hergenreder, John C. Latino, Douglas C. Sears, 761 Main Ave M/S 695, 079, 648, Norwalk, CT 06859

A simultaneous multielement GFAA with a new high optical throughput echelle spectrometer and a custom made solid state detector is used to evaluate arsenic detection limits in environmental samples. Various parameters that effect the signal to noise in both simultaneous and multielement mode are investigated. Also investigated are the effects of signal processing, the use of increased sample volumes and the use of new graphite tube that incorporate end caps.

The new echelle spectrometer's signal to noise is compared to a state of the art single element GFAA. The systems performance in environmental samples is also reported.

- 42 ANALYSIS OF URANIUM & RADIUM IN ENVIRONMENTAL SAMPLES BY ICP-MS. William R. Tnon, USX Texas Uranium, George West, Texas 78022 & Rob Henry, r isons Instruments, PO Box 20460, Boulder, CO 80304.

The tailings from Uranium processing as well as ground waters are required to be monitored to meet regulatory levels for total Uranium and traces of Radium 226. The technique of soil digestion and subsequent Radium precipitation followed by alpha counting is well proven but time consuming. The high sensitivity and element specificity of ICP-MS has been instrumental in the development of methods for the analysis of long lived radionuclides including Uranium and Radium. Traditional sample preparation was used and the resulting preconcentrated sample was analyzed quantitatively using ICP-MS equipped with an Ultrasonic nebulizer. The analytical data were compared with counting methods and it was found that a reliable measurement at lower levels than the regulated 5 pCi/g Radium 226 in soil was easily achieved.

**ARSENIC SPECIATION IN SOIL USING HIGH PERFORMANCE LIQUID CHROMATOGRAPHY - INDUCTIVELY COUPLED PLASMA - MASS SPECTROMETRY (HPLC-ICP-MS).** Dean A. Bass, Judith S. Yaeger, Kathleen J. Parish, Jeffrey S. Crain, James T. Kiely, and Mark Gowdy, Argonne National Laboratory, Argonne, IL 60439-4831; and Greg B. Mohrman, Rocky Mountain Arsenal, Commerce City, CO 80022-2180

A method has been developed by Argonne National Laboratory to identify and quantify As(III), As(V), and organoarsenic compounds in soil samples from the Rocky Mountain Arsenal (RMA). The soils were extracted using a phosphate buffer (pH=6) and sonication. Extraction efficiencies and stability of the arsenic species during the extraction process will be presented. The arsenic species were separated by reversed-phase HPLC. The HPLC column effluent was introduced into an ICP-MS using a direct injection nebulizer. Detection limits of less than 1 pg (as injected on the column) for each arsenic species were readily obtained. Extraction, separation, and ICP-MS conditions will be presented, and the effects of varying these conditions will be discussed. Quality control measures recommended to increase accuracy and precision will also be presented. Soil samples spiked with arsenic oxide, sodium arsenate, dimethylarsinic acid (DMAA), and chlorovinyl arsenious acid (CVAA) were extracted, identified and quantified with the HPLC-ICP-MS system. Soil samples were analyzed in support of the analytical needs of a thermal desorption treatability study being conducted at the RMA. (Work supported by the U. S. Army and the U. S. Department of Energy under Contract W-31-109-ENG-38.)

**44 USING POLYMERIC MICROENCAPSULATION ARRAYS TO CONCENTRATE TRACE METAL IONS FROM DILUTE AQUEOUS SOLUTIONS.** Veronica M. Cepak, Ranjani Parthasarathy, and Charles R. Martin, Colorado State University, Department of Chemistry, Fort Collins, Colorado, 80523, (970) 491-6160

A template approach can be used to prepare microstructures of organic conductive polymers inside the pores of a microporous membrane filter. The conductive polymer, polypyrrole, adheres to the inner pore walls of these membranes by means of a templating effect to form hollow polymer tubules. These polypyrrole tubules can be capped and used as a microencapsulation device to hold a water soluble chelating polymer. An array of microcapsules can be produced in which the chelating polymer cannot escape from the capsules, but metals ions can diffuse through the porous walls of the polypyrrole capsules. This process allows direct concentration of metals ions from dilute aqueous solutions. There are many advantages of using these polypyrrole microcapsular arrays to concentrate trace metal ions from aqueous solutions. This method can be specific or universal based on the selection of the polymeric chelating agent used. The use of water soluble chelating polymers is of interest because an aqueous-organic interface does not exist where unfavorable mass transfer resistance can occur. The array of microcapsules also allows much more surface area to be exposed, which should improve the efficiency of concentrating metal ions compared to other methods. Finally, metal ions can be concentrated without requirement of filtration steps which are needed in other methods.

**45 TRENDS IN USEPA METHODOLOGY FOR THE DETERMINATION OF TRACE ELEMENTS IN ENVIRONMENTAL SAMPLES.** Theodore D. Martin and John T. Creed, U. S. Environmental Protection Agency, National Exposure Research Laboratory, Aquatic Research Division, 26 W. Martin Luther King Dr., Cincinnati, OH 45268.

The analytical methods and quality control requirements specified by the Agency for use in the various compliance monitoring programs have increased in complexity over the years. This trend in complexity has been dictated by a need to document and verify the quality of data being produced. The Chemistry Research Branch of the Aquatic Research Division (formally EMSL-Cincinnati) has attempted to bring consistent quality control practices to methods developed for the analysis of drinking water and wastewater. In this presentation the evolution and purpose these practices will be discussed as incorporated in the manual, "Methods for the Determination of Metals in Environmental Samples - Supplement I". This manual contains 7 methods prepared using the adopted Environmental Monitoring Management Council (EMMC) format. Four of the spectrochemical methods have been approved for the analysis of drinking water, however, these methods have yet to be proposed as the updated EPA reference methods for NEDES wastewater analyses.

- 46 **METHOD EVALUATION WITH ROUND ROBIN TECHNIQUES USING ARSENIC DETERMINATION BY SPE-AA, HG-AA AND HG-ICPMS.** Andrew Eaton, Maria Tikkanen  
Montgomery Laboratories, 555 East Walnut Street, Pasadena, CA 91101 and Association of California  
Water Agencies 910 K Street, Sacramento, CA 95814

Due to the potential for a significant reduction in the Maximum Contaminant Level for Arsenic, several new techniques were developed with the potential for routine measurement of arsenic or individual arsenic species at concentrations as low as 0.1 ug/L. These techniques were evaluated in several laboratories to determine their ruggedness for determination of either As-III or Total As at sub ppb levels. The methods included a solid phase extraction technique followed by conventional graphite furnace detection and two hydride generation methods (cold trapping with AAS detection and on line ICPMS). All three methods appeared to be rugged when tested in the individual laboratories where the methods were developed, with both good precision and minimal bias. However when the methods were field tested in laboratories with less experience it was found that they were not as precise as expected. In each case at least a single lab was able to generate reliable data, but when multiple lab data was combined the precision and accuracy deteriorated significantly. In addition, the results showed that preservation techniques for arsenic species were highly dependent on the specific matrix, suggesting that the only reliable way to determine arsenic speciation is by field separation. Work is continuing on this project to make the methods more rugged.

- 47 **IMPROVING DRINKING WATER ANALYSIS PRODUCTIVITY BY EPA METHOD 200.8.** Rob Henry, Chris Tye, Paul Sigsworth, Tom Rettberg, Fisons  
Instruments, P.O. Box 20460, Boulder, CO 20460-3460

Since EPA approved Method 200.8 in 1994, ICP-MS analysis of drinking water has been implemented in many laboratories in the USA. Method 200.8 allows the analysis of all Primary and Secondary regulated elements in drinking water, including Mercury. Since the number of analyses required by the Safe Drinking Water Act is immense, the implementation of a single analytical technique is the most cost effective solution for improving sample throughput and reducing analysis costs. The application of new sample introduction techniques which automate sample preparation as well as unattended evaluation of the data as it is produced will further improve sample throughput. Data will be presented to show compliance with EPA Method 200.8 with high sample throughput.

- 48 **EVALUATION OF GEOLOGIC AND LAND-USE FACTORS THAT PRODUCE URANIFEROUS WATERS, ARKANSAS RIVER VALLEY, SOUTHEASTERN COLORADO.** Robert A. Zielinski, Sigrid Asher-Bolinder, Allen L Meier, Craig A. Johnson, and Barney J. Szabo, U.S. Geological Survey, Denver, Colorado 80225.

Irrigation of alkaline soils of the semi-arid Western United States can salinize soil and contaminate surface and ground water with high concentrations of dissolved salts and toxic trace elements such as uranium (U). We investigated the geologic and land-use controls on dissolved U in the Arkansas River valley of southeastern Colorado (an area previously documented to contain high-U waters). Seventy-seven surface water and spring samples collected in April 1991 contained <1 to over 100 ppb dissolved U. Uranium concentrations in excess of the proposed USEPA drinking water standard of 20 ppb were confined to waters draining areas of the High Plains that are largely underlain by uranium-bearing (2-8 ppm) Upper Cretaceous marine shales and limestones. In areas where the above lithologies underlie intensively irrigated lands and where surface waters are heavily impacted by irrigation return, dissolved U concentrations were anomalously high and variable (30 to > 100 ppb). Uranium is transported in these oxygenated waters primarily as uranyl-carbonate complexes and is further concentrated by evaporation. A separate study of U isotopes in nitrate-rich irrigation return waters discounted U-bearing fertilizers as possible U sources. Oxidized, weathered sulfidic shale is the probable source of uranium. Approximately 3 to 20 percent of the U in 50 shaley soils was leachable with 0.1 M sodium bicarbonate solution. The results suggest other areas of the West may have potentially harmful levels of dissolved U produced by a combination of natural processes and human activities.

49

**-MICROWAVE ASSISTED DIGESTION OF PAINT CHIPS AND AIR FILTERS FOR LEAD ANALYSIS**  
 Sara Littau, CEM Corporation, 3100 Smith Farm Road, Matthews, NC 28105.

The adverse health affects resulting from exposure to environmental lead has received increasing attention. Studies have shown chronic exposure can result in impairment to the central nervous system. The major sources of exposure to lead are paint, soil, dust, and airborne particulate.

Inductively coupled plasma atomic emission spectrometry (ICP-AGS) has been widely applied to the analysis of lead from these sources. The traditional technique for preparing samples for lead analysis for ICP-AES is acid digestion on a hot plate. However, this technique is very tedious and creates an acid vapor exposure problem for the operator.

In this paper, we will present lead recovery data using a closed "Vessel microwave digestion system to prepare paint chip, dust, and air filter samples. The benefits of this approach are (1) speed of the decomposition, (2) improved recoveries, (3) elimination of glassware contaminating ajld (4) minimal operator exposure to acid vapors.

50 PREPARATION OF FREE AVAILABLE BROMINE SPECIES AND MEASUREMENT OF MOLAR ABSORPTIVITIES USING UV-VISIBLE SPECTROPHOTOMETRY AND IODOMETRIC ANALYSIS. Gary L. Emmert, Renee D. Gauw and Gilbert Gordon, Department of Chemistry, Miami University, Oxford Ohio 45056.

The importance of the free available bromine species (FAB:  $\text{Br}_2$ , HOBr, and OBr) in the formation of bromate ion during water and wastewater treatment is incontrovertible. However, prior to our work, fundamental limitations in the measurement of the molar absorptivities ( $\epsilon$ ) of these FAB species existed. Published measurements were reported at only one cell pathlength and over a narrower wavelength region than currently required. Our work circumvents these limitations by measuring the  $\epsilon$  of each FAB species at several pathlengths, several concentrations, and over a broader wavelength region than previously published. In order to accomplish these measurements, it was necessary to prepare each FAB species in pure form. Details of the preparation the FAB species and the subsequent measurement of the molar absorptivity using UV-Visible spectrophotometry and iodometric analysis will be discussed as well as implications to kinetic measurements during water and wastewater treatment processes.

- 51 GLYCINE AS A QUENCHING AGENT FOR OZONE IN BROMATE ION FORMATION STUDIES. Gary L. Emmert and Gilbert Gordon, Department of Chemistry, Miami University, Oxford, Ohio 45056.

In studies of bromate ion formation when ozone is reacted with bromide ion, many researchers have typically used nitrogen gas to remove ozone from sample thereby minimizing the reaction with bromide ion. Ideally, subsequent measurement of the samples collected over time would show the rate of bromate ion formation. However, results from our laboratory indicate that with typical degassing methodologies, as much as 0.5 mg ozone/L can remain in solution to continue to react after the reaction has been supposedly quenched. This unfortunately leads to skewed values for the rate of bromate ion formation and may account for some of the discrepancies that have appeared in the literature.

Our research has shown that glycine, which has long been used to quench ozone reactions will not effect bromate ion concentration levels. The reaction between ozone and glycine is very rapid and virtually all ozone is effectively removed when compared to nitrogen degassing. Results from experiments where bromate ion was measured potentiometrically both in the presence of and without glycine will be discussed. Work is currently underway in our laboratory to adapt this quenching agent to ion chromatographic measurements.

- 52 CIRCULAR DICHROISM FOR DETECTING MICROORGANISMS MODELED WITH LIGHT SCATTERING THEORY. David L. Rosen and J. David Pendleton, U.S. Army Research Laboratory, Battlefield Environment Directorate, ATTN: AMSRL-BE-S, WSMR, NM 88002-5501

Potential methods of measuring circular dichroism from microorganisms were analyzed using Bohren's theory of light scattering from optically active spheres. Detection of microorganisms by light scattering is possible because of circular dichroism. Circular dichroism is caused by optically active substances, which nonbiological processes seldom produce. The mathematical analysis shows conditions for which induced circular polarization on scattered light would indicate a microorganism. Computer calculations show that deviation from these conditions could produce an induced circular polarization signal that would cause a false detection of microorganisms. Possible methods of removing the false signal were analyzed. Reducing the false signal would broaden applications of circular dichroism spectroscopy. Potential applications include remote sensing of microorganisms, fast measurement of microorganisms in water, and pharmaceutical analysis of chiral drugs. A computer code for analyzing light scattered from optically active spheres is now available to qualified users from the authors.

- 53 THE ANALYSIS OF CYANOBACTERIAL TOXINS IN FRESHWATERS. Kevin J. James and Ian R. Sherlock, Ecotoxicology Research Unit, Chemistry Department, Cork RTC, Bishopstown, Cork, IRELAND.

Reports of cyanobacterial (blue-green algal) blooms in freshwaters have increased dramatically in recent years and a number of toxic incidents have been reported. A particular cause for concern is that waters used for human and animal consumption may contain blooms of a toxigenic species, such as *Aphanizomenon*, *Anabaena*, *Oscillatoria* and *Microcystis*. They are known to produce two classes of neurotoxins, saxitoxins and anatoxins, as well as hepatotoxic compounds (microcystins) which have also been shown to be potent tumour promoters. The determination of these compounds in water at levels below parts per million presents an enormous analytical challenge. Direct analysis of these toxins using HPLC is insufficiently sensitive. However, a combination of toxin concentration, using solid phase extraction (SPE), and fluorimetric derivatisation permits satisfactory HPLC determination of these toxins. A new sensitive method for the determination of anatoxin-a has been developed and was used to confirm the role of this toxin in incidents of fatal canine neurotoxicosis in Ireland. Efficient extraction of the toxin from its matrix was achieved using SPE on a weak cation exchanger and fluorimetric detection was possible after derivatisation with 4-fluoro-7-nitrobenzoxadiazole (NBD-F).

**54 MEMBRANE INTRODUCTION AND ION TRAP MASS SPECTROMETRY**  
 R. Graham Cooks, Dept. of Chemistry, Purdue University, West Lafayette, IN 47907

This presentation describes the operating principles of ion trap mass spectrometer\* and illustrates them with simulations of ion motion calculated for collections of trapped ions. The program ITSIM yields multipartite simulations and mimic\* realistic scan functions. Demonstrations of the simulation in real time display the effects of buffer gas collisions, resonant ejection, dc excitation and other ion trap experiments. The output is presented in the form of two-dimensional animations or trajectory plots showing velocities and positions vs. time. Current capabilities including such high performance features as an extended mass-to-charge range, high resolution, MS\* capabilities, and exquisite sensitivity are summarized. The improved dynamic range resulting (from the use of mass-selective Ionization, specifically that based on the SWIFT (selected waveform inverse fourier transform) method) is illustrated.

The use of semi-permeable membranes for sample introduction in conjunction with SWIFT, allows direct measurement of even sub-parts per trillion levels of volatile organic compounds directly from aqueous solution. A variety of membrane interface! is reviewed. The on-line monitoring capabilities of the MIMS experiment are also illustrated in the case of detection of volatile organics in air, and in monitoring the progress of chemical reactions and fermentations. New MIMS experiments which are selective to compounds with particular functional groups are described and methods in which monitoring is performed from organic solutions are also discussed.

**55 DEVELOPMENT OF AN IMPROVED, DIRECT METHOD FOR THE DETERMINATION OF HALOACETIC ACIDS.** Viorica Lopez-Avila, California Operations Director and Yan Liu, Principal Chemist, Midwest Research Institute, 625-B Clyde Avenue, Mountain View, CA 94043  
 Ruth Hund, Senior Project Manager, AWWA Research Foundation, 6666 W. Quincy Avenue, Denver, CO 80235

The Information Collection Rule requires all drinking water utilities which serve more than 10,000 people to monitor for haloacetic acids. The current EPA methods (552 and 552.1) involve tedious derivatizations that are hazardous. The reliabilities of these methods are substantially dependent on the skill of the analyst and recoveries are highly variable. In addition, the current methods analyze for only six of the nine haloacetic acids.

Researchers at Midwest Research Institute, in conjunction with Dionex Corporation, are developing a direct ion chromatography method for all nine haloacetic acids. The method uses a preconcentration technique and then analysis on an AS-11 column with conductivity detection. Either High Performance Centrifugal Chromatography (HPCPC) or a preconcentration cartridge or disk will be used to lower the detection limits to less than 10 ppb for each analyte. The direct analysis will decrease the time of analysis, increase the safety and reliability of the method.

**56 CHARACTERIZATION OF IODINATION DISINFECTION BYPRODUCTS BY SOLID-PHASE MICROEXTRACTION.** Paul A. Frazee, Robert M. Barkley, and Robert E. Sievers, NASA Specialized Center for Research and Training (NSCORT) in Space Environmental Health, Global Change and Environmental Quality Program, Cooperative Institute for Research in Environmental Sciences, Department of Chemistry and Biochemistry, University of Colorado, Boulder, Colorado 80309-0216.

N.A.S.A. has chosen iodine to disinfect recycled water on long-duration manned space missions. Chlorine disinfection of both natural surface waters and waste water produces chlorine disinfection byproducts (DPs), compounds that are hazardous to human health and are regulated by the EPA. Chlorine DPs are well characterized, but much less is known about iodination disinfection byproducts (IDPs). To date, most analysis of DPs and IDPs in water have been based on either purge and trap or solvent extraction techniques. These methods involve either multi-step procedures or the use of toxic organic solvents. Recently developed solid-phase microextraction (SPME) offers a simple and solvent-free alternative to these traditional methods. SPME uses sorbent coated fused silica fibers to achieve rapid extractions. After extraction, the fibers can be directly desorbed into a gas chromatograph (GC) for analysis. We have developed a new method for IDP analysis based on SPME coupled to GC/MS, GC/FID, and GC/ECD. The characterization of IDPs in flask experiments and in a closed-loop water recycle system will be discussed.

- 57 **MICROWAVE SOLVENT EXTRACTION OF CHLORINATED PESTICIDES FROM SOIL**  
lamie Fish, FAS Analytical Services, P.O. Box 533, Monroe, NC, 28111: Robert Revesz, CEM Corporation, P.O. Box 200, Matthews, NC 28106-0200 (704) 821-7015

Microwave assisted solvent extraction of chlorinated pesticide residues from soil can provide an efficient contemporary alternative to standard Soxhlet or sonication methods. The need for modifications of current EPA methods is becoming paramount as the scientific community attempts to reduce the usage of large amounts of hazardous solvents in routine analysis. This study explores the application of the microwave assisted extraction as an alternative extraction technique for EPA Method 8081 in the determination of organochlorine pesticides in soil. Spiked soil samples were used to determine the extraction efficiencies of various solvents and solvent mixtures over a range of extraction temperatures. Since recoveries of spiked matrices naturally exceed those of real world samples, subsequent analysis of certified reference materials provided the opportunity to optimize operating parameters and compare results to those obtained using current EPA methods. Investigations were also conducted to examine the effect of microwave heating on potential sources of interference including thermally labile pesticide breakdown. EPA methodologies for soil spiking sample preparation and gas chromatography were followed. Only the extraction portion of Method 8081 was changed, thus eliminating the need for major changes in laboratory standard operating procedure. The resulting microwave solvent extraction protocol utilizes a solvent system comparable to the standard Soxhlet method but with at least a 50% reduction in solvent volume. Extraction time is also reduced from hours to minutes with recoveries that equal or exceed those for EPA methods.

- 58 **RESIDUAL POLYMER ANALYSIS BY IMMUNOASSAY**, Andrew I. Dunham, and Robert L. Wetegrove, Nalco Chemical Company, One Nalco Center, Naperville, IL, 60563-1198.

Synthetic polymers are widely used in the production of drinking water. However, analytical methods for trace level determination of polymer residues have been missing. The state-of-the-technology has included colloidal titrimetric or gel permeation chromatographic methods. Both of these techniques are subject to common interferences and neither has the sensitivity to detect trace level concentrations (parts-per-billion).

This paper will discuss the development of a highly specific technique for the analysis of free polymer residuals at parts-per-billion (ppb) concentrations. The analytical technique is based upon immunoassays for specific polymer chemistries. We have developed simple and rugged tests which can detect specific polymers at concentrations as low as 10 ppb. The tests are selective for unbound, residual polymer and detect polymer in complex matrices. Data will be presented from simulations of sedimentation and filtration processes.

- 59 **A COMPARISON OF RURAL AND URBAN CARBONYL CONCENTRATIONS.**  
Mary Ann Magoun, Larry G. Anderson, Randolph Eisenhardt, CU-Denver, Chemistry Dept., Campus Box 194, P.O. Box 173364, Denver, CO 80217-3364

Combustion yields low molecular weight aldehydes and acetone as by-products. Once in the atmosphere, these compounds undergo photolysis to create free radicals, oxidizing hydrocarbon fragments and ultimately increasing the concentration of aldehydes. The presence of these by-products has known toxicological consequences on plant and animal life, necessitating a quantitative evaluation of the compounds. The objective of this research project is the determination of the concentrations of these aldehydes and ketones sampled from a rural site, (Barr Lake State Recreational Park), and the comparison to those from an urban site (Denver Auraria Campus), for which a database has already been established. An intercomparison of the two allows analysis of the photochemistry occurring in the atmosphere as air migrates from an urban area to a rural site. Differences in concentrations of aldehydes and ketones between urban and rural sampling sites have been noted. Levels at Barr Lake are generally higher, most notably for acetone. Data for Barr Lake during the winters of 1994 and 1995 shows a marked increase in overall levels of acetaldehyde and acetone as compared to the previous year.

- 60 ANALYSIS OF ENVIRONMENTAL SAMPLES FOR EXPLOSIVES AND EXPLOSIVES DEGRADATION PRODUCTS BY THERMOSPRAY LIQUID CHROMATOGRAPHY-MASS SPECTROMETRY. Paul M. Gates, Edward T. Furlong, Christopher E. Lindley, and Mark R. Burkhardt, U.S. Geological Survey, National Water Quality Laboratory, 5293 Ward Road, Arvada, CO 80002.

Nitroaromatic explosives and their degradation products are regulated water-soluble contaminants that may be significant water contaminants. A major shortcoming of most explosives analyses is reliable confirmation of identity, particularly the identity of degradation products. To overcome this shortcoming, we applied liquid chromatography-mass spectrometry to determine compound molecular weights and tandem mass spectrometry to confirm molecular structure. A Waters liquid chromatograph with UV-diode array detection and a Finnigan TSQ-70 were coupled by a Thermospray interface. Compounds were separated isocratically using methanol-water on an octadecylsilane column. The identities of known nitroaromatic explosives were confirmed by combined optical absorbance and negative ion mass spectra. For best detection of known compounds, selected ion monitoring mass spectrometry was used. Calibration curves fit quadratic models; correlation coefficients typically exceeded 0.995 over two orders of magnitude. Detection limits ranged from 2.5 to 10 nanograms per injection. Unknown analytes (indicated by optical spectra) were identified by full scan and tandem mass spectrometry experiments on either sample extracts or isolated extract fractions.

- 61 GETTING STARTED IN EPR. S. I. Weissman, Department of Chemistry, Washington University, St. Louis, MO 63130.

This abstract is prepared under duress—the discovery that I am listed as a speaker and a deadline imposed by Sandra Eaton for its delivery. The talk deals with muddling through despite conceptual errors and experimental blindness. I will discuss averaging of anisotropies by molecular reorientation at high and zero external fields, commutation and ~~time~~ evolution, getting rescued from the consequences of one's folly by able and compassionate coworkers.

- 62 MICROWAVE FREQUENCY DEPENDENCE OF CTDEP. Noboru Hiroa, Masahide Terazima, Keishi Ohara, Yuji Miura, Department of Chemistry, Faculty of Science, Kyoto University, Kyoto 606, Japan

CTDEP measurements are conducted in the X-, S- and L-band microwave regions and frequency dependence of the CTDEP spectra of radicals produced by laser photolysis is investigated in detail. The systems studied are : 1) tetraphenyl porphyrin (TPP) and p-benzoquinone / ethanol or 2-propanol or 2-methylpropanol, 2) acetone / 2-propanol, 3) pyrazine / 2-propanol, 4) maleic anhydride / 2-propanol, and 5) xanthone and di-t-butylphenol / SDS micelle. The observed CTDEP spectra strongly depend on the observing microwave frequency. The causes of this dependence include the frequency dependences of TM (Triplet Mechanism), ST<sub>n</sub>M RPM (Radical Pah-Mechanism) due to g-value difference and ST<sub>M</sub> RPM, but the main cause is ascribed to the TM. The TM contribution is estimated for each system. The TM contribution in the TPP system is found to increase with the decrease of the microwave frequency, but in the pyrazine and maleic anhydride systems opposite trends are observed. These results are examined on the basis of the Atkins-Evans theory taking account of the differences in the rotational correlation times, the zero-field splittings and the reaction rates of the precursor triplet molecules. The observed results are explained reasonably well by the Atkins-Evans theory. Frequency dependence of the spectra of spin-correlated radical pairs are also studied in viscous solution and micelle.



63

ANGLE SELECTED ENDOR SPECTROSCOPY; EPR SPECTRA AS 3-DIMENSIONAL ENERGY SURFACES. Boklye Kim, S.P. Greiner and Robert Kreilick, Department of Chemistry, University of Rochester, Rochester, NY 14627

Analysis of ENDOR spectra from randomly oriented solid samples requires knowledge of all polar angles which contribute to fixed resonance fields in the EPR spectrum of the sample. We have found that EPR resonance fields of such randomly oriented samples can be represented as a series of concentric ellipsoids in which each ellipsoid represents a given nuclear spin state. The surface of these ellipsoids gives the resonance fields for a given nuclear spin state. Axonometric plots of these surfaces clearly show the angle dependence of the resonance fields. Slices of these surfaces at constant  $\theta$  or constant  $\phi$  show how the resonance field varies with a given polar angle. Contours taken from the surface at constant resonance field strength yield plots of  $\theta$  versus  $\phi$  for any given field strength. We have analyzed EPR spectra from a series of Cu complexes and some free radicals to determine which angles contribute to ENDOR spectra. The resonance field surfaces of molecules with rhombic and axial  $g$  and hyperfine tensors have been analyzed. Cases in which the 3 principal components of both the  $g$  and hyperfine tensors have significant differences and those in which the  $x$  and  $y$  components of the  $g$  tensor and hyperfine tensor are closely spaced but differ from the  $z$  components have been analyzed. We have also analyzed the case in which there is a very small  $g$  anisotropy and a relatively large hyperfine anisotropy. Magnetic energy surfaces were determined for each of these cases along with angle paths at fields near the EPR turning points. Our analysis shows field values where single crystal like ENDOR spectra should be observed as well as angle paths where 2-dimensional or 3-dimensional ENDOR spectra should be seen. Examples of analysis of proton and nitrogen ENDOR spectra through use of these angle paths will be given.

#### 64 APPLICATIONS OF FT-EPR IN STUDIES OF PHOTOCHEMICAL REACTIONS.

Hans van Willigen, Chemistry Department, University of Massachusetts at Boston, Boston, Massachusetts 02125

With FT-EPR the formation and decay of free radicals formed in pulsed-laser initiated chemical reactions can be monitored with nanosecond time resolution (1). The high spectral resolution of EPR makes it possible to identify transient free radicals. In addition analysis of the time profiles of the resonance peaks gives information on rates of formation and decay. Generally, the FT-EPR spectra in the early time domain (nanoseconds to microseconds after laser excitation) show the effects of Chemically Induced Dynamic Electron Polarization (CIDEP) mechanisms. Analysis of CIDEP contributions contributes to the understanding of the mechanisms of photochemical reactions. This contribution will be concerned with the application of the technique in studies of electron transfer and photoionization reactions in homogeneous and heterogeneous media.

(1) H. van Willigen, P.R. Levstein, and M.H. Ebersole, Chem. Rev. 1993, **93**, 173.  
Supported by the Division of Chemical Sciences, Office of Basic Energy Sciences, DOE.

#### 65 PROBING ELECTRON TRANSFER WITH LOW AND HIGH FIELD EPR. James R. Norris, Department of Chemistry, University of Chicago, Chicago, Illinois 60637-1403.

We have developed experimental as well as theoretical EPR approaches for characterizing electron transfer in one and two dimensional aggregates. Electron transfer in the integral membrane protein antenna complex LHI of *Sphaeroides* is probed by changes in the EPR line shape of bacteriochlorophyll cations generated by chemical oxidation unaided by light. At room temperature a narrow EPR signal is observed while near 10 K a broad EPR line is detected. The EPR line width measurements reveal that electron transfer occurs rapidly at room temperature while the process is halted or substantially slowed at low temperatures. By exploring these electron transfer events in a variety of magnetic fields and with protonated and deuterated samples the electron transfer parameters and aggregation size and shape can be extracted independently. For example, high field EPR of fully deuterated samples permits the examination of the  $g$ -tensor not revealed in these antenna complexes with  $x$ -band EPR. As the rate of electron transfer increases in the LHI complex, the  $g$ -tensor becomes more cylindrical or almost isotropic. The averaged  $g$ -tensor depends on the relative orientations of the bacteriochlorophylls attached to the protein helices as well as the electron transfer rate. Once rates are firmly established for electron transfer in antenna complexes as a function of temperature, modeling of chemistry in integral membrane proteins can be extended to a new level of understanding.

- 66 High Field (140 GHz / 5T) Electron Paramagnetic Resonance and Dynamic Nuclear Polarization G.J. Gerfen, B.F. Bellew, L.R. Becerra, D. Hall, S. Inati, H. Spindler, D J. Singel, W. van der Donk, J. Stubbe, and R.G. Griffin, Francis Bitter Magnet Laboratory, and Dept. of Chemistry, MTT, Cambridge, MA 02139

High field EPR spectra facilitate structural studies in polycrystalline systems. Specifically, spectra arising from multiple paramagnetic species, which overlap at low fields, may be resolved on the basis of differences in g-values. The increased spectral dispersion arising from the g-anisotropy permits accurate studies of the relative orientation of the principal axes of the g- and nuclear hyperfine coupling which may not be possible at low fields. We demonstrate these features and their role in the elucidation of enzymatic mechanisms with spectra of protein based free radical species from ribonucleotide reductase .

Dynamic nuclear polarization (DNP) transfers the polarization of unpaired electrons to nuclei and thus significantly enhances the signals in nuclear magnetic resonance (NMR) spectra. High frequency DNP has been implemented in solid state NMR experiments using a 140 GHz gyrotron as a microwave source and nitroxide radicals as the paramagnetic polarizing agent in a watenglycerol frozen solution. The  $^1\text{H}$  and  $^{13}\text{C}$  NMR signal strengths of both the solvent and an amino acid solute have been enhanced by a factor of 185, which represents a reduction of  $>10^3$  in sample size requirements or  $>10^4$  in signal acquisition time. These experiments using a water: glycerol: nitroxide system open the possibility of acquiring DNP enhanced NMR spectra of large proteins, membranes and other macromolecular samples.

- 67 PHOTOINDUCED ELECTRON TRANSFER AND SPIN POLARIZATION IN HYDROCARBON-POLYANION/ALKALI-METAL COMPLEXES. HaimLevanon, Vladimir Rozenshtein, Gil Zilber, and Mordecai Rabinovitz, Institute of Chemistry and the Farkas Center for Light-Induced Processes, The Hebrew University of Jerusalem, Jerusalem 91904, Israel.

Redox reactions in polycyclic-hydrocarbon/alkali-metal solutions result in multicharged ion-bound complexes, held together by coulombic interactions that restrict mutual diffusion of the charged constituents. Photoexcitation of these donor-acceptor systems induces fast geminate electron transfer (ET) reactions, which are typified by different electron spin polarization (ESP) mechanisms, as reflected by the time-resolved EPR (TREPR) spectra. These reactions are of considerable interest, which provide means for studying ion-pair coulombic interactions, ion solvation, electron spin dynamic and their effects on ion-pair photoinduced ET chemistry. By employing selective laser excitation and pulsed-EPR (Fourier transform) detection, several systems have been studied: 1) rubidium/THF; and 2) conjugated polycyclics/alkali-metals/THF. The TREPR spectra, reveal unique time- and temperature-dependent ET processes, involving highly spin polarized species such as photoelectrons, radical-anions, radical-trianions, and spin correlated pairs. Analyses of the observed phenomena was carried out within the framework of Marcus theory combined with known ESP mechanisms, and two newly proposed mechanisms, namely secondary radical-triplet pair and triplet pair annihilation.

- 68            LIGHT-INDUCED NUCLEAR COHERENCES IN PHOTO SYNTHETIC REACTION CENTERS. Stefan Weber\*\*, Ernst Ohmes\*, Marion C. Thurnauer\*\*, James R. Norris\*\* and Gerd Kothe\*. \*) Department of Physical Chemistry, University of Freiburg, Albertstr. 21, D-79104 Freiburg. \*\*) Chemistry Division, Argonne National Laboratory, Argonne Ill. 60439, USA.

Spin-correlated radical pairs are generated as short-lived intermediates in the primary energy conversion steps of natural and artificial photosynthesis. In this contribution we report observation of *nuclear coherences* in reaction centers of plant photosystem I using a high time resolution CW EPR technique. Suspensions of fully deuterated cyanobacteria *Synechococcus lividus* were irradiated with 2 ns pulses of a Nd:YAG laser and the transient magnetization of the secondary radical pair  $p^*_{\text{aq}} A\sim$  was monitored for various static and microwave magnetic fields. Due to *zero quantum coherence* between two electron spin eigenstates fast *quantum beat oscillations* are observed at early times ( $t < 130$  ns) after laser excitation. At lower temperatures, additional slow persisting oscillations appear which cannot all be assigned to Torrey precessions. Similar observations have recently been reported for bacterial reactions centers. Model calculations show that these slow oscillations represent *nuclear coherences* associated with the non-adiabatic change of the spin Hamiltonian at the instant of the laser pulse. Since the initial nuclear spin configurations are not eigenstates of the radical pair spin Hamiltonian, the light pulse induces a coherent time evolution of the nuclear spin system. This *nuclear coherence* is then transferred to observable electron coherence by means of the continuous microwave magnetic field. The frequencies of the oscillations are equal to differences between nuclear spin levels and thus correspond to ENDOR frequencies. Detection of *nuclear quantum beats* is intimately related to other coherence phenomena in EPR such as coherent Raman beats and ESEEM. Note, however, that in the present case *nuclear coherence* is generated by a short laser pulse and does not require preparation by pulsed microwaves. This represents a unique feature of rapid charge separation such as in photosynthesis. At present accurate values for the  $^{15}\text{N}$  hyperfine tensors interactions in  $p^*_{\text{aq}}$  do not exist. Even the total number of  $^{15}\text{N}$  nuclei involved in coupling is not unambiguously known. Additional studies of the light-induced *nuclear quantum beats* may provide the desired information.

- 69            FROM CONVENTIONAL TO ECHO-DETECTED TRANSIENT NUTATION OF THE PHOTO-EXCITED TRIPLET STATE. T. Tom Lin, Vladimir Kouskov, David J. Sloop and S. I. Weissman, Department of Chemistry, Washington University, St. Louis, Missouri 63130

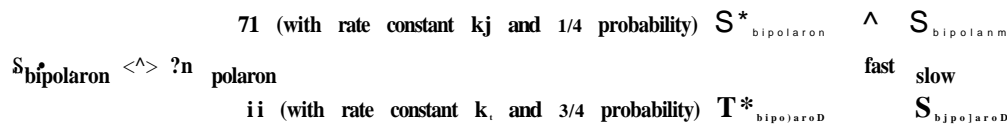
Transient nutation (TN) techniques have been employed to investigate the transient spin dynamics of the photo-excited triplet state of pentacene in *j*-terphenyl crystals by using cw and pulsed EPR spectrometers (X-band). The time evolution of the longitudinal magnetization of the triplet state is monitored in the electron-spin-echo detected TN experiments. We observed different transient responses for the low-field and the high-field transitions. Also the deuteration of the guest and the host molecules affect the observed TN decay signals. We believe these differences arise from the effectiveness of the electron-nuclear cross polarization which is governed by the non-secular hyperfine tensor elements. Spin coherence effects in the cross polarization have been observed in the time resolved DNP experiments induced by a nutation (microwave) pulse.

**70** TRANSIENT EPR WITH NO RF PULSE — A FAST FIELD SWITCHING EXPERIMENT. David J. Sloop, Tien-Sung Lin, J.J.H. Ackerman and S. I. Weissman, Department of Chemistry, Washington University, St. Louis, Missouri 63130

We have succeeded in performing transient EPR without using an RF pulse - a fast field switching (FFS) experiment. The essence of the experiment is the following: a polarizing magnetic field is turned off and an orthogonal observation field is turned on in a time short compared to the paramagnetic spin relaxation processes of the sample while the response of the sample magnetization is measured *via* high speed digitizing network. The experiment is performed in a 185 MHz (67.2 Gauss) FFS spectrometer. Switching-polarizing-field transients aside, the absence of short high power radio/microwave B, sample interrogation pulses greatly reduced receiver dead time. The dead time reduction may allow the study of a variety of paramagnetic centers based on their chemical/biological merits rather than solely on their relaxation time properties.

**71** DOUBLET AND TRIPLET ESR ABOVE AND BELOW  $T_c$  IN  $(\text{BEDT})_3\text{Ta}_2\text{F}_2$ ; Juana Vivo, Acrivos and Lei Chen, San Jose State University, One Washington Square, San Jose CA 95192-0101.

The energy loss near zero field and, the ESR absorption (9.36 GHz) by doublet and triplet states ( $AS_{\pm}=\pm 1$  and  $AS_{\pm}=\pm 2$ ) in the organic conductor are compared above and below  $T_c$  to superconducting cuprates (Acrivos et al, *J. chem. phys.* 86, 60 (1987); *Phys. Rev.B* so, 13710 (1994)). Diamagnetic shifts and changes in the doublet ESR absorption line shapes occur below  $T_c=150\pm 10$  K; the triplet state ESR absorption is observed only below  $T_c$ . The bipolaron model for superconductivity (Alexandrov and Mott (1994)) obtains a lattice polarization in the neighborhood of a free spin  $D_{\text{polaron}}$ , above a ground state singlet  $S^{\wedge\wedge}$ , by  $VzRA$  ( $A \gg T$ ); diffusion and combination of spin polarons leads to the formation of r-inter-site bipolaron singlet  $S^*_{\text{bipolaron}}$ ,  $S_{\text{bipolaron}}$ , and triplet  $T^*_{\text{bipolaron}}$  conduction states, involving at least an equilibrium and several rate processes:



The ESR equilibrium constant is  $K_{H4}^{\wedge} i^{\wedge} / [S_{\text{bipolaron}}^{\wedge}] = Q^{\text{me}}$ ,  $AA(298 \text{ K}) \approx 3E3$  K decreases to  $10^3$  K near  $T_c$  and to 30 K just above  $T_c$ . ESR line widths vs T obtain  $k_i = A \exp(AS/R \cdot AU/RT)$ ; ( $AU/R, A \text{ g e}^{\wedge *}$ ) = (115 K,  $3.5 E7 \text{ s}^{-1}$  above  $T_c$ ); (11 K,  $0.7 E7 \text{ s}^{-1}$  below  $T_c$ );  $D_{\text{diff}} \text{Bion}^{\wedge} B^{\wedge\wedge} \approx 2 \cdot 5E-3 \text{ cm}^2/\text{s}$  and  $A, pk, T_c/h = 1.46 \text{ E}11 \text{ s}^{-1}$ . A AS increase of  $= 2R$  above  $T_c$  can be explained by the disorder introduced by two possible spin flips for each of the three singlet states formed by antiparallel pairing along each of the principal axes of spin-spin interaction, each contributing  $k_B \ln 2$  to the entropy when triplet pairing is not allowed. The  $T^*_{\text{bipolaron}}$  ESR transitions  $AS_{\pm}=\pm 2$  observed above and below  $T_c$  are orientation independent, sharp for the organic conductor with  $A B^{\wedge\wedge} B \text{ mT}$  and, two orders of magnitude broader for cuprates, i.e., AS is greater due to disorder and/or AU is lower due to stronger polarization for the cuprates. We thank Mott, Alexandrov and NSF grants in aid DMR 9307387, INT 9312176.

**72** TWO-CENTER MODEL FOR RADIATION-INDUCED ALUMINUM HOLE CENTER IN STISHOVITE: HIGH PRESSURE PHASE  $\text{SiO}_2$ . Kazutoshi Ogoh, Chihiro Yamanaka, Motoji Bceya and Eiji Ito, Department of Earth and Space Science, Faculty of Science, Osaka University, Toyonaka Osaka 560. Institute for Study of the Earth's Interior, Okayama University, Misasa 682-02, Japan

Stishovite is an octahedrally coordinated phase of  $\text{SiO}_2$  which can be synthesized under high pressure condition over 10 GPa and has potentiality to be a useful material. EPR has been measured for stishovite samples synthesized from high purity  $\text{SiO}_2$  glass or natural quartz and irradiated by y-rays both at room temperature and at 77 K. The prominent signal detected at 77 K has anisotropic g-factors of orthorhombic symmetry,  $g_x = 2.0155$ ,  $g_y = 2.0094$  and  $g_z = 2.0033$ , and hyperfine sextets ( $7=5/2$ ) with  $A_x = 0.394 \text{ mT}$ ,  $A_y = 0.372 \text{ mT}$  and  $A_z = 0.436 \text{ mT}$ . The g-factors and the hyperfine structure constants have been confirmed by spectrum simulation and compared with those of aluminum hole center in quartz and  $\text{O}_2^{\cdot -}$  radical in anhydrite ( $\text{CaSO}_4$ ). It is concluded that the newly found signal is due to a two-center type oxygen hole center,  $\text{O}_2^{\cdot -}$ , associated with an aluminum atom at the silicon site in stishovite.

- 73 **ELECTRON PARAMAGNETIC RESONANCE STUDY OF TRANSITION ION DIMERS FORMED IN CeO<sub>2</sub>-** Edmond Abi-Aad<sup>1</sup>, Abdelrhani Bennani<sup>1</sup> and Antoine Aboukais<sup>2</sup>. <sup>1</sup>-Laboratoire de Catalyse Heterogene et Homogene, URA CNRS 402, Universite des Sciences et Technologies de Lille, 59655 Villeneuve d'Ascq Cedex France. <sup>2</sup>-Laboratoire de Catalyse et Environnement, Universite du Littoral, 17 Avenue Bleriot, 62100 Calais Cedex France.

MeCeO oxides (Me=transition ion metal) with different atomic ratios Me/Ce, have been prepared by coprecipitation and impregnation methods. The solids were calcined under oxidizing or reducing atmospheres at given temperatures. An EPR study evidenced the presence of transition ion dimers in CeO<sub>2</sub>. Well resolved fine structures have been obtained for CuCeO and MeCeO oxides. The signals at half magnetic field intensity ( $A_m = 2$ ) of spectra, characteristic of dimers were presents in all the solids. The transition ions forming the dimers are located in oxygen vacancies near Ce<sup>3+</sup> ions present in the solid before their introduction. The distance between the ions has been evaluated to 3.5+0.3Å. All the measured EPR parameters values have been confirmed from simulated spectra. The environment symmetries of ions have been determined. They change from octahedral to tetrahedral following the cation nature.

- 74 **RECENT DEVELOPMENTS OF THE DYNAMIC IMAGING OF DIFFUSION ESR TECHNIQUE IN THE APPLICATION OF POLYDISPERSED POLYMER SAMPLES**

Dajiang Xu, Jozef K. Moscicki, Jack H. Freed, Elizabeth Hall, and Christopher K. Ober  
Baker Laboratory, Cornell University, Ithaca, NY 14853-1301

A new methodology utilizing the DID-ESR (dynamic imaging of diffusion by ESR) technique has been developed for its application to polydispersed polymer samples. Due to polydispersity the spin-labeled polymer molecules have a wide range of molecular weight, and this is also true for the matrix polymer molecules. The work presented here includes a complete theoretical derivation of the new DID-ESR method in the presence of polydispersity, plus its first application for measuring translational diffusion coefficients of liquid crystalline (LC) polymer melts. This includes a detailed analysis of the reliability of the method, the proper interpretation of average diffusion coefficients, and how the molecular weight dependence of the diffusion coefficient may be obtained from even a single experiment on a sample with wide polydispersity. The results obtained by our new method are consistent with those from the FRES (forward recoil spectroscopy) technique on the same model system. A comparison is made between these two techniques, and future experiments which combine them to further study LC polymer diffusion mechanisms are proposed.

- 75 **AN ESR AND ENDOR STUDY OF RADICAL CATIONS GENERATED FROM ARYLSILANES AND GERMANES,** Manfred Lehnig, Heino Klaukien and Susanna Reiß, Fachbereich Chemie, Universitat Dortmund, D-44221 Dortmund, Peter Such, BRUKER Analytische Meßtechnik, D-76287 Rheinstetten, Silberstreifen,

In the radical anions of a 1-alkyl- and silylbenzenes, the antisymmetric s-orbital of the unperturbed benzene is occupied in the former, the symmetric T-orbital in the latter, Whereas the symmetric i-orbital is occupied in the radical cation of alkylbenzenes, it has been shown by ESR spectroscopy in the solid state that it is the SOMO in radical cations of silylbenzenes as well, This result will be confirmed by ESR investigations in solution, Radical cations were generated by irradiation with Hg(CF<sub>3</sub>COO)<sub>2</sub> in CF<sub>3</sub>COOH,



In some cases, radical cations from R-Ph-R are observed, Radical cations of germylbenzenes were not formed, During reaction of diphenylsilanediol with AlCl<sub>3</sub> in CH<sub>2</sub>Cl<sub>2</sub>, the appearance of the radical cation has been reported, However, after treating arylsilanes and germanes with AlCl<sub>3</sub> in CH<sub>2</sub>Cl<sub>2</sub>, radical cations of substituted anthracenes are observed, Hexamethylgermane gives a mixture of highly methylated anthracene radical cations,

**76** A STUDY OF THE STRUCTURE OF SURFACE BOUND SURFACTANT AGGREGATES:  
APPLICATION TO SHEAR FLOCCULATION

Martin G. Bakker and Dexter D. Murphy, Department of Chemistry, The University of Alabama, Tuscaloosa, Al 35487-0336

Surfactant aggregates bound to particle surfaces are involved in many important applications including mineral processing, waste water remediation, chromatography and preparation of nanoparticles. The size and structure of these aggregates substantially affects these various applications, but has been little studied. Indeed there is considerable controversy as to the existence of the various aggregate structures postulated. EPR is an ideal tool to address these issues.

Work carried out on shear-flocculation (a type of particle aggregation process used in mining) will be used to illustrate how EPR can provide insight into surfactant aggregation during this process. Spin-labeled hexadecyltrimethylammonium bromide (HTAB) has been used to determine the extent of surfactant aggregation on silica and to probe the equilibrium between the various surfactant aggregate structures. Preliminary work indicates that when FITAB binds to the surface significant alteration in the mobility of the headgroup occurs. Further information about the structure of the aggregates can be gained using paramagnetic broadeners. Work with potassium ferricyanide suggests that counterions are included among the surfactant headgroups adsorbed at the particle surface as predicted by theoretical studies. Potentially EPR can also be used to determine the size of surfactant aggregates.

**77** COMBINING TIME-RESOLVED FLUORESCENCE QUENCHING AND EPR TO STUDY STATISTICAL DISTRIBUTIONS AND COLLISION RATES OF ADDITIVE MOLECULES IN MICELLES, Barney L. Bales and Christopher Stenland, California State University at Northridge 91330 and Mats Almgren, University of Uppsala, Sweden.

Time-resolved fluorescence quenching (TRFQ) has been used to study dynamics in micelles for many years, while EPR has only recently been employed for this purpose. Both techniques employ an indicator (fluorescent molecule with a long life time for TRFQ — nitroxide free radical for EPR) and both rely upon measuring the effect of added molecules (quenchers or paramagnetic broadeners). Since nitroxide free radicals and some other paramagnetic molecules effectively quench fluorescence, it is relatively easy to design experiments to study essentially the same system using both techniques, substantially increasing the information available. The two techniques are compared within the context of one such system: sodium dodecyl sulfate (SDS) in the concentration range 25 - 200 mM with  $\text{Cu}^{++}$  as the quencher/broadener. The indicator is pyrene for TRFQ and a hydrophobic nitroxide free radical for EPR. Invoking a small electrostatic repulsion between  $\text{Cu}^{++}$  ions residing upon the same micelle, improves the agreement between theory and experiment for both experiments. The aggregation numbers increase linearly as the one-fourth power of the SDS concentration with a coefficient of correlation,  $r = 0.999$ . The fluorescence quenching rates and the spin exchange rates are quantitatively similar leading to the conclusion that the quenching rate is nearly diffusion controlled with a diffusion coefficient near that of  $\text{Cu}^{++}$  in water. The quenching rate follows an inverse square dependence upon the micelle radius with  $r = 0.994$ . EPR measurements show that the polarity and the microviscosity of the environment of the indicator vary linearly with micelle size and that the addition of  $\text{Cu}^{++}$  causes the micelles to grow less than about one molecule.

- 78 **BIOLOGICAL EFFECTS OF THE NITROGEN DIOXIDE RELEASING-AGENT AMMONIUM DINITRAMIDE. AN EPR/SPIN-LABELING STUDY.** Alasdair T. Carmichael<sup>1</sup>, J. Armengol<sup>1</sup>, A. Young<sup>1</sup>, K. Dean<sup>2</sup>, M.D. Pace<sup>3</sup>, L. Steel-Goodwin<sup>2</sup>. <sup>1</sup>AFRRI, Bethesda, Maryland 20889, <sup>2</sup>OL AL HSC/OETB, WPAFB, Dayton, OH 45433, <sup>3</sup>Code 6120, NRL, Washington, D.C. 20375

EPR/spin-labeling was used to measure the effects of active nitrogen intermediates on transferrin and lactoferrin binding to WB344 hepatocytes. Chemicals absorbed through the gastroenteric system are metabolized mainly by the liver. The effects of the  $\text{NO}$ , generating oxidizer, ammonium dinitramide (ADN), on receptor function in WB344 hepatocyte membranes was studied. The iron-saturated proteins were treated with the spin-labeling reagent, 3-[[[(2,5-dioxo-1-pyrrolo-dinyl)oxyl]carbonyl]-2,5-dihydro-2,2,5,5-tetramethyl-1H-pyrrolyl-1-oxy, which reacts with peptide amino groups yielding a nitroxide-labeled protein molecule. EPR spectra were recorded following addition of the labeled proteins to hepatocyte suspensions and their binding to these cells. The procedure was repeated with hepatocyte cells incubated with ADN for twenty minutes prior to the addition the labeled proteins. The results show that ADN decreased both lactoferrin and transferrin binding to WB 344 receptors. The binding of labeled proteins to the WB 344 hepatocytes was characterized by EPR generating a binding curve resulting from the titration of cell suspensions with spin-labeled protein.

- 79 **THE FAST REACTION STOPPED FLOW EPR TECHNIQUE/AS APPLIED TO THE UNFOLDING OF PROTEINS/LIMITATIONS AND POTENTIAL REMEDY,** Raymond E. Hansen, Update Instrument, Inc., 6701 Seybold Road, Madison, WI 53719

The phenomenon of flow birefringence was first reported by Maxwell in 1873. The phenomenon is made apparent when a beam of linearly polarized light incident upon the flowing medium emerges elliptically polarized. It has been reported that the phenomenon is not only observable in flowing liquids, but also in certain flowing gases (e.g., nitrogen and carbon dioxide).

In stopped flow EPR, in the investigation of radicals during the condition of steady flow, if the E-field impinges upon the H<sub>z</sub>-field within the sensitive volume of the resonator, the phenomenon will modulate the resonance frequency congruously with the nature of the flow. Thus, in the case of turbulent flow (and by its decay after the bulk flow has been arrested), the modulation will be random, i.e., the recorded signal will be noisy. Consider the investigation of the unfolding process of proteins (by urea or guanidine) employing spin label addends. Since the earliest state of the process is measurable (by rapid field scanning) during steady flow, this noise imposes a limitation upon the detection of the initial interval of the process. This limitation and the instrumental means for overcoming it will be presented.

- 80 **WHEN IS A G-VALUE NOT A G-VALUE AND A SYMMETRY NOT A SYMMETRY IN EPR OF PROTEINS WITH HIGH SPIN FERRIC IRON ?**

Betty J. Gaffney, Chemistry, Johns Hopkins Univ., Baltimore, MD 21218

We have specialized in quantitative lineshape analysis of EPR spectra resulting from non-heme iron centers in proteins for many years. Phenylalanine hydroxylase, transferrin and lipoxigenases have been the subjects of study. The purpose of this presentation is to highlight the reasons for the quantitative approach and point out problems with more qualitative approaches to spectral analysis. The ferric transferrin complexes with several anions provide excellent examples of the problems. For the carbonate complex, direct analysis from the X-band EPR spectrum would lead to the erroneous conclusion that the lower and middle Kramers doublet transitions correspond to different zero-field splittings. For the oxalate complex, the distribution in zero field splittings could lead more than one interpretation regarding the symmetry of the complex. For lipoxigenases, we have completed the x-ray structure. The aim of current studies is to correlate EPR information about symmetry with the x-ray structure information.

**81 APPLICATION OF ANGLE SELECTED ENDOR FOR STRUCTURE DETERMINATION.**  
Devkumar Mustafi, Department of Biochemistry and Molecular Biology, The University of Chicago,  
920 East 58th Street, Chicago, Illinois 60637.

Electron nuclear double resonance (ENDOR) is the most accurate means to measure electron-nuclear hyperfine couplings. On the basis of ENDOR-determined principal hyperfine couplings, precise electron-nucleus dipolar separations can be estimated. Therefore, application of ENDOR should provide very high resolving power for study of molecular structure. Except for single crystal studies, however, there has been limited application of ENDOR to assign structure and conformation of molecules. We have demonstrated that dipolar electron-nucleus distances can be determined over a 3-11 Å range with less than 5% uncertainties through application of "angle selected ENDOR" to molecules in polycrystalline and frozen glassy systems. Angle selected ENDOR is based not only on dipolar separations, which are scalar quantities, but also the dependence of the hyperfine patterns on relative coordinates with respect to magnetic axes in the molecule. With specific reference to the two paramagnetic systems, namely nitroxyl spin-labels and the vanadyl ( $V^{2+}$ ) ion, application of angle selected ENDOR rests on the fact that in both systems the  $g$  tensors exhibit low anisotropy and are nearly axially symmetric, and the  $g_z$  component for both is perpendicular to the molecular  $xy$  plane. Examples of these relationships and how they can be determined by using angle selected ENDOR for structural analysis will be discussed with reference to spin-labeled penicillin, a specific substrate for  $\beta$ -lactamases, and vanadyl-reconstituted kidney stone inhibitor protein nephrocalcin. (Supported by GM 21900).

**82 SATURATION RECOVERY EPR OF  $Cu(CATECHOL)_2$ .** W. Froncisz,<sup>§</sup> W. E. Antholine, C. C. Felix, and J. S. Hyde, <sup>^</sup>Institute for Molecular Biology, Jagiellonian University, Krakow, Poland, and Biophysics Research Institute, Medical College of Wisconsin, Milwaukee, WI 53226.

$Cu(catechol)_2$  is a low molecular weight, square-planar cupric complex with four oxygen donor atoms. Dilution of the sample from 3 to 0.4 mM has no effect on the line position and little effect on the lineshape of the CW-EPR spectrum, whereas easily detectable changes in the saturation-recovery signals are observed. Little changes in the saturation-recovery signals are observed upon dilution of the sample from 0.4 to 0.1 mM. The changes above 0.4 mM are interpreted in terms of dipole-dipole interactions between  $Cu(catechol)_2$  complexes. The results are relevant for the determination of the distance between two similar paramagnetic copper complexes. The saturation recovery signals are best fit to at least double exponentials. The prefactor of the exponential function for the longer relaxation time,  $T_{1L}$ , increases, and the prefactor for the shorter relaxation time,  $T_{1S}$ , decreases as the pump width varies from 1  $\mu$ s to 1 ms. The dependence of the relaxation time,  $T_{1L}$ , on magnetic field at 16.7 K varies by less than 20% from the  $g_{\parallel}$  region to the  $g_{\perp}$  region with little  $M_j$  dependence in either region. Results are discussed with respect to previous reports for other cupric complexes in which  $T_1$  dependence on magnetic field is 2-fold between the  $g_{\parallel}$  and  $g_{\perp}$  region and with respect to mechanisms involving copper or proton nuclear relaxation. The work is supported by NIH grants RR01008 and GM27665.

**83 EPR STUDY OF EXTRINSIC DEFECTS IN AMORPHOUS SILICA**  
William R. Austin and Robert. G. Leisure, Dept. of Physics  
Colorado State University, Fort Collins, CO 80523.

Exposure of amorphous silica to ionizing radiation is known to produce EPR active defects associated with degradation of the covalently bonded **SiO<sub>2</sub>** network. The presence of trace impurities in the lattice results in additional extrinsic spin defects, indicating the impurity atoms act as precursors for radiation damage. Suprasil 1, a commercial silica glass, is known to contain ~1200 ppm network bonded hydroxy 1, which may serve as a source of radiolytic free hydrogen. Other spin defects in this material have been attributed to interstitial carbon monoxide<sup>^</sup> and network bond<sup>^</sup>M **nitrogen<sub>2</sub>**. In this work, extrinsic spin defects in Suprasil 1 are studied vs. x-ray irradiation dose, irradiation temperature, and post irradiation anneal. Results are interpreted with emphasis on what can be learned about the mechanism(s) of radiation damage.

<sup>^</sup>Work supported by the Office of Naval Research under Contract N00014-91-J-1607.

<sup>^</sup>D.L. Griscom, M. Stapelbroek and E.J. Friebele, *J. Chem. Phys.* **78**,1638 (1983)

<sup>^</sup>T. E. Tsai, D.L. Griscom and E.J. Friebele, *Phys. Rev. B* **38**, 2140 (1988)



IS A SECOND RADICAL INVOLVED IN THE HEMOGLOBIN AUTOXIDATION UNDER HYPOXIA ?. C. Balagopalakrishna, O.O. Abugo, and J.M. Rifkind, Laboratory of Cellular and Molecular biology, National Institutes of Health, National Institute on Aging, 4940, Eastern Avenue, Baltimore, Maryland 21224.

The autoxidation of hemoglobin has been studied by EPR at low temperatures (235 K) to facilitate the observation of various intermediates. The results reveal that autoxidation of hemoglobin under hypoxia is a two step process, involving the initial formation of a peroxy-like heme complex, which then decomposes to give methemoglobin and superoxide radical. The EPR spectrum corresponding to the superoxide radical which has features in the  $g = 2$  region and which grows over the signal of the methemoglobin, could not be simulated with a two component model, involving methemoglobin and superoxide radical. A third isotropic component is necessary to reproduce the experimental spectrum. The origin of this third species, with  $g = 2.1053$ , is not clear and is postulated to arise from the protein. Both the superoxide and the protein radical features disappear on thawing the sample, indicating their instability at room temperature. These features which are seen only in partially oxygenated hemoglobin samples, indicate a new mechanistic pathway for autoxidation under hypoxia.

### 85 $^{51}\text{V}$ ESE-ENDOR STUDIES OF VANADIUM COMPLEXES,

James A. Ball and R. David Britt,

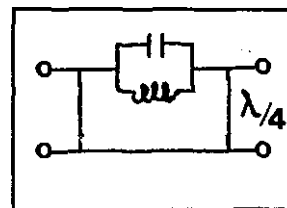
Department of Chemistry, University of California, Davis, CA 95616

We are exploring the high frequency  $^{51}\text{V}$  electron spin echo - ENDOR spectroscopy of the vanadyl ion ( $\text{VO}^{2+}$ ) complexed with various ligands. By using the large anisotropy present in the EPR spectra of vanadyl systems, we obtain high quality angle-selected ENDOR spectra which provide a reliable measure the small quadrupole interaction of  $^{51}\text{V}$ . To date we have found that in  $\text{VO}^{2+}(\text{H}_2\text{O})_5$  the quadrupole parameter is about twice as large as in  $\text{VO}^{2+}(\text{H}_2\text{O})_6$  (Py  $\ll$  0.097 MHz vs. P|| fa 0.55 MHz). Because vanadyl nucleoside complexes are used as inhibitors or mimics of phosphate biochemistry, such characterization on different complexes should yield useful structural data for biological systems.

### 86 THE DESIGN OF MIMS-STYLE TRANSMISSION CAVITIES FOR PULSED EPR

Chris Bender. *Albert Einstein College of Medicine, Bronx, NY 10461.*

The so-called Mims cavity is a transmission mode sample resonator that features low quality and filling factors, and it is well suited to conducting the repertoire of pulsed EPR measurements (ESEEM, LEFE, ENDOR) in liquid helium immersion dewars. Analysis of the structure by using a network analyzer verifies that the design is based on the concept of a bandpass filter in which a  $X/2$  resonator is spanned by  $X/4$  shunts on either side (see figure). The waveguide sections on both transmitter and receiver sides of the cavity feature tapered transitions. The taper on the transmitter waveguide section reduces the height of the guide in the E-plane, and the length of the taper is very much larger than  $X/2$  in order to minimize transmission VSWR. The receiver side of the transmission line is likewise tapered, but the taper length is on the order of  $X/2$  in order to maximize VSWR of any reflections that would return to the cavity. Electroformed prototypes spanning 4 - 18 GHz will be on display.



87 EXPERIMENTAL INVESTIGATIONS OF THE LINEAR ELECTRIC FIELD EFFECT.  
Chris Bender. *A Ibert Einstein College of Medicine, Bronx, NY 10461.*

The linear electric field effect is a measure of the shift of the Zeeman (i.e. EPR) spectrum in response to an electric field applied perpendicular to the microwave field, and this regard, it is a form of Stark spectroscopy. Although LEFE can be measured from a direct measure of the perturbed cw-EPR spectrum, the spin echo-detected method is more sensitive to small shifts. A series of case studies of the LEFE was conducted with geometrically constrained model complexes. The aim of these experiments was to evaluate the resolving power of the measurement and determine whether unambiguous variations among a given class of compounds could be detected. Systems under study include copper pyridinecarboxamide complexes, among which the spacing between  $g\uparrow$  and  $g\downarrow$  varies, and strained 'sandwich' complexes.

88 PULSED EPR STUDIES OF THE TYPE I COPPER CENTER OF RUSTICYANIN.  
Chris Bender, Danilo Casimiro, H. Jane Dyson. *Albert Einstein College of Medicine and The Scripps Institute.*

Rusticyanin is a blue copper protein derived from *Thiobacillusferrooxidans* that features a copper binding site analogous to other Type I copper proteins, namely one cysteine, methionine, and two histidines. ESEEM spectra of this protein resemble those of other Type I proteins (e.g. azurin, plastocyanin, stellacyanin), which are dominated by  $^{14}\text{N}$  modulation phenomena. The spectra consist of effective zero field NQR transitions of the remote (amino) imidazole nitrogen atom, which indicate that  $e^2Qq/h \ll 1.35$  MHz and  $r_j \ll 0.95$ . The double quantum line suggests that  $A^{\wedge} \ll 2.1$  MHz. These values differ from those of azurin, which has a similar copper coordination motif. Azurin, however, features an  $e^2Qq/h \gg 1.42$  MHz and distinctly resolved pair of  $A_{iso}$  (1.7 & 2.2 MHz); The differences may reflect variation in metal-ligand interactions among the proteins.

89 PULSED EPR STUDIES OF 'ENGINEERED' YEAST SUPEROXIDE DISMUTASE.  
Chris Bender, Yi Lu, Joy Goto, Joan Valentine, Jack Peisach. *Albert Einstein College of Medicine and UCLA.*

ESEEM investigations of the copper center of yeast SOD were conducted on several forms of the protein subjected to point amino acid substitutions in the vicinity of the copper/zinc binding site. The w.t. yeast SOD ESEEM spectrum resembles those previously obtained from bovine SOD,<sup>1</sup> both of which reveal splittings among the intense lines commonly assigned to NQR transitions in  $\text{Cu}(\text{imid})_x$  complexes. The splitting has been attributed to differences in the quadrupole parameters of His-46, -48, -120 versus the bridging Cu-His63-Zn. Variations in the  $^{14}\text{N}$  modulation spectra of ligand imidazoles to copper (His46, His48, His63, His120) are detected and interpreted in context of known structural changes inferred from studies using NMR and x-ray techniques. One of the two imidazole types can be resolved by  $g$ -selection, suggesting that the imidazoles differ with respect to their relative orientation to the molecular axis in addition to nuclear quadrupole parameters.

<sup>1</sup>Fee, J.; Peisach, J.; Mims, W. *J. Biol. Chem.*, 256, 1910 (1981).

- 90 UNPAIRED ELECTRON DELOCALIZATION IN ACCEPTOR-BRIDGE-DONOR MOLECULAR STRUCTURES. R. Krzyrniniewski\*, A. Bielewicz\*, 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 the progress that has been achieved in the study of electron delocalization in acceptor-hydrogen bridge-donor molecular structure using EPR spectroscopy. New measurements on the role that substitutional acid groups play in the alternation of the degree of delocation of an electron created by  $\nu$ -irradiation. Specific results are reported on polycrystalline piperidine modified by trifluoroacetic, perchloric and dichloroacetic acids. It is found that the degree of delocalization increases as the electronegativity of the hydrogen bridge increases. Measurements on stilbene and stilbene with different substitutional groups after  $\nu$ -irradiation are also reported. The objective of these measurements is to evaluate the suitability of these and other materials with similar structures for use in non-linear molecular electronics and optics.

- 91 CONTINUING OXIDATION STUDIES OF MOTOR OILS AT TYPICAL CRANKCASE TEMPERATURES. J. Kudynska and H.A. Buckmaster, Department of Physics and Astronomy, University of Victoria, P.O. Box 3055, Victoria, B.C., Canada. V8W 3P6

The change in the free radical concentration present in eight selected SAE 10W-30 motor oils as they were aged at a crankcase temperature of 150 °C is reported. The 9 GHz CW-EPR measurements were made at 293 K at appropriate time intervals over -1500 hours. It is found that this selection of domestic motor oils manufactured by six different petroleum companies exhibit widely different behaviour. These variations are believed to be due to the different proprietary additives that manufacturers include in their virgin oils as anti-oxidants, detergents, sludge dispersants and varnish inhibitors. These oils are blended to minimize viscosity and thermal breakdown. It is found that the spin concentration increases with age during the measurement interval. The rate of increase was greatest in the one synthetic oil included in this study and was the smallest in two of those oils intended for gasoline fueled internal combustion engines. These results will be compared with those reported previously at crankcase temperatures of 100 °C and 200 °C.

- 92 ANISOTROPIC ROTATIONAL DYNAMICS OF MRI PARAMAGNETIC CONTRAST AGENTS. J.W. Chen, R.B. Clarkson, R.L.Belford, Illinois EPR Research Center, 506 S. Mathews, Urbana, IL 61801.

Rotational dynamics is an important determinant of the relaxation enhancement abilities of paramagnetic contrast agents (PCA) used in magnetic resonance imaging. Much of the work on PCA's to date assumes an isotropic rotational correlation time. However, anisotropic rotation may arise in many situations either coincidentally *in vivo* or by design. We have used EPR experiments and simulations to investigate rotational dynamics of model small-chelate PCA's (such as EDTA and DTPA) in viscous environments, utilizing vanadyl as the dynamic probe. We have used both isotropic and two-motion anisotropic model to describe the EPR spectra. In this environment, even though these complexes are nearly spherical, in the intermediate motional regime only simulations based on an anisotropic model can accurately simulate the motionally-modulated EPR spectra. As we alter the environment toward the fast limit or the rigid limit, the different motions become similar in time scale, and hence anisotropy becomes small; an isotropic model then fits the spectra nearly as well as the anisotropic model. The results from this study and similar studies can be used to study the relaxation enhancement behavior of PCA's undergoing anisotropic rotational dynamics. Research supported by the NIH (GM-42208 with resources provided by RR01811).

- 93 PBN SPIN TRAP INHIBITS KUPFFER CELL PHAGOCYTOSIS AND LIVER NITRIC-OXIDE SYNTHASE. Jane Z. Chen,\* Lester A. Reinke,\* S. Yamashiro, Guoman Chen, Betty Anne Quinn, Tony Hayes and Edward G. Janzen. Departments of Clinical Studies, Biomedical Sciences, and Pathology, Ontario Veterinary College, University of Guelph, Guelph Ontario, N1G 2W1; \* on leave from College of Pharmacy, Oklahoma Health Sciences Center, University of Oklahoma, Oklahoma City, OK, 73104.

We have published the observation that PBN (C-phenyl terf-butyl nitron) inhibits edema formation caused by carbon tetrachloride in the rat liver. The MRI intensity of the hydropic regions (edema) is markedly diminished after treatment with relatively small doses of PBN (1). PBN was also found to inhibit well known signs of  $CCl_4$  toxicity in hepatocytes judged by electron microscopic (EM) investigation. When it was shown that gadolinium chloride also inhibits formation of liver hydropic regions from  $CCl_4$  (2), our attention was directed towards liver Kupffer cells, since gadolinium chloride protects Kupffer cells from  $CCl_4$  toxicity. The question we wanted to answer was does PBN also inhibit Kupffer cell function. Well known EM methods were applied using carbon particles from India ink to show that PBN does in fact inhibit Kupffer cell phagocytosis. This observation led to the next question, namely does the inhibition of Kupffer cell function by PBN involve nitric oxide and/or nitric oxide synthase (NOS). This poster will show that PBN does inhibit liver (and lung) NOS function as judged by reduced nitric oxide production. Rat lung microsomal dispersions and rat hepatocytes were used in this study.

(1.) E.G. Janzen, *et al.*, *Free Rad. Res. Commun.*, 9, 325 - 335. (1990).

(2.) R.A. Towner, *et al.*. *Can. J. Physiol. Pharmacol.*, 72, 441 - 446. (1994).

- 94 PULSED ENDOR AT 35 GHz

Clark E. Davoust. Brian M. Hoffman, Peter E. Doan, Victoria J. DeRose, Department of Chemistry, Northwestern University, Evanston, IL 60208-3113.

Our group has constructed and tested a 35 GHz ('K<sub>1</sub>-band') electron-spin echo spectrometer for the purpose of obtaining pulsed ENDOR on metalloproteins. This spectrometer has shown large signal-to-noise enhancements over our 9.5 GHz (X-band) pulsed ENDOR spectrometer, making many experiments that were essentially impossible at X-band, routine. Details concerning the microwave bridge, pulse architecture and resonator designs will be given. A survey of results of both Mims and Davies ENDOR will be shown that compare and contrast our 9 and 35 GHz pulsed spectrometers.

- 95 INVESTIGATION OF THE DINUCLEAR FE CENTER OF METHANE MONOOXYGENASE BY ADVANCED PARAMAGNETIC RESONANCE TECHNIQUES: ON THE GEOMETRY OF DMSO BINDING. Victoria J. DeRose. Katherine E. Liu\*, Stephen J. Lippard\*, Brian M. Hoffman, Departments of Chemistry, Northwestern University, Evanston, IL 60208-3113 and **Massachusetts** Institute of Technology, Cambridge, MA 02139.

We have performed an extensive characterization of the mixed-valence form of the dinuclear Fe center of methane monooxygenase hydroxylase ( $MMOH_{m.v.}$ ) by using advanced paramagnetic resonance spectroscopy to study enzyme from *Methylococcus capsulatus* (M<sub>c</sub>) (Bath). The techniques used in this study include continuous wave and pulsed electron nuclear double resonance (ENDOR) spectroscopy, both at Q-band microwave frequencies, to examine  $^{14,15}N$ ,  $^1H$ ,  $^{13}C$ , and  $^{57}Fe$  nuclei in native  $MMOH_{m.v.}$  and in  $MMOH_{m.v.}$  treated with DMSO. A procedure for describing the  $^1H$  hyperfine tensor of the bridge hydroxide proton predicts the orientation of the g-tensor relative to the cluster framework. Q-band pulsed  $^1H$  and  $^{13}C$  ENDOR measurements of labelled DMSO show that this inhibitor binds in a distinct site with a well-ordered structure, and further indicate that it is O-bound to the Fe ion of the mixed-valence cluster. The analysis, coupled with  $^1H$  X-band electron spin-echo envelope modulation data, places limitations on the possible orientation of the bound DMSO.

- 96 ELECTRON SPIN ECHO ENVELOPE MODULATION SPECTROSCOPIC ANALYSIS OF ALTERED NITROGENASE MoFe PROTEINS FROM *AZOTOBACTER VINELANDII*. Victoria J. DeRose, Chul-Hwan **KW**, John Peters<sup>1</sup>, William E. Newton\*, Dennis R. Dean<sup>1</sup>, and Brian M. Hoffman Department of Chemistry, Northwestern University, Evanston, IL 60208-3113 and department of Biochemistry and Anaerobic Microbiology, Virginia Polytechnic Institute and State University, Blacksburg, VA 24061.

Electron spin echo envelope modulation (ESEEM) spectroscopy has been used to study changes in the polypeptide environment of the FeMo-cofactor that were elicited by amino-acid substitutions within the nitrogenase MoFe protein  $\alpha$ -subunit. Two separate types of modulation due to weakly-coupled <sup>14</sup>N have been identified in wild-type and mutant MoFe proteins. The appearance of the <sup>14</sup>N ESEEM correlates in part with the activity of the enzyme, and is a delicate probe of the local structure of the FeMo cofactor. Simulations of ESEEM data obtained at both 9- and 35-GHz microwave frequencies will be presented.

- 97 THE COUNTOUR LINESHAPE OF CROSS-PEAKS IN TWO-DIMENSIONAL ESEEM SPECTRA OF ORIENTATIONALLY-DISORDERED SPIN SYSTEMS  $S=1/2$  and  $1=1/2$ . Sergei A. Dikanov<sup>1</sup> and Michael K. Bowman<sup>2</sup>, <sup>1</sup>Macromolecular Structure & Dynamics, Environmental Molecular Sciences Laboratory, Pacific Northwest Laboratory, Richland WA 99352, <sup>2</sup>Institute of Chemical Kinetics and Combustion, Novosibirsk 630090, Russia.

At present two variants of 2D-ESEEM experiments based on three-pulse ( $n/2-x-x/2-T-n/2$ ) and four-pulse ( $7t/2-T-7\tau/2-t,-7t,-7\tau/2$ ) sequences were proposed. In the first case the set of stimulated echo patterns is measured as a function of time  $(t+T)$  at different values of  $t$ . In second experiment, usually called HYSORE (hyperfine sublevel spectroscopy), the amplitude of the four-pulse stimulated echo is measured as a function of times  $t$ , and  $t_1$ . The important advantage of both 2D techniques lies in the creation of cross peaks whose coordinates nuclear frequencies from opposite electron spin manifolds ( $v_{0(p)}, v_{p(a)}$ ) in three-pulse and ( $\pm v_{s(p)}, \pm v_{p(a)}$ ) four-pulse 2D ESEEM spectra. Among the two indicated 2D techniques, HYSORE finds increasing application due to its equal resolution in both dimensions and phase sensitivity. The present work gives a simple analytical description of countour lineshapes from the nuclear spin  $1=1/2$  at arbitrary values of isotropic and anisotropic hyperfine coupling and nuclear Zeeman frequency. These results indicate that the countour lineshape is a very informative experimental representation which clearly reflects the variation of different experimental parameters and can be easily used for their determination.

Pacific Northwest Laboratory is a multiprogram national laboratory operated by Battelle Memorial Institute for the U.S. Department of Energy under contract DE-AC06-76RLO 1S30. This research was supported by Associated Western Universities, Inc. Northwest Division (AWU NW) under Grant DE-FG06-89ER-75522 or DEFG92RL-12451 with the U.S. Department of Energy.

- 98 ORIENTATION SELECTION IN ENDOR AND ESEEM: TOWARDS A SET OF GUIDELINES FOR INTERPRETING COMPLEX ENDOR AND ESEEM PATTERNS, Peter E. Doan, Brian M. Hoffman, Department of Chemistry, Northwestern University, Evanston, IL 60208-3113.

ENDOR and ESEEM spectra in metalloproteins often exhibit extremely complicated lineshapes due to the processes of orientation-selection. During the past two years, our group has been reviewing and revising our understanding of the underlying mathematics of orientation-selection. Numerical methods that are based on an *ad hoc* parameterization of the problem that were first derived for increasing execution speed of our simulation programs have a tremendous additional benefit: they provide extremely powerful tools for predicting the patterns without the need of simulation. A simple set of rules have been devised for nuclear spin Hamiltonian information for  $1=1/2$  and  $1=1$  nuclei in orientation selected ENDOR patterns. We are now attempting to extend these rules to understanding ESEEM spectra as well.

- 99** MASS SPECTROMETRIC STUDY OF PBN SPIN TRAPPING PRODUCTS FROM HYDROXYL RADICAL GENERATING SOURCES. Coit M. DuBose, Edward G. Janzen and Hong Sang, National Biomedical Center for Spin Trapping and Free Radicals, Free Radical Biology and Aging Research Program, Oklahoma Medical Research Foundation, 825 N. E. 13th Street, Oklahoma City, Oklahoma 73104, USA.

The detection of hydroxyl (HO $\cdot$ ) radicals by spin trapping with nitrones has been studied for many years. The predominant and persistent chemical product has been assumed to be produced by the conventional spin trapping route with the HO $\cdot$  adding to the carbon atom of the nitrono function group. Little or no attention has been paid to other reaction routes or products which may occur in these systems. Using tandem mass spectroscopy and deuterated analogs of PBN (C-phenyl N-ferf-butyl nitrono, *-di*, *-dg* and *-di*,), evidence will be presented indicating the aromatic addition of HO $\cdot$  to the phenyl group of PBN. Data from chemical (photolytic, Fenton, Udenfriend, etc.) and biological (microsomal and animal) systems will be presented.

- 100** 250GHz EPR Studies of Solvent Cage Structure in o-terphenyl (OTP)  
Keith A. Earle, Nino Polimeno, Jozef Moscicki, Jack H. Freed  
Baker Laboratory, Cornell University, Ithaca, NY 14853-1301

We have performed a set of experiments on the organic glass OTP with three spin probes: perdeuterated TEMPONE (PDT), perdeuterated MOTA, similar to PDT but with a short flexible tail, and cholestane (CSL), a rigid cigar shaped spin probe. Using a recently developed theoretical model of Polimeno and Freed, we can study the degree to which probe size affects the local dynamic structure of the solvent cage.

Above the melting transition of OTP at 69C, our 250GHz data suggest that the solvent has no long-lived modes that would give rise to a local orienting potential. Below the melting transition, the high field CSL and MOTA data indicate that there is a local ordering that increases as the temperature is lowered. Supplemental experiments at X-band indicate that the MOTA- and PDT/OTP systems consist of a rapidly exchanging component due to expelled spin-probe dimers and a normally diffusing component.

Our results suggest that OTP in the solid state has a clathrate structure that is too large to significantly effect the rapidly diffusing spectral component of PDT/OTP. The large CSL probe experiences significant aligning torques due to the local dynamic cage potential and probe and cage diffusional rates monotonically approach the rigid limit as the temperature is reduced. The MOTA data suggest behavior intermediate to these two extreme cases.

- 101** SILICON GRAPHICS IMPLEMENTATION OF PROGRAMS FOR SPECTRAL SIMULATION IN METAL ION EPR

KUTBUDDIN S. DOCTOR, BRENDAN C. MAGUIRE AND BETTY J. GAFFNEY

This presentation is primarily an announcement that we have implemented our S=5/2 simulation programs on the SGI UNIX systems. Using an Indigo X22, run times are approximately 20 times faster than our previous applications on Macintosh systems. The SGI code is available.

- 102** A High Frequency EPR Study of the Radical Formed Upon Inhibition of *E. coli* Ribonucleotide Reductase with a Substituted Deoxynucleotide.  
Gary J. Gerfen,<sup>1,2</sup> Brendan F. Bellew,<sup>1,2</sup> Wilfred van der Donk,<sup>2</sup> David J. Singel,<sup>3</sup>  
Robert G. Griffin,<sup>1,2</sup> and JoAnne Stubbe.<sup>2</sup>

Francis Bitter Magnet Laboratory and<sup>3</sup>Department of Chemistry, MIT, Cambridge, MA 02139.<sup>3</sup>Department of Chemistry and Biochemistry, Montana State University, Bozeman, Montana 59717.

Ribonucleotide reductases (RNRs) catalyze the conversion of nucleotides to deoxynucleotides and thus provide the building blocks for DNA synthesis. In *E. coli* RNR, the postulated reduction mechanism involves initiation by a tyrosyl radical which, through a series of long range coupled electron and proton transfer reactions, generates sulfur-containing radicals in the substrate nucleotide binding site. This mechanism is supported by kinetic and site-directed mutagenic studies which have identified five catalytically essential cysteines and by a recent x-ray crystallography study which reveals that three of these cysteines are located within 6 Å of one another in the substrate binding pocket. Inhibitors of *E. coli* RNR consisting of substituted nucleotides have been developed which yield relatively stable radicals upon enzyme inactivation. We have characterized the structure of the radical formed upon enzyme inactivation with 2'-azido-2'-deoxyuridine 5'-diphosphate (NUDP) using 140 GHz and 9 GHz EPR spectroscopy. Determination of g-values, nitrogen hyperfine coupling constants, and relative principal axis orientations indicate that the radical has the structure [X-N $\leftarrow$ S-R]. EPR spectroscopy of the radical upon incorporation of deuterated cysteine into RNR and <sup>15</sup>N-azide into the nucleotide inhibitor substantiate this assignment. Possible structures and their implications for the mechanism of inhibition are presented. These results provide strong support for the involvement of radical based intermediates in nucleotide reduction.

- 103** S-B AND STEPPED-FIELD ELECTRON ELECTRON DOUBLE RESONANCE SPECTROSCOPY, Barnard T. Ghim, Richard W. Quine, George A. Rinard, Sandra S. Eaton, and Gareth R. Eaton, Departments of Engineering and Chemistry, University of Denver, Denver, CO 80208.

ELDOR measurements were made on an irradiated L-alanine sample using a stepped field in conjunction with an inversion recovery 180-Ti-90-T2-180-T2-observe echo sequence at 3.4 GHz. With our locally-constructed pulsed magnetic field system, one can step the magnetic field to a new location in the spectrum to excite the spins that contribute to one portion of the EPR spectrum, and then return the magnetic field back to the original location in the spectrum and sample the spin system at this resonant field with subsequent microwave pulses (e.g., a two-pulse echo sequence). The spins can be sampled as quickly as 500 ns after the field jump, depending on the magnitude of the jump. When AB = 25 gauss, room temperature STELDOR measurements showed an enhancement of the L-alanine spin echo signal.

- 104** SPIN LABELING OF UNSATURATED LIPIDS WITH NITROSO-COMPOUNDS. Thierry Guiberteau, Lawrence J. Berliner. Department of Chemistry, The Ohio State University, Laboratory of In-Vivo Electron Spin Resonance, 120 W. 18th Ave., Columbus, Ohio 43210.

Nitrosobenzene and nitrosotoluene are important xenobiotics which display mutagenic, carcinogenic and cytotoxic effects *in vivo*. They react with unsaturated fatty acids via a pseudo Diels Alder mechanism to form a free radical adduct, easily detectable by EPR spectroscopy. Recently, a broad three line spectrum, characteristic of the reaction of nitrosobenzene with lipids, was detected from a mouse in an L-band EPR experiment (Hirota Fujii, Baolu Zhao, Janusz Koscielniak, Lawrence J. Berliner, Magn. Reson. Med., 31, 77 (1994)). In order to elucidate how these nitroso compounds are metabolized, where they might be localized, and with which unsaturated fatty acid they react preferentially, we have undertaken the study of the reaction between nitrosobenzene or nitrosotoluene and different fatty acids such as docosahexaenoic acid, arachidonic acid, nervonic acid, linoleic acid and linoleic acid. We present the studies concerning the measurements of the hyperfine coupling of the free radical adducts, studies of formation and degradation kinetics and the studies of the stoichiometry of the reaction between nitrosobenzene and polyunsaturated fatty acids. The presented data could be used as control in the studies of nitroso-compounds in *in vivo* EPR experiments.

- 105 VISCOSITY MEASURED IN ANIMALS WITH DEUTERATED SPIN LABELS AND VERY LOW FREQUENCY EPR: SIGNIFICANCE AND LIMITS. HJ Halpern, GVR Chandramouli, ED Barth, University of Chicago, Chicago, IL 60637

Differences in the solution spectrum linewidths of magnetic substrate manifold have been related in simple theoretical and experimental studies to rotational correlation times of the observed EPR substrate. The analysis of Nordio has been modified for very low frequency operation. A similar simple analysis between rotational correlation time and solvent viscosity yields a measurement of the viscosity of the compartment in which the EPR substrate distributes. These are measurements of diffusion of a sugar size molecule in solution; they do not recapitulate  $T_2$  MRI measurements. Serum viscosity diminution has long been associated with states of chronic disease. Both simple chemical reactions and enzyme catalysed reactions are slowed by diminution of solvent viscosity. We report measurements with very low frequency EPR of linewidth differences from  $^{15}\text{N}$ -2,2,5,5-tetra-deuterio-methyl-l-pyrrolinyl-oxide (mHCTPO) (MW=95) in samples of glycerol (MW= 87)/water and aqueous fetal bovine serum albumen (MW~15,000), a globular serum protein. These show surprisingly similar linewidth differences at equal viscosities. Using very low frequency EPR linewidth differences in tumors and normal tissues have been measured. Analysis of this data will be presented in pursuit of tumor and normal tissue differences.

- 106 PRIMARY NUCLEAR SPIN ECHOES IN EPR INDUCED BY MICROWAVE PULSES. **Michael Hubrich, Eric C. Hoffmann and Arthur Schweiger**, Swiss Federal Institute of Technology, CHN-G32, CH-8092 Zurich, Switzerland.

Primary nuclear spin echoes in electron-nuclear spin systems, created and detected by exciting electron spin transitions only, are presented. Two different pulse sequences for the generation of this new type of echo in magnetic resonance are presented. The first sequence consists of two *semi-selective* microwave pulses with flip angles  $\theta$  and  $2\theta$  followed by a weak microwave probe pulse for detection. Remarkably, the flip angles have to be *doubled* compared to the ones used in the usual primary spin echo experiment. In the second sequence the nuclear spin echo is created by non-selective microwave pulses and observed as a modulation on top of the electron spin echo. The theoretically predicted features are verified experimentally, in particular, the separation of the primary echoes from the coherence-transfer echoes by using two-dimensional representations of the data in the frequency domain. As an example of application the determination of the phase memory time of nuclei coupled to the electron spin is discussed and an experimental demonstration is given.



- 107 PULSE TRAIN-DETECTED ELECTRON SPIN ECHO ENVELOPE MODULATION. Eric C. Hoffmann, Michael Hubrich and Arthur Schweiger, Swiss Federal Institute of Technology, CHN-G32, CH-8092 Zurich, Switzerland.**

One-, two- and three-dimensional electron spin echo envelope modulation (ESEEM) spectroscopy is extensively used to determine the structure of paramagnetic compounds. Of particular interest are experiments which measure the free evolution of the nuclear coherence that decays with the phase memory time of the nuclei. Most of these experiments are based on the three-pulse stimulated echo sequence. A new type of detection for the stimulated echo and its modulation is presented that consists of a train of short and weak microwave pulses creating a train of stimulated echoes. In principle, with such a pulse train the whole ESEEM pattern can be recorded in a single shot experiment; thus leading to a time advantage, which in particular becomes important for recording more dimensional spectra. First experimental data are presented. The signal to noise ratio is compared with that one of the probe pulse detection (coherent Raman beat) and the standard three-pulse method.

- 108 ADVANCED EPR, CW AND PULSED ENDOR, AND ESEEM, STUDIES OF BIS(MALEONITRILE-DITHIOLATO)-NICKEL(III) COMPLEXES. Jennifer E. Huyett, Suranjan B. Choudhury\*, Michael J. Maroney\*, Brian M. Hoffman, Department of Chemistry, Northwestern University, Evanston, IL 60201. department of Chemistry, University of Massachusetts Amherst, Amherst, Ma 01003.**

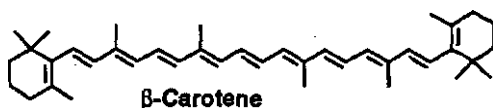
Expanding on studies of Maki et al. (A.H. Maki, N. Edelstein, A. Davison and R. H. Holm, / *Am. Chem. Soc.*, 6,4580 (1964)) and Heuer et al. (W. B. Heuer, A. E. True, P. Swepston and B. M. Hoffman, *Inorg. Chem.*, 27,1474 (1988)), we have applied the titled methodologies to measure hyperfine couplings and thereby the spin densities in bis(maleonitrile-dithiolato)-nickel(III). Using ligands labelled with  $^{13}\text{C}$  at the olefinic carbons or with  $^{13}\text{C}$  cyanide along with natural abundance  $^{14}\text{N}$  and labelled  $^{15}\text{N}$  on the cyanide, the spin density for the molecule has been determined. The results show the spin is located almost entirely on the **MS4** core with surprisingly small  $n$  delocalization throughout the molecule.

- 109 MULTI-FREQUENCY EPR MEASUREMENT OF THE ZERO-FIELD SPLITTING OF MRI PARAMAGNETIC CONTRAST AGENTS. H. Kang, J.H. Hwang, R.B. Clarkson, R.L. Belford, Illinois EPR Research Center, 506 S. Mathews, Urbana, IL 61801.**

Accurate measurement of the zero-field splitting (ZFS) is important in the development of paramagnetic contrast agents (PCA) used in magnetic resonance imaging. The ZFS controls the electron relaxation rate which affects the proton relaxivity; it also reveals important relationship between the PCA chelate structure and the PCA's effectiveness. Whereas previous ZFS measurements of gadolinium contrast agents consisted of indirect methods of measuring the EPR linewidth, we obtain their ZFS parameters, D and E, by characterizing their powder spectra at several EPR frequencies. The EPR powder spectra of frozen glasses of GdCl<sub>3</sub>, GdDTPA, GdEDTA, GdTTHA, and GdDOTA at L-band, X-band, and Q-band (1.5 GHz, 9.5 GHz, and 35 GHz) are measured. Varying the frequency controls the relative magnitude of the ZFS and the Zeeman interactions, resulting in changes in the powder lines. These are interpreted with the aid of a spectral simulation program for an  $S = 7/2$  powder spectrum. Research supported by the NIH (GM-42208 with resources provided by RR01811).

**A TIME-RESOLVED EPR (35 GHZ) STUDY OF CAROTENOID CATION RADICALS.** A. S. Jeevarajan<sup>1</sup>, N. I. Avdievich<sup>2</sup>, M. D. E. Forbes<sup>2</sup> and Lowell D. Kispert<sup>1</sup>. a) Department of Chemistry, The University of Alabama, Tuscaloosa, AL-35487. b) Venable and Kenan Laboratories, Department of Chemistry, CB# 3290, University of North Carolina, Chapel Hill, NC 27599.

The importance of carotenoids in photosynthesis as a photoprotector and an auxiliary antenna pigment is well established. However, the role of the carotenoid cation radical in the photosynthetic apparatus is not well understood. Further, in order to incorporate the photoprotect character of the carotenoids in artificial solar devices, the decomposition processes should be understood. As part of this research effort, the cation radicals of carotenoids were generated photochemically by irradiating a flowing solution of carotenoids in carbon tetrachloride with 308 nm laser light. The time-resolved EPR signal measured in a 35 GHz EPR cavity is polarized. The polarized EPR signals from the anion radical of the solvent and the cation radical of carotenoid are seen. The electron transfer occurs from the excited singlet state of the carotenoids as deduced from the polarization pattern. The Q band frequency measurements resolve the two radicals with quite different g factors more efficiently than the X band EPR measurements. This work was supported by the Division of Chemical Sciences, Office of Basic Energy Sciences, Department of Energy, under grant DE-FG-05-86ER13465.



- 111**      **DECAY RATES OF NITROXIDE RADICALS IN THE PRESENCE OF BIOLOGICAL REDUCING AGENTS.** Yashige Kotake, Zhenqiang Yu, and Edward G. Janzen, National Biomedical Center for Spin Trapping and Free Radicals, Free Radical Biology and Aging Research Program, Oklahoma Medical Research Foundation, Oklahoma City, OK 73104.

The loss of nitroxide free radicals in biological systems due to their reaction with endogenous reducing agents hampers experiments in spin trapping, spin labeling and spin probing, including the use of nitroxides as contrast reagents in magnetic resonance imaging. We have investigated structural factors that determine the stability of nitroxides in the presence of biological reducing agent. Second order decay rate constants ( $k_2$ ) of various nitroxide radicals in the reaction with ascorbate were determined at room temperature. The experimental setup consists of a stopped-flow system combined with an EPR flow-cell. Sodium ascorbate in phosphate buffer was mixed with an aqueous buffer solution of nitroxide and the decay of the EPR signal was recorded after an abrupt stop of the flow. Significant dependence of the decay-rate constants on the structure of the nitroxide was found. For example,

4-hydroxy 2,2,5,5-tetramethylpyrrolidine 1-oxyl (TEMPOL)	$k_2 = 1.4 \text{ M}^{-1} \text{ Y}^{-1}$
4-oxo 2,2,5,5-tetramethylpyrrolidine 1-oxyl (TEMPONE)	$k_2 = 2.6 \text{ M}^{-1} \text{ Y}^{-1}$
3-phenyl 4-imidazolyl 2,2,5,5-tetramethyl pyrrolidine 1-oxyl	$k_2 = 24.2 \text{ M}^{-1} \text{ Y}^{-1}$

We are in the process of screening various kinds of nitroxide radical using this method.

- 112**      **ELECTRON NUCLEAR DOUBLE RESONANCE (ENDOR) STUDIES OF THE CARBON MONOXIDE INHIBITED MoFe PROTEIN OF NITROGENASE.** Hong In Lee,<sup>1</sup> Rob C. Pollock,<sup>2</sup> Linda M. Cameron,<sup>3</sup> Victoria J. DeRose,<sup>1</sup> Brian J. Hales,<sup>3</sup> W. H. Orme-Johnson,<sup>2</sup> and Brian M. Hoffman,<sup>1</sup> Departments of Chemistry, <sup>1</sup>Northwestern University, Evanston, IL 60208, <sup>2</sup>MIT, Cambridge, MA 02139, Louisiana State University, Baton Rouge, LA 70803.

Nitrogenase, consisting of an Fe and a MoFe protein, catalyzes the reduction of dinitrogen to ammonia. The MoFe protein contains the P-cluster ( $\text{Fe}_7\text{S}_7$ ) pair and the FeMo-cofactor ( $\text{Fe}_7\text{S}_7\text{Mo}:\text{homocitrate}$ ). In the resting state, the MoFe protein shows an EPR signal arising from an  $S=3/2$  center of the FeMo-cofactor. The reduction of dinitrogen is inhibited under CO atmosphere. Under turnover conditions with CO inhibition, the  $S=3/2$  EPR signal disappears and two new signals, associated with the FeMo-cofactor, are observed: one at low CO pressure with  $g_{\parallel} < 2$  (2.09, 1.97, 1.93) and one at high CO pressure with  $g_{\parallel} > 2$  (2.17, 2.06, 2.06).

<sup>13</sup>C, <sup>1</sup>H, and <sup>57</sup>Fe Q-band ENDOR studies have been performed to characterize the CO inhibited MoFe protein. <sup>13</sup>C ENDOR revealed that a single CO is bound to a cluster of the MoFe protein at low CO pressure and at least one and possibly two CO molecules are coupled to a cluster at high CO pressure. This is the first direct observation of a small molecule bound to a metal center of the enzyme. In this presentation, the characteristics of the CO inhibited protein including the identification of the bound cluster and the magnetic properties of the inhibitor will be addressed by <sup>13</sup>C, <sup>1</sup>H, and <sup>57</sup>Fe ENDOR studies of turnover samples prepared under various conditions.

- 113** FAR-INFRARED ESR OF SOME DISTORTED TETRAHEDRAL MANGANESE (II) COMPLEXES. W. Bryan Lvnch<sup>a</sup>, Richard M. Wood<sup>b</sup>, Debra M. Stucker<sup>b</sup>, and Jack H. Freed<sup>c</sup>, department of Chemistry, University of Evansville, 1800 Lincoln Avenue, Evansville, IN 47722; department of Chemistry, Gettysburg College, Gettysburg, PA 17325; <sup>c</sup>Baker Laboratory of Chemistry, Cornell University, Ithaca, NY 14853.

We will present ESR spectra at 250 GHz for the compounds Mn(triphenylphosphine oxide)<sub>2</sub>X<sub>2</sub>, where X = Cl, Br, and I. The compounds were studied as powders at room temperature. The spectra are highly resolved and reveal features which are highly dependent upon the magnitudes of the axial (D) and rhombic (E) zero-field distortion parameters. Acceptable fits of the spectra were made using field-swept, third-order perturbation theory of all five electron spin transitions in the high-field limit. We find that these compounds have large amounts of axial and rhombic distortion. Both D and E increase with increasing size of the halogen, but the ratio E/D decreases with increasing size. The value of D ranges from 0.17 cm<sup>-1</sup> to 0.91 cm<sup>-1</sup>; values for **T** range from 0.28 to 0.25. Attempts will be made to correlate the zero-field parameters with the structures of the complexes. Supported by: NM Grant No. RR07126, a Research and Professional Development Grant from Gettysburg College, and The Undergraduate Research Committee at the University of Evansville.

- 114** ESE-ENDOR STUDIES OF PARAMAGNETIC CENTERS OF PHOTOSYSTEM II  
R. David Britt, David W. Randall, M. Lane Gilchrist, Jr. and James A. Ball,  
Department of Chemistry, University of California, Davis, CA 95616

Electron Spin Echo ENDOR experiments performed on a broad radical EPR signal observed in photosystem II particles depleted of Ca<sup>2+</sup> indicate that this signal arises from the redox-active tyrosine Yz. The tyrosine EPR signal width is increased relative to that observed in a manganese-depleted preparation due to a magnetic interaction between the photosystem II manganese cluster and the tyrosine radical. The manganese cluster is located asymmetrically with respect to the symmetry related tyrosines Yz and Yq. The distance between the tyrosine and the manganese cluster is estimated to be approximately 4.5 Å. Based on the close proximity of the Mn cluster to the redox active tyrosine Yz, we propose that this tyrosine abstracts protons from substrate water bound to the Mn cluster. In addition, <sup>55</sup>Mn ESE-ENDOR experiments are revealing new details about the electronic structure of mixed valence Mn model compounds and the Mn cluster of PS II.

- 115** INVESTIGATION OF THE ELECTRONIC STRUCTURE OF THE PRIMARY ELECTRON DONOR IN BACTERIAL PHOTOSYNTHESIS BY HIGH-FREQUENCY (95 GHz)/HIGH-FIELD EPR  
Martina Huber<sup>\*</sup>, Jens T. Tórring<sup>b</sup>, Uwe Fink<sup>o</sup>, Reiner Feickl<sup>c</sup>, Craig C. Schenck<sup>e</sup>, Wolfgang Lubitz<sup>a</sup>, Klaus Mdbius<sup>a</sup> "Institut für Organische Chemie, Freie Universität Berlin, D-14195 Berlin, Takustr.3; "Institut für Molekulphysik, Freie Universität Berlin, D-14195 Berlin; <sup>e</sup>Technische Universität Berlin, D-10623 Berlin; <sup>c</sup>Universität München, D-80638 München <sup>a</sup>Colorado State University, Ft. Collins CO 80523

The anisotropy of the G-tensor (**G**) of the primary electron donor (D) cation radical (D<sup>+</sup>) is investigated. D is a dimer of bacteriochlorophyll molecules. Due to the small anisotropy of G the determination of G-tensor components requires high-field EPR methods, e.g. microwave frequencies of 95 GHz (W band). A systematic study of the principal values of the G-tensor of various bacterial organisms and site specific mutants is performed (e.g. of *Rhodobacter sphaeroides*, *Rhodospseudomonas viridis*, *Chloroflexus aurantiacus*). In addition to principal values the directions of the tensor axes are needed, which can only be obtained through single crystal experiments. Here we investigate a heterodimer mutant, HL (M202), in which one BChl of D is replaced by bacteriopheophytin. This causes the unpaired electron to be localized on the BChl, which is the D<sub>l</sub> half of the dimer. Consequently, (3 properties of this mutant reflect properties of the monomer. Surprisingly, the direction of the smallest G-tensor component deviates from the normal of the plane of the 7r-electron system. The axes of **Q** are close to those of the native system suggesting a strong contribution of D<sub>l</sub> to the G-tensor of the dimer.

- 116** ENDOR AND ESEEM EXPERIMENTS ON THE RADICAL CATION OF THE PRIMARY DONOR,  $P700^+ >$  IN PHOTOSYSTEM I. Hanno Kafi, Petra Fromme, Lars E. Andreasson\*, Freidhelm Lendzian, Horst T. Witt, and Wolfgang Lubitz, Max-Volmer-Institut für Biophys. und Phys. Chemie, Technische Universität Berlin, StraB des 17. Juni 135, D-10623 Berlin, Germany, \*Dept. of Biochemistry and Biophysics, University of Gdteborg, Medicinaregatan 9C, S-41390 Goteberg, Sweden

In the light-induced charge separation of photosynthesis an electron is transferred from a primary donor P to a series of electron acceptors. The electron transport chain is located in a transmembrane protein complex. In this work the hyperfine couplings (hfc's) of the oxidized primary donor cation radical,  $P700^+ >$  investigated in photosystem (PS) I. The radical cation of chlorophyll a serves as a model system and is also characterized by EPR, cw-ENDOR, 2-dimensional stimulated echo ESEEM and HYSORE (P. Hofer et al., *Chem. Phys. Lett.* 1986, 132, 279). Proton and nitrogen hfc's have been determined. To facilitate the interpretation of the ESEEM spectra, a  $^{15}N$  ( $I=1/2$ ) labeled PS I preparation from spinach was investigated. Several  $^1H$ -hfc tensors were determined by cw-ENDOR applied to PS I single crystals from *Synechococcus elongatus* (for 6 Å X-ray structure see N. Krauß et al. *Nature* 1993, 361, 326). The analysis yielded the orientation of  $P700^+ >$  relative to the symmetry axes of the crystal unit cell. ESEEM also has been applied to  $P700^+ >$  PS I crystals.

- 117** EPR AND ESEEM DETERMINATION OF THE STRUCTURE OF A FREE RADICAL INTERMEDIATE IN THE REACTION OF LYSINE 2,3 AMINOMUTASE  
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Lysine 2,3 aminomutase catalyzes the interconversion of L-lysine and L-freta-lysine in Clostridia. The enzyme contains an iron-sulfur cluster [1] and pyridoxal 5' phosphate (PLP). The classical role of PLP is to form a Schiff's base linkage with  $N_\epsilon$  of a protein-based lysine residue; this adduct generally serves to stabilize a negatively-charged, diamagnetic reaction intermediate. In the present system, however, the reaction has been shown to pass through a free-radical intermediate, whose unpaired electron is concentrated upon  $C_\alpha$  of the *substrate* lysine [2]. It was proposed [2] that PLP forms an adduct to  $N_\epsilon$  of the substrate lysine, in order to stabilize an azacyclopropyl carbinyl radical intermediate, which converts quickly into a  $C_\alpha$ -based radical to which PLP remains linked. To test this hypothesis, PLP was prepared with deuterium at C4. Deuterium peaks in the three-pulse ESEEM spectra showed well-resolved splittings at most magnetic field settings on the absorption line. Analysis of the ESEEM results confirms that the  $C_\alpha$  radical is a PLP adduct, and supports the proposed catalytic mechanism.

1) R. M. Petrovich, F. J. Ruzicka, G. H. Reed, & P. A. Frey. *J. Biol. Chem.* 266,7656 (1991).

2) M. D. Ballinger, P. A. Frey, & G. H. Reed. *Biochemistry* 31,10782 (1992).

Supported by grants DK28607, GM35752, and GM25052 from the NIH, USPHS.

- 118** ANALYSIS OF STATIC CONFORMATIONAL DISTRIBUTIONS IN THE SOLID STATE BY  $^3H$  ESEEM SPECTROSCOPY: ANGULAR DISPERSION IN SIDE CHAIN ORIENTATIONS IN AMINO ACID TYROSINE RADICALS. Kurt Warncke, Gerald T. Babcock & John McCracken, Department of Chemistry, Michigan State University, East Lansing, MI 48824.

The experimental analysis of static distributions in hydrogen hyperfine interactions in randomly-oriented radicals in the solid state by using  $^3H$  electron spin echo envelope modulation spectroscopic techniques has been examined systematically. The hyperfine interaction between the two (3-methylene  $^1H$  nuclei and coupling  $\rho$ -spin density ( $\rho^\wedge$ ) at ring carbon atom  $C_i$  in the tyrosine neutral radical trapped in low temperature aqueous glass were addressed specifically. Successful simulation of the stimulated echo envelope modulation depths and lineshape responses to changes in  $T$  and magnetic field strength were achieved by using two distributed  $f3$ - $^3H$  hyperfine tensors. The principal tensor distribution is caused by variation in the isotropic coupling owing to a distribution in rotamers about the  $C_i$ - $C_p$  bond. The extent of the distribution for the weakly- and strongly-coupled  $B$ - $^3H$  is  $|0_\omega|=60^\circ-92^\circ$  and  $|0_\omega|=60^\circ-28^\circ$ , where  $\phi_i$  is the dihedral angle between  $C_p$ - $H_p$  and the  $P_{rf}$ -orbital axis. The value of  $\rho^\wedge$  at  $C_i$  is  $0.35 \pm 0.03$ . Relative rotamer populations are given by the conformational weighting function required for exact reproduction of the lineshapes. The relative rotamer populations represent the quantum mechanical probability amplitudes for the  $C_i$ - $C_p$  torsional oscillator. Three potential minima about  $C_i$ - $C_p$  are revealed, which are caused by different  $C_p$ - $C_y$  conformations. The potential energy curves and frequencies, and their dependence on  $Q$ - $C_p$ , identify key factors that control the reactivity of tyrosine radical catalytic centers in enzymes. The analysis has been applied to tyrosine radicals in the photosystem II enzyme. **Support: NIH GM-37300 (G.T.B.) & GM-45795 (J.M.).**

- 119** THE NATURE OF THE Cu<sub>A</sub> SITE IN NITROUS OXIDE REDUCTASE FROM *PSEUDOMONAS STUTZERI* Frank Neese<sup>a</sup>, Walter G. Zumft<sup>b</sup>, William E. Antholine<sup>c</sup> and Peter M. H. Kroneck<sup>a</sup>, "Universitat Konstanz, Fakultat fur Biologie, W-78434 Konstanz, FRG, <sup>b</sup> Lehrstuhl fur Mikrobiologie, Universitat Karlsruhe, W-76128 Karlsruhe, FRG, <sup>c</sup> Biophysics Research Institute, Medical College of Wisconsin, Milwaukee WI53226, USA

We have investigated the Cu<sub>A</sub> site in the multicopper enzyme nitrous oxide reductase from *Pseudomonas stutzeri* by applying multifrequency EPR and MO calculations. <sup>63</sup>Cu/<sup>65</sup>Cu enriched enzyme samples show distinct EPR spectra at S-, C-, X- and Q-band which are interpreted in terms of a [Cu(1.5)Cu(1.5)]<sub>2</sub> S=1/2 mixed-valence site. The application of mixed valence theory leads to an *effective spectroscopic model* with non-colinear **g** and A<sup>Cu</sup> tensors. The model is successfully applied to simulate the EPR spectra at different frequencies. *Iterative Extended Hueckel* calculations in conjunction with a perturbation theoretical treatment of the system **g** and the ligand SHF tensors are used to set up a *structural model* for the site. The final model involves a *copper-copper bond* and bis-Cysteine coordination and is consistent with the model proposed by Blackburn et al. (*Biochemistry*, 33 (1994), 10401-10407). The calculations also provide further insight into the nature of the mixed-valence phenomenon in copper dimers. The dependence of the double exchange parameter on distance, geometry and nature of bridging ligands is discussed.

- 120** TIME-DOMAIN EPR DETERMINATION OF INTERSPIN DISTANCES IN SPIN-LABELED HEMOGLOBINS, Vladimir Budker, Jing-Long Du, Michael Seiter, Gareth R. Eaton, and Sandra S. Eaton. Department of Chemistry, University of Denver, Denver, Colorado USA 80208

Nitroxyl free radical electron spin relaxation times for spin-labeled low-spin methemoglobins were measured between 6 and 120 K by two-pulse ESE and by SR EPR. As temperature is increased, the relaxation rates for the Fe(III) become comparable to and then greater than the iron-nitroxyl spin-spin splitting, which collapses the splitting in the continuous wave EPR spectra of the nitroxyl and causes an increase and then a decrease in the nitroxyl ESE decay rate. Throughout the temperature range examined, interaction with the Fe(III) increases the spin-lattice relaxation rate (1/T<sub>1</sub>) for the nitroxyl. The relaxation rates for the Fe(III), measured by SR and ESE, were used to analyze the temperature-dependent changes in the spin echo decays and in the SR data for the interacting nitroxyl and to determine the interspin distance, *r*. The values of *r* for three spin-labeled methemoglobins were between 15 and 15.5 Å. Analysis of the nitroxyl ESE and SR data also provides values of the iron relaxation rates at temperatures where the iron relaxation rates are too fast to measure directly by SR or ESE spectroscopy.

- 121** TIME-RESOLVED ELECTRON SPIN RESONANCE STUDIES OF SPIN TRAPPING: QUANTITATIVE ASPECTS OF NITRONE SPIN-TRAPPING. Keith P. Madden and Hitoshi Taniguchi, Radiation Laboratory, University of Notre Dame, Notre Dame, IN 46556-0579.

The utility of the nitrone spin trap DMPO (5,5-dimethyl-1-pyrroline-N-oxide) resides in its ability to efficiently produce a characteristic spin-adduct aminoxyl radical from a given transient parent radical. Quantitative measurement of the rates of radical spin trapping and the efficiency of the trapping reaction have previously been attempted using kinetic optical spectrophotometry. However, the weak optical absorption of the DMPO spin adducts have necessitated the use of indirect competition experiments to measure the trapping rate of DMPO with highly reactive radicals such as the hydrated electron and hydroxyl radical. Time-resolved ESR experiments with DMPO offer the opportunity to directly observe the yield of spin adducts from the reaction of DMPO with the hydroxyl radical and the hydrated electron produced by water radiolysis. These measurements result in a more accurate evaluation of the kinetics and efficiency of these spin trapping reactions.

## 122 QUANTITATIVE EPR SPIN TRAPPING 1. NITRITE IONS IN ALKALINE SOLUTION

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In this paper, quantitative spin trapping methodology is reported to measure nitrite ion ( $\text{NO}_2^-$ ) concentrations in strong alkaline aqueous solution. The spin trap used for this experiment is the nitromethane *aci* anion ( $\text{CH}_2=\text{NNO}_2^-$ ) reaction. In alkaline aqueous solution, nitromethane *aci* anion is produced by the following equilibrium:  $\text{CH}_2-\text{NO}_2 + \text{OH}^- \rightleftharpoons \text{CH}_2=\text{NNO}_2^- + \text{H}_2\text{O}$ . In strong alkaline solution (pH ~ 12), the equilibrium is shifted to the right-hand side of this equation. Nitrite ions are excited by ultraviolet light ( $\text{NO}_2^-$ )<sup>\*</sup> and react with water to give hydroxyl ion (OH<sup>-</sup>), nitric oxide (NO), and hydroxyl radical (\*OH). The self-scavenging of \*OH by nitrite ions in turn produces nitrogen dioxide ( $\text{NO}_2^*$ ) radicals. The EPR signal detected during photolysis of nitrite ions in  $\text{H}_2\text{O}$  is an adduct of  $\text{NO}_2^*$  and the *aci* anion to form dinitromethyl radical dianion:  $\text{CH}_2=\text{NNO}_2^- + \text{NO}_2^* \rightarrow \text{O}_2\text{N}-\text{CH}=\text{NO}_2^-$  • (I). In this study, we show that the spin concentration of (I) is proportional to the  $\text{NO}_2^-$  ion concentration in alkaline solution. This has potential application in evaluation of catalysts designed to decompose waste explosives and propellants (energetic materials). Application to energetic materials is demonstrated by using the spin trapping EPR method to measure  $\text{NO}_2^-$  concentrations of energetic nitramines in alkaline solution; thereby determining the extent of initial nitramine decomposition.

123 COULD NITROSYL CHLORIDE (CINO) BE PRODUCED BY HUMAN SKIN KERATINOCYTES AND SULFUR MUSTARD (HD)? A MAGNETIC RESONANCE STUDY. Carmen M. Arroyo and Clarence A. Broomfield, U.S. Army Medical Research Institute of Chemical Defense, Aberdeen Proving Ground, Maryland 21010-5425.

Nitrosyl chloride (CINO), a strong oxidizing agent [ $E^0(\text{CINO}/\text{NO}^+, \text{Cf}) = 1.0 \text{ V}$ ], is capable of nitrosylating organic compounds and thereby generating mutagens or promutagens [1]. We have examined the expression of interleukin-1 beta (IL-1 $\beta$ ) in normal human epidermal keratinocytes (NHEK) in culture by immunocytochemistry upon exposure to sulfur mustard (HD). Neonatal NHEK exposed to HD (1 mM) tends to increase the release of IL-1 $\beta$ . However, the response of NHEK breast adult tends to decrease upon exposure to the same concentration of HD. Therefore, this pro-inflammatory cytokine IL-1 $\beta$  was shown to decrease in an age-dependent manner in keratinocytes. The response was inversely related to the donor age of the cell cultures. Recently, evidence has been shown that IL-1 $\beta$ -induced the formation of EPR-detectable iron-nitrosyl complexes in Islet of Langerhans [2]. Furthermore, nitrogen monoxide (NO) has been implicated as the effector molecule that mediates interleukin-1 $\beta$ . Chloride ion ( $\text{Cl}^-$ ) is released from sulfur mustard ( $\text{Cl}-\text{CH}_2-\text{CH}_2-\text{S}$ ) upon cyclization to the sulfonium ion which is its electrophilic form. The Gibbs energy of formation of nitrosyl chloride, the nitrosyl cation and chloride, has been published [1] and the formation of nitrosyl chloride is energetically feasible. References: [1] W.H. Koppenol, FEBS Letters, 347, 5-8 (1994). [2] J.S. Corbett et.al, FASEB J., 7, 369-374 (1993).

124 ESEEM STUDIES OF  $^{25}\text{Mg}$  COUPLING IN PHOTOSYSTEM I: ELECTRONIC STRUCTURE DETERMINATION OF  $\text{P}_{700}^+$

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Oxygenic photosynthesis in higher plants and cyanobacteria requires the interplay of two pigment protein reactions, Photosystem I and Photosystem II (PSI and PSII). In each of these reaction centers the primary charge separation event proceeds via the light induced generation of a chlorophyll *a* cation radical species. In PSI, this species is known as  $\text{P}_{700}^+$  and is the primary electron donor in an electron transfer chain that ultimately effects the reduction of NADP<sup>+</sup>. Although both monomelic and dimeric structures of chlorophyll *a* have been suggested for  $\text{P}_{700}^+$ , neither have been proven conclusively and the ambiguity surrounding its nuclearity remains. The electronic structure of the cation radical is

controversial as well. The pulsed-

EPR technique of electron spin echo envelope modulation (ESEEM) was used to identify an interaction between the unpaired  $n$  electron in  $\text{P}_{700}^+$  and the  $^{25}\text{Mg}$  nucleus ( $I=5/2$ ; natural abundance, 10%) in  $^{14}\text{N}$  labeled PSI reaction centers from the cyanobacterium, *Synechocystis* PCC 6803. The magnitude of this coupling ( $a \sim 9.4 \text{ MHz}$ ) and the resulting unpaired spin density on the  $^{25}\text{Mg}$  indicates a monomelic electronic structure for the radical.

**125 MULTIFREQUENCY 2-DIMENSIONAL ESEEM OF (VO)(SALICYLALDOXIME) MODEL COMPLEXES.**

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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 ESEEM allows to overcome some of these difficulties.

We will present a multifrequency ESEEM study of a model oxovanadium complex (VO)(Salox). Our one and two dimensional ESEEM measurements cover the range of C- and X-band frequencies. 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 and sign of the nitrogen spin coupling parameters.

**126 COMPARATIVE ANALYSIS OF CONFIGURATION-RELATED RADIATION-INDUCED DEFECTS IN AMORPHOUS SILICON DIOXIDE AND SILICON NITRIDE\* V. A. Mashkov and R. G. Leisure, Physics Department, Colorado State University, Fort Collins, CO 80523**

Hole trapping is a general mechanism of stimulated paramagnetic defect production both in amorphous silicon dioxide and silicon nitride. However, the published data regarding silicon nitride deal only with the light-induced metastable changes in optical and ESR spectra. It is well known that two major defects in a-SiO<sub>2</sub> created under ionizing radiation are the E center and peroxy radical, i.e., the oxygen-vacancy related center and bound O-O molecule. The role of vacancies in a-Si<sub>3</sub>N<sub>4</sub> under irradiation is not well understood. On the basis of similarity in chemical bonding in both materials, we discuss possible radiation induced defect reactions in a-Si<sub>3</sub>N<sub>4</sub>, based on known effects in a-SiO<sub>2</sub>. In particular we discuss possible electronically and configurationally related defect centers, i.e., oxygen- and nitrogen-vacancy related centers and radicals (bound O-O and N-N molecules) in both materials. The role of different charge states and defect configurations will be discussed. \*Research supported the Office of Naval Research under Contract N00014-91 - J-1607.

**127 PBN SPIN TRAP INHIBITS LPS-INDUCED NITRIC OXIDE GENERATION IN MICE. A SPIN TRAPPING STUDY. Takashi Miyaiima and Yashige Kotake, National Biomedical Center for Spin Trapping and Free Radicals, Free Radical Biology and Aging Research Program, Oklahoma Medical Research Foundation, Oklahoma City, OK 73104**

Phenyl N-fert-butyl nitron (PBN) has many pharmacological effects such as decreasing mortality due to lipopolysaccharide (LPS)-induced septic shock in rats and reversing age-related parameters in Mongolian gerbils. The implication of nitric oxide (NO) in PBN's pharmacological effects have not been investigated. We hypothesized that PBN could inhibit NO generation and thus reduce the mortality in LPS-induced septic shock animal model. *Experimental:* Mice (Balb/c) were injected with PBN(6mg/20g) before or after the LPS (1mg/20g) injection. In 6 hrs, NO spin trap (N-methyl glucarnine dithiocarbamate [MGD] plus FeSO<sub>4</sub>) was injected and in 0.5 hr liver specimen was obtained. The specimen was placed in a tissue flat cell and EPR spectra were recorded. Mouse peritoneal macrophage were activated by LPS/interferon- $\gamma$  (3 hr) in an EPR flat cell and incubated for 8 hrs. PBN (5 - 10 mM) was added to the activation/incubation medium at various time. MGD-Fe was infused before the EPR recording. *Results:* When PBN was administered 0.5 hr before LPS injection, NO spin adduct in the liver decreased to 1/7 of that of control. Such decrease was not observed when PBN was administered 3 hrs after LPS injection. Whereas NO-synthase(NOS) inhibitors were effective in suppressing EPR signal independent of injection timing. Macrophage NO generation was also inhibited when PBN was present in the activation medium but not in the incubation medium. These results suggest that PBN is a potent inhibitor of the induction of NOS but not an inhibitor of NOS.

**128 PHOTO-ENHANCED PRODUCTION OF THE SPIN-ADDUCT DMPO-OH IN AQUEOUS MENADIONE SOLUTION, S. Monroe and S. S. Eaton, Department of Chemistry, University of Denver, Denver CO 80208**

Menadione (2-methyl-1,4-naphthoquinone) is an inhibitor of mitochondrial respiration. When menadione was used in a DMPO (5,5-dimethyl-1-pyrroline N-oxide) spin-trapping experiment with mitochondrial preparations, enhanced production of DMPO-OH- was observed. However, a similar enhancement in DMPO-OH- production was observed in the absence of mitochondria. The production of DMPO-OH- was decreased when samples were handled in the dark and increased by deliberate exposure of the spin-trapping solution to light from a fluorescent lamp. The production of DMPO-OH- in these systems is increased by addition of superoxide dismutase although addition of H<sub>2</sub>O<sub>2</sub>, catalase, or bovine serum albumin has little impact. Removal of oxygen decreases the production of DMPO-OH-. Photoredox and redox-cycling reactions that may be responsible for the DMPO-OH- production will be discussed.

**129 DEVELOPMENT OF AN EDUCATIONAL EPR MODULE FOR TEACHING THE PRINCIPLES OF MRI. Alex I. Smirnov<sup>1</sup>, Reef (Philip P.. ID Morse), and R. Linn Belford<sup>2\*</sup>, Department of Chemistry<sup>1</sup>, Illinois State University, Normal IL 61790-4160 and College of Medicine<sup>2</sup>, Department of Chemistry<sup>3</sup>, University of Illinois, Urbana, IL 61801.**

Electron paramagnetic resonance (EPR) spectroscopy is well suited for teaching fundamental principles of magnetic resonance imaging - the use of magnetic field gradients to encode spatial information, which is common for both EPR and nuclear magnetic resonance (NMR) imaging. Here we describe an educational module aimed at the first year physical chemistry student. The module includes instructional materials such as lecture notes and overheads, air-cooled thin anti-Helmholtz coils for generating one-dimensional magnetic field gradient, a goniometer stage for rotating the sample, a commercial computer-controlled power supply, data acquisition software and hardware, test samples for laboratory exercises, and spectra taken from more exotic samples (e.g., stressed polymers, etc.). These materials are sufficient for a two-hour lecture and three-hour laboratory followed by approximately 3-6 hours of student data evaluation (processing projection sets, deconvolution, image reconstruction from projections, data presentation and plotting). The module is also suitable for undergraduate research projects. This work was supported by NSF grant DUE-9352362 (PDM) and used the resources of the Illinois EPR Research Center (NIH Grant RR01811).

**130 SIMULTANEOUS EPR MEASUREMENTS OF KINETICS OF OXYGEN AND SPIN LABEL CONSUMPTION BY BABY HAMSTER KIDNEY CELLS. Reef (Philip P.. ID Morse) and Alex I. Srnirnov<sup>1</sup>, Department of Chemistry<sup>1</sup>, Illinois State University, Normal IL 61790-4160 and College of Medicine<sup>2</sup>, University of Illinois, Urbana, IL 61801.**

Nitroxide spin probes have several potential medical applications which involve measurement of cell redox activities and oxygen concentration with the use of EPR. Current experimental methods of such measurements have difficulties in handling cellular samples which may result in experimental artifacts and data misinterpretation. We describe a better method for accurate and simultaneous measurement of nitroxide reduction and oxygen concentration based on fitting of EPR spectra using a fast convolution least-squares algorithm. Improved accuracy in determination of both linewidth and double-integrated intensity allowed us to do the experiments with fewer cells (typically about  $1.5 \times 10^6$  cells/ml; to prevent cell crowding) and at initial nitroxide concentrations of 1 mM to ensure that nitroxide reduction is not diffusion-limited. Examples of this method include experiments at X-band (9.5 GHz) with cultured normal and transformed Baby Hamster Kidney cells and nitroxide radicals TEMPOL and TEMPONE. Under these experimental conditions, the rates of nitroxide reduction are independent of oxygen concentration. These new data lead us toward a better understanding of nitroxide kinetics in the living systems. This work was supported by NTH grant GM44365-01 to PDM and used the resources of the Illinois EPR Research Center (NTH P41-RR01811).



- 131 **CURRENT STATUS OF HIGH-FREQUENCY (95 GHZ) EPR METHODS FOR MEASURING NITROXIDE REDUCTION BY A SINGLE MAMMALIAN CELL.** Alex I. Smirnov<sup>1</sup> and Reef (Philip P.. U) Morse<sup>2</sup>. College of Medicine<sup>1</sup>, University of Illinois, Urbana, IL 61801 and Department of Chemistry<sup>2</sup>, Illinois State University, Normal IL 61790-4160.

Nitroxide reduction experiments are usually carried out at X-band (8.8-9.5 GHz) with a relatively large number of cells (typically 10<sup>7</sup> cells in 100 ul). Such a large number of cells is not always available for experimentation. For example, it is of interest to probe cellular metabolism during transformation by adenovirus, when, initially, few cells are involved. Additionally, high concentrations of cells in X-band experiments often result in inhomogeneous cell distribution in a sample tube and eventually in long diffusion paths for the metabolites and complicated apparent kinetics. We have already shown (Rocky Mountain Conference, 1994) that the number of cells in the nitroxide reduction experiments can be reduced to only 900 by use of a W-band (95 GHz) EPR spectrometer developed at the Illinois EPR Research Center (IERC). By applying a resonator with a higher Q-value, careful sample positioning, and lineshape fitting software we were able to decrease this number to six cells in a sample. We have measured the reduction rate of TEMPONE (T=36.6 °C) at both X-band (3x10<sup>7</sup> cells in 30 pi) and W-band (6 cells in 7.5 nanoliters). The rate measured from W-band experiments (3.5 x10<sup>-10</sup> molesxmin'xcell<sup>-1</sup>) was essentially the same as that found at X-band (3.3 x10<sup>-10</sup> moles xmin'xcell<sup>-1</sup>). From signal-to-noise considerations, we infer that it will be possible to observe nitroxide reduction by a single cell at W-band. This would open the path towards measurements of cell redox changes in which only a few cells participate. This work was supported by NTH grant GM44365-01 to PDM and used the resources of the IERC (NTH P41-RR01811).

- 132 **CHOOSING STANDARDS FOR EPR CONCENTRATION MEASUREMENTS: EFFECT OF SPIN HAMILTONIAN PARAMETERS ON LINE INTENSITIES.** Vitaly Yu. Nagy. Dmitry P. Sokolov, Vernadsky Institute of Geochemistry and Analytical Chemistry, Russian Academy of Sciences, Moscow 117975, Russia

Accurate EPR concentration measurements with a standard with different paramagnetic centers comprise using values of transition probabilities, which can be calculated from spin Hamiltonian parameters. In practice, values of these parameters are often not known exactly, and an analyst needs some guidelines to reasonably choose a standard ensuring least error without exact calculations of differences in the transition probabilities. We performed systematic quantum-mechanical calculations to reveal dependencies of line intensities on values of spin Hamiltonian parameters for paramagnetic centers of various types. Computations were made for the field-swept spectrometry; exact numerical matrix diagonalization was used. The results obtained may be used in estimating errors in concentrations measurements coming from inequalities of (uncertainties in) values of spin Hamiltonian parameters, in selecting standards that provide signals of about the same specific intensity as the species to be determined, and, for single-crystal measurements, in selecting spectral lines least sensitive to uncertainties in the parameter values. This data helps a worker to decide which of available reference materials is really "most similar" to the test sample. The work was supported in part by International Science Foundation Grant MHC 000.

- 133 **ELECTRON AND LIGHT MICROSCOPY STUDIES ON PARTICULATE PROBES LITHIUM PHTHALOCYANTNE, FUSINITE AND SYNTHETIC CHARS.** Shone Wan Norby . \* Harold M. Swartz and Robert B. Clarkson, College of Medicine, Department of Veterinary Qinical Medicine, Illinois EPR Research Center, University of Illinois, 506 S. Mathews, Urbana, IL 61801, 'Dartmouth Medical School, Hanover, NH 03755.

The development of particulate probes sensitive to both oxygen and nitric oxide has generated oximetry studies and nitric oxide measurements by electron paramagnetic resonance spectroscopy. The probes used in these studies are lithium phthalocyanine, fusinite and synthetic chars. All of these probes can be used in conjunction with conventional soluble nitroxides for measuring intra- and extracellular oxygen simultaneously. They have been used in various *in vitro*, *in vivo* and *in situ* studies. We are studying the gross and fine structure of these probes with light, scanning ,and transmission electron microscopy. The structural information obtained should provide valuable inputs in the further understanding of the probes' response to either oxygen or nitric oxide. If a correlation exists between form and function, the results would help us synthesize better probes (e.g. char) with improved sensitivity to both gases. In addition, microscopic studies of these probes phagocytosed by cells or injected into tissues will help to deterrnine if there are any detectable detrimental effects. This information is vital to our goal of using these probes for future clinical applications.

Partial support was received from NIH (GM 42208 and RR01811).

**134 IN VITRO SPIN TRAPPING OF NITRIC OXIDE IN ACTIVATED NERVE CELLS AND MACROPHAGES.** Shong Wan Norby and Robert B. Clarkson, College of Medicine, Department of Veterinary Oinical Medicine, Illinois EPR Research Center, University of Illinois, 506 S. Mathews, Urbana, IL 61801.

The role of nitric oxide (NO) as a bioregulatory molecule has been reviewed in the literature and its importance in the immune and nervous systems is emphasized. We studied the production of NO in nerve cells (N1E and NG108 cells) and macrophages (ANA-1 and RAW cells) *in vitro*. Our results show that NO was produced when N1E or NG108 cells were stimulated with IFN $\gamma$ , N-methyl-D-aspartate, or KCl and CaCl $_2$ . Electron Paramagnetic Resonance spectroscopy was used to measure NO by means of spin trapping with a water soluble spin trap, Fe $^{2+}$ -Methyl-glucamme-dithiocarbamate. Similarly, *in vitro* real time detection of NO production was made in ANA-1 and RAW cells when activated with IFN $\gamma$ , LPS or both. The production of NO could be inhibited in various degrees by introducing the inhibitor L-NMMA in the culture medium. Complete inhibition of NO production could be achieved by culturing three or more generation of cells in L-arginine free medium prior to activation with any of the stimulants.. These inhibition results indicated that NO was an intermediate in the L-arginine to NO $^*$ , NO $^*$  and citrulline pathway. Partial support was received from NIH (GM 42208 and RR01811).

**135 ELECTRON TRAPPING OXYGEN VACANCY CENTERS IN COESITE AND STISHOVITE : HIGH PRESSURE PHASE SiO $_2$ .** Kazutoshi Ogoh, Chihiro Yamanaka, Motoji Dceya and Eiji Ito, department of Earth and Space Science, Faculty of Science, Osaka University Toyonaka, Osaka 560. <sup>2</sup>Institute for Study of the Earth's Interior, Okayama University Misasa, Tottori 682-02, Japan

Coesite and stishovite are high pressure phases of SiO $_2$  over 2GPa and 8GPa, respectively, which have potentiality to be useful materials. EPR studies were made on radiation induced defects in coesite and stishovite. Samples were synthesized in a static condition from high purity SiO $_2$  glass, and were irradiated by  $\gamma$ -rays both at room temperature and at 77 K. In coesite, an axial signal with  $g_{\parallel} = 2.0027$  and  $g_{\perp} = 1.9993$  and an orthorhombic one with  $g_{zz} = 2.0004$ ,  $g_{yy} = 1.9993$  and  $g_{xx} = 2.0048$  are compared with those of defects in ZrSiO $_4$ . Two non equivalent oxygen sites in coesite may be associated with these signals. In stishovite, only an axial signal with  $g_{\parallel} = 2.0052$  and  $g_{\perp} = 2.0023$  is detected, probably due to the oxygen vacancy center of a kind.

**136 PULSED EPR STUDIES OF PHOTOSYSTEM II SEMIQUINONE RADICALS,** Jeffrey Peloquin and R. David Britt, Department of Chemistry, University of California, Davis, CA 95616

Two pulse and three pulse ESEEM and Mims and Davies ESE-ENDOR experiments were performed on the QA radical of cyanide-treated PSII core complexes isolated from the cyanobacterium *Synechocystis* PCC 6803. ESE modulations with frequencies 0.75, 2.06 and 2.85 MHz are assigned to the quadrupole transitions of a single  $^{14}\text{N}$  nucleus strongly coupled to the quinone radical. The calculated electric quadrupole couplings parameters are  $e^2qQ=3.29$  MHz and  $\eta=0.50$ . These quadrupole values are characteristic of a  $^{14}\text{N}$  in a peptide bond and are tentatively assigned to arise from the peptide nitrogen of an alanine amino acid residue hydrogen bonded to the quinone. From the double quantum transition at 5.0 MHz, the hyperfine coupling constant is calculated to 2.0 MHz. Three pulse experiments performed on PSII core complexes isolated from cyanobacterium grown on  $^{15}\text{N}$  support the assignment of a single nitrogen nucleus strongly coupled to the quinone radical. There is evidence in both the  $^{14}\text{N}$  and  $^{15}\text{N}$  ESEEM and ESE-ENDOR spectra that additional nitrogen nuclei are weakly coupled to the quinone radical.

**137 BIMODAL S-BAND LOOP-GAP RESONATOR.** Woiciech Piasecki, Wojciech Froncisz, and James S. Hyde, Biophysics Research Institute, Medical College of Wisconsin, Milwaukee, 53226

A new class of bimodal loop-gap resonators for EPR spectroscopy is proposed. These resonators contain two axially placed one-loop—one-gap resonators. In mode I, the axial magnetic components of the microwave field of both resonators are parallel. In mode II, these fields are in opposite directions similar to the counter rotating current loop-gap resonator previously described (1). The resonant frequency of mode II can be adjusted independently of the resonant frequency of mode I by changing the capacitance between the two one-loop—one-gap resonators. The isolation between these two modes for a prototype S-band resonator was measured to be better than 60 dB for either equal or different resonant frequencies of the two modes. The resonators have a very high filling factor—close to unity when used in the reflection configuration of the microwave bridge and 0.5 for transmission. The resonator was tested in regular EPR experiments as well as in CW ELDOR and multi-quantum EPR experiments. As a consequence of the microwave field distribution, the new resonator cancels the unwanted FID signal in saturation-recovery EPR experiments.

1. W. Froncisz, A. Jesmanowicz, J. B. Kneeland, J. S. Hyde, Counter rotating current coils for high resolution magnetic resonance imaging, *Magn. Reson. Med.* 3, 590-603 (1986).

**138 FOLDING OF ISO-1 CYTOCHROME C PROBED AT SITE-SPECIFICALLY SPIN LABELED CYS<sup>102</sup> - EQUILIBRIUM AND EPR STOPPED-FLOW KINETICS.** Kunbin Ou\*, Jeffrey Vaughn\*, Jacquelyn Fetrow\*, Andrzej Sienkiewicz\*, and Charles P. Scholes\*; Departments of \*Physics, +Chemistry and †Biological Science, SUNYA, ALBANY, NY 12222

Yeast iso-1 ferricytochrome *c* (cyt *c*) was spin labeled with the cysteine-specific spin label MTSSL (methane thiosulfonate spin label) at its only accessible cysteine, Cys<sup>102</sup>. To analyze protein folding/unfolding, the shape and amplitude of the label's EPR line were monitored for change in probe mobility. Guanidine hydrochloride (GuHCl) equilibrium denaturation and thermal melting were studied by conventional EPR of the labeled protein and by circular dichroism (CD) and UV-vis of labeled and non-labeled protein; the results were consistent with a two-state, folded/unfolded equilibrium. All these equilibrium spectroscopic methods showed that GuHCl-induced unfolding of labeled protein was completely reversible at room temperature. In contrast, thermal unfolding of the spin labeled cyt *c* was only partially reversible after the protein had been heated to > 70 C. Our newly developed Dielectric Resonator (DR)-based EPR Stopped-Flow system was used to study protein folding/unfolding kinetics. GuHCl concentration at pH 6.5 was step-wise changed in the EPR stopped-flow apparatus to initiate protein unfolding or folding. The unfolding brought on by an increase of GuHCl from 0 to 0.7 M was well fit to a single exponential with a time constant of about 0.3 s, whereas the refolding induced by a decrease of GuHCl from 1.4 to 0.7 M was faster and more complex. Molecular modeling and mechanics studies are underway to predict the position and flexibility of the spin label and to assay the label-induced perturbation to the protein conformation.

**139 ESEEM STUDIES OF OXO-Mo(V) CENTERS IN MODEL COMPOUNDS AND SULFITE OXIDASE.** Partha Basu, Arnold M. Raitisring, Petr Borbat, Andrew Pacheco, Nikolai V. Shokhirev, and John H. Enemark, Department of Chemistry, University of Arizona, Tucson, Arizona 85721

EPR is an important technique for probing oxo-Mo(V) centers. However, ligand hyperfine interactions from coordinated <sup>14</sup>N atoms are rarely resolved in CW-EPR spectra of compounds of this 4d metal center. We have begun systematic ESEEM studies of mononuclear oxo-Mo(V) complexes of known stereochemistry that contain N atoms at well defined coordination sites. Preliminary ESEEM results at 8.8 GHz using 2- and 3-pulse echo techniques at various fields, i.e. different orientations of the Mo-N bonds relative to the magnetic field, will be reported for *fac*- and *mer*-MoOCl<sub>3</sub>(bpy), for several adducts of [MoOClJ<sup>+</sup> with N-containing molecules, and for [MoOCl<sub>3</sub>(amp)]<sup>+</sup>. ESEEM spectroscopy on the Mo center of sulfite oxidase shows weak <sup>14</sup>N modulation for the high pH form that is absent in the low pH/high Cl form. The enzyme results will be discussed in light of spin density calculations and spectral simulations on model compounds with known structure. The <sup>31</sup>P modulations of the phosphate inhibited form of sulfite oxidase will also be presented.

- 140** "1+2" TRAIN - A NEW VARIETY OF PULSE ADJUSTABLE ESEEM SPECTROSCOPY. A.Raitsimring, P.Borbat\* , Department of Chemistry, University of Arizona, Tucson, AZ 85721. ' On leave Institute of Chemical Kinetics and Combustion RAS, Novosibirsk 630090, Russia.

We report the further development of Pulse Adjustable ESEEM Spectroscopy (PA ESEEM) which exploits the evolution of electron spins under the influence of electron-nuclear interaction during the action of mw-pulses. This variety of PA ESEEM where the first pulse is "1+" pulse with adjustable duration and amplitude detects only fundamental frequencies and may be used as an improved substitute of stimulated ESEEM. Using as a model system a hydroquinone radicals in frozen solution of the phosphoric acid we have shown that the non-modulating part of the "1+2" signal have been decreased in twenty times that of stimulated echo leaving the absolute magnitude of modulation amplitude slightly more than in stimulated echo. This technique allowed one to resolve the interaction of electron spin with the nearest protons (first shell), the distinct protons (second shell), and <sup>31</sup>P nuclei as well. For a case of the weak hyperfine interaction the analytical expression of the "1+2" signal modulation have been derived.

This work was supported by NSF Grant No.BIR 9224431.

- 141** ESEEM AND ESE-ENDOR STUDIES OF MANGANESE CLUSTERS, David W. Randall and R. David Britt, Department of Chemistry, University of California, Davis, CA 95616

We are performing ESEEM and Electron Spin Echo ENDOR experiments on mixed valence manganese clusters that serve as models for the catalytic Mn clusters of the photosynthetic oxygen-evolving complex and the Mn catalase enzyme. ESEEM and ESE-ENDOR are being used to characterize ligand interactions in these model compounds. In addition, <sup>55</sup>Mn ESE-ENDOR experiments are revealing new details about the electronic structure of these Mn model compounds. The pulsed EPR results on the model compounds are compared to the results on the enzyme clusters.

- 142** COPPER RE-ENTRANT STYLE LOOP-GAP RESONATORS FOR MULTI-FREQUENCY EPR. George A. Rinard, Barnard T. Ghim, Minoru Sueki, and Gareth R. Eaton, Departments of Engineering and Chemistry, University of Denver, Denver, CO 80208

Re-entrant style loop-gap resonators have been developed for use with our multifrequency bridges (1-8 GHz). The LGRs are machined out of a block of copper using a numerically-controlled milling machine. The resonator halves are then electroplated with gold to decrease background signals and bolted together. Slots are cut into the sample area to allow 100 kHz magnetic field modulation to pass with about 50% penetration. The program to cut the halves of the LGR is versatile and a variety of these LGRs have been constructed. For example, L-band (1-2 GHz) LGRs have been made with sample diameters of 4.2 mm and 30 mm. The CW and pulsed EPR performance of these resonators will be presented.

- 143 EPR INVESTIGATION OF THE EFFECT OF ULTRASONICATION ON THE PENETRATION OF MODEL SPIN PROBES AND SPIN-LABELED ANTIBIOTICS THROUGH BACTERIAL CELL WALLS. Rodney W. Pope and Natalva Y. Rapoport. Department of Bioengineering, 108 F Biomedical Polymer Research Building, University of Utah, Salt Lake City, Utah 84112.

The mechanism of the previously discovered synergistic effect between antibiotics and ultrasound in eliminating bacterial infections on implants was investigated using the EPR technique. The effect of ultrasonication on the uptake of various spin probes by *Pseudomonas aeruginosa* was studied. Hydrophilic Tempone, hydrophobic 16-doxyl stearic acid, and 4-oxymethyloxirane-Tempo - labeled gentamicin were used as spin probes. All probes underwent the reduction to corresponding hydroxylamins upon the incubation with *P. aeruginosa*, the rate of reduction being effected by the sonication. In non-sonicated samples the reduced Tempo was quantitatively re-oxidized by potassium ferricyanide, which implies its extra-cellular localization. In sonicated samples the re-oxidation was not quantitative unless the cells were lysed before the re-oxidation. We did not see the EPR signal in the spun-out and washed cells before cell lysis, which was attributed to high local concentrations of probes in the interior of the cells; the EPR signal re-appeared after the lysis of the cells. The intracellular concentration of probes was higher in the sonicated cells. The results imply an enhanced penetration of spin probes through bacterial cell walls under ultrasonication.

- 144 SPONTANEOUS RADICAL FORMATION FROM 1,3-DIPOLAR MOLECULAR ADDITION OF HALOCARBONS TO C-PHENYL N-tert-BUTYL NITRONE (PBN). Hong Sang, Edward G. Janzen and J. Lee Poyer, National Biomedical Center for Spin Trapping and Free Radicals, Free Radical Biology and Aging Research Program, Oklahoma Medical Research Foundation, 825 N.E. 13th Street, Oklahoma City, OK 73104, USA.

The reaction between halocarbons which contain a cyanyl group and PBN in hexane was studied by electron ionization (EI) tandem mass spectroscopy (MS/MS), GC-MS spectroscopy and electron paramagnetic resonance (EPR). Four different such kind of halocarbons were studied in this work. They are CCLCN, CHClCN, Br<sub>2</sub>CHCN and BrCH<sub>2</sub>CN. Precursor ion scan of  $m/z$  57 was recorded during MS/MS analysis to find ions potentially due to PBN spin adducts. The MS/MS results shows that these halocarbons can react with PBN to form 1,3-dipolar molecular addition products. The molecular addition products between CCLCN, CHClCN and PBN are stable enough to be detected by GC-MS. The fragment ion at  $m/z$  [M-77]<sup>+</sup> was found by both EI MS/MS and GC-MS to be a common fragment for these molecular addition products, which is very different from other PBN spin adducts. PBN radical spin adducts were also formed in these systems and detected by EPR method. At least two different radicals were formed in each system; one is a carbon-centered radical adduct, the other is the oxidized PBN radical. These radical adducts were not detected by MS spectroscopy, because these species are detected at very low concentration by EPR and molecular addition gives the main product.

- 145 NUCLEAR AND ELECTRON SPIN RELAXATION IN PARAMAGNETIC SOLUTIONS CONTAINING TRANSITION METAL AND LANTHANIDE IONS WITH SPIN > 1/2  
Robert R. Sharp, Dept of Chemistry, The University of Michigan, Ann Arbor, MI 48109

Nuclear spin relaxation phenomena in paramagnetic solutions depend profoundly on the electron spin precessional motion. For  $S > 1/2$  ions, these motions are driven both by the electronic Zeeman interaction and by the zero-field splitting (zfs) interaction which couples the electron spin to the electrostatic potential of the crystal field. In the Zeeman-limit the quantization axis of precession is that of the external magnetic field; in the zfs limit, precession is quantized along the molecule-fixed principal axes of the zfs tensor. In the Zeeman-limit (at high field strengths where  $H_{zeem} \gg H_{f.}$ ), spin relaxation is described by the classical Solomon-Bloembergen-Morgan (SBM) theory. In the zfs-limit ( $H_{f.} \gg H_{zeem}$ ), nuclear spin relaxation is more complex, depending on the position, angular as well as radial, of the nuclear spin in the molecule-fixed principal axis system, as well as on the dipolar spectral density function. In the intermediate regime, nuclear spin relaxation rates depend additionally on the zfs energy parameters (D, E, etc.) of the electron spin Hamiltonian. Nuclear spin relaxation data obtained outside the Zeeman-limit are potentially a much richer source of molecular structure and spin Hamiltonian information than is Zeeman-limit data. Our long term objective is the development of new theoretical methods and experimental strategies suitable for extracting this information. New computer methods for visualizing and simulating electron spin dynamics in solutions of  $S > 1/2$  d-block and lanthanide ions will be described, as well as new approaches to the calculation of solution-phase electron and nuclear spin relaxation times outside the Zeeman-limit

- 146 SIMPLE ANALYTICAL MODEL FOR THE DESCRIPTION OF CIDN(E)P FORMATION IN RADICAL(-ION) PAIRS. Nikolai V. Shokhiev, University of Arizona, Tucson, Arizona 85721, Marc B. Taraban, Tatjana V. Leshina, Institute of Chemical Kinetics and Combustion, Novosibirsk, 630090, Russia.

CIDNP has become a powerful method for the investigation of reactions including the stages of radical recombination. The correct interpretation of such experiments, especially for arbitrary magnetic fields, requires fast and reliable calculations of spin states for products and radicals, which have escaped into the bulk. Using the analytical approximation of the Green's function for diffusion motion in the Coulomb potential, we derived general expressions for the spin density matrix in solvents of arbitrary polarity. The case of contact recombination with the step-wise exchange interaction was considered. A comparison of the analytical and precise numerical calculations shows good accuracy of the proposed approach. The theory was applied to the description of CIDNP in Sn-containing radical pairs. Also discussed are the limits of the high-field approximation for radicals with large HFI constants and accuracy of the step-wise exchange model for different solvent polarity and viscosity.

- 147 TUNABLE Q-BAND CAVITY FOR EPR AND ENDOR EXPERIMENTS - APPLICATION TO <sup>17</sup>O-OXYGEN BOUND TO ACTIVATED BLEOMYCIN. Andrzej Sienkiewicz\*, Andrei Veselov\*. Brian Smith\*, Harold Taylor\*, Richard Burger\*, and Charles P. Scholes\*; Departments of \*Physics and +Chemistry, SUNYA, Albany, NY 12222, †Laboratory of Chromosome Biology, Public Health Research Institute, 455 1<sup>st</sup> Av., NYC, NY 10016

We present a tunable Q-Band microwave probe head suitable for EPR and/or ENDOR experiments. The cylindrical cavity, resonating in a TE<sub>011</sub> mode, has a loaded Q of 3600 and is coupled to the waveguide through a 2.9 mm iris at the side wall. The body of the resonator is made of non-magnetic, gold-plated brass, and the 100 kHz magnetic field modulation and the radio frequency (RF) posts are located inside the cavity cylinder. These posts are firmly anchored to the upper lid, whereas they pass freely through a set of holes in the movable bottom part of the cavity. This design enables one to tune the resonant frequency and to adjust the coupling with the cavity immersed in pumped liquid helium over a range of +/- 350 MHz around a center frequency of 34 GHz - a critically important feature, since our Bruker Q-band Gunn diode source has less than 100 MHz of tunability. The Q-Band probe head was used for obtaining information on oxygen bound to the chemo-therapeutic drug bleomycin [BLM] in the oxygen-activated [Act-BLM] form that leads to DNA damage. Hyperfine couplings for <sup>17</sup>O were resolved from Q-Band ENDOR, the largest being 27 MHz at  $g = 2.17$ . Consistency between EPR line broadening and the ENDOR information points to strong hyperfine coupling to a single liganding oxygen atom. Such coupling is compatible with end-on ligation to one oxygen of the hydroperoxide which has been proposed as the iron ligand for Act-BLM (Sam, J.W. *et al*; *J. Am. Chem. Soc.* 1994, 116, 5250).

- 148 ESR SPECTROSCOPIC STUDIES OF PHENOLIC ANTIOXIDANT FOOD ADDITIVES. A PHYSICAL-BIOCHEMICAL EXPERIMENT FOR ADVANCED UNDERGRADUATE LABORATORIES. Herbert J. Sipe, Jr., R. J. Geiger, Jr., T. W. Johnson, D. M. Goldin, and C. St. John. Department of Chemistry, Hampden-Sydney College, Hampden-Sydney, Virginia 23943.

We report conditions and procedures, based on the previous work of Valotti, Sipe, *et al.*, for ESR studies of phenoxy radicals produced by oxidation of phenols with Horse Radish Peroxidase enzyme [HRP, EC 1.11.1.7]. HRP, a robust enzyme, is commercially available in suitable purity. We report optimum conditions for sample preparation and ESR observation that are suitable for use by undergraduates in laboratories in physical chemistry or physical biochemistry. We find phenoxy radicals from phenolic food additives and their analogs to be appropriate for studies by undergraduates. The radical of 2,6-di-tert.butyl-4-hydroxyanisole is easily formed, relatively long-lived ( $t_{1/2} > 2$  hours), well-resolved, and suitable for spectral simulations if desired. Students completing this project gain experience with buffers, small scale sample preparations, as well as ESR spectrometer operation, and data reduction. The parent molecule is suitable for semiempirical calculations, e.g., Huckel or Huckel-McLachlan molecular orbital calculations, or more sophisticated calculations if desired. Extensions of the project can include studies of other, less stable, phenoxy radicals such as those produced by HRP oxidation of the food additives 2-tert.butyl-4-hydroxytoluene (BHT) and 2-tert.butyl-4-hydroxyanisole (BHA).

- 149 **EFFECT OF ETHANOL ON OXYGEN PERMEABILITY OF MODEL PHOSPHOLIPID BILAYER.**  
**Alex I. Smirnov<sup>1</sup> and R. Linn Belford<sup>2</sup>, College of Medicine<sup>1</sup>, Department of Chemistry<sup>2</sup>, University of Illinois, Illinois EPR Research Center, Urbana, IL 61801.**

Permeability of a phospholipid bilayer to oxygen and the oxygen transport parameter through the membrane is usually measured with nitroxide spin probes placed at a known location (x) of the phospholipid bilayer, by comparing the relaxation rates (e.g.,  $1/T_1$ ) measured with and without oxygen (e.g., see Subczynski, W. K.; Hyde, J. S.; and Kusumi, A. *Proc. Natl. Acad. Sci. USA.* 86: 4474, 1989). Development of spin-label oximetric methods for continuous-wave (CW) EPR spectroscopy has been complicated by the complexities in the spectral shapes of slow-tumbling nitroxides in anisotropic media. Only a few attempts, such as measurements of the peak-to-peak linewidth of the central component of the nitroxide spectrum over few characteristic data points and theoretical predictions on slow-tumbling EPR spectra, have been documented. Here we describe how oxygen broadening can be extracted by comparing anisotropic nitroxide CW EPR spectra taken at various oxygen concentrations. We have found that, within the accuracy of the experiment, the oxygen broadening is homogeneous and therefore a fast convolution algorithm can be applied for accurate fitting of the experimental spectra. Using this technique, we have observed that ethanol concentrations as low as 1% increase the permeability of the 1<sup>^</sup>-dipalmitoyl-sn-glycero-3-phosphatidylcholine (DPPQ) bilayer to oxygen. This work used the resources of the Illinois EPR Research Center (NIH Grant RR01811).

- 150 **ACCURACY OF OXYGEN MEASUREMENTS IN  $T_1$  (LINEWIDTH) EPR OXIMETRY.**  
**Tatyana I. Smirnova<sup>1</sup>, Alex I. Smirnov<sup>2</sup>, R. B. Clarkson<sup>2</sup>, and R. Linn Belford<sup>1,3</sup>, Departments of Chemistry<sup>1</sup>, Veterinary Medicine<sup>2</sup>, College of Medicine<sup>3</sup>, and the Illinois EPR Research Center, University of Illinois, Urbana, Illinois 61801.**

EPR oximetry is used for *in vivo* and *in vitro* measurements of oxygen in biological systems, including experimental animals. The accuracy of oxygen measurements in  $T_1$  (linewidth) EPR oximetry is significantly improved if least-squares simulation is used to extract the linewidth parameters. The oxygen effect on the EPR spectra of nitroxide solutions and aqueous suspensions of fusinite can be described as an additional homogeneous broadening that modifies the EPR spectrum of the oxygen-free probe. This allows one to use a one-parameter linewidth model in most cases. The simulations were carried out with the use of a fast-convolution algorithm followed by Levenberg-Marquardt optimization. The validity of error estimates provided by this method was tested on sets of experimental spectra taken under common conditions. It is shown that the accuracy of oxygen measurements in linewidth ( $T_1$ ) oximetry is determined not only by the probe sensitivity (rate of linewidth change vs. oxygen concentration), but also by the signal-to-noise ratio, inhomogeneous contribution to the lineshape (e. g., unresolved proton superhyperfine structure), and the spectral window. The accuracy of oxygen measurements is compared for aqueous solutions of two nitroxide radicals with different superhyperfine structure and for aqueous suspensions of fusinite. Supported by NIH GM42208 with resources provided by P41-RR01811 (NIH) and the University of Illinois Fellowship awarded to T.I.S.

- 151 **ESEEM AND ENDOR STUDIES OF NON-KRAMERS SPIN SYSTEMS NEAR ZERO FIELD.** **Bradley E. Sturgeon,\* Judy M. Nocek,\* Brian M. Hoffman,\* Katherine E. Liu,\* Stephen J. Lippard\*DougBurdi, WingH. Tong/ JoAnne Stubbe,<sup>†</sup> Nishi Gupta,<sup>®</sup> and DonaldM. Kurtz, Jr.<sup>®</sup> \*Northwestern University, Department of Chemistry, Evanston, Illinois 60208. Massachusetts Institute of Technology, Department of Chemistry, Cambridge, Massachusetts 02139. <sup>†</sup>Massachusetts Institute of Technology, Department of Chemistry and Biology, Cambridge, Massachusetts 02139 <sup>®</sup>University of Georgia, Department of Chemistry, Athens, Georgia 30602.**

It was at last year's EPR conference that we first presented ESEEM and ENDOR data collected on the diiron centers of hemerythrin (Hr) and methane monooxygenase hydrolase (MMOH) poised in the *diferrous* state. In these spin systems the two ferrous irons are ferromagnetically coupled resulting in a non-Kramers spin system ( $S=4$ ). The continuous wave X-band EPR spectra from these centers consists of a broad featureless resonance extending from 0 to approximately 1000 G. In contrast to the EPR characteristics, these same samples generate an observable electron spin echo only over a range of small magnetic field values (<100 G). Although the electron spin echo is a maximum at zero field, no modulation is observed. The application of very low parallel magnetic field (>1 G) leads to a rich modulation pattern arising from nitrogen coordination to the *diferrous* center. These observations have led us to further investigate the spin physics of non-Kramers systems. ESEEM results will also be presented for a suite of diiron proteins.

- 152 **COMPUTER PROGRAMS FOR ANALYSIS OF EPR AND ENDOR SPECTRA OF GENERAL SPIN SYSTEMS USING METHODS OF EXACT CALCULATION.** Joshua Telser, School of Science and Mathematics, Roosevelt University, 430 S. Michigan Ave., Chicago, IL 60605.

A series of FORTRAN computer programs has been written for the analysis of EPR and ENDOR spectra. The programs calculate transition energies and probabilities for general spin systems by diagonalization of the spin Hamiltonian matrix using EISPACK subroutines. The programs run on micro- (PC), mini- or main-frame computers. The input parameters can be entered interactively or read from a batch file. Output is in the form of ASCII files listing the input parameters and x,y points (intensity vs. magnetic field or RF) suitable for use by any spreadsheet/plotting software. The programs DDZHQR and DDPOWH calculate either EPR or FJvDQR transitions for systems of one electronic spin ( $1/2 < S < 5/2$ ) and one nuclear spin ( $0 < I < 7/2$ ) either at user-specified magnetic field orientations or generates powder pattern spectra (using the igloo method), respectively. The user provides the electronic spin and the appropriate zero-field splitting parameters through fourth order (in  $\text{cm}^{-1}$ ), and the intrinsic principal  $g$  values. The user also provides the isotope number of the nucleus of interest ( $I$  and  $g_n$  are obtained from a look-up table), the hyperfine coupling principal values and quadrupole coupling constants (in MHz). The hyperfine and quadrupole coordinate systems each can be rotated separately with respect to the electronic coordinate system by Euler angles  $\alpha$ ,  $\beta$  and  $\gamma$ . The programs DJDZ and DDPOWJ calculate EPR transitions for systems of two electronic spins ( $1/2 < S_1 < 5/2$ ), respectively as above. The user provides the electronic parameters for each spin and the spin-exchange coupling parameter,  $J$ , as  $J_x, J_y, J_z$ , (in  $\text{cm}^{-1}$ ). The second spin can be rotated with respect to the first by Euler angles. Lineshape parameters are also needed for the powder patterns.

- 153 **EVIDENCE OF NON-CURIE LAW EPR BEHAVIOR IN SAMPLES OBTAINED FROM ILLINOIS NO. 6 COAL.** Robert L. Thompson, Kurt S. Rothenberger, and Herbert L. Retcofsky, U.S. Department of Energy, Pittsburgh Energy Technology Center, P.O. Box 10940, Pittsburgh, PA 15236.

Variable temperature EPR studies of coals and coal samples treated with electron donors and acceptors have been performed which fail to reveal any evidence of deviation from Curie Law, suggesting that the EPR signals arise from non-interacting doublet states. We have observed weak EPR signals, however, for some coal samples near  $g = 4$ , which has been assigned by others to a  $\Delta m = \pm 2$  transition and can arise only from thermally accessible triplet states. The pyridine extract of Illinois No. 6 coal has been separated by column chromatography and EPR analysis confirms that the acid fraction, in agreement with all previous coal samples that we have studied, does not deviate from Curie Law. The aromatic and base fractions, however, do deviate weakly from Curie Law, suggesting that at least some of these spins arise from triplet states. Attempts to observe  $\Delta m = \pm 2$  transitions in the aromatic and base fractions were unsuccessful and our observation of EPR signals in the coal near  $g = 4$  are attributed to clay impurities. This signal is enhanced when the mineral matter is concentrated by triboelectric separation, but disappears in the coal ash obtained from low temperature plasma oxidation. Also, this signal does not disappear at low temperatures, which would be expected for a  $\Delta m = \pm 2$  transition.

- 154 **THE NEW LOW-POTENTIAL C-TYPE CYTOCHROME FROM SHEWANELLA PUTREFACIENS.** Alexandre I. Tsapin, K.H. Nealson, Milwaukee, Center Great Lakes Studies, 600 E. Greenfield ave., Milwaukee, WI 53204

The new low-potential c-type cytochrome has been isolated and purified from *Shewanella putrefaciens*, strain MR-1. Different methods - EPR, optical and atomic absorption spectroscopy, PAGE and volt-amperometric titration have been used to characterize the novel cytochrome. This new cytochrome is a water-soluble tetraheme cytochrome of MW  $\approx 12,000$  D with a redox potential  $-220$  mV. The  $p_i$  of the protein is 5.6 - 5.8. The presence of water-soluble cytochrome with such low redox potential can explain the possibility of *Shewanella putrefaciens* to grow using a variety of different electron acceptors.



- 155 RECONSTRUCTION OF THE 2Fe-2S CENTER AND G=1.90 EPR SIGNAL INTO OVERPRODUCED WILD-TYPE AND MUTANT FORMS OF THE RIESKE PROTEIN. Alexandre I. Tsapin, T.Kallas, Y.-S. Cho, X.WU, and B.Holton, UW-Oshkosh, UW-Milwaukee, Center Great Lakes Studies 600 E. Greenfield ave., Milwaukee, WI 53204

The Rieske 2Fe-2S center is an essential subunit of the photosynthetic electron transport chain. We have been able to overproduce this protein by expression in *E.coli* of the petC(Rieske) gene from the cyanobacterium *Vostoc* PCC 7121. The 2Fe-S center with pet its characteristic g=1.90 EPR signal has been restored to the overproduced protein by means of an in vitro reconstruction procedure. EPR spectra have been used for estimation of the number of restored paramagnetic centers. We constructed several mutant forms of Rieske protein with N-terminal deletions of several residues. We have shown that after deletion of less than 20 residues the structure of the active center of Rieske protein does not differ from the structure of the non mutant form of Rieske protein. However, after deletion of 43 residues the structure of the active center (according to EPR data) has been changed. We observed also a correlation between the line shape of the EPR-signal at g=4.3 and the line shape of EPR bands at g=2.03 and g=1.90 in the reconstructed samples.

- 156 EPR STUDIES RELATED TO ARSENATE BINDING IN ZEOLITE/CEMENT COMPOSITES  
Gregory L. Turner, Martin G. Bakker, Department of Chemistry, The University of Alabama Tuscaloosa, Al 35487-0336 and Patrick M. Brown, U.S. Bureau of Mines, Twin Cities Research Center, Minneapolis MN 55417-3099

The Bureau of Mines has developed a process for containment of high level arsenic bearing waste using a zeolite-cement matrix. The unusually high arsenic loading levels warrant a study of the mechanism(s) of containment. EPR methods based on TEMPO spin probes and on Cu<sup>2+</sup> ion-exchanged into the zeolite into zeolites are being used to study arsenate binding, and the mobility of organic components in the composite. Questions that need to be addressed include: does the zeolite survive incorporation into the cement? Are the zeolite pores closed by the cement? Is the arsenate ion bound to copper ions?

The EPR spectra from the TEMPO spin probes show a number of different species when incorporated into the zeolite/cement composites. These are assigned to the spin-probe in a located in a zeolite cavity and in water pools in the cement. As the cement dries the spin probes migrate back into the zeolite as the resulting also in increases in the local concentration of the spin probe in the water pools that remain. This is clear evidence that the zeolite survives incorporation in the cement and that the zeolite pores are not sealed off in the early to middle stages of the cement drying process.

- 157 **MAGNETIC FIELD (g-VALUE) DEPENDENCE OF PROTON HYPERFINE COUPLINGS OBTAINED FROM ESEEM MEASUREMENTS: DETERMINATION OF AXIAL LIGAND ORIENTATION IN GLASSY SAMPLES OF LOW-SPIN IRON(III) PORPHYRINATES.** F. Ann Walker, Tatjana Kh. Shokhireva, Peter Borbatand Arnold M. Rattsimring, Department of Chemistry, University of Arizona, Tucson, Arizona 85721

Electron spin echo envelope modulation studies were utilized to characterize a coupling between protons of axially bound imidazole and pyridine ligands (L) and the unpaired electron of low-spin Fe(III) porphyrinate-L<sub>2</sub> complexes. Samples were prepared in mixed-solvent glasses to maximize the resolution of the EPR signals. X-band two- and four-pulse ESEEM experiments at 4.2 K demonstrated that this coupling results in 0.2-0.85 MHz shifts of the  $\nu_i + \nu_s$  proton sum combination peak from twice the Larmor frequency. These shifts have been investigated across the EPR absorption spectra of the low-spin Fe(III) complexes. Two- and four-pulse ESEEM spectra were simulated at different magnetic field positions. For the simulations, the orientation of the nearest four protons of the ligands with respect to the g-tensor of the complex, the Fe(III)-proton distance and g-strain were taken as input parameters. Comparison of the experimental data and computer simulations allows evaluation of the orientation of the hyperfine coupling tensor of the protons in coordinates of the g-tensor principal axes.

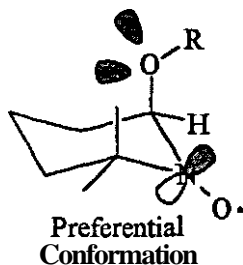
- 158 **MICROELECTRODE-DETECTED ESR SIGNALS OF FREE RADICALS IN ELECTROLYTE SOLUTIONS.** H. Yokoyama, T. Satoh, H. Ohya-Nishiguchi,\* and H. Kamada, Institute for Life Support Technology, Yamagata Technopolis Foundation, Numagi, Yamagata990, Japan.

The detection method of ESR signal by electric current change is a state-of-the-art technique investigating the semiconductive devices and atomic-level lattice defects. Based on similar method we have tried to detect free radical in electrolyte solution. We have succeeded to observe the ESR signal of typical organic free radicals in electrolyte solutions. The instrument constructed consists of a combination of a conventional EPR spectrometer and an electrochemical voltammogram: The sample cell consists of a thin sample tube with inner diameter of 1 mm and two microelectrodes, one is a working electrode with the surface area of 0.05 mm<sup>2</sup> and the other a reference/counter electrode, which were both inserted in the sample solution and set in a cavity resonator. A potentiostat was connected to the electrodes and operated with a current flow of 100 nA to 1 mA. The excitation of EPR resonance was carried out by usual way with low-frequency magnetic modulation. The AC component of the current due to the resonance was filtered by a transformer in the circuit and amplified by a lock-in-amplifier, followed by recording on the spectrometer. Its detection limit was estimated to be 10<sup>11</sup> spins. It is expected that the application of this method to biological science will be effective to detect very small amount of bioradicals in vivo.

- 159 **MOBILE OXYGEN IN HIGHLY-IRRADIATED, OXYGEN-DEFICIENT  $\alpha$ -SiO<sub>2</sub>**  
Lin Zhang and Robert. G. Leisure, Dept. of Physics  
Colorado State University, Fort Collins, CO 80523.

The EPR signal of peroxy radicals was observed in oxygen *deficient* amorphous silica samples which were subjected to high doses of x-irradiation followed by a soft anneal (225°C, 10 min). The peroxy radical has previously been reported only in oxygen *excess* silica. EPR signals were measured at 4.2 K following irradiation at doses up to 400 Mrad. Predominant defects in this material were E', and E' centers. A small non-bridging oxygen hole center (NBOHC) signal was observed before the soft anneal. A weak peroxy radical signal was observed after the soft anneal in highly irradiated samples (accumulated dose > 200 Mrad). During the anneal the E' concentration remained the same value while the NBOHC concentration was slightly reduced. The evidence suggests that radiolytic oxygen atoms diffused during the soft anneal and were captured at the sites of NBOHC, creating peroxy radicals:  $sSi-O^{\bullet} + O \rightarrow sSi-O-O^{\bullet}$ .  
\*Research supported by Office of Naval Research: Contract No. N00014-91-J-1607.

- 160 **ANOMERIC CONFORMATIONS OF SIX-MEMBERED CYCLIC AMINOXYLS WITH A B-ALKOXYL SUBSTITUENT.** Yong-Kang Zhang, OMRF Spin Trap Source, Free Radical Biology and Aging Research Program, Oklahoma Medical Research Foundation, 825 N. E. 13th Street, Oklahoma City, Oklahoma 73104 USA



The addition reaction of  $CH_3(CH_2)_nO\cdot$ ;  $(CH_3)_2CHCH_2O\cdot$ ;  $(CH_3)_2CHCH_2CH_2O\cdot$  ( $CH^{\wedge}CO^{\cdot}$  and  $(CH_3)_2C(CN)O\cdot$ ) radicals to a novel six-membered cyclic nitroxide, 6,6-dimethyl-3,4,5,6-tetrahydropyridine 1V-oxide ( $M_2PyO$ ), generates the corresponding 6-alkoxyl-2,2-dimethylpiperidine-1-oxyl aminoxyl (nitroxide) spin adducts. In QHg solution at room temperature, the preferential conformation of these spin adducts appears to be the anomeric conformer with the alkoxy group in the axial position according to EPR spectroscopic conformational analysis of these aminoxyls. The anomeric effect in these aminoxyls might be the combination of electrostatic and molecular orbital interactions.

- 161 **RESONANT ENHANCEMENT IN FID-DETECTED EPR BEATS.**  
Y.C. Zhong, Department of Physics, Monash University, Clayton, Victoria 3168, Australia

EPR beats at proton Larmor frequency have been observed for the first time by detecting free-induction-decay (FID) signals whilst changing the length of a microwave pulse in an  $S=1/2$  and  $I=1/2$  system. It has been shown that the amplitude of such EPR beats are significantly enhanced when the electron spin nutation frequency equals to the nuclear Larmor frequency, i.e.  $\gamma_e B_1 = \gamma_n B$ , where  $\gamma_n$ , is the nuclear geomagnetic ratio,  $\gamma_e$  the electron geomagnetic ratio,  $B_1$  the amplitude of the microwave magnetic field and  $B$  the static magnetic field. Implications of this finding are discussed in relation to electron-nuclear cross polarization and its application in ESEEM and pulsed-ENDOR studies.

- 162 **THE SG1 DEFECT: A Ge DANGLING BOND IN OXYGEN IMPLANTED SiGe**  
Mary Ellen Zvanut and Patricia J. Macfarlane\*. Department of Physics, University of Alabama at Birmingham, Birmingham, AL 35294-1170 and  
W.E. Carlos, Naval Research Laborator, Washington DC 20375

Recently there have been reports of light emission from Si and SiGe-based structures. Among the several systems which appear to emit light one consists of Ge implanted  $SiO_2$  [1]. Although the mechanism of light emission remains unclear, here we suggest that it may be related to (or limited by) the presence of Ge dangling bonds which are stable in a Ge/ $SiO_2$  system.

We present results of electron paramagnetic resonance (EPR) work on a Ge centered defect in oxygen implanted crystalline SiGe material. A major emphasis of this investigation is the study of the interface between the SiGe alloy and oxide precipitates formed during oxygen implantation. By varying the implantation conditions, anneal temperature, and implanted species, we deduce that the defect is a Ge dangling bond at the interface with  $SiO_2$  precipitates. Because the center appears only in the presence of  $SiO_2$  we suggest that it exists also at the Ge nanocrystal/ $SiO_2$  interface in Ge implanted  $SiO_2$ .

•Supported by the Office of Naval Research #N00014-93-0777

1. K.V. Shcheglov et. al. Appl. Phys. Lett. 66, 745 (1995).

163

**A Novel Reflection Mode Spectrometer for 250GHz****Keith A. Earle, Jack H. Freed****Baker Laboratory, Cornell University, Ithaca, NY 14853-1301**

We have designed and are developing a novel reflection mode bridge for use in a 250GHz ESR spectrometer. Spectrometers in this frequency range have, until now, only been successfully operated in a transmission mode. Instead of using conventional microwave components, which are either not available, or have very high losses, we instead use techniques that are common in the far infrared (FIR), but are not yet widely known to the ESR community. The bridge uses a new method of polarization coding to discriminate power incident on the sample resonator from the signal reflected from the resonator. We also discuss quasi-optical techniques for varying the coupling into and out of the resonator in order to optimize the resonator performance.

We discuss the expected improvements in S/N that will accrue from the new bridge design and we estimate such performance parameters as insertion loss and the isolation between the transmit and receive arms. We will also discuss the bandwidth of the bridge and evaluate its suitability for incorporation into a pulsed or frequency swept spectrometer.

- 164 **MULTIFREQUENCY AND HIGH-FREQUENCY (95 GHz) EPR IN STUDIES OF FAST MOLECULAR DYNAMICS IN LIQUIDS.** **Alex I. Smirnov<sup>1</sup>, Tatyana I. Smirnova<sup>1</sup>, R. B. Clarkson<sup>1</sup>, Reef (Philip D., II) Morse<sup>2</sup>, and R. Linn Belford<sup>1</sup>, Illinois EPR Research Center<sup>1</sup>, University of Illinois, Urbana, IL 61801 and Department of Chemistry<sup>2</sup>, Illinois State University, Normal IL 61790-4160.**

Many dynamics processes in liquids fall into the picosecond rotational motion regime (correlation times,  $T_c \ll 10^{-10} - 10^{-12}$  sec), which is difficult to probe by conventional EPR at 8.8-9.5 GHz (X-band). At 94 GHz (W-band), the range of  $T_c$  measured by a typical nitroxide radicals is extended by a factor of seven towards short times. Additionally, the EPR spectra become more sensitive to the anisotropy of rotational diffusion. For multicomponent systems, such as aqueous and lipid phases of biological membrane, tenfold enhanced g-value resolution of W-band spectroscopy allows one to differentiate nitroxide signals and therefore to extract the molecular dynamics information from different phases. The use of multifrequency EPR data in these studies is essential for accurate inclusion of inhomogeneous lineshape contributions and, as was shown by the group of Prof. Freed at Cornell, for determination of the full rotational diffusion tensor. This presentation summarizes some recent results obtained at the Illinois EPR Research Center (IERC) with a particular emphasis on dynamics of nitroxides with complex superhyperfine structure, effect of drugs on molecular dynamics, and partitioning of small spin-labeled solutes in model phospholipid bilayers. This work used the resources of the IERC (NTH P41-RR01811).

- 165 **NOVEL EFFECTS IN PULSED ENDOR**

**Peter E. Doan, Brian M. Hoffman, Department of Chemistry, Northwestern University, Evanston, IL 60208-3113.**

Mims (stimulated-echo) ENDOR spectroscopy has proven to be a valuable tool in studies of metalloproteins. This technique combines high signal-to-noise with exquisite resolution for nuclei with weak hyperfine interactions with the metal center. In addition, we have found that there is little interference from 'distant' ENDOR effects that often plague parallel CW spectra on the same samples. By decreasing the dead-time of our spectrometer to less than 100 ns, we have been able to investigate weakly coupled <sup>1</sup>H nuclei ( $A^H < 5$  MHz) without interference from  $x$  suppression effects that occur when  $A^H(\text{MHz}) \times (\mu\text{s}) = 1, 2, 3, \dots$ . In these studies, we have observed interesting lineshape effects that are dependent upon  $x$ , but are not related to the standard suppression arguments. Interpretations and possible applications of these effects will be discussed.

166

**NUCLEAR DIPOLAR DEPHASING IN ENDOR SPECTROSCOPY,  
Marcelino Bernardo & Hans Thomann, EXXON Corporate Research, NJ**

The heteronuclear Spin Echo Double Resonance (SEDOR) experiment was first introduced by Hahn and coworkers for the indirect detection of the NMR spectrum for an  $I_2$  nucleus. In SEDOR, the refocusing of the coherence for nucleus  $I_1$  is partly defeated by reorienting the nuclear moment of a second nucleus,  $I_2$ , which is dipolar coupled to  $I_1$ . In the original experiment, SEDOR was used to indirectly detect the spectrum of an  $I_2$  nucleus by step wise incrementing the frequency of an rf pulse applied to the  $I_2$  nucleus in successive pulse sequence iterations. More recently, Slichter and coworkers used the SEDOR experiment to measure inter-nuclear distances from the dephasing of the  $I_1$  coherence. These two types of the SEDOR experiments can also be applied to nuclei in paramagnetic molecules with sufficiently long electron spin relaxation times. This SEDOR-ENDOR experiment can be applied as a "nuclear dipolar filter" by step-wise incrementing the rf pulse on  $I_2$  on successive pulse sequence iterations in which the coherence for a selected  $I_1$  transition is indirectly observed. Inter-nuclear distance measurements can be made using the same SEDOR-ENDOR pulse sequence by indirectly observing the dephasing of the  $I_1$  coherence measured as a function of the evolution time/2. The local field originating from the hyperfine interaction serves to shift the resonance frequencies of the  $I_1$  and  $I_2$  nuclei so that the SEDOR-ENDOR experiment can be applied to both homo and heteronuclear spin pairs. The SEDOR-ENDOR experiment, theory, and results will be presented.

- 167** INCREASING THE SENSITIVITY OF MEASUREMENT OF RADIATION INDUCED HYDROXYL RADICALS IN LIVING ANIMALS WITH NOVEL SPIN TRAPPING SYSTEMS AND VERY LOW FREQUENCY EPR. HJ Halpern, GVR Chandramouli, ED Barth, S Pou and GM Rosen, U. Chicago, Chicago, IL and U. Maryland, Baltimore, MD.

We recently reported the measurement of markers of radiation induced hydroxyl radicals in the tumor of a living mouse (PNAS 92, 796 (1995)). This involved administration, intratumorally, 0.2ml aqueous solution of 1.7 M EtOH, 0.5 M cc-(4-pyridyl-1-oxide) N-tert-butyl nitron (4-POBN) in buffer followed by application of a tourniquet to the tumor bearing leg and giving 3000 Gy radiation. This radiation dose was extremely high. We are undertaking a simple series of measurements to optimize the sensitivity of the system. This involves diminishing the time of radiation (and the consequent dose), methods and amounts of spin trapping solution injection. The basic spin trapping system, however, will remain unchanged. We expect to be able to demonstrate spectra from substantially lower doses of radiation. Further methodological improvements (multiple timed measurements for back extrapolation to the end of radiation and calibration in model systems) should allow rough estimates of the concentration of the hydroxyl radical evolved.

**168** **A NEW MILLIMETER-WAVE EPR SPECTROMETER AND ITS CW AND PULSED OPERATION**

G.G. Maresch, P. Hbfer, K. Holczer\*, and D. Schmalbein, Bruker Analytische Messtechnik, 76287 Rheinstetten, Germany, and \*University of California, Los Angeles

High-frequency / high-field EPR spectroscopy is a well-known tool to obtain spectral information which in many cases is not accessible at lower frequencies. Nitroxide radicals in disordered systems are good examples to demonstrate the various aspects of the performance up to the limits with respect to physical theory and practical achievements. Precision determination of the g-tensor components is reached using the Bruker 94 GHz CW and pulsed EPR spectrometer. Besides structural studies of radical electrons in polymers, electron spin-echoes, relaxation measurements, and two-dimensional (2D) EPR spectra are presented. As a result from these experiments we obtain information about molecular motions with correlation times in the range from  $10^{-12}$ s to  $10^{-9}$ s. The enhancement of spectral resolution in high-frequency EPR in combination with the different pulsed EPR experiments adds valuable information for the interpretation for chemical, physical or biological problems.

- 169 SPECTROSCOPY OF VARIOUS BLACK CARBONS (SOOT). Abdul R. Chughtai, Brian Konowalchuck, and Dwight M. Smith, Department of Chemistry, University of Denver, Denver, CO 80208

Fourier transform infrared (FTIR) spectroscopy has been the most definitive analytical tool in a comprehensive program on the structure and reactivity of black carbon (in the form of n-hexane soot). In combination with other techniques, it has revealed the soot structure, as produced by high temperature incomplete combustion, to be predominantly aromatic with a surface coverage by oxygen-containing functional groups of about 0.5. Particularly well suited to following net changes in surface groups, and gas phase reactant/product concentrations, FTIR has been the key technique in determining the kinetics and mechanisms of some important heterogeneous reactions of black carbon with gas phase oxidant molecules. For example, the reaction of NO<sub>2</sub>/N<sub>2</sub>O<sub>2</sub> with soot follows a dual path mechanism, down to 2 ppm, which is reflected in the rate law: Initial rate = (k<sub>1</sub> + k<sub>2</sub>[soot]<sup>n</sup>) P<sub>NO<sub>2</sub></sub>. On the other hand, catalytic decomposition initiates the reaction with ozone, followed by the formation of surface carboxylic groups and gaseous CO and H<sub>2</sub>O. The evidence suggests that dissociation of ozone yields a steady-state concentration of excited oxygen atom which is actually the oxidant. FTIR combined with chemical measurements has proven that a high solubility observed for carbon particles exposed to ozone has its origin in the hydrolysis of the surface carboxylics. Significant effects of simulated solar radiation on the reactions, especially in the soot/SO<sub>2</sub>/H<sub>2</sub>O/O<sup>3</sup> system, has been revealed by FTIR. Infrared will continue its central role in the examination of increasingly complex systems containing black carbon, particularly through its interface with ancillary techniques.

- 170 DIAMOND ATR: THE UNIVERSAL APPROACH FOR FT-IR ANALYSIS. Steve Hill. ASI/Applied Systems

The diamond is generally acknowledged to be the most rugged and inert optical material used for infrared measurements. Two diamond elements mounted as opposing pressure plates are traditionally used to restrict the transmission thickness of strongly absorbing and scattering materials. This has been especially effective for the study of thin fibers, forensic trace evidence, and pressure-sensitive materials. The diamond anvil cell requires adept handling to avoid damage to the diamond element and spectral artifacts from the diamond lattice response at 2400-1950cm<sup>-1</sup> and fringing by the empty cell background.

A new sampling approach utilizes a single diamond element cleaved as a trapezoidal ATR crystal. The 4mm crystal is sealed in a Hastelloy mount to provide an inert durable sampling station, or Durasample IR™. The optical design efficiently delivers 25% throughput from the 6-12 sample contacts at the diamond surface. A pressure clamp and liquid flow cell adapter have been designed for rigid solids and liquid stream applications. Spectra will be presented for a variety of challenging polymers and inorganic applications.

A diamond ATR immersion probe provides a means to sample most liquid and resin-based chemical systems. Mounted in a 16mm or 25mm tubular Hastelloy body, DiComp™ probe is mated to either ground glass fittings or high pressure NPT seal. The probe is compatible with all chemical processes operating at temperatures in excess of 200°C, 2000 PSI., and aqueous pH systems from 1-14. With liquid agitation, emulsions and solid dispersions may be accurately analyzed. A kinetic FT-IR analysis can provide real-time data on reaction kinetics, concentrations of reaction species, per cent conversion as well as information on reaction pathways. Applications will be presented for observation and analysis of a wide range of corrosive reactions including chlorinations, brominations, nitrations, and sulfonating.

- 171 MEASUREMENT OF WAX CLOUD POINTS IN LIVE CRUDE OILS BY INFRARED SPECTROSCOPY. James E. Tackett, Marathon OU Company, P.O. Box 269, Littleton CO 80160. (303) 347-5470

Measurement of the temperature at which the first wax crystal appears upon cooling a crude oil (cloud point) is of interest to the petroleum industry because solid wax can deposit on crude oil production facilities and even shut down pipelines. Although it is important to be able to measure cloud points on live oils under high pressure reservoir conditions, very few techniques have this capability. A lack of visible light transmission by the dark oils prohibits use of the standard ASTM technique. DSC, cross-polarization microscopy, filtration, and various scattering techniques have been used to measure dark oil cloud points at low pressures. Signal changes can be observed as the temperature is decreased, but the cause is not always obvious. We have developed an FT-IR based cloud point technique that combines the use of baseline shifts and spectral subtraction. Baseline shifts at non-absorbing wavelengths are used to locate the cloud point, while spectral subtraction in the 730 - 720 cm<sup>-1</sup> region is used to confirm the shift is due to wax. This method has been applied to live crude oils at pressures as high as 7,000 psig.

- 172 **FOURIER TRANSFORM INFRARED SPECTROSCOPY OF 5,8-DIHYDROXYQUINOLINE.** Fedri M. Marrugo, Stephen D. Wathen, and Donald C. Zapien, Department of Chemistry, University of Colorado at Denver, Denver, CO 80217

Oxine, or 8-hydroxyquinoline, is a compound well known for its ability to form strong complexes with a variety of metal ions. Infrared measurements used to probe molecular changes in oxine due to complexation in solution require that the frequencies and intensities of characteristic bands in both the complexed and uncomplexed forms of oxine be monitored. IR spectra have been collected of oxine and its derivatives in solution, in spectral regions where the solvent absorption is minimal. In addition, spectra have been collected of oxine in the presence of metal ions. Absorption measurements, using the method of corresponding solutions, are being used to determine the formation constants of oxine-metal complexes. However, due to the overwhelming absorption of the solvent, 15 micron path lengths are used. The measurement of the small absorbances of the ligand and complexes are aided by the signal averaging capability of FTIR. The absorption measurements are made in a high concentration regime of oxine, and therefore the formation constants obtained with FTIR are compared with those obtained with methods in which oxine concentrations are amenable to equilibrium measurements.

- 175 **IMPROVED DETERMINATION OF BARIUM BY FLAME AES.** John Schmelzel, Susan Martin, Gerald Dulude, and David Pfeil, Thermo Jarrell Ash, 8E Forge Pkwy., Franklin, MA 02038.

For the same reason that barium is a difficult element to measure by AAS (intense emission from itself and concomitants), it is a very sensitive element to measure by atomic emission. Using an Inductively Coupled Plasma Optical Emission Spectrometer, barium is handily measured but care must be taken to correct for the potentially severe background emission interferences. In this work, a flame AAS/AES spectrometer which utilizes a galvanometer based wavelength drive mechanism was employed to simultaneously correct for off-peak emission in the determination of barium. A nitrous oxide/acetylene combustion flame was used as the atomization/excitation source. Accuracy, precision, and limits of detection will be compared with and without off-line background correction.

- 176 **A MINIATURIZED, AUTOMATED DOC FRACTIONATION PROCEDURE.** Charles F. Tabor and Larry B. Barber, II, U.S. Geological Survey, 3215 Marine Street, Boulder, Colorado 80303.

Dissolved organic carbon (DOC) fractionation was used to characterize organic matter in water by isolating hydrophobic (HP0) and hydrophilic (HPI) acid, base, and neutral organic solutes. The use of a Waters Millilab 1A robotics system, Sep-Pak cartridges containing small-diameter macroreticular resins, and automated data collection has reduced operating time and improved accuracy and precision of the method. A 125 ml water sample (pH 7) was passed through the methacrylic resin Amberlite GC-71 to isolate the HP0 base/neutral fraction. The base fraction was eluted with H<sub>2</sub>SO<sub>4</sub>. The sample was acidified to pH 2, then passed through the GC-71 again to isolate the HPI acid fraction. The remaining HPI solutes were separated into acid, base and neutral fractions using Amberlite IRA-910 strong anion exchange resin and Amberlite 200 strong cation exchange resin. Most fractions were determined by difference in the cartridge influent and effluent. Sample flow rates through all cartridges were 4 mL/min. Six samples were analyzed in triplicate to examine analytical variability. The average relative standard deviation (RSD) for all fractions from all samples was 20%, with a range of 2-90%. High RSD values resulted from fractions that were < 2% of the total DOC. DOC fractionation done by a commercial laboratory produced an average RSD of 41%, with a range of 9-141%. The fractionation at the commercial lab took 2.6 man-hours/sample, while the automated method took 0.5 man-hours/sample.

- 177 **NEURAL NETWORK PATTERN RECOGNITION OF PHOTOACOUSTIC FTIR SPECTRA AND KNOWLEDGE-BASED TECHNIQUES FOR DETECTION OF TOXIGENIC FUNGI IN CORN**  
**Sherald H. Gordon, Donald T. Wicklow, Bruce C. Wheeler, Robert B. Schudy, and Richard V. Greene, USD A, ARS, National Center for Agricultural Utilization Research, Peoria, IL 61604**

Fourier transform infrared photoacoustic spectroscopy (FTIR-PAS), a highly sensitive probe of the surfaces of solid substrates, is used to detect pathogenic fungal contamination in com. Kernels of corn infected with toxigenic fungi, such as *Aspergillus flavus*, display FTIR-PAS spectra that differ significantly from spectra of uninfected kernels. Photoacoustic infrared spectral features were identified, and an artificial neural network was trained to distinguish contaminated from uncontaminated corn by pattern recognition. Software was written for computer extraction of the infrared spectral features and neural network classification. A friendly graphical user interface allows a non-chemist to easily discover spectral features useful in the analyses. Work is in progress to integrate epidemiological information about cereal crop fungal disease into the spectral pattern recognition program to produce a more knowledge-based, and hence, more reliable technique. A model of a hierarchically organized expert system is proposed, using epidemiological factors such as plant stress and susceptibility to infection, weather, insect vectors, handling and storage conditions, in addition to the analytical data to predict *A.flavus* and other kinds of toxigenic fungal contamination that might be present in food grains.

- 179 **SILICA GEL, TENAX, AND CARBON MEDIA ADSORPTION TUBE FOR THE SAMPLING OF A WIDE VARIETY OF ORGANIC COMPOUNDS IN AIR.**  
**Steven F. Baugh, Havelick & Associates, Ltd., 60 Garden Center Suite 201, Broomfield, Colorado, 80020.**

An air sampling tube containing silica gel, Tenax, and carbon is used to sample air containing either unknown contaminants or a mixture of a wide variety of organic compounds, varying in boiling points, functionality and overall polarity. The sampling tube presented here, HAL1, is only one of several possible tube configurations utilizing a variety of adsorption materials in differing combinations, amounts, and different sampling devices or methods. HAL1 is prepared and assembled in a common (EPA TO-1) configuration for thermal desorption and subsequent analysis by GC/MS. Thermal desorption eliminates solvent extractions and deposits the entire sample in the instrument for increased method sensitivity while eliminating solvent peak fronts from masking low level analytes which coelute. This sample collection tube will allow rapid collection and analysis of a wide variety of organic compounds, affording subsequent analysis by an appropriate analytical technique using commercially available thermal desorption tube sample introduction systems.

- 180 **DETERMINATION OF METHANOL AND ETHANOL IN AMBIENT AIR BY GAS CHROMATOGRAPHY WITH FLAME IONIZATION DETECTION.** Debra L. Kirschenman. Larry G. Anderson; John A. Lanning, University of Colorado, PO Box 1733364, Campus Box 194, Denver, Colorado, 80217.

The increased use of methanol and ethanol gasoline blended fuels is expected to increase the concentrations of these alcohols in ambient air. Currently there is no specific and sensitive technique available for the quantification of methanol and ethanol in ambient air. Our objective was quantifying these alcohols in the ambient air of Denver, Colorado by using a standard gas chromatograph with a flame ionization detector (GC-FID). In our procedure ambient air samples were trapped on a solid adsorbent. The analytes were then thermally desorbed and cryofocused onto a GC capillary column. The GC column was rapidly heated injecting the analytes. The detection limits of the system were in the ppbv range for both methanol and ethanol. Ten ambient air samples of three to twelve liters were collected at the Auraria Ambient Air Sampling Station on the University of Colorado Campus in downtown Denver, Colorado between November 11, 1994 and December 3, 1994. The concentration of methanol in Denver's air ranged from 1.7-12 ppbv with an average of  $5.9 \pm 3.7$  ppbv, and ethanol ranged from 0.70 - 3.4 ppbv with an average of  $2.3 \pm 1.2$  ppbv.



- 181 SULFURIC ACID/CHARRING CLEAN-UP METHOD FOR PCBS IN GAS CONDENSATE. Sandy K. Brown, Public Service Company of Colorado, 1500 West Hampden, Building 5-G, Englewood, Colorado, 80110.

A method for cleaning up gas condensates to remove the sulfur contamination has been implemented at Public Service Company of Colorado, Applied Sciences Department laboratory. It is a sulfuric acid/charring technique, utilizing Gas Chromatography/Electron Capture Detector. There are three other clean-up procedures referenced in SW-846, Method 3660; copper, mercury, and TBA-sulfite. In the past there was an attempt to use the mercury clean-up procedure and also the copper clean-up procedure, but they were not able to adequately remove the sulfur contamination, associated with the mercaptan odorant, which interferes with the quantitation of arochlors 1221 and 1242. The Hall detector is used in some cases, but it is quite expensive and it is not able to get a detection limit better than four parts per million and the industry standard detection limit is less than two parts per million. The charring procedure was initially developed in California where the detection limit requirement is one ppm, so it is quite adequate for a two ppm detection limit. Spike and duplicate recoveries are well within the acceptable range for EPA standards. The advantages of this procedure are it doesn't require the purchase of any new high tech, expensive equipment since it works with ECD, which most laboratories already have and it doesn't generate any excess hazardous metal waste.

- 182 ANALYSIS OF LOW LEVEL ANIONS IN POWER GENERATION SYSTEMS. Cheryl A. Quinlin, Becki L. Sheridan, Public Service Company of Colorado, 1500 West Hampden, Building 5-G, Englewood, Colorado 80110.

A method for determining low-level anions in power generation systems was developed at Public Service Company of Colorado, Applied Sciences Department laboratory, located in Englewood, Colorado, to accommodate a growing need for component analysis. The method was developed utilizing ion chromatography to monitor water quality throughout the feedwater/boiler system and was in response to changes in chemical treatment programs and EPRI guidelines for anions in steam. As hydroquinones replaced hydrazine as an oxygen scavenger, weak organic acids were observed in routine monitoring for anions. The low level method is capable of analyzing several anions simultaneously with the advantages of increased sensitivity and separation. Currently, the six anions of concern are acetate, formate, chloride, nitrate, sulfate, and phosphate. The method is not limited to the above mentioned anions and could be expanded to include other anions of interest. These anions can be detected in the parts per billion range with a minimum detection limit of one part per billion. Considerations when using this method include sampling contamination, water purity, and analyzing within suitable holding times. The method has been implemented to measure the quantity of anions in feedwater, boiler, steam, and condensate systems and has been beneficial in meeting the growing demands of our industry.

- 183 IMPURITY DETECTION OF GC-FT-IR DATA EMPLOYING THE ASSESSMENT OF SINGULAR VALUE EVOLVING PROFILES. Nickev J. Messick, Gregory A. Rakken, and John H. Kalivas, Department of Chemistry, Idaho State University, Pocatello, ID 83209.

An approach to impurity detection previously developed [1] for high performance liquid chromatography with ultra violet visible spectrochromatograms is tested using gas chromatography Fourier transform infrared spectrochromatograms. This method entails the use of singular value evolving profiles (SVEP) to determine the presence of an impurity. The analysis requires no assumptions and reference spectra are not required. However, a reference spectrum of the analyte is required when the resolution between the impurity and the analyte is at or near zero and the impurity has the same bandwidth as the analyte. With a resolution of zero, a detection limit was found to be 0.1% impurity. A detection limit was found to be 0.5% impurity with a resolution equal to one.

[1] G.A. Bakken and J.H. Kalivas, *Anal. Chim. Acta*, 300 (1995) 173.

- 184 **SAMPLE DEPENDENT PRINCIPAL COMPONENT REGRESSION.** Dixie R. Long-Reitel and John H. Kalivas, Department of Chemistry, Idaho State University, Pocatello, Idaho 83209.

A new method of choosing principal components for predicting individual unknown concentrations by principal component regression (PCR) is proposed. The classical approach of PCR includes performing singular value decomposition (SVD) on the calibration response matrix. The singular values are then evaluated for non-error singular values. In determining which singular values are non-error singular values, the analyst needs to determine a singular value magnitude to represent the cut off point. Once the cut off point is determined, the singular values above it are considered the non-error singular values. The non-error corresponding principal components are used to predict the individual unknown concentrations. By using non-error principal components, the prediction error should be lower than compared to using all principal components, i.e., least squares. This classical approach shall be referred to as top-down selection. New criteria are proposed that select principal components that should generate equal or lower prediction errors compared to the top-down selection. These criteria involve a combination of mathematical analysis and a series of plots. The mathematical analysis is the decomposition of the equation that estimates the unknown concentration. The plots are used to visually confirm why the selected principal components should be used. Although this new method of choosing principal components is still under investigation, this poster demonstrates it as a promising alternative for improved prediction results compared to the classical top-down approach.

- 185 **A COMPARISON OF THE DETECTION OF DECOQUINATE USING HPLC/UV AND HPLC/EC.** Jeffrey A. Hurlbut, David H. Desandre, and Patrick B. Cooper of MSCD; Joseph M. Storey, and Carolyn A. Geisler of FDA; Chemistry Department, Metropolitan State College of Denver, P.O. Box 173362, Denver, Colorado 80127

Decoquinatone is a veterinary drug which is added to animal feed in order to control certain diseases. Typical analysis of decoquinatone involves extraction of the drug from feed, liquid-liquid extraction clean-up, and HPLC/UV separation and detection. The typical HPLC separation procedure is tedious because of the use of a normal phase silica column and a nonpolar mobile phase. We have developed a procedure which uses a short C3 reverse phase column and a methanol/aqueous mobile phase. The methanol/aqueous mobile phase coupled with the fact that decoquinatone contains an oxidizable phenolic group allowed us to use an electrochemical detector. This work compares the HPLC/UV and the HPLC/EC detection systems; gives the limits of both methods; and presents an SPE clean-up procedure.

- 186 **ANALYTICAL COMPARISON OF EPHEDRINES IN NUTRITIONAL SUPPLEMENTS AND HERBAL PREPARATIONS BY CE, HPLC, GC/FID and GC/MS.** Barbara S. Portz, Kent C. Faul, Terri L. Thomas, Jeffrey H. Cutting, Jennifer C. Pensoneau and Jeffrey A. Hurlbut, Food and Drug Administration, General Chemistry Section, Denver Federal Center, Denver, CO 80225-0087.

Ephedrine is frequently found in nutritional supplements and herbal products. There have been recent health concerns related to these drugs. The compounds of interest are ephedrine, pseudoephedrine, methylephedrine, methylpseudoephedrine, norephedrine and norpseudoephedrine. A cleanup procedure using SPE columns has been developed which allows interference free analysis by both HPLC and GC methods. The GC/FID and GC/MS analysis utilizes a capillary chiral column for separation of the ephedrine isomers. HPLC analysis, using a phenyl column, separates the isomers of importance. Previously, preparation of herbal products was difficult. Traditional acid-base cleanup procedures were tedious, time consuming, high solvent usage and resulted in lower recoveries. A buffered solvent extraction did not remove all of the interfering components. Capillary electrophoresis is a very rapid method for separating and analyzing the ephedrine isomers and does not require extensive cleanup. Quantitation of the ephedrine isomers at the levels found in the products is possible by CE method, however the identification by GC/MS requires a clean sample. A combination of these methods are used in our laboratory.

- 187 Analysis of Methylene Blue in Catfish Tissue. Sherri B. Turnipseed, Jose E. Roybal, Allen P. Pfenning, Jeffrey A. Hurlbut, Austin R. Long, Food and Drug Administration, Animal Drugs Research Center, Denver Federal Center, Denver, CO 80225-0087

Methylene Blue (MB) is a thiazine dye which may be used as an antifungal agent in the aquaculture industry. MB is a suspected carcinogen, therefore it is important to develop analytical methods to monitor for this compound in fish tissue. The metabolism of MB in fish is not known at this time. Based on the metabolic profiles of other dyes in fish, it may be reduced to its leuco form. We have found that the leuco form of MB is very unstable and cannot be isolated, but solutions of leuco MB do convert completely back to the chromic dye when analyzed by HPLC. MB can be isolated from catfish tissue with an acetonitrile/acetate buffer solution containing hydroxylamine and toluenesulfonic acid. It is then extracted into methylene chloride, and these extracts are cleaned-up using alumina and carboxylic acid solid phase extraction cartridges. The dye is then analyzed by HPLCA/IS at 660-665 nm. Recoveries of catfish fortified with MB at the 10 ng/g level are  $75.4 \pm 6.3\%$ . Leuco MB can also be recovered from catfish tissue at this level with recoveries of over 80%.

- 188 **DETERMINATION OF OXOLINIC ACID RESIDUES IN SHRIMP BY HIGH PERFORMANCE LIQUID CHROMATOGRAPHY-FLUORESCENCE/UV DETECTION** Allen P. Pfenning, Robert K. Munns, Sherri B. Turnipseed, Jose E. Roybal, Austin R. Long, Food and Drug Administration, Animal Drugs Research Center, Denver Federal Center, Denver, CO 80225-0087

As the aquaculture industry expands, efforts to monitor edible seafood tissue for residues of drugs used to treat bacterial infection have increased. A multi-residue method for the determination of four quinolones [flumequine (FLU) and oxolinic (OXO), nalidixic (NAL), and piromidic (PIR) Acids] in catfish by Munns, *et al.*, was adapted to shrimp. All four quinolones were analyzed in fortified shrimp tissue at 0, 5, 10 and 20 ppb. The target level (X) for the method is 10 ppb for each analyte. The recoveries (n=6) of fortified shrimp tissue at X are: FLU 81% (RSD=3.7); OXO 89% (RSD=8.9); NAL 94% (RSD=6.2); PIR 85% (RSD=13). Two levels of OXO incurred shrimp tissue were prepared and analyzed. A third level was prepared by mixing control blank shrimp with the lower level of incurred tissue. The results of the incurred analysis (n=6) are: Group A 40 ppb (RSD=2.9); Group B 78 ppb (RSD=3.9); Group C 9.3 ppb (RSD=8.6).

- 189 LIQUID CHROMATOGRAPHIC SEPARATION AND ANALYSIS OF INORGANIC COLLOIDS SYNTHESIZED IN INVERSE MICELLES. S. Craft, and J.P. Wilcoxon, Sandia National Laboratories, MS1421 Albuquerque, NM 87185-1421.

We have developed a novel method to synthesize inorganic colloids in a water-free organic environment. The technique relies on the use of surfactant molecules to solubilize metal salts (e.g.  $\text{CoCl}_2$ ,  $\text{FeCl}_3$ ) in inert, low dielectric constant solvents such as octane. The surfactants form into droplet-like structures called inverse micelles with the inorganic salt in the interior. Subsequent reduction of the salt using strong organic reducing agents leads to dispersions of metal colloids. We have examined the chemical byproducts and the colloids themselves using HPLC. Gases released during the reduction are analyzed using head-space analysis and GC-TCD. We use HPLC to separate the inorganic colloids from the surfactants, organic molecules, and inorganic salts produced in the reaction and to study the inherent optical properties of the colloids, including photoluminescence. We observe highly structured UV-visible spectra by PDA detection of the eluting components which we attribute to the small size and discrete transitions found in nanosize metals and semiconductors. This is illustrated with nanosize Si and Ge colloids. Characterization of Fe and Co colloid size using SEC methods is compared to other size measurements on the purified colloids using HRTEM, x-ray and light scattering.

- 190 USE OF RESPONSE SURFACE METHODOLOGY IN OPTIMIZATION OF REVERSED-PHASE HPLC CHIRAL SEPARATION OF AMINO ACID AND AMINO ACID ANALOGS. John A. Blackwell and William L. Champion. The DuPont Merck Pharmaceutical Co., DuPont Chambers Works/PRF (S-1), Deepwater, NJ 08023.**

Commercially available chiral HPLC are routinely used to perform chiral separation of amino acids. This poster shows application of response surface methodology to better understand the separation of enantiomers of several amino acids and amino acid analogs. The factors investigated include pH, Cu(II) Concentration and organic modifier concentration of the mobile phase and temperature of the column.

- 191 A BLIND QUALITY ASSESSMENT STUDY OF THE BRANCH OF GEOCHEMISTRY. Belinda Arbogast, U.S. Geological Survey, MS 973, Box 25046, Denver, CO 80225.**

The purpose of this investigation is to assess the bias of analytical results and cost effectiveness. The Quality Assurance Coordinator conducts the study and submits reference materials (RM) samples to the Analytical Chemistry Services Group (ACSG) as "routine jobs." The situation for acceptable bias is defined to be within 80-120 percent Recovery for values greater than or equal to 5x the lower reporting limit. Values less than 5x the lower reporting limit have controls of  $\pm$  the lower reporting limit. The ACSG has been tested since 1991 with excellent agreement between ACSG results and certified RM values by quantitative techniques; the 1993 study indicated an average 97 percent Recovery. Multi-element techniques, dominated by DC-arc atomic emission spectroscopy, inductively coupled plasma-atomic emission spectroscopy, and X-Ray fluorescence spectroscopy remain the most cost efficient methods of choice for acquiring analytical results. The INAA technique generally gives the lowest reporting limits available but at the highest cost. Results of this study are summarized on an annual basis that may be used for addressing discrepancies in analytical results and improvements in production efficiency.

- 192 A COMPARISON OF FLUORIMETRIC DERIVATISATION METHODS FOR THE HPLC ANALYSIS OF DIARRHETIC SHELLFISH TOXINS. K.J. James, E.P. Carmody and S.S. Kelly, Ecotoxicology Research Unit, Chemistry Department, Cork RTC, Bishopstown, Cork, IRELAND**

Diarrhetic shellfish poisoning (DSP) produces gastroenteritis in humans following the ingestion of bivalve molluscs, particularly mussels and scallops. Most outbreaks of DSP are due to the presence of okadaic acid (OA). However, dinophysistoxin-1 (DTX-1) and an isomer of OA, named dinophysistoxin-2 (DTX-2) have also been implicated in DSP. These toxins originate in marine microalgae and accumulate in shellfish that feed on these flagellates. The determination of DSP toxins is possible using fluorimetric liquid chromatographic analysis following pre-column derivatisation with 9-anthryldiazomethane (ADAM). Although this method is very sensitive, the problems associated with reagent instability present difficulties. 1-bromoacetylpyrene (BAP) has been successfully applied to the analysis of the diarrhetic shellfish toxins, OA, DTX-1 and DTX-2, with good linear calibration (OA,  $r=0.996$ ). In addition, the same solid phase extraction and liquid chromatographic conditions can be used for both the anthrylmethyl and pyrenacyl esters. The progress of the isolation of toxins was also monitored by the examination of fractions using the above liquid chromatographic procedures.

**THE ANALYSIS OF VOLATILE ORGANIC COMPOUNDS IN SOIL USING SOLID PHASE MICROEXTRACTION FOR HEADSPACE GAS CHROMATOGRAPHY.** Kevin J. James and Mary A. Stack. Ecotoxicology Research Unit, Chemistry Department, Cork RTC, Bishopstown, Cork, IRELAND.

193

Solid phase microextraction (SPME) has recently been applied as a useful extraction technique for organic compounds present in a variety of solid matrices. We have applied this method to sample the headspace above a soil matrix and used gas chromatography - mass spectrometry (GC-MS) for the analysis of a number of target organic compounds. Xylene, ethylbenzene, trichloroethene, tetrachloroethene, dichloromethane and hexane were determined in soil samples. These analytes are adsorbed directly from the headspace sample onto a fused-silica fiber that is coated with a polydimethylsiloxane-coated fibre. While the fiber is inserted in the headspace sample, the analytes partition from the sample matrix into the stationary phase until equilibrium is reached. The fiber is then inserted into the injector port of the GC where the analytes are rapidly thermally desorbed onto a capillary column. Time profiles for the extraction the target compounds were determined at various temperatures (20°-90° C) using a 100um fibre. Calibrations for these solvents in soil were rectilinear (0.1-10 ug/g). Finally, the method was applied to determine the VOC's in soil samples from landfill sites.

194 **STRUCTURE ANALYSIS OF TWO NOVEL ALKALOIDS FROM SPERANSKIA TUBERCULATA (BGE.) BAILL.** Jiangong Shi, Hanging Wang and Min Wang, Lanzhou Institute of Chemical Physics, Chinese Academy of Sciences, Lanzhou 730000, P.R. China

*Speranskia tuberculata* (Bge.) Bail! (Euphorbiaceae) is a Chinese medicinal plant used for treatment of rheumatic arthritis, tumors, tendon contractures, sores, swelling and gynecological problems. By silica column chromatography, two optically active novel alkaloid atropisomers (1 and 2) were isolated from the acetone extract of the whole plant. The elemental analysis gave the same molecular formula,  $C_{20}H_{24}O_{10}N_2$ , for both. Their EI-MS spectra exhibited a molecular ion peak of M/Z 452 and similar fragment peaks. Both IR spectra showed absorption bands for hydroxy and carbonyl groups. Their structures were finally elucidated by 1D  $^1H$ ,  $^{13}C$  and DEPT NMR spectra and 2D H,H COSY H,C COSY and HMBC experiments. The structures were further confirmed by X-ray crystallographic analysis, which indicated that the dihedral angle between ring least-square planes 88.21° for compound 1 and 85.20° for compound 2.

195 **LASER ABLATION ICP/MS ANALYSIS OF LOW LEVEL HANFORD TANK WASTE AND SIMULANTS: OPTIMIZING EXPERIMENTAL PARAMETERS.** Michael L. Alexander, Monty R. Smith, David W. Koppelaar, and John S. Hartman, Battelle, Pacific Northwest Laboratories, Battelle Blvd., P3-08, Richland, WA 99352.

A laboratory demonstration system has been constructed to demonstrate the feasibility of using laser ablation ICP/MS to rapidly scan and analyze radioactive material from the Hanford Tank Farms. The integration of diverse types of instrumentation allows the variation and measurement of a large number of parameters relevant to the laser ablation of material, transport to the ICP and measurement by the mass spectrometer. These include laser wavelength, pulse length, pulse energy and beam area at the sample surface. Correlations are made between these parameters and elemental fractionation as measured by the mass spectrometer. The particle size distribution of the ablated material is monitored both at the point of ablation and at the entrance to the ICP/MS. The particle size distribution is also correlated with the laser parameters. Several sample matrices are studied and the parameters are correlated to determine the conditions for obtaining optimum sensitivity, precision and accuracy. Ultraviolet ablation wavelengths produce smaller overall particle sizes and superior analytical data for the samples studied.

- 196 DETERMINATION OF CHALCOPHILIC ELEMENTS IN GEOLOGICAL MATERIALS BY LASER ABLATION INDUCTIVELY COUPLED PLASMA MASS SPECTROMETRY. Xun Guo and Frederick E. Lichte, US Geological Survey, M/S 973, Box 25046, Denver Federal Center, Denver, CO 80225

The determination of chalcophilic elements is extremely important for many environmental and mineral exploration studies. These elements include: As, Se, Ag, Cd, In, Sb, Te, Tl, Pb, and Bi. In the presence of sulfur, they follow the siderophile elements and at high concentrations are a problem in the NiS fire assay method used for platinum group elements (PGEs). This method employs a LiB<sub>3</sub>O<sub>8</sub> fusion of the sample in the presence of nickel and sulfur. For this study, we optimized the fusion conditions for the chalcophilic elements instead of the PGEs and concentrated them into a NiS mini-bead (30mg) from a 0.3 gram sample. The mini-bead was then directly analyzed by laser ablation inductively coupled plasma mass spectrometry. Recovery of the chalcophilic elements was >95 percent. The limits of detection ranged from <1 (Ag) to 100 (Te) ng/g. Stable isotopes were used to compensate for variations in mass response and ablation efficiency.

- 197 GEOLOGICAL AND ENVIRONMENTAL ANALYSIS USING A NEW UV LASER ABLATION MICROPROBE COUPLED TO AN ICP-MS. Rob Henry, Angelica Raith, Fisons Instruments, P.O. Box 20460, Boulder, CO 20460-3460 William T. Perkins, Institute of Earth Studies, University of Wales, Aberystwyth, SY23 3DB, Wales, UK

An Ultraviolet Laser Ablation Microprobe system has been developed for the analysis of both geological and environmental materials. The laser is a frequency quadrupled Nd:YAG operating at 266 nm with up to 5 mJ power output which produces crater sizes in minerals of between 5 and 50 microns. A computer controlled high precision sample stage allows for accurate and comprehensive traverses across large samples. Data will be presented for a series of geological and environmental applications including: a) distribution of Pb and Sr in the shell of *Artica islandica* which may indicate metabolic changes during the lifetime of the shell as well as uptake of Pb due to environmental pollution, b) the content of Cd and Zn in a weathered sphalerite and zonation of other metals such as Mn & Fe. c) the analysis of polished petrological thin sections for a range of elements to ppm levels. Data will be presented from zoned olivine phenocrysts in basaltic rocks.

- 198 TECHNIQUES FOR VALIDATING TRACE ELEMENT DETERMINATIONS IN ENVIRONMENTALLY RELATED MATERIALS BY ICP-MS. Ronald C. Antweiler and Howard E. Taylor, U.S. Geological Survey, 3215 Marine St, Boulder, CO 80303

Post-analysis techniques for the improvement of the accuracy and precision of data acquired by inductively-coupled plasma mass-spectrometry (ICP-MS) are necessary for optimal data processing. The implementation of these techniques requires that the analyses be done by a carefully specified protocol. Each sample must be analyzed in triplicate using a randomized design. Three to four Standard Reference Materials should be analyzed at least every sixth sample and blanks should be analyzed a minimum of five times, interspersed throughout the suite of samples. A minimum of five calibration standards should be used; if the ratio between the highest concentration calibrant and the lowest concentration calibrant is greater than 30, the concentrations of the remaining calibrants should be geometrically spaced. In addition, at least four different Standard Reference Materials should be analyzed covering the entire calibration range. There are four post-analysis techniques which are employed: 1) the "manual calculation" of concentrations directly from the calibration curve (rather than having the instrument software calculate them); 2) the adjustment of concentrations using one of the Standard Reference Materials; 3) the computation of detection limits; and 4) the detection and systematic removal of outliers. An experiment was conducted using twelve blind Standard Reference Materials from three different sources (the National Bureau of Standards, the U.S. Geological Survey Standard Reference collection and High Purity Standards) as samples to assess the efficacy of each of these four techniques. It is demonstrated that the optimal solution to improve both the accuracy and precision of a data set requires appropriate implementation of all four techniques.

**TRACE ANALYSIS OF CORROSIVE GAS PRODUCTS BY ICP/MS, Greg W. Johnson and Jude Proctor, Matheson Gas Products, 1861 Lefthand Circle, Longraont, Colorado 80501.**

The ICP/MS has proven to be an invaluable tool in analysis of corrosive gases for elemental constituents present at trace concentration levels. To date, methods for the analyses of tungsten hexafluoride, hydrogen bromide, hydrogen chloride, chlorine, and boron trichloride gases have been devised. Production lots of material are sampled by both residue and hydrolysis methods. ICP/MS is used routinely to determine elemental concentrations for more than sixty elements in the resulting samples, with ICP/AES used for Ca concentration determinations, GFAA for Fe and Si, and Flame Emission for Na and K. Determination of method detection limits and guidelines for assurance of analytical accuracy described in document C10-94 promulgated by Semiconductor Equipment Manufacturers International (SEMI) have been adopted into our standard operating procedure. Isotope selection/isobaric interference correction, reagent blank control, ICP/MS standardization, data reduction, report generation, statistical process control, and data archiving constitute the other essentials of our standard operating procedures. Using residue sampling procedures, a production lot can be certified to contain less than one microgram of any elemental contaminant of interest per kilogram product, or less than 200 micrograms total metal impurity per kilogram product, using predominantly the ICP/MS instrumentation.

**200 ANALYSIS OF SNOW-CORE SAMPLES FROM ALASKA'S NORTH SLOPE USING SUB-BOILING EVAPORATIVE CONCENTRATION AND ICP-MS. John R. Garbarino and Gerald L. Hoffman, U.S. Geological Survey, 5293 Ward Road, MS 407, Arvada, CO 80002 and Elaine Snyder-Conn, U.S. Fish and Wildlife Service, 101 12th Ave., Box 19, Room 232, Fairbanks, AK 99701.**

The concentration of heavy-metal contaminants in dissolved and particulate phases of the 1994 snowmelt from Alaska's North Slope was studied to identify possible local sources of contamination, and to obtain baseline data for snow as an air-pollutant indicator. Snow cores were collected and sealed in perfluoroalkoxy-polymer bags at 11 sampling sites, 2 in the Prudhoe Bay oil field and 9 in the Arctic National Wildlife Refuge. A major difficulty in quantifying selected heavy-metal concentrations in snowmelt is the extremely low concentration present. A subboiling evaporative concentration technique was developed to concentrate snowmelt in polypropylene beakers by a factor of up to 50 in less than 3 days using a custom-built graphite heating block operated at 85°C. Contamination was minimized by conducting the experiments inside a Class-100 clean room and laminar-flow clean benches. The effective detection limits using inductively coupled plasma-mass spectrometry (ICP-MS) were less than 10 nanograms per liter (ng/L) for all heavy metals measured. The accuracy of the technique was determined by evaporating diluted certified natural-water samples with the snowmelt samples. Recoveries of nearly 100 percent were obtained for most heavy metals with precision for four replicate evaporations over a 3-week period ranging from 3 to 5 percent at the 100-ng/L concentration level.

**201 USE OF ISOTOPE DILUTION-INDUCTIVELY COUPLED PLASMA-MASS SPECTROMETRY TO DETERMINE MERCURY IN NATURAL WATER SAMPLES. D. A. Roth and H. E. Taylor, U.S. Geological Survey, 3215 Marine Street, Boulder, Colorado 80303**

Ensuring the accuracy of analytical results can be achieved by two basic methods. Accuracy of the results can be inferred by comparing results obtained for standard reference materials, provided that the matrices are similar in nature. Alternatively, methods that are inherently accurate, such as isotope dilution-inductively coupled plasma-mass spectrometry (ID-ICP-MS) O'neumann, K.G., 1988; Isotope Dilution Mass Spectrometry: in *Inorganic Mass Spectrometry*. Adams, F., Gijbels, R., and Greiken, R. Van, eds. John Wiley and Sons, New York, pp. 301 - 319 and Gray, A.L., 1988; Inductively Coupled Plasma Source Mass Spectrometry: in *Inorganic Mass Spectrometry*. Adams, F., Gijbels, R. and Greiken, R. Van, eds. John Wiley and Sons, New York, pp. 257-300), can be used to accurately determine trace concentrations of poly-isotopic elements, independent of matrix interferences. ID-ICP-MS is ideal for the determination of analyte concentrations in materials that are to be used as standard reference materials. This method can be extended to determine analyte concentrations in unknown environmental samples with high accuracy and precision. A mercury cold-vapor generator was coupled with an ICP-MS to obtain the sensitivity necessary to determine mercury concentrations at the nanogram per liter levels which naturally occur in environmental water samples. Data generated by this technique were used to confirm the mercury concentrations in standard reference materials used in the determination of mercury utilizing a cold vapor-atomic fluorescence spectroscopy (CV-AFS) technique (Roth, D. A., 1994; Ultratrace Analysis of Mercury and Its Distribution in Some Natural Waters in the United States. Ph.D. Dissertation, Colorado State University, Fort Collins, Colorado; 309 p). The accuracy, precision, and efficiency of the ID-ICP-MS method was compared with the CV-AFS method used routinely for the determination of ultratrace mercury concentrations in environmental samples.

**202 MICROWAVE INDUCED PLASMA TIME-OF-FLIGHT MASS SPECTROSCOPY OF CHLORINATED VOCs.** Alex F. Schreiner, Chung H. Sin, and Jon W. Carnahan, Department of Chemistry, Northern Illinois University, DeKalb, IL 60115-2862

A microwave induced plasma source is coupled with a reflectron time-of-flight mass spectrometer. The MIP is a stable and powerful ionization source which produces parent ions as well as atomic species. The reflectron TOFMS can compensate for the relatively large energy distributions of the ions. The ions are cooled initially by the supersonic jet expansion, but still contain thermal and kinetic energy from the MIP source as the linear spectra indicate. The mass spectrometer is used to quantify the parent species of some volatile organic compounds containing chlorine in addition to the identification and quantification of the atomic species produced through the volatile organic compounds. The chlorine ion is of particular interest for the helium and argon helium doped MIP torch. It is known that the chlorine emission line is very intense for the helium plasma. This is attributed to the energy overlap of the excited state  $\text{Cl}^{+*}$  and  $\text{He}^+$ . The charge transfer reaction between  $\text{He}^+$  and  $\text{Cl}$  leads to high abundance of chlorine ion. When argon is present, the chlorine ion emission is much lower. This can be related to a reduction of ionized helium. The sensitivity of the current configuration is limited by the collision induced dissociation leading to broad peaks and loss of the parent ion. The fundamental studies of chlorinated ions and the helium/argon system will be presented.

**203 DEVELOPMENT OF A SECOND GENERATION HIGH RESOLUTION ICP-MS AND ITS APPLICABILITY TO TRACE ELEMENT ANALYSIS IN REAL SAMPLE MATRICES.** Rob Henry, Nicola Reed, Robert Hutton, Fisons Instruments, P.O. Box 20460, Boulder, CO 20460-3460

Since the first high resolution ICP-MS using a double focussing magnetic sector mass analyzer was installed in Japan in 1989 many laboratories around the world have recognized the value of interference free ICP-MS analysis of complex sample matrices. However like most first generation instruments the early instruments had some limitations. A second generation high resolution ICP-MS has now been developed which incorporates a new high resolution mass analyzer and sophisticated software control. The enhanced performance of the new system will allow much lower detection limit capability in complex matrices where high resolution is required to resolve the polyatomic species present in the argon plasma. In addition the speed of data acquisition and automation of the five resolution settings has been designed to increase sample throughput. The implementation of digital mass scanning of the magnet combined with the fast electrostatic sector also allows accurate and precise isotopic ratio measurements. Data will be presented for a range of sample matrices to illustrate the analytical capabilities of the system.

**204 PRACTICAL EXPERIENCE WITH A DIN-HR-ICP/MS IN THE SEMICONDUCTOR INDUSTRY.** Barton D. Tillotson, Anthony J. Schleisman, Texas Instruments, Inc., P.O. Box 650311, M/S 301, Dallas, Texas 75265

Past and present technology in the semiconductor industry employ the application of an ICP/MS for the determination of metallic contaminants in certain chemicals. However, this technology is quickly becoming obsolete due to its limitation concerning low detection limits and resolving polyatomic interferences. This is still evident even after extensive research in improving the instrument capabilities. This lack of progress has created a mass rush by the semiconductor industry to search for other instrumentation that will achieve the next level of analytical capabilities. One avenue is the utilization of a High Resolution Inductively Coupled Mass Spectrometer (HR-ICP/MS). Due to the fact that the HR-ICP/MS is new technology, a fundamental question often arises concerning its capabilities to achieve both present and future requirements set by the semiconductor industry. Furthermore, can the instrument act both as a research instrument and a production instrument? This presentation will focus on our practical experience when analyzing ultra pure chemicals with a Direct Injection Nebulizer coupled to HR-ICP/MS.



- 205 **PROTOCOL DEVELOPMENT FOR QUANTITATIVE MULTI-ELEMENT ANALYSIS OF BIOLOGICAL SAMPLES BY INDUCTIVELY COUPLED PLASMA-MASS SPECTROMETRY, Chiung-Sheng Hsiung, Joseph D. Andrade. K.Owen Ash, ARUP, 500 Chipeta Way, Salt Lake City, UT 84108**

During the last decade, inductively coupled plasma-mass spectrometry (ICP-MS) has emerged as a promising and versatile means for trace element analysis in biological specimens. Our goal is to determine conditions for simultaneous analysis of multiple elements in biological specimens. High salt content in biological samples results in matrix induced signal suppression, polyatomic interference and changes in ion stabilities and detection limits. Using a Perkin-Elmer SCIEX ELAN 5000 ICP-MS, we investigated the feasibility of chemical modification with ethanol while varying two instrument parameters:

- Nebulizer gas flow rate—15 flow rate intervals of 0.025 liters/minute.
- Radio frequency power—1.0 to 1.4 Kilowatts at 100 Watt intervals.

Ion signal variations were assessed for more than 39 elements spiked in water. Optimized conditions for gas flow and radio frequency power produced patterns which were mass dependent. We confirmed reported findings that ethanol increases sensitivity for some element, while lowering gas flow requirements and increasing power requirements. These findings provide a base for continued development of simultaneous multi-elements analysis in biological specimens.

- 206 **CHARACTERIZATION AND DETERMINATION OF BENZO(A)PYRENE-DNA ADDUCTS AND THEIR HYDROLYSIS PRODUCTS VIA SOLID-MATRIX LUMINESCENCE. R. J. Hurtubise, Y. Chu, and S. W. Tjioe, Department of Chemistry, University of Wyoming, Laramie, Wyoming 82701.**

Benzo(a)pyrene [B(a)P] can covalently bind to DNA and initiate chemical carcinogenesis. Thus, very sensitive and selective analytical methods are needed for the characterization and determination of B(a)P-DNA adducts and their hydrolysis products. Because there are different conformations of covalently bound DNA adducts, the selectivity of the analytical methodology for distinguishing the adducts is of considerable importance. Solid-matrix luminescence techniques offer both sensitivity and selectivity. Several solid matrices have proven to be very effective for acquiring room-temperature fluorescence and phosphorescence from B(a)P-DNA adducts and their hydrolysis products. Different types of filter paper, cyclodextrin salt mixtures, trehalose salt mixtures, and thallium nitrate-sodium acetate mixtures have proven to be very effective. With these solid matrices, both room-temperature fluorescence and phosphorescence were obtained from the B(a)P-DNA adducts at very low levels. Also, the solid-matrix luminescence approach permitted the general characterization of different forms of the DNA adducts. Several significant results from these studies will be presented.

- 207 **HEAVY-ATOM EFFECT ON THE ROOM-TEMPERATURE PHOSPHORESCENCE (RTP) OF 2-AMINO-1-METHYL-6-PHENYLIMIDAZO[4,5-B]PYRIDINE (PHIP) IN GLUCOSE AND TREHALOSE GLASSES AS SOLID MATRICES. Jiangshan Wang and Robert J. Hurtubise, Department of Chemistry, University of Wyoming, Laramie, WY 82071**

Nal and T1N0<sub>3</sub> were used as heavy-atom salts in glucose and trehalose glasses to study the RTP of PHIP. PHIP is a toxic substance found in foods. It was discovered that both Nal and T1N0<sub>3</sub> had a strong heavy-atom effect on the RTP of PHIP. Various percentages of Nal and T1N0<sub>3</sub> from 1 to 15% were added to glucose and trehalose. The results showed that as the percentage of Nal or T1N0<sub>3</sub> increased, the RTF intensity decreased significantly and the RTP intensity increased substantially until the RTP intensity reached a plateau. The RTP intensity increased about 3 to 10-fold and RTF decreased about 3-fold compared with the respective RTP and RTF intensities with no heavy atom present. However, the RTF did not disappear completely, and it was still strong enough for analytical use. Also, T1N0<sub>3</sub> not only affected the intensities of the RTF and RTP signals, but also shifted the positions of the main RTF and RTP peaks of PHIP to longer wavelengths in the glucose and trehalose glasses. However, Nal affected only the intensities of the RTF and RTP spectra of PHIP, but not the position of the peaks. The heavy-atom effect on several other organic compounds in glucose and trehalose glasses will also be briefly introduced.

- 208 **MEASURING THE TEXTURE OF A SURFACE USING EXCITATION ENERGY TRANSPORT.** T. Gregory Dewey, Department of Chemistry, University of Denver, Denver, CO 80208.

The effect of surface texture or lacunarity on the dynamics of excitation energy transport is investigated. The problem of Foerster transport between multiple donors on a complicated surface is considered. The Greens function associated with the dynamics of this problem can be calculated approximately using a density expansion. This Greens function can be experimentally determined by measuring the time resolved fluorescence anisotropy of the system. The multiple donors are assumed to be distributed on a surface that can be characterized by a fractal surface dimension. However, this parameter alone is not sufficient to describe the texture of the surface. Rather one must introduce a lacunarity function to determine this property. The fractal properties of the surface enter directly into the density expansion of the Greens function and the predominant contribution is contained in the two-body correlation term. The three body correlation term will also contain contributions from the lacunarity function. Using lacunarity functions determined on model surfaces, the magnitude of the "texture effect" can be determined. The experimental constraints in measuring surface textures are discussed.

- 209 **PROBING THE BINDING PROPERTIES OF AGGREGATE MATERIALS WITH THE TRIPOSITIVE EUROPIUM IONS.** Leo V. Azarraga, U.S. Environmental Protection Agency, Environmental Research Laboratory, 960 College Station Road, Athens, GA 30605-2700.

Florescence from  ${}^7F_0, + - {}^5D_0, {}^7F_1, * - {}^5D_0$  and  ${}^7F_2, * - {}^5D_0$  transitions of tripositive Eu ions is used to study binding properties of the aqueous suspensions of naturally occurring heterogeneous solid aggregates. The ratio of the intensity of the magnetic dipole allowed transition,  ${}^7F_x, * - D_0$  to the intensity of the hypersensitive,  ${}^7F_2, * - {}^5D_0$ , transition is used to determine the extent of binding of the probe ions on the heterogeneous matrix. A titration curve is developed to estimate the maximum binding capacity of the solids. The technique is applied to a number of aquifer materials, well water and silica suspensions as well as aqueous solutions of pure substances. The estimated maximum binding capacity may be input into the Continuous Multilegand Distribution Model of Susetyo et. al. (Anal. Chem., 1990, 62, 1215) to obtain the mean binding constant and the width of the binding site distribution of the suspended solids.

- 210 **AN ORGANIZED MEDIA ENHANCED FIBER OPTIC LUMINESCENCE SENSOR FOR ENVIRONMENTAL MONITORING.** P.M. Hanlon, Seton Hall University, L.J. Cline Love, Chemistry Department, Seton Hall University, DeLyle Eastwood, Lockheed (LESAT), Las Vegas, Nevada, 89119, and K. Rubelowsky, Spex Ind., Inc. Edison, New Jersey, 08820.

The authors of this research will present positive proof of concept data for the detection of polycyclic aromatic hydrocarbons (PAHs) with a specific fiber optic luminescence sensor utilizing an organized media reservoir cell. This luminescence sensor possesses the potential for wide application in field site characterization of PAHs. The apparatus features the novel addition of a membrane enclosed reservoir cell containing micelles and/or cyclodextrins as the organized media. Key advantageous features inherent to the system will be displayed in spectra of naphthalene, anthracene and a real world sample, JP-8 Air Force jet fuel. The data confirming these properties are evidenced by: (1) A pronounced preconcentration effect of PAHs within the reservoir cell. (2) Luminescence enhancement by protection of the PAH from quenching interferences (humic acids or metals) due to the favorable microenvironment offered by the organized media and protective membrane. (3) Specific selectivity provided to the PAHs by either organized media based on dimensional and stoichiometric consideration in guest/host complexes.

211 **FLUORESCENCE ANISOTROPY MEASUREMENTS IN THE DETERMINATION OF HUMIC ACID ASSOCIATIONS.** Regginal R. Engehretson and Ray von Wandruszka, Chemistry Department, University of Idaho, Moscow, Idaho 83844

2,5-Diphenyloxazole (PPO) was used as a fluorescent probe to assess the pseudomicellar character of five aqueous humic acids. Fluorescence anisotropy measurements, in conjunction with fluorescence quenching and size-exclusion chromatography, showed the importance of size and secondary structure in the association of humic acids with extraneous species. An anisotropy-based parameter, including the effects of temperature and cations, was devised to describe the strength of interaction between the fluorescent probe and the humic acids.

**LUMINESCENCE AND PHOTOCHEMICAL REACTION DETECTION IN CAPILLARY ELECTROPHORESIS AND HPLC.** Robert E. Milofsky, Matt Odom, Samantha Spaeth, Emily Halvorson, and Derek Taylor, Department of Chemistry, Fort Lewis College, Durango, CO 81301.

Analytes that are poor chromophores present a significant challenge for sensitive detection in capillary electrophoresis (CE) and HPLC. Detection is even more challenging in CE, where path lengths on the order of 5-75  $\mu\text{m}$  limit the sensitivity of UV-VIS absorption measurements. We are interested in the development of sensitive detection schemes for CE and HPLC based on singlet oxygen ( $^1\text{O}_2$ ) photochemistry. While photochemical amplifiers based on  $^1\text{O}_2$  chemistry have been used to improve UV-absorbance detection in HPLC under predominantly organic conditions (Shellum, C.L. & Birks, *J.W. Anal Chem.* 1987, 59, 1834), the application of these techniques to enhanced UV detection in CE has not been demonstrated. This talk will cover new detection techniques for CE and HPLC based on  $^1\text{O}_2$  photooxidation reactions. Recent work in the area of micelle-enhanced  $^1\text{O}_2$  photooxidation reactions, and the application of micellar-enhanced photooxidation to detection in CE will also be presented.

213 **CHARACTERIZATION OF POLYMERIC MATERIALS BY FLUORESCENT CHARGE-TRANSFER PROBES,** J.W. Hofstraat, H.J. Verhey<sup>1</sup>, J.W. Verhoeven<sup>1</sup>, M. Ktimke<sup>2</sup> and L.B. McCown<sup>2</sup>, Akzo Nobel Central Research, Department RGL, P.O. Box 9300, NL-6800 SB Amhem, The Netherlands. <sup>1</sup> University of Amsterdam, Department of Physical Organic Chemistry, Amsterdam, The Netherlands, <sup>2</sup> Duke University, Department of Chemistry, Durham, NC, USA.

The fluorescence of molecules which undergo intramolecular charge-transfer upon excitation strongly depends on the polarity of the solvent. Since the change in fluorescence wavelength and intensity is caused by a dynamic process, the reorientation of the solvent cage surrounding the guest molecule in order to maximize their interaction, also the intrinsic viscosity of the system plays a role. It will be shown that charge-transfer fluorescent molecules, which report "from within" on subtle changes on a molecular scale, offer unique possibilities for the characterization of polymeric systems. A few examples which will be discussed are: 1) the characterization and study of the swelling of polystyrene latices; 2) the in-situ study of polymerization reactions of polystyrene latices, e.g. the formation of core-shell latices; 3) the study of coating formation; 4) the study of polymers under external, e.g. mechanical, stress. Apart from steady state fluorescence techniques, also time-resolved fluorescence methods have been applied. The advantage of the use of temporal resolution will be illustrated at the hand of the latex systems. Finally, the application of solvatochromic studies for the characterization of polymers with non-linear optical molecules as side chains will be discussed.

- 214 **DIAGNOSTICS FOR SIMULTANEOUS QUANTITATION OF DISSOLVED OXYGEN CONCENTRATION, PARTICLE SIZE, AND SURFACE MASS DEPOSITION RATE IN THERMALLY STRESSED AVIATION FUEL.** James R. Oord, Wright Laboratory, Aero Propulsion & Power Directorate, Wright-Patterson Air Force Base, OH 45433-7103; William L. Weaver and Viroj Vilimpoc, Systems Research Laboratories, Inc., 2800 Indian Ripple Road, Dayton, OH 45440-3696; and Steven W. Buckner, Department of Chemistry & Geology, Columbus College, Columbus, GA 31907-5645.

Aircraft performance improvements are often accompanied by increased thermal stress on the fuel-the primary coolant for on-board heat sources. Fuel thermal decomposition leads to fuel-system fouling and aircraft downtime. To address these concerns, three techniques have been integrated into a single instrumented rig designed for real-time simultaneous quantitation of dissolved oxygen concentration, particle size and growth rate, and surface mass deposition rate in thermally stressed aviation fuel. Dynamic quenching of the time-resolved fluorescence of pyrene-doped fuel is used to monitor dissolved oxygen concentration. Photon Correlation Spectroscopy (PCS) provides particle size and growth rate information. A Quartz Crystal Microbalance (QCM) is employed to record deposition during thermal stressing. The combined diagnostics yield data essential to the elucidation of fundamental fouling mechanisms and evaluation *of fuel additive performance*.

- 215 **ENERGY-GAP LAW AND SOLID-MATRIX ROOM TEMPERATURE PHOSPHORESCENCE.** S. M. Ramasamy and R. J. Hurtubise, Department of Chemistry, University of Wyoming, Laramie, WY 82071-3838.

Polycyclic aromatic hydrocarbons (PAH) adsorbed on solid matrices gave a range of room-temperature phosphorescence (RTP) emission areas depending on the nature of the PAH. In this work, the energy-gap law was shown to be applicable to the RTP of PAH adsorbed on cyclodextrin/salt mixtures. Eleven PAH that were adsorbed on 10%  $\alpha$ -cyclodextrin/sodium chloride and 30%  $\beta$ -cyclodextrin/sodium chloride solid matrices were studied with no heavy atom present. The RTP lifetimes of PAH were found to increase with an increase in the energy gap between the lowest excited triplet state and ground state of the phosphor. Also, the RTP lifetimes of PAH were correlated with the magnitude of rate constants for nonradiative transition from the triplet state to ground state of the phosphor. In addition, the solid-matrix RTP emission areas were found to increase as the energy gap between the triplet state and ground state increased. These correlations permit one to predict the strength of phosphorescence of the PAH. The approach developed was extended to predict the nature of phosphorescence of the tetrols of benzo(a)pyrene adsorbed on 10%  $\alpha$ -cyclodextrin/sodium chloride.

- 216 **THE STUDY OF THE MOISTURE-QUENCHING OF SOLID-MATRIX ROOM-TEMPERATURE PHOSPHORESCENCE WITH INFRARED SPECTROSCOPY.** Jie Chen and Robert J. Hurtubise, Department of Chemistry, University of Wyoming, Laramie, WY 82071

The mechanism of moisture quenching of solid-matrix room-temperature phosphorescence was investigated with filter paper as a solid matrix. Generally, it is believed that the rigidity of filter paper is very important for room-temperature phosphorescence to be observed from phosphors. The intermolecular hydrogen bonding network in filter paper is the major source of the rigidity for paper. In this study, infrared spectroscopy was used to investigate the changes in hydrogen bonds in filter paper upon the adsorption of moisture. The results were correlated to the Young's modulus of filter paper and the room temperature phosphorescence intensity changes of adsorbed phosphors. The results showed that the changes in the infrared intensity of hydroxyl bands from filter paper and the changes in the Young's modulus of filter paper with moisture adsorption were almost linearly related. The results support the conclusion that rearrangement of the hydrogen-bonding network in filter paper, which resulted in a less rigid matrix, caused a significant amount of room-temperature phosphorescence quenching.

- 217 **Effect of dissolved oxygen and soft thermal annealing on the x-ray induced luminescence of amorphous silicon dioxide.** A.J. Miller, V.A. Mashkov, Lin Zhang and R.G. Leisure, *Department of Physics, Colorado State University, Fort Collins CO 80523.*

The x-ray induced luminescence (XRL) spectra of several types of high purity, bulk amorphous silicon dioxide ( $a\text{-SiO}_2$ ) of differing dissolved O<sub>2</sub> content were studied as a function of accumulated x-ray dose and thermal history. Spectra were collected at room temperature using a diffraction grating spectrograph and charge-coupled device (CCD) detector. XRL Peaks centered at 1.9, 2.5, and 2.7 eV were observed and the integrated areas under those peaks estimated numerically using non-linear least squares fitting. Irradiation was interrupted at regular intervals and the samples were annealed at 225°C for periods of time ranging from 10 to 120 minutes. After annealing, the samples were again irradiated, more XRL spectra acquired, and the peak intensities compared with their values immediately before the anneal. We compare these intensities with  $E'$ , NBOHC, and PROHC paramagnetic defect densities measured by electron spin resonance under identical conditions and discuss the correlations between the spin-active and optically-active defects. A simple model explaining these correlations, as well as the role of dissolved oxygen molecules participating in the annealing of radiation-induced luminescent defects, is presented. fWork supported by the Office of Naval Research under Contract N00014-91-J-1607.

- 218 **EFFECTS OF STABILIZERS ON DISCOLORATION OF EVA ENCAPSULANT FOR PV MODULES.** S. H. Glick, and F. J. Pern, National Renewable Energy Laboratory, 1617 Cole Boulevard, Golden, Colorado 80401-3393.

Ethylene vinyl acetate copolymer (33%/wt vinyl acetate) encapsulant, formulated with conventional stabilization additives and used as an adhesive encapsulant in contemporary PV modules may degrade and discolor photochemically and/or thermochemically. Effects of two stabilizers, Lupersol 101<sup>TM</sup> (a peroxide curing agent) and Cyasorb UV 531<sup>TM</sup> (2-Hydroxy-4-n-(octyloxy)benzophenone, a UV absorber) were studied in this work, utilizing accelerated UV-exposure of laminated samples. Concentrations of  $\alpha,\beta$ -unsaturated carbonyls (impurity chromophores) that originally exist in the base polymer QZlva<sup>TM</sup> 150W<sup>TM</sup> decreased gradually when exposed to enhanced UV-light. Films that contained only Lupersol 101<sup>TM</sup>, incorporated via solution phase before lamination and curing, displayed similar behaviors. Other samples incorporated only Cyasorb. None of these samples exhibited significant discoloration after ~ 1500 h of exposure. A substantial increase in integrated peak areas was observed in emission spectra after ~ 600 to 800 h exposure for the Cyasorb sample. In contrast, specimens containing both additives eventually discolored appreciably and had integrated emission peak areas which increased steadily over time, indicating a synergistic effect on encapsulant discoloration had probably resulted. Excitation spectral analysis for all samples containing Cyasorb showed this additive was depleted by illumination that appeared to cause concomitant red shifts after the first ~ 600 to 800 h of exposure. Results of transmission analysis indicate that discoloration is accompanied by slowly increasing concentrations of elongating polyenic chromophore mixtures in the base polymer in agreement with earlier findings. Work performed at NREL under DOE Contract No. DE-AC02-83CH10093.

- 219 **STABILIZING EFFECTS OF UV-FILTERING GLASS AND GAS PERMEABLE POLYMER SUPERSTRATES ON DISCOLORATION OF EVA ENCAPSULANT FOR PHOTOVOLTAIC MODULES.** F. J. Pern, National Renewable Energy Laboratory, 1617 Cole Blvd., Golden, CO 80401

The stabilizing effects of UV-filtering glass and gas permeable polymer superstates for the ethylene-vinyl acetate (EVA) copolymer encapsulant in laminates upon accelerated UV exposure were investigated by using fluorescence spectrophotometry together with UV-visible transmission and spectroradiometric measurements. The results show that the UV-filtering glasses studied can reduce significantly the rate of EVA yellowing when the UV wavelengths below 320 nm is effectively filtered by at least 90%, such as by a window glass that has a 10% transmittance (T) at 320 nm. PPG's Airphire<sup>TM</sup>, with a 10% T at 342 nm, provides an even greater shielding for the EVA from yellowing. In comparison, the EVA yellowing rates are faster and greater when borosilicate (10% T at 290 nm) and PPG's Starphire<sup>TM</sup> (10% T at 270 nm) are used. In addition, when Starphire<sup>TM</sup> glass was used for both, a fast-cure EVA shows a considerably slower discoloration rate than a slow-cure EVA. The results also show that none of the samples laminated with Du Pont's Tefzel<sup>TM</sup> films as superstate exhibits any visible or significant EVA yellowing after 1000-h exposure. Results from fluorescence analysis indicate that the initial chromophores in the slow-cured EVA are rapidly destroyed or decomposed photochemically into shorter chromophores. This is attributed to the oxygen permeability, which is  $\sim 800 \text{ cm}^3/\text{m}^2\text{-d-atm}$  for a 2 mil Tefzel<sup>TM</sup> film, into the EVA where photobleaching reactions may take place more effectively than photo-induced discoloration reactions. This work was performed at NREL under DOE Contract no. DE-AC36-83CH10093.

- 220 **F2-ISOPROSTANE ANALYSIS BY ELECTROSPRAY MASS SPECTROMETRY.** Russell J. Waugh and Robert C. Murphy, Department of Pediatrics, National Jewish Center, 1400 Jackson Street, Denver, Colorado 80206.

Isoprostanes are a family of novel products of arachidonic acid derived by nonenzymatic, free radical processes and isomeric to the prostaglandins generated by cyclooxygenase. Interest in these molecules stems from the fact that their generation is initiated by free radical lipid peroxidation within cells and that several have been identified as having significant biological activity working through endogenous receptors. The isoprostanes of the PGF<sub>20C</sub> family were the first isoprostanes to be detected and are prototypic of this class of molecule. F<sub>2</sub>-isoprostanes have as a common structural feature, 1,3-diol cyclopentane structure and each member of the family differ by the size of the two attached side chains and positions of a single hydroxyl group. Four different family subtypes are possible in theory. To date only one definite family member subtype has been identified, that being 8-epi-PGF<sub>20c</sub>. We have developed a strategy to identify the distribution of isoprostanes as to family member subtype using a combination of HPLC/MS separation and GC/MS analysis of reduced isoprostanes. The isoprostanes are first separated by RP-HPLC and elution of the isoprostanes detected by on line electrospray MRM monitoring of the transition m/z353 to m/z309. Those fractions containing isoprostanes are then reduced with RII/AI<sub>2</sub>O<sub>3</sub> and derivatized to their methyl ester trimethylsilyl ether derivative. Subsequent electron ionization-GC/MS is used to detect the characteristic a-fragmentation ions which are unique for each family of isoprostane subtype. This strategy has been tested using arachidonic acid oxidized by Fenton reaction conditions (Cu<sup>2+</sup>/H<sub>2</sub>C<sub>2</sub>>2) as a means to generate hydroxyl radical to initiate formation of isoprostanes from arachidonic acid.

- 221 **PYROLYSIS-QUADRUPOLE ION TRAP MASS SPECTROMETRY OF PATHOGENIC BACTERIA.** Franco Basile, Ted L. Hadfield', and Kent J. Voorhees, Dept. of Chemistry, Colorado School of Mines, Golden, Colorado 80401; 'Armed Forces Institute of Pathology, Washington, D.C. 20306.

The need for an automated, real-time detection of chemical and biological warfare agents (CWA and BWA) has led to the development of the Chemical/Biological Mass Spectrometer or CBMS. The CBMS consists of an infrared pyrolyzer and a non-linear quadrupole ion trap (Bruker-Franzen Analytik). The ion trap uses a non-linear ejection mode which results in an increased resolution at a faster scan rate while using air as the buffer gas. A silicon membrane interfaces the pyrolyzer and the vacuum system. In this study, four human pathogens, *Bacillus anthracis*, *Brucella spp.*, *Francisella tularensis*, and *Yersinia pestis*, were pyrolyzed and then mass analyzed with the CBMS. Pattern recognition of the resulting data set identified useful biomarkers for the identification and differentiation of these pathogens. Results will be compared with established bacterial-lipid profiling chemotaxonomic techniques.

Research sponsored by the U.S. Army Research Office/ERDEC, Grant #: DAAL03-92-G-003.

- 222 **FAST METASTABLE ION DECAY PROCESSES IN MATRIX-ASSISTED LASER DESORPTION/IONIZATION.** Robert S. Brown and Duane Reiber, Department of Chemistry and Biochemistry, Utah State University, Logan, UT 84322-0300

Fast, metastable ion decay can be observed in MALDI generated ions through the utilization of delayed, pulsed ion extraction with a linear TOF instrument. This pseudoprompt decay is over within 350 ns of the ionization event. Sequence specific fragmentation is observed for peptide/protein ions and the fragmentation is dominated by C<sub>n</sub>, Y<sub>n</sub> and Z<sub>n</sub> series ions. This is in contrast to the A<sub>n</sub>, A<sub>n</sub>-17, B<sub>n</sub> and B<sub>n</sub>-17, series ions that have been observed with the longer time frame post source metastable ion decay experiment. It will be shown that the matrix employed for MALDI has a pronounced effect on the extent of fragmentation. This suggests a chemical and not a collisional process (i.e., unimolecular decay) is involved. Our current working model for this fast fragmentation process centers around the proton transfer event in the MALDI process. A fast proton transfer reaction that is sufficiently exothermic to induce bond cleavages on the short nanosecond time scale is believed to be responsible. The added lack of similar cleavage products for cationized molecular species supports this model. Recent experimental results utilizing additional laser wavelengths and their implications to the fragmentation model will be discussed. Preliminary results with negative ion ([M-H]<sup>-</sup>) metastable ion decay will also be presented.

- 223 REACTIVITY AND SECONDARY KINETIC ISOTOPE EFFECTS IN SOME  $S_N2$  REACTIONS OF OXIGEN AND SULPHUR CONTAINING NUCLEOPHILES.** Gustavo E. Davico, Charles H. DePuy and Veronica M. Bierbaum., Department of Chemistry and Biochem., University of Colorado at Boulder, Campus Box 215, Boulder, Colorado 80309-0215.

Simple anions and radical anions containing oxygen and sulfur and with similar basicities were used as nucleophiles in reaction with a variety of alkyl halides using our FA-SIFT apparatus. Secondary deuterium Kinetic Isotope Effects (KIE) were measured in several cases and correlated with substitution and elimination reactions.

We calculated the KIE for some of the reactions studied experimentally using ab initio methods and Transition State Theory (TST) in order to understand the origin and nature of this effect. The values were factored into translational, rotational and vibrational contributions. Further, the vibrational parts of the total KIE were separated into contributions from different groups of frequencies associated with different modes.

- 224 PYROLYSIS MASS SPECTROMETRY OF OLIGOPEPTIDES RANGING FROM SIX TO FIFTY AMINO ACID UNITS IN LENGTH.** Alan D. Hendricker and Kent J. Voorhees, Dept of Chemistry and Geochemistry, Colorado School of Mines, Golden, CO 80401

**A long term goal of this research group has been the characterization and differentiation of microbial organisms using pyrolysis tandem mass spectrometry (Py-MS). This study examines oligopeptides ranging from 6 to 50 amino acid units in length using Py-MS. The results indicate that peaks of taxonomic significance are observed for peptides under 20 amino acid units in length. Pyrolysis mass spectra become more complex and more alike as the chain size of the oligopeptide increases. Several fragmentation pathways of the oligopeptides will be discussed, including formation of cyclic dipeptides (diketopiperazines), substituent cleavages and backbone fragmentation. In addition, the ability of pyrolysis mass spectrometry to differentiate oligopeptides of any chain size will be discussed.**

- 225 ELECTROSPRAY IONIZATION LC/MS CHARACTERIZATION OF OXIDIZED PHOSPHOLIPIDS.** Kathleen A. Harrison\* and Robert C. Murphy, National Jewish Center for Immunology and Respiratory Medicine, 1400 Jackson Street, Denver, CO 80206 and \*Rocky Mountain Instrumental Labs, 456 S. Link Lane, Fort Collins, CO 80524.

Phospholipids have been difficult to characterize using traditional techniques owing to the lack of a chromophore and their amphipathic nature. With the advent of new ionization techniques, such as fast atom bombardment and electrospray, mass spectrometry has enabled the analysis of complex mixtures of phospholipids to be carried out relatively easily. Oxidized phospholipids that occur as a result of lipid peroxidation have been postulated to be important in the pathology of several diseases including atherosclerosis and ischemia/reperfusion injury. We have used model systems of lipid peroxidation in vitro to produce oxidized phospholipids that mimic the biological activity of platelet activating factor, an enzymatically produced phospholipid mediator of inflammation. Electrospray ionization LC/MS and tandem mass spectrometry was used to characterize these oxidized phospholipids. Selective derivatizations were also used followed by flow injection ESI-MS analysis to characterize the oxygen functional groups.

**227 GAS PHASE CHEMISTRY OF METHYL CATION (CH<sub>3</sub><sup>+</sup>) AND BORON CATION (BH<sub>3</sub><sup>+</sup>)**

**Joseph A. Hankin**, Ed Motell, C. H. DePuy, and Robert Damrauer, Department of Chemistry, University of Colorado at Boulder, Boulder, Colorado 80309-0215.

A Flowing Afterglow - Selected Ion Flow Tube (FA-SIFT) apparatus uses a quadrupole mass filter to select out specific ions formed in a flowing afterglow plasma. (VanDoren, J.M.; Barlow, S.E.; DePuy, C.H.; Bierbaum, V.M. *J. Am. Chem. Soc.* 1987, 109, 4412) These ions are entrained in a thermalizing flow of helium and injected into a reaction flow tube where they are characterized by their chemistry with a variety of neutral reagents. The gas phase chemistry of methyl cation (CH<sub>3</sub><sup>+</sup>) with acetylene, ethylene, allene and ethane has been studied in the FA-SIFT. Reaction mechanisms and energetics have been elucidated using isotopically labelled methyl cations (CD<sub>3</sub><sup>+</sup>, <sup>13</sup>CH<sub>3</sub><sup>+</sup>, and <sup>13</sup>CD<sub>3</sub><sup>+</sup>) which were formed from isotopically enriched samples of methanol. This chemistry is contrasted to studies of the cations B H 2 <sup>+</sup> and B D 2 <sup>+</sup> in reactions with the same set of neutral reagents.

**228 USE OF PY MS/MS TO STUDY BIOMARKER PYROLYSIS MECHANISMS IN WHOLE CELLS.**

**Christy Abbas-Hawks**, Dave Sickenberger<sup>1</sup>, and Kent J. Voorhees, Department of Chemistry and Geochemistry, Colorado School of Mines, Golden, Colorado 80401; <sup>1</sup>U. S. Army ERDEC, Aberdeen Proving Ground, MD 21010, USA.

A detailed study has been performed on the whole bacterial cells of *Brucella neotomae* using pyrolysis tandem mass spectrometry. The purpose of the study was to determine possible pyrolysis mechanisms for the formation of the observed biomarker ions when pyrolyzing whole cell microorganisms. The results indicate that biomarkers of interest are a collection of fragments from peptides, nucleic acids, and lipids. The pooling of previous analysis on pure cell components with the data collected from the whole cell facilitates the goal of developing rapid chemotaxonomic assays for microorganism identification. In addition, similar pyrolysis pathways are observed for deoxydinucleotide monophosphates and peptides when either pure components or whole cells are pyrolyzed. The fragmentation mechanisms of several important biomarkers will be presented.

**229 EVIDENCE FOR NONENZYMATIC METABOLISM OF PAF VIA FREE RADICAL OXIDATION.** **Lisa M. Nickelson** and Robert C. Murphy, National Jewish Center for Immunology and Respiratory Medicine, 1400 Jackson St., Denver, CO 80206

Platelet activating factor (PAF; 1-hexadecyl-2-acetyl-*w*-glycero-3-phosphocholine) is a lipid mediator in mammalian tissue with a variety of biological activities including platelet aggregation, hypotension, and bronchoconstriction and is inactivated by enzymatic metabolism to lyso PAF (1-hexadecyl-5/*i*-glycero-3-phosphocholine). Stimulation of polymorphonuclear leukocytes generates PAF as well as active oxygen species such as superoxide anion, hydrogen peroxide, and hydroxyl radical which are known to initiate lipid peroxidation. However, nothing is known about the chemical reaction of free radical oxygen species with PAF. We have found that radical species such as hydroxyl radicals efficiently hydrolyze the various ester bonds in PAF to yield numerous metabolites including lyso PAF. Structure elucidation of these metabolites will be performed using several different mass spectrometric techniques after TLC and HPLC separation. The chemical reaction of oxygen free radical species to metabolize PAF may present a novel mechanism to limit the biological activity of this important lipid mediator.



- 230 **Confirmatory Analysis by On-line Photodegradation and Liquid Chromatography-Mass Spectrometry, Dietrich A. Volmer\* and Jon G. Wilkes, US Food and Drug Administration/National Center for Toxicological Research, 3900 NCTR Drive, Jefferson, AR 72079**

The effect of on-line photodegradation on the sensitivity and specificity in the liquid chromatography-mass spectrometry (LC-MS) analysis of pesticides has been investigated. Parameters such as irradiation time, irradiation wavelength and solvent composition have been investigated. Furthermore, the effect of postcolumn addition of different photosensitizers on the degree of photochemical degradation of the analytes and on the sensitivity of their detection was investigated. By using different photosensitizers, both the formation of structure specific dissociation products and transformation products for either structure elucidation and molecular weight confirmation can be achieved.

It is demonstrated, that the on-line combination of photodegradation and LC-MS can increase spectral information and thus the specificity of LC-MS without losing sensitivity as is often observed in CAD experiments. Furthermore, the characterization of several isomeric and isobaric pesticides, which has usually been performed by using MS/MS techniques, is readily possible by on-line photodegradation/LC-MS. For example, isomeric triazines can be distinguished by means of their photodegradation mass spectra. In general, the usefulness of combining on-line photodegradation with LC-MS for the structure elucidation of daughter compounds formed by photochemical degradation is shown in this study.

- 231 **Enhancement of Electrospray Detectability for Nitrosamines by Photochemical Degradation. David L. Vollmer and Jack Lay Division of Chemistry, Nat'l Center for Toxicological Research, 3900 NCTR Road, Jefferson, AR 72079**

Formation of gas-phase ions by electrospray ionization (ESI) is usually limited to analytes that are ionic in solution or that can be ionized in solution. Current research, however has demonstrated the analytical potential of producing ions that are amenable to ESI by way of bimolecular, electrochemical, or photochemical derivitization. These approaches often improve the detectability of the analytes and may increase their selectivity by analyte-specific reactions.

Here, we report the analytical utility of an on-line photochemical reactor as a way of enhancing the detectability of nitrosamines by ESI. Nitrosamines are of great interest because they are considered carcinogenic and they have been found in many food constituents and in drinking water.

Under photochemical conditions, the nitrosamines are observed to give characteristic degradation products that can be used to increase the specificity of the analysis and, in most cases, enhance the total amount of signal. Moreover, nitrosamine isomers can be distinguished by means of photochemical degradation. Factors such as irradiation wavelength, irradiation time, solvent composition, and solvent pH are also studied to determine their effect on detectability.

232

*Ultra-Sensitive Detection in Complex Matrices by Quadrupole Ion Trap Mass Spectrometry, William Schnute and Siu Teng, Finnigan MAT, 355 River Oaks Parkway, San Jose, California 95134.*

This paper will discuss the ways in which new Ion Trap technology can be applied to the identification and quantitation of trace level organics in various complex matrices. The ultra-sensitive nature of the Ion Trap allows processing of samples with concentrations in the part per trillion level. Analysis of products meant for human consumption are generally complex in nature and require these low detection levels.

The additional use of MS/MS and negative ion techniques extend the range and capabilities of the Ion Trap. MS/MS simplifies the detection of suspected components in extremely complex matrices by eliminating interferences and co-eluting compounds. When combined with negative ion capabilities, the chromatographer can achieve extremely sensitive and specific detection of electrophilic compounds.

- 244 **NEW APPROACHES TO PROTEIN STRUCTURE DETERMINATION BY SOLID STATE NMR.** Robert Tvcko and David P. Weliky, Laboratory of Chemical Physics, NIDDK, National Institutes of Health, Building 5, Room 112, 9000 Rockville Pike, Bethesda, Maryland 20892-0520.

We are currently setting up a new laboratory to develop and apply solid state NMR methods for determining protein and peptide structures and interpreting the structural information in terms of biochemical function. The goal is to obtain qualitative and quantitative information about systems that can not be studied in detail by other structural methods, e.g., membrane-bound proteins, peptides, and complexes, partially-folded proteins in frozen solution, and proteins in noncrystalline solid form. Two aspects of this work will be discussed: (1) the use of two-dimensional exchange spectroscopy to probe protein secondary structure, and (2) the use of multidimensional correlation spectroscopy to assign MAS spectra of isotopically labeled proteins and to probe secondary and tertiary structure.

- 245 **HIGHER RESOLUTION THROUGH HIGHER DIMENSIONAL SOLID-STATE NMR EXPERIMENTS,** Ayyalusamv Ramamoorthy, Chin Hsiang Wu, and Stanley J. Opella, Department of Chemistry, University of Pennsylvania, Philadelphia, PA 19104.

A family of three- and four- dimensional high resolution solid-state NMR experiments are being developed and applied to the study of  $^{15}\text{N}$  and  $^{13}\text{C}$  sites in biomolecules. These experiments are generally applicable to powder, single crystal, and uniaxially oriented samples, in the presence and absence of magic angle sample spinning. And there are a wide variety of spectroscopic, structural, and dynamic findings that can be obtained, notably the full determination of  $^{15}\text{N}$  and  $^{13}\text{C}$  (or  $^{15}\text{N}$  or  $^{13}\text{C}$ ) chemical shift and dipolar tensors from powder samples. High resolution is obtained in all dimensions through the use of efficient homonuclear and heteronuclear decoupling procedures, especially phase and frequency shifted Lee-Goldburg pulse sequences. Typical linewidths (within a spectral range of 10 kHz) in the heteronuclear dipolar coupling dimension are 45 Hz with magic angle spinning of a powder and 180 Hz with a stationary single crystal, and the  $^1\text{H}$  resonance linewidths (within a spectral range of 15 ppm) are 0.8 ppm.

- 246 **A CPMAS NMR CHARACTERIZATION OF THE CONDUCTING POLYMER POLYANILINE.** 1Matthew Espe, ^Ben Mattes, and 1 Jacob Schaefer, \* Department of Chemistry, Campus Box 1134, Washington University, St. Louis, MO 63130; ^Los Alamos National Laboratory, CST-6, mail stop J963, Los Alamos, NM, 87545.

Polyaniline,  $(-\text{C}_6\text{H}_4\text{NH}-)_x$ , in addition to being a conducting polymer, is effective for gas separation, even for gases with similar size. Solid-state magic-angle spinning NMR has been used to characterize the structure and dynamics of this polymer to understand better its conductivity and gas separation capabilities. The CPMAS  $^{19}\text{F}$  NMR spectrum shows broad lines (13 ppm) which result from structural and packing heterogeneity; T2 measurements show that the natural linewidth is 2-5 ppm. Relaxation studies demonstrate that the polymer consists of a single phase with little or no crystallinity, and that it undergoes molecular motion in the low-kHz regime. Structural heterogeneity and lack of main-chain cooperative motion is evident in the dipolar rotational spin echo (DRSE) spectrum. Only 15% of the phenyl rings undergo  $180^\circ$  ring flips. The  $^{19}\text{F}$  NMR spectrum, following doping of the polymer with HF to the conductive form, indicates that there are at least two distinct  $^{19}\text{F}$  environments, which differ in chemical shift and strength of  $^{19}\text{F}\cdots\text{H}$  dipolar coupling. Fluorines are likely monitoring the different environments of polarons and bipolarons, both of which are present upon protonation of the polymer. REDOR and XY-8 DRAMA experiments to determine  $^{19}\text{F}\cdots^{19}\text{F}$   $^{19}\text{F}\cdots^{15}\text{N}$  (main-chain) distances are underway to aid in assignment of the fluorine spectrum.

- 247 **NMR AND THE OVERTHROW OF ZEOLITE SUPERACIDITY.** James F. Haw, Larry Beck, David Ferguson, Tom Krawietz and Teng Xu. Department of Chemistry, Texas A&M University, College Station, TX 77843. John Nicholas. DOE Pacific Northwest Laboratories, Richland, WA 99352.

A major theory in catalysis is built around the widely and long accepted belief that zeolites and other solid acids are "superacidic", i.e., stronger than 100% sulfuric acid. This theory is used to generate explanations for a wide variety of phenomena. A large number of NMR and other measurements as well as density functional calculations at the highest practical levels with current CPUs and methodologies strongly rebut the theory of zeolite superacidity for the more common materials. A variety of evidence suggests that the acid reaction function of zeolites is complex and that acid catalysis precedes on materials that are substantially less acidic than 100% sulfuric acid.

This talk will highlight the excitement of work in solid acids with NMR-related examples including  $^{29}\text{Si}$ - $^1\text{H}$  and  $^{15}\text{N}$ - $^1\text{H}$  double resonance, studies of reactive species and new experimental methodologies for MAS studies of reactivity on short time scales.

- 248  $^{29}\text{Si}$ - $^1\text{H}$  and  $^{15}\text{N}$ - $^1\text{H}$  CP/MAS REDOR IN ZEOLITES: A NEW WAY TO CHARACTERIZE SURFACE ACTIVE SITES. Alexander L. Blumenfeld, Dominique J. Coster, and Jose J. Fripiat, Department of Chemistry and Laboratory for Surface Studies, University of Wisconsin-Milwaukee, PO Box 413, Milwaukee, WI 53201.

Rotational Echo Double Resonance (REDOR) technique allows one to reintroduce heteronuclear dipolar interactions into conventional CP/MAS NMR spectra and thus provides valuable structural information. Included in the presentation will be the results obtained with  $^{29}\text{Si}$ - $^1\text{H}$  and  $^{15}\text{N}$ - $^1\text{H}$  CP/MAS REDOR for various active catalysts, namely, USY, H-mordenites and HZSM-5 zeolites prepared under controlled atmosphere using chemisorbed  $^*\text{NH}_3$  as a surface probe. A new approach is proposed that allows to describe REDOR evolution curves when the "isolated pair approximation" does not hold. The procedure is based on the inhomogeneous nature of the heteronuclear dipolar coupling and calls for the heteronuclear  $^{29}\text{Si}$  (or  $^{15}\text{N}$ ) -  $^1\text{H}$  second moment as a single fitting parameter. It is successfully tested with model compounds with known structures, such as kaolinite and dickite minerals,  $\text{KHSi}_2\text{O}_5$  and  $^*\text{NH}_4\text{Cl}$  salts. The discussion is concentrated on the distribution of the active sites on zeolite surfaces and on the role of non-framework alumina species in the formation of such sites.

- 249 **APPLICATIONS OF XENON NMR IN SOLIDS: CHEMICAL SHIFT ANISOTROPY.** Igor L. Moudrakovski, Hirokazu Nakayama, Chris. I. Ratcliffe and John A. Ripmeester, Steacie Institute for Molecular Sciences, National Research Council of Canada, Ottawa, Ontario K1A 0R6, Canada.

There are remarkably few reported instances of anisotropic chemical shift powder lineshapes for xenon in solids, and consequently much emphasis has been placed on the interpretation of isotropic shifts. However, cases where anisotropy is observed can potentially yield much more detailed information about the behaviour of the xenon. Some new applications of  $^{129}\text{Xe}$  NMR spectroscopy are presented which use the properties of adsorbed xenon to learn about structure and exchange: 1) Results showing loading-dependent anisotropic chemical shifts in sieves such as ZSM-12, ALPO-5, SSZ-24, ALPO-8 and VPI-5 which have 1D channels with increasing cross-section, along with 2D EXSY NMR data, have allowed modelling of the distribution of xenon atoms in these low-dimensional pore systems. 2) Studies of amorphous codeposits of Xe and water prepared at 10K and annealed to progressively higher temperatures provide useful information about the formation of hydrogen bonded water cages around Xe atoms and the formation of crystalline xenon clathrate hydrate.

- 250 **NMR DETERMINATION OF HYDROGEN COORDINATES AND DYNAMICS IN INORGANIC SOLIDS.** Herman Cho, Robert Maxwell, Donald Stec, and Chaoying Rong, Environmental Molecular Sciences Laboratory MSIN P7-55, Pacific Northwest Laboratory, Richland, Washington 99352.

We are exploring the use of solid state proton and deuterium NMR spectroscopy in combination with numerical simulations as a method for measuring hydrogen coordinates and dynamics in inorganic solids of environmental concern. Questions regarding hydrogen position and motion arise in our studies of anhydrous minerals with hydrous defect sites, synthetic model minerals, multi-component oxide glasses that have been exposed to water, and Brønsted acid sites and adsorbates on the surface of oxide catalysts. In systems such as these, which frequently contain small, discrete groups of hydrogen atoms in close proximity to one another or in a repeating pattern, spectra with enough resolved structure to make definitive determinations of hydrogen positions, trajectories, and rates can be obtained.

The Pacific Northwest Laboratory is operated for the U.S. Department of Energy by the Battelle Memorial Institute under Contract DE-AC06-76RLO 1830.

- 251 **NMR STUDY OF THE BEHAVIOR OF PESTICIDES IN SOIL AND SOIL COMPONENTS.** I-Ssuer Chuang, Mark Seger and Gary E. Maciei. Department of Chemistry, Colorado State University, Fort Collins, CO 80523

$^{31}\text{P}$  NMR spectra, based on magic-angle spinning (MAS) and on direct polarization (DP) or cross polarization (CP) signals, have been obtained on samples of pesticides adsorbed on soil and on clays and humics. For a given pesticide, nearly the same isotropic  $^{31}\text{P}$  chemical shifts are observed for all samples studied, but dramatic differences in molecular mobilities are observed in terms of variations in spinning sideband patterns and CP-vs-DP characteristics. Much greater pesticide hydrolysis activity is noted in pesticide/clay samples than in pesticide/humic samples. Patterns of relaxation times are useful in characterizing the state of a pesticide in these systems; and  $^{13}\text{C}$  NMR shows promise for following the fate of a pesticide.

- 252 **CFC ALTERNATIVES: CHARACTERIZATION OF ADSORPTION SITES FOR HYDROFLUOROCARBONS IN BASIC ZEOLITES**

Clare P. Grey

SUNY Stony Brook, Chemistry Department, Stony Brook, NY 11794-3400

The adsorption of a series of hydrofluorocarbons (HFCs) on basic zeolites is probed using  $^{19}\text{F}$  variable temperature NMR. The HFCs are most strongly bound to the most basic zeolite studied, NaX, rigid complexes being formed at 125K. The mobility of the HFCs in the pores of the zeolite varies with the HFC: e.g. HFC-134 is less mobile than HFC-134a. A correlation is observed between the Sanderson electronegativity of the zeolite and the mobility of the HFC. The interaction with the cations in the sodalite cages is studied with  $^{23}\text{Na}$  and  $^{133}\text{Cs}$  NMR. Attack of the zeolite framework occurs above  $250^\circ\text{C}$  in the more basic zeolites, and tetrahedrally coordinated aluminum fluoride species are formed. These are clearly visible in the  $^{19}\text{F}$  to  $^{27}\text{Al}$  cross-polarization spectrum. On exposure of the zeolite to moisture, hydrolysis occurs, and six-coordinate aluminum fluoride species are now seen. Attack of the zeolite, is correlated with the basicity of the zeolite.

**253 NOISE SPECTROSCOPY IN SOLID STATE NMR AND NQR**

**David B. Zax, Ming-Yuan Liao and Benjamin G.M. Chew,**

**Department of Chemistry, Baker Laboratory, Cornell University, Ithaca, NY 14853.**

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 to 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.

**254 TIME-DOMAIN ANALYSIS OF SOLID-STATE NMR SIGNALS: ISOTROPIC ALTERNATIVES TO THE FOURIER TRANSFORM**

**Karl T. Mueller and Thomas P. Jarvie,**

**Department of Chemistry, The Pennsylvania State University, 152 Davey Laboratory, University Park, PA 16802-6300 (814)863-8674**

We have found analytic solutions for the time-evolution of dipolar signals from heteronuclear and certain homonuclear two-spin systems in randomly-oriented solids. The solutions are non-periodic, decay in time, and Fourier transformation reproduces the well-known lineshapes of solid-state NMR in the absence of magic-angle spinning. Similar solutions have also been found for the dynamics of signals observed from REDOR, TEDOR, and related methods, which utilize radiofrequency pulses to retain an average dipolar coupling under MAS conditions. Using an analysis method based on constrained optimization in the time domain, we are able to extract dipolar coupling frequencies from the dynamics of the magnetization. We present both theoretical and experimental findings, as well as a discussion of the prospects for this alternative to Fourier transform techniques for spin interactions that are not cylindrically symmetric.

**255 THE EFFECT OF DECOUPLING ON CARBON-13 LINESHAPES IN SOLID-STATE NMR.**

**Joseph R. Sachleben,<sup>§</sup> Stefano Caldarelli,<sup>^</sup> and Lyndon Emsley.<sup>§</sup> <sup>§</sup> Department of Chemistry, University of Illinois, Chicago, II60607, <sup>t</sup> Section de Chimie, University de Lausanne, CH-1005 Lausanne, Switzerland, <sup>\$</sup> Ecole Normale Supérieure de Lyon, 69364 Lyon, France**

We present theoretical and experimental studies of the effect of on-resonance proton decoupling on carbon-13 lineshapes in solid-state NMR. Average Hamiltonian calculations of the lineshapes can produce misleading results because acquisition is not synchronous with the appropriate cycle time. We have therefore adopted an approach towards calculating carbon lineshapes under conditions of proton irradiation which uses an operator representation of second-order degenerate perturbation theory. This allows us to obtain analytical expressions for the spectrum. Our results suggest that, when the spin system is effectively limited to less than around 15 protons, the spectrum under conditions of on-resonance decoupling should consist of a single line of constant width which increases in amplitude with increasing decoupling field strength. This line is superimposed on a very broad (often unobservable) component which decreases in amplitude with increasing decoupling field strength. It is only in the limit of a thermodynamic reservoir of protons and carbons that we obtain the semi-classical behavior, predicted using stochastic theories, of a center line whose width depends on the decoupler field strength. Our predictions are confirmed by experiments on liquid crystals and organic solids.

**<sup>13</sup>C NMR RELAXATION VIA PARAMAGNETIC NITROGEN CENTERS IN SYNTHETIC DIAMOND.**D. Blane Baker and James. P. Yesinowski. Code 6120, Naval Research Laboratory, Washington DC 20375-5342.

256

Static and MAS <sup>13</sup>C NMR spin-lattice relaxation measurements have been performed on various synthetic high-pressure high-temperature diamond powders containing substitutional paramagnetic nitrogen. The <sup>13</sup>C relaxation is dominated by the paramagnetic centers, which are characterized by EPR to be PI nitrogen centers (*pins* other radicals in high surface area samples) and found to be present in high concentrations (~ 10<sup>20</sup> cm<sup>-3</sup>). The magnetization recovery data for static samples fit a stretched exponential of the form  $M(t) = M_0(1 - \exp(-(t/T')^n))$ , with  $n=0.54$  to  $0.56$  and  $T'$  on the order of minutes. These results are surprising in view of the previously determined long electron  $T_1$  (~0.1 ms), and since rapid spin-diffusion should be present and lead to exponential relaxation behavior ( $n=1.0$ ). We propose that a distribution of electron correlation times gives rise to the observed <sup>13</sup>C relaxation behavior, as a consequence of a distribution of electron-electron dipolar interactions of randomly distributed nitrogen centers. High-speed (10 kHz) <sup>13</sup>C MAS reveals that spin-diffusion is *not* quenched, and that the observed stretched-exponential behavior is not due simply to direct relaxation as had previously been assumed. In addition, we have analyzed the effect of spinning at the magic-angle and other angles upon direct relaxation by paramagnetic impurities, by taking into account the relevant angular averages in the proper way. The differences predicted in the relaxation behavior vis-a-vis earlier treatments are rather minor.

258 A COMPARISON BETWEEN <sup>13</sup>C-CPMAS AND <sup>2</sup>D-CPMAS EXPERIMENTS. Shimon Vega and David Marks, Department of Chemical Physics, The Weizmann Institute of Science, Rehovot 76100, Israel

A theoretical model will be presented that describes the spin dynamics of  $S=1/2$  and  $S=1$  spins during CPMAS experiments on a system containing a rare  $S$ -spin coupled to a set of abundant  $I=1/2$  spins. The analogies between the cross-polarization processes in spinning and non-spinning samples will be shown. For the spinning cases the Floquet formalism will be utilized. Multi-quantum and adiabatic cross-polarization methodologies will be explained in terms of the theoretical model. Results of CPMAS experiments on deuterium will be presented and the practical aspects of <sup>2</sup>D-NMR on deuterated compounds will be discussed. The extension of the model to CPMAS experiments on spins with  $S>1/2$  will also be mentioned.

259 MULTIDIMENSIONAL NMR TECHNIQUES INVOLVING QUADRUPOLEAR NUCLEI. Jay Shore, Shuanhu Wang, Susan DePaul, Rebecca Taylor, Matthias Ernst, Alexis T. Bell, and Alexander Pines, Lawrence Berkeley Laboratory, and University of California, Berkeley, CA 94720, USA

With NMR, an experimenter has the unprecedented advantage of being able to manipulate the Hamiltonian of the system being measured, using radio frequency pulses and sample spinning, among other techniques. Combining this ability with multidimensional NMR enables the direct correlation and/or deconvolution of multiple interactions. Recently, at Berkeley we have used these ideas in the study and utilization of quadrupolar nuclei to address the deficiencies in sensitivity and resolution of NMR of inorganic solids, employing two different approaches: 1) We have used two-dimensional switched angle spinning (SAS) experiments on quadrupolar nuclei to determine quadrupolar and CSA tensors elements, as well as the relative orientation between the two principal axis systems. This technique can be applied to correlate quadrupolar and dipolar interactions, as well as can be extended to a three-dimensional experiment by incorporating a purely isotropic dimension. 2) We have used <sup>23</sup>Na/<sup>29</sup>Si and <sup>27</sup>Al/<sup>29</sup>Si double resonance techniques to improve sensitivity and measure heteronuclear correlations. For example, we have used <sup>27</sup>Al-to-<sup>29</sup>Si cross polarization to enhance the <sup>29</sup>Si NMR signal-to-noise ratio of crystalline albite by a factor of 5, and have utilized the corresponding twenty-five fold saving in time to perform isotropic-anisotropic, homonuclear and heteronuclear correlation experiments.

- 260 INVESTIGATION OF THE MIXED ALKALI EFFECT IN (Na,Li) DISILICATE GLASSES BY NMR AND CONDUCTIVITY MEASUREMENTS Mark C. Jermey<sup>a</sup>, Fatima Ali<sup>b</sup>, A.V. Chadwick<sup>c</sup>, G.N. Greaves<sup>c</sup>, Mark E. Smith<sup>a</sup> a) Physics Laboratory, University of Kent, Canterbury, Kent, CT2 7NR, U.K., 011 44 1227 827686 b) Chemical Laboratory, University of Kent, Canterbury, Kent CT2 7NH, U.K. c) EPSRC Daresbury Laboratory, Warrington, Cheshire, WA4 4AD, U.K.

Information on the local structure and ionic motion in glasses of composition 33%(xLi<sub>2</sub>O)(1-x)Na<sub>2</sub>O«67%SiO<sub>2</sub> has been obtained in an effort to improve understanding of the Mixed Alkali Effect. The local structure was studied by <sup>29</sup>Si, <sup>7</sup>Li, and <sup>23</sup>Na MAS NMR spectroscopy. The <sup>29</sup>Si NMR results suggest there is relatively little change of network structure with alkali composition. The <sup>7</sup>Li and <sup>23</sup>Na MAS linewidths and shifts vary continuously with x, suggesting the alkali ions are intimately and uniformly mixed. The ionic motion was studied by <sup>7</sup>Li NMR relaxation and by ac conductivity measurements. The activation energy from conductivity shows a distinct maximum at x=0.5, whereas the NMR activation energy shows only a small increase as x decreases. Cooperativity between the motion of the ions can partially explain this, a manifestation of the Mixed Alkali Effect, and can be quantified in terms of the Kohlrausch exponent.

- 261 ELUCIDATING THE STRUCTURE OF INORGANIC MATERIALS: PROGRESS BY NEW AND OLD CONCEPTS Christian Jager<sup>1)</sup>, Karin Herzog<sup>2)</sup>, Berthold Thomas<sup>2)</sup>, Martin Feike<sup>1,3)</sup>, Hans-Wolfgang Spiess<sup>1)</sup>

<sup>1)</sup> Max Planck Institute for Polymer Research, POB 3148, D-55021 Mainz, Germany

<sup>2)</sup> Freiberg University of Mining, Institute of Analytical Chemistry, D-09596 Freiberg/Sa., Germany

The recent progress for the investigation of the micro structure of glasses is presented using REDOR, Satellite Transition (ST) Spectroscopy and 2D Exchange NMR. REDOR has been used to study the structural incorporation of protons in glasses. The REDOR theory has been extended to many spin interactions. Theoretical curves and applications to glasses, minerals and sol-gel materials are presented. Connectivities can be determined among Q<sup>n</sup> units in phosphate glasses by 2D Exchange NMR. Both connectivities in glasses as well as the crystallization can be investigated. The principles of the experiment and applications are shown. Similarly, HETCOR NMR und REDOR has been used to probe connectivities of AlO<sub>4</sub> and PO<sub>4</sub> units in glasses. Multiple boron sites in glasses have been determined in the past by 2D DAS NMR. We present an alternative approach using MAS NMR only. Multiple BO<sub>3</sub> and even BO<sub>4</sub> sites in borate glasses are found. Examples are presented including bulk glasses and hydrated layers of electrode glasses. Also, all relevant information (chemical shift, quadrupole interaction) can be recovered from the ST MAS spectra.

- 262 <sup>17</sup>O DYNAMIC-ANGLE SPINNING NMR STUDIES OF THE STRUCTURE OF NETWORK-MODIFIED SILICATE GLASSES. P. J. Grandinetti<sup>1)</sup>, P. Florian<sup>1)</sup>, K. E. Vermillion<sup>1)</sup>, I. Farnan<sup>2)</sup>, and J. F. Stebbins<sup>3)</sup>, department of Chemistry, Ohio State University, Columbus, OH, <sup>2)</sup>CRPHT, CNRS, 45071 Orleans, CEDEX 2, France, <sup>3)</sup>Department of Geology, Stanford University, Stanford, CA,

We have obtained <sup>17</sup>O Dynamic-Angle Spinning (DAS) results on crystalline K<sub>2</sub>Si<sub>2</sub>O<sub>6</sub> and the three disilicate glasses: K<sub>2</sub>O • 2 SiO<sub>2</sub>, Na<sub>2</sub>O • 2 SiO<sub>2</sub>, and KNaO • 2 SiO<sub>2</sub>. Comparison of the <sup>17</sup>O DAS spectra of crystalline K<sub>2</sub>Si<sub>2</sub>O<sub>6</sub> and glassy K<sub>2</sub>O • 2 SiO<sub>2</sub> suggests that the mean coordination number of the non-bridging oxygen in the glass is similar to the crystal. In addition, the Si-O-Si bond angle distribution in the K<sub>2</sub>O • 2 SiO<sub>2</sub> glass has a maximum near the crystalline K<sub>2</sub>Si<sub>2</sub>O<sub>6</sub> values, and is shifted to lower values compared to SiO<sub>2</sub> glass. The isotropic lineshape of the non-bridging oxygen in the KNaO • 2 SiO<sub>2</sub> glass has a shape that is consistent with a binomial distribution of sodium and potassium cations coordinated around it, indicating that the alkali cations are intimately mixed and randomly distributed throughout the glass.

- 263 SOLID STATE AND  $^{15}\text{N}$  NMR INVESTIGATIONS OF NOVEL PYRIDINES, PYRTMIDINES, AND THEIR N-OXIDES.** Karen L. Altmann, Lawrence H. Merwin, Robin A. Nissan, and William S. Wilson, Chemistry & Materials Branch, Naval Air Warfare Center Weapons Division, China Lake, CA 93555

Important characteristics in the development of novel energetic materials include increased energy content and reduced thermal and shock sensitivity. The challenge of incorporating these two seemingly contradictory criteria has been addressed in the past with a variety of different classes of heterocyclic compounds, including azines, azoles, benzazoles, and derivatives of TACOT (tetranitrodibenzotetraazapentalene). In the present investigation, we have approached the problem by using the inherent stability of the pyridine and pyrimidine ring systems and incorporating alternating nitro and amino groups to add further stability and insensitivity. In addition, the energy content is supplemented by including one or two N-oxide functionalities at the ring nitrogens. Solid state  $^{13}\text{C}$  and  $^{15}\text{N}$  NMR data have been obtained for a series of such compounds. It is found that the chemical shifts correlate well with known substituent effects and with the degree of intramolecular and intermolecular O—H bonding that can occur between nitro and amino groups. In addition, the effects of crystal packing in the solid state are evident in some of the NMR data, where magnetic nonequivalences are observed.

- 264 NUMERICAL SIMULATION OF PULSE SEQUENCES IN SOLID-STATE NMR: PULSAR.** J. P. Amoureux, C. Fernandez and Y. Dumazy, Universite de Lille, Villeneuve d'Ascq, F59655, France.

Spectral lineshape distortions arising from the actual RF pulses are impossible to describe analytically for quadrupolar nuclei.

Therefore, we have written PULSAR, which is able to simulate any spectra corresponding to:

- i) All powder samples: static or rotating around 1 or 2 axes.
- ii) All nuclei simultaneously subjected to CSA, dipolar and quadrupolar interactions.
- iii) All kinds of preparation periods including several RF pulses.

As an example of PULSAR abilities, we analyse:

- i) Several pulse sequences for sideband suppression (TOSS, CELTICS, RISC).
- ii) The MAS spin-locking experiment for quadrupolar semi-integer spins.

- 265 OFF-RESONANCE DOR NUTATION EXPERIMENTS.** J. P. Amoureux, C. Fernandez and Y. Dumazy, Universite de Lille, Villeneuve d'Ascq, F59655, France.

In addition to the V.A.D.O.R. technique, another obvious two-dimensional extension of the D.O.R. technique concerns the nutation experiment. On D.O.R. probes the RF field is limited at present to 30 kHz approximately and this is not enough for classical nutation techniques. Happily, recently, a very elegant method has been described by Kentgens: the off-resonance nutation spectroscopy. For a given RF field this new method greatly extends the applicability of the nutation technique to a larger range of quadrupolar coupling constants. Moreover, it is possible to obtain several spectra with different resonance offsets on one spectrometer, thus facilitating the determination of the interaction parameters.

The extension of this technique to D.O.R. involves two major problems:

- \* a computing problem which can be overcome with our new program PULSAR,
- \* a technical problem: the RF homogeneity must be very good.



- 266 **NEW 1 AND 2D METHODS FOR DOUBLE ROTATION EXPERIMENTS.** J. P. Amoureux. C. Fernandez and Y. Dumazy, Universite de Lille, Villeneuve d'Ascq, F59655, France.

We propose a new geometry for DOR (DOuble Rotation) probes ( $\theta_e = 70.124^\circ$ ,  $\theta_i = 54.736^\circ$ ) which suppresses first-order interactions (CSA and dipolar) more efficiently than the geometry ( $\theta_e = 54.736^\circ$ ,  $\theta_i = 30.556^\circ$ ) presently employed.

We also describe a new 2D high-resolution technique for nuclei with semi-integer spins subjected to strong quadrupole interactions. This VADOR (Variable Angle DOR) technique separates anisotropic spectral patterns according to the isotropic shift of each species. No sudden sample reorientation is needed for VADOR which can then be used regardless of the "relaxation times". VADOR can also be utilized to characterize slow molecular reorientations in 2 or 3D experiments.

267

MAS  $^{13}\text{C}$  AND DNP NMR STUDY OF HIGH TEMPERATURE CROSSLINKING IN PMR POLYIMIDES

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PMR crosslinked polyimides are extremely temperature resistant polymers that are used as matrix materials in carbon fiber composites. This family of crosslinked polyimides shows an increase in glass transition temperature after postcuring at 371 °C. This increase is accompanied by an improvement in the elevated temperature mechanical properties of the polyimide/fiber composites. Crosslinking in the polyimides occurs at the endgroups, which consist primarily of aliphatic carbons. NMR and EPR have been used to clarify the crosslinking process occurring in these polyimides during high temperature treatment. The MAS  $^{13}\text{C}$  NMR shows a decrease in the aliphatic carbon spin count that is commensurate with the increase in aromatic carbon spin count. Dynamic nuclear polarization (DNP) experiments show a solid effect enhancement that is indicative of isolated unpaired electrons. The DNP enhancement for an analogous, noncrosslinked polyimide is smaller, suggesting that free radical formation occurs at the crosslinking sites. These results indicate that upon postcuring at 371 °C, the endgroups undergo additional crosslinking and rearrangement to form a conjugated system capable of supporting unpaired electrons. A structure for the high temperature crosslinking network in PMR polyimides is proposed which is consistent with these results.

- 268 **NMR IMAGING OF WATER DISTRIBUTIONS AND DIFFUSION IN ENGINEERED FIBROUS SUBSTRATES.** Haskell W. Beckham. Wallace W. Carr *School of Textile and Fiber Engineering, Georgia Institute of Technology, Atlanta, GA.* Carsten Fiilber, H. W. Spiess *Max-Planck-Institut für Polymerforschung, D-55021 Mainz, Germany.*

The location and mobility of small-molecule penetrants in complex polymeric materials are important to characterize for such properties as transport, binding, and exclusion. The performance of textile substrates used in filtration and barrier systems depends on these properties of the polymers from which they are constructed. NMR imaging is particularly suited for conducting these types of characterizations. Initial work in this area will be presented for carpet. NMR imaging of a carpet sample initially loaded to 50% water (based on the weight of the dry sample) has shown that the water is not homogeneously distributed, but does leave the carpet homogeneously as a function of free-convection time. Drying rate curves can be generated for the different regions of these multilayered textile substrates. These carpet studies are aimed at elucidating drying mechanisms for different drying techniques (e.g., convection, infrared, microwave), thereby allowing optimization of this energy-intensive industrial process.

- 269 **170 NMR STUDIES OF ZEOLITES** Ray Dupree, Jay Shore, Young K. Lee, Lucy M. Bull, Sheryl L. Gann, Anthony K. Cheetham and Alex Pines, Materials Research Laboratory, University of California, Santa Barbara, CA 93106, Department of Physics, University of Warwick, Coventry, CV4 7AL, U.K., Department of Chemistry, University of California, Berkeley, CA 94720.

Relatively few  $^{17}\text{O}$  NMR studies have been performed on zeolites because the problems of dealing with a quadrupolar nuclei are compounded by the disordered nature of the local oxygen environment arising from distributions of aluminum in the framework and the presence of charge compensating cations. In addition, many zeolite structures have large numbers of symmetry inequivalent oxygen sites, complicating the  $^{17}\text{O}$  NMR spectrum still further. Using a combination of MAS, DAS and DOR NMR techniques, and also various enrichment techniques, we have studied one of the simplest zeolite systems, siliceous faujasite (Sil-Y), which has four oxygen sites in the asymmetric unit and no aluminum. We will compare the relative strengths of these techniques and correlate our NMR results with a recent neutron diffraction study of this system. We shall also discuss the influence of sorbate molecules on  $^{17}\text{O}$  NMR spectra of zeolites.

- 270 **A MULTIPLE-QUANTUM  $^1\text{H}$ -NMR STUDY OF CONFORMATIONAL BIASING OF BIPHENYL IN A NEMATIC LIQUID CRYSTAL.** T. Chandrakumar, James M. Poison, and E. Elliot Burnell, Department of Chemistry, University of British Columbia, 2036 Main Hall, Vancouver, B. C, Canada V6T1Z1.

Multiple-quantum  $^1\text{H}$ -NMR spectroscopy was used to simplify the analysis of the complicated one-quantum spectrum of the ten-spin molecule biphenyl dissolved in a nematic solvent. The eight-quantum spectrum, which was acquired indirectly from projections of two-dimensional experiments, was analyzed to obtain all dipolar coupling constants and chemical shifts, which were used as a starting point to solve the one-quantum spectrum. The dipolar couplings from the one-quantum spectrum were used to obtain orientational order parameters and geometrical parameters. The effective internal rotation potential was found to be shifted slightly towards a more planar configuration relative to the gas-phase potential, with an equilibrium dihedral angle of  $37.1^\circ$ .

- 271 **MULTI-NUCLEAR NMR STUDIES ON BIOMINERALS.**  
B.A. Concannon\*, P.D. Ellis<sup>1</sup>, A.S. Lipton\*, R.A. Santos<sup>2</sup>, R.A. Wind<sup>3</sup>, and R.J. Wuthier\*.  
<sup>1</sup>Environmental and Molecular Sciences Laboratory, Battelle, Pacific Northwest Laboratories, P.O.Box 999, MS P7-55, Richland, WA.99352. <sup>2</sup>Department of Chemistry and Biochemistry, University of South Carolina, Columbia, SC, 29208.

The main objective of this research is to investigate the early phases of calcium-phosphate formation involved in biological mineralization, and to determine the sequence of events leading to the formation of mature bone. To this end  $^{13}\text{C}$  CRAMPS, 31P MAS and 1H-31P heteronuclear experiments are performed on synthetic and natural minerals to determine their structure and identify the phases present. Mineral extracted from matrix vesicles after initiation of calcification is used. These vesicles are the initial sites of mineralization and contain the most nascent calcium-phosphates phases. Mineral extracted from these vesicles will represent the earliest calcium-phosphates ever studied by NMR. We have also investigated the possibility of using cadmium as a spin spy to replace the calcium atoms. It has been shown crystallographically that cadmium substitution does not perturb the overall structure of these synthetic minerals, and the shielding tensor of the  $^{113}\text{Cd}$  substitution is sensitive to the coordination environment as opposed to the relative insensitivity of  $^{31}\text{P}$  shielding. Results on these systems are shown here. Pacific Northwest Laboratory is a multiprogram laboratory operated by Battelle Memorial Institute for the U.S. Department of Energy under contract DE-AC06-76RLO1830. BAC, RAS and ASL are supported by the Associated Western Universities, Inc., Northwest Division under grant DE-FG06-89ER-75522 under the U.S. Department of Energy.

- 272 SULFUR-33 SOLID-STATE NMR WITH MAS AND CROSS-POLARIZATION AT LOW AND HIGH MAGNETIC FIELD STRENGTHS. William A. Paunch and Peter L. Rinaldi, Department of Chemistry, The University of Akron, Akron, Ohio 44325-3601

After almost a decade of near-dormancy in the area of solid-state  $^{33}\text{S}$  NMR, the first notable results involving the study of  $^{33}\text{S}$  in the solid state have been obtained. With significant improvements in magnetic field-strength, NMR hardware and probe technology, the experimentalist has only recently been equipped with the proper tools to collect extensive information about the chemical nature of what is still considered to be one of the more demanding nuclei to study by NMR. In this poster, many of these advances and how they ultimately relate to improvements in sensitivity and the reduction of problems related to second-order quadrupolar broadening effects will be discussed. Also, **sensitivity enhancements due to the application of high-speed magic angle spinning (MAS) as well as the first application of  $^1\text{H} \rightarrow ^{33}\text{S}$  cross-polarization will be described.**

- 273 APPLICATION OF  $^{17}\text{O}$  MAS NMR TO MIXED OXIDE GELS, GLASSES AND PEROVSKITE TYPE MATERIALS. Peter J. Dirkeir<sup>7</sup>, Ray Dupree<sup>\*</sup>, Mark E. Smithy Harold J. Whitfield<sup>a</sup> *a*: Physics Laboratory, University of Kent at Canterbury, Canterbury, Kent CT2 7NR, UK. *b*: Department of Physics, University of Warwick, Coventry CV4 7AL, UK. *c*: CSIRO Division of Materials Science and Technology, Private Bag 33, Rosebank MDC, Clayton, Victoria 3169 Australia, *d*: Department of Applied Physics, Royal Melbourne Institute of Technology, Box 2476W, Melbourne, Victoria 3001, Australia.

$^{17}\text{O}$  MAS NMR has been applied to a variety of technologically important materials. Amorphous  $\text{SiO}_2$ - $\text{TiO}_2$  and  $\text{SiO}_2$ - $\text{ZrO}_2$  gels and glasses (up to 40 mol%  $\text{TiO}_2$ / $\text{ZrO}_2$ ) were prepared by the hydrolysis of the metal alkoxides and subsequent heat treatment up to 600 °C (for Si/Ti system).  $^{17}\text{O}$  NMR is much more informative than  $^{29}\text{Si}$  NMR and shows, that the Ti and Zr are incorporated in the silica network by forming Ti-O-Si and Zr-O-Si bonds. These bonds each have a distinct NMR resonance at 260-280 and 150-160 ppm, respectively. In case of the Ti/Si mixed oxide system, these bonds persist up to 600 °C. Unexpectedly, hydrolysis behaviour in the Zr/Si system differs from that in the Si/Ti system, in that Zr is incorporated in the silica network at much higher Zr contents.  $^{17}\text{O}$  MAS NMR has also been applied to perovskite type  $\text{ABO}_3$  structures (A=Li, Ba, Sr, Ca; B=Ti, Zr, Sn) and  $^{17}\text{O}$  NMR chemical shifts are related to the crystallographic structures.

- 274 MEASUREMENT OF  $^{13}\text{C}$ - $^{13}\text{C}$  DISTANCES IN SOLID DNA USING DIPOLAR RECOUPLING WITH A WINDOWLESS SEQUENCE (DRAWS)

David Gregory, Dan Mitchell, Manish Mehta and Gary Drobny  
Departments of Chemistry and Physics, University of Washington, Seattle, WA 98195

This poster pertains to the use of solid state magic angle spinning experiments to elucidate the local structure of DNA molecules. Recently, solid state NMR techniques have been developed which enable the detection of direct nuclear dipolar couplings between spin 1/2 nuclei in biopolymers. New developments in synthetic and biochemical procedures allow site-specific  $^{13}\text{C}$ -labeling in DNA and thus one can monitor the interactions between  $^{13}\text{C}$  nuclei in DNA.

We have developed a new NMR pulse sequence, Dipolar Recoupling with a Windowless Sequence (DRAWS), for measuring dipole-dipole coupling strengths in rotating solids. This is similar to the DRAMA pulse sequence (R. Tycko & G. Dabbagh, *Chem. Phys. Lett.*, 173 (1990) 461). DRAWS, however, has better compensation for chemical shift anisotropy and offset effects. We have used DRAWS to determine  $^{13}\text{C}$ - $^{13}\text{C}$  distances within spinning samples of DNA. We will demonstrate how these give us insight into the relative orientations of adjacent bases in DNA.  $^{13}\text{C}$ - $^{13}\text{C}$  distance measurements have also been determined for model compounds to further support the DNA measurements. In addition, distances measured with DRAWS Recoupling will be compared to distances measured with a related technique, Radio Frequency-driven Dipolar;

275

**NMR STUDY OF A THERMOTROPIC LIQUID CRYSTALLINE POLYESTER AND BLENDS AT ELEVATED TEMPERATURES AND PRESSURES.** Michael B. Gentzler, Morton M. Denn and Jeffrey A. Reimer, Department of Chemical Engineering, University of California at Berkeley, Berkeley, California 94720-9989.

The response of fully-aromatic main-chain thermotropic liquid crystalline polyesters (LCPEs), like poly[*p*-hydroxybenzoic acid(73%)-co-*p*-hydroxynaphthoic acid(27%)] (Vectra-A), to thermal treatments above the glass transition temperature is complex and not satisfactorily understood. Annealing near the melt temperature increases mechanical strength due to a "crystallization" / ordering process that likely involves both conformational changes and transesterification reactions in the melt. Initial molecular order (chain alignment and defect texture) and control of gas evolution in the melt should be important. Our goal is a molecular understanding of this behavior in the LCPE and partly-miscible polymer blends containing it. We are currently measuring  $^1\text{H}$  T1 and T2 in Vectra-A resin and oriented fibers between room temperature and 340°C at pressures up to 50 atm. Blends with poly[ethylene terephthalate] are being prepared for related experiments.  $^1\text{H}$  CP-MAS experiments can be performed up to 160°C if useful. These measurements provide structural and dynamic information such as the average molecular alignment, as well as activation energies for, and indications of heterogeneity in, polymer back-bone motions. Our results will be presented in context with SEM and DSC characterization of the processed blends.

276

**RADIAL DISTRIBUTIONS OF  $^7\text{Li}$  IONS IN POLYETHYLENE OXIDE IN A CYLINDRICAL CAVITY IMAGER.** Rex E. Gerald II, Jerome W. Rathke, and Robert J. Klingler, Argonne National Laboratory, Chemical Technology Division, 9700 S. Cass Avenue, Argonne, Illinois 60439.

An NMR imaging technique based on Rotating Frame Microscopy (RFM) has been developed to image  $^7\text{Li}$  ions in a lithium polymer-electrolyte consisting of polyethylene oxide and lithium triflate (PEO/LiCF<sub>3</sub>SO<sub>3</sub>). This method provides a one dimensional radial profile of the  $^7\text{Li}$  ion concentration as a function of the distance from the central conductor in a detector with cylindrical symmetry. The central conductor is also used as the working electrode in an electrochemical cell. A second spatial dimension is possible by employing a static magnetic field gradient applied along the axis of the cavity thereby allowing the analysis of the  $^7\text{Li}$  ion concentration at several positions along the length of the working electrode. An estimate of the resolution for this imaging method by Abbe's criterion from optical theory is determined to be several microns. This technique provides sufficient resolution to map the lithium ion concentration in the region immediately surrounding the electrode in a polarized electrochemical cell. Time dependent measurements of the  $^7\text{Li}$  ion distribution yields quantitative NMR determinations of the lithium ion transport number in polymer electrolytes.

277

**HIGH-FIELD DYNAMIC NUCLEAR POLARIZATION: POLARIZATION TRANSFER IN A FROZEN AQUEOUS SOLUTION.** Dennis Hall, Gary Gerfen, Lino Becerra, Souheil Inati, Henry Spindler, David Singel, Robert Griffin, Department of Chemistry and Francis Bitter National Magnet Laboratory, Massachusetts Institute of Technology, Cambridge, MA 02139.

Dynamic Nuclear Polarization (DNP) transfers the high polarization of unpaired electrons to nuclei, giving rise to NMR signal enhancements of up to 2 orders of magnitude. DNP experiments were performed on a frozen water-glycerol solution containing the free radical TEMPO at 5 Tesla (140 GHz EPR). A cyclotron resonance maser, or gyrotron, has been implemented as a high-power (~100 W) microwave source. Proton polarization enhancements up to 185 were achieved, and this polarization was subsequently transferred to solute nuclei via cross-polarization. The potential utility of this experiment for studying macromolecular biological systems is discussed.

The polarization transfer proceeds through a combination of three pathways, the direct and indirect thermal mixing effects, and the solid effect. The signal enhancements are studied as a function of microwave power and magnetic field to gauge the relative efficiencies of the three pathways.

In addition, we have implemented magic-angle spinning (MAS) on this system, to combine the sensitivity enhancement of DNP with the resolution enhancement of MAS.

- 278 **DISTRIBUTION OF CESIUM IN SYNROC. A CESIUM-133 MAGIC ANGLE SPINNING NMR STUDY.** J. S. Hartman. Department of Chemistry, Brock University, St. Catharines, Ontario L2S 3A1, Canada, and E. R. Vance, Australian Nuclear Science and Technology Organization, Menai, New South Wales 2234, Australia.

Characterizing the cesium site locations in nuclear wasteforms is important because Cs<sup>+</sup> is a very labile ion and contributes a very significant fraction of the short-term (<1000 yr) beta/gamma activity of high-level reprocessing waste (Cs-134, t<sub>1/2</sub>~2 yr, and Cs-137, t<sub>1/2</sub>~30 yr), and a significant fraction of the long-term activity (Cs-135, t<sub>1/2</sub>~3,000,000 yr). We will present our cesium-133 MAS NMR studies of the cesium environments that can exist in Synroc, a ceramic made from a reactive mixture of Al, Ba, Ca, Ti, and Zr oxides which is proving to be an effective medium for immobilization and long-term storage of nuclear wastes (E. R. Vance, MRS Bulletin, XIX, December 1994, pp. 28-32, and reference 8 therein). Cs-133 with its 100% natural abundance, high sensitivity, and very small quadrupole moment is well suited for nmr monitoring of such systems. Cs-133 spectra of cesium-substituted model systems including cesium hollandite and cesium-containing simulated high-level nuclear waste samples show wide variations, with at least three different kinds of cesium environment present. Cesium-substituted titanate hollandites that contain both Ti(III) and Ti(IV) give a strongly Knight-shifted resonance (600 - 700 ppm from 0.5 molal aqueous CsCl), indicating a cesium environment with considerable metallic character at the channel sites.

- 279 **STRUCTURES OF ALKALI THIOBORATE M<sub>2</sub>S-B<sub>2</sub>S<sub>3</sub> (M=Li, Na, Rb) GLASSES STUDIED BY MULTI-NUCLEAR MAS and DOR NMR**

Son-Jong Hwang,<sup>1</sup> D. P. Lang<sup>1</sup>, Jaephil Cho<sup>2</sup>, S. W. Martin<sup>2</sup>, C. Fernandez,<sup>3</sup> J. P. Amoureux,<sup>3</sup> and M. Pruski<sup>1</sup>

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<sup>3</sup>Univ. des Sci. et Tech., de Lille, Villeneuve d'Ascq, France.

Multinuclear high-speed MAS and DOR NMR were used to study the structural transformation of glass and crystalline thioborates xM<sub>2</sub>S + (1-x)B<sub>2</sub>S<sub>3</sub> (M=Li, Na, Rb). Central transition of <sup>11</sup>B, <sup>7</sup>Li, <sup>23</sup>Na and <sup>87</sup>Rb were monitored under 8-10 kHz MAS, to elucidate the chemistry of network modification upon increasing concentration of alkali metals. The experimental results were aided by the computer simulation of the MAS and DOR spectra.

- 280 **INVESTIGATIONS OF THE LOCAL DISORDER IN THE API MICROPOROUS FRAMEWORK**

Michael Janicke,\* Dirk Demuth,\* Ferdi Schüth,\* Christian Jäger,t and Bradley F. Chmelka.\*

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Recent research efforts have focused on the use of high resolution solid-state NMR to analyze microporous aluminophosphates (AIPO4-5) and silicon aluminophosphates (SAPO-5) in an effort to better characterize these unsolved crystal structures and to investigate the effect of silicon substitution on the framework, specifically the API system. Examination of the long-range order in these materials using powder X-ray diffraction, scanning electron microscopy, and optical microscopy has established the incorporation of silicon induces profound morphological deviations from the aluminophosphate system. To correlate these measurements with the local structure of the materials, several solid-state NMR techniques have been employed to probe the changes in the aluminum and phosphorous sites that accompany the incorporation of silicon into the AFI structure. <sup>31</sup>P MAS and variable field <sup>27</sup>Al Double Rotation (DOR) NMR studies confirm the existence of three resolvable tetrahedral sites in the AIPO4-5 molecular sieve. Substitution of silicon into the framework results in the gradual loss of resolution in the <sup>31</sup>P MAS and <sup>27</sup>Al DOR spectra, reflecting increased disorder in the material. <sup>27</sup>Al Satellite Transition Spectroscopy (SATRAS) confirms that this disorder produces a distribution of quadrupolar parameters associated with the spin-5/2 nuclei <sup>27</sup>Al. These results show that the local ordering of the aluminum sites in the AFI framework can be significantly diminished by replacing only a small percentage (ca. 1%) of the tetrahedral atoms with silicon.

281 A LOW TEMPERATURE PROBE FOR THE MAGIC ANGLE TURNING EXPERIMENT

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The Magic Angle Turning (MAT) experiment introduced several years ago by Gan provides a simple method to obtain a 2D isotropic - CSA correlation spectrum. In this presentation a probe optimized to perform this experiment and capable of low temperature operation is described. For this MAT experiment the spinning rate needed is usually about 30 Hz. Therefore, the problems of sample heating common in high speed MAS probes are avoided and sample temperatures down to about -140°C can be reached. In the design used, the sample is contained in a section of a standard 12 mm diameter NMR tube which is placed in a large diameter holder, resulting in a sample volume of about 1.5 cm<sup>3</sup>. This holder can be rotated by room temperature bearing gas only, for the slower speed of about 1-5 Hz. The spinning rate is insensitive to small fluctuations in bearing gas pressure. The cooling gas is isolated from the bearing gas region, and is transferred to the sample region by a dewar which has a bend at the magic angle and connects to the probe with a Teflon joint. The sample temperature achieved is a function of the flow rate of the cooling gas, eliminating the need for a heating circuit. The system design and experimental results will be shown and discussed in the presentation.

282 USE <sup>31</sup>P-SOLID NMR FOR THE INVESTIGATION OF THE INTERFACIAL STRUCTURE OF POLYPHOSPHAZENE-PHOSPHATE MOLECULAR COMPOSITES.

William D. Samuels, Li-Qiong Wang, and Gregory J. Exarhos, Pacific Northwest Laboratory, MS; K2-44, Richland, WA 99352.

Jami K. Kimble, University of Colorado, and Lawrence Carter, Xavier University of Louisiana; Student Interns at Pacific Northwest Laboratory, MS; K2-44, Richland, WA 99352.

Solid NMR spectroscopy has been applied to changes in structure of inorganic polymer/phosphate glass composites. Single Pulse Block Decay, CP-MAS, and CRAMPS techniques have been used to study the interfacial structures. Strong interfacial bonding between the component phases is also inferred from electron micrographs. Mutual solubility of inorganic polymers, typified by the polyphosphazene, -[N=PR<sub>2</sub>]-, and metal phosphate glasses in a solvent such as water allows intimate mixing on the molecular scale. Solvent evaporation followed by thermal processing generates material having nanoscale microstructure which can be modified by appropriate choice of processing parameters.

283 PHYSICO-CHEMICAL CHARACTERIZATION OF CREAMS AND OINTMENTS BY DIFFUSION NMR. W. Kuhn and M. Szayna, Fraunhofer Institute for Biomedical Engineering, Magnetic Resonance Department, Ensheimer Str. 48, D-66386 St. Engbert, Germany.

Pharmaceutical drugs provided as ointments and beauty care products, like cosmetic creams, are usually prepared as water in oil or oil in water emulsions. In addition to these two components they may contain vitamins, amino acids, penetration enhancers such as urea, etc. The effectiveness of creams and ointments with regard to the penetration of the skin depends strongly on their composition with respect to the physico-chemical properties of the emulsions. Parameters offered by NMR, which can be used to characterize the emulsions, are the relaxation times and diffusion coefficients of the different compounds. In particular, the relative contribution of differently bound water present in the creams seems to be one of the important parameters describing the potentials of skin care products. We present the chemical selective characterization of creams and ointment using the measurement of NMR relaxation times and diffusion coefficients for the different compounds. The performed measurements reveal the presence of water bound in at least two different stages, which is reflected in diffusion coefficients measured not only for water but lipids and other ingredients as well. From the diffusion values the average free moving distance of the molecules could be estimated giving an idea about the droplet size of water in the emulsion. Also aging process and, as its consequence, the phase separation of water and fat, can be investigated by this technique.

- 284 **<sup>13</sup>C NMR STUDY OF COMPONENT DYNAMICS IN AROCLOR / POLY(VINYLETHYLENE) MIXTURES.** Kenneth J. McGrath and C. Michael Roland, Naval Research Laboratory, Code 6120, Washington, DC 20375-5342

Solid state <sup>13</sup>C magic angle spinning, dipolar decoupling NMR experiments were carried out on Aroclor 1248, a small molecule glass former, a low molecular weight, high vinyl polybutadiene (PVE), and a 50% mixture of the two liquids. The temperature dependent NMR line broadening closely correlates with the temperature dependence of the relaxation times measured by dielectric spectroscopy. Previous work had shown that addition of PVE speeds up the mixture's bulk relaxation. The present NMR experiments reveal that the individual motions of both components become faster. For the Aroclor, this is unusual, since the polymer has a higher glass transition temperature. From these results we conclude that an increase in available volume, occasioned by the positive excess volume of mixing, is the mechanism giving rise to faster Aroclor dynamics in the mixture. At least in this system, any changes in the degree of intermolecular cooperativity of the local motions accompanying the mixing do not play a primary role.

- 285 **RESOURCE FOR SOLID-STATE NMR OF PROTEINS.** R. McNamara, K. Valentine, T. Le and S. J. Opella, Department of Chemistry, University of Pennsylvania, Philadelphia, Pennsylvania 19104.

A new NDH 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 solid-state NMR spectroscopy. One spectrometer has a wide-bore (89 mm) 12.9T Magnex magnet with a <sup>1</sup>H resonance frequency of 550 MHz. The second spectrometer currently under construction has a mid-bore (62 mm) 17.6T Magnex magnet with a <sup>1</sup>H resonance frequency of 750 MHz. The high resonance frequencies give substantial boosts in sensitivity and resolution, and are having their greatest impact by making <sup>1</sup>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. Members of the staff will be present to discuss opportunities for service, collaborative, and core research at the Resource.

- 286 **ORIENTATION AND ROTATION OF AXIAL LIGANDS IN (PORPHYRINATO)-IRON(III) COMPLEXES.** Konstantin I. Momot, Nikolai V. Shokhirev, Tatjana Kh. Shokhireva, and F. Ann Walker, Department of Chemistry, University of Arizona, Tucson, Arizona 85721.

Modified MM2 potentials have been used to study the equilibrium geometry of low-spin (porphyrinato)iron(III) complexes such as [TPPFe(I-MeIm)<sub>2</sub>]<sup>+</sup> and [TMPFe(1,2-diMeIm)<sub>2</sub>]<sup>+</sup>, where TPP and TMP are tetraphenylporphyrin and tetramesitylporphyrin, respectively. Monte Carlo multiple minimum analysis has been used to obtain local energy minima along with the global minimum. The "adiabatic" potential energy surface for rotation of axial ligands (minima achieved in all degrees of freedom but with constrained internal rotation coordinates for the two ligands) can be computed by combining a Ramachandran-type dihedral drive with Monte Carlo single minimum analysis. Effects of the rates of axial ligand rotation in unsubstituted complexes, [PorFe(L)<sub>2</sub>]<sup>+</sup>, on 1D and 2D NMR spectra can be also modelled by means of molecular mechanics and MM-based molecular or stochastic dynamics, and the results applied to the calculation of rate constants for axial ligand rotation from EXSY cross peak intensities. The validity of molecular and stochastic dynamics for the description of the hindered rotation of axial ligands and spectroscopic properties of complexes will be discussed.

- 287 **HETERONUCLEAR CORRELATION EXPERIMENTS WITH HIGH-RESOLUTION FOR QUADRUPOLEAR NUCLEI** Karl T. Mueller, Robert M. Wenslow, and Thomas P. Jarvie, Department of Chemistry, The Pennsylvania State University, 152 Davey Laboratory, University Park, PA 16802-6300 (814)863-8674

We present studies using high-resolution NMR techniques for quadrupolar nuclei, such as dynamic-angle spinning (DAS) NMR, in two-dimensional heteronuclear correlation experiments. The DAS experiment allows spectral resolution of broad, overlapping resonances from nuclei such as  $^{11}\text{B}$ ,  $^{17}\text{O}$  and  $^{23}\text{Na}$ . Heteronuclear correlation is achieved through mixing schemes such as cross-polarization or TEDOR pulse sequences. Correlated resonances appear as cross-peaks in a well-resolved two-dimensional map. Examples include  $^{23}\text{Na}/^{31}\text{P}$  DAS/CP/MAS spectra from polycrystalline solids obtained with high-resolution in both spectral dimensions.

- 288 **A STUDY OF THE MOLECULAR MOTIONS IN ASPHALTS USING VARIABLE TEMPERATURE DIPOLAR DEPHASING  $^{13}\text{C}$  NMR.** Daniel A. Netzel, Francis P. Miknis, J. Calhoun Wallace, Jr., Clinton H. Butcher, and Kenneth P. Thomas, Western Research Institute, 365 N. 9th Street, Laramie, WY 82070-3380

The nature and extent of the mobile components in asphalt at various temperatures significantly influences a variety of physical properties such as viscosity, glass transition temperature, and, in general, the viscoelastic properties. These viscoelastic properties play a major role in determining overall pavement performance. Carbon-13 spin-lattice and spin-spin relaxation times were measured for the aromatic and aliphatic carbons in several asphalts as a function of temperature (+20 to -45°C). The relaxation data indicate considerable motions still persist for the aromatic as well as the aliphatic methylene and methyl carbons at -45°C. Weight percent of rigid and mobile carbons in the various asphalts and the activation energies for segmental motions of the  $(\text{CH}_2)_n$  carbons and for rotational motions for the branched/aromatic and terminal  $\text{CH}_3$  carbons will be presented.

- 289 **TRANSIENT INTERMEDIATES IN SOLID STATE REACTIONS. A CARBON-13 NMR STUDY OF MONOSUBSTITUTED BULLVALENES.** Raphy Poupko, Klaus Muller, Herbert Zimmermann and Zeev Luz, The Weizmann Institute of Science, Rehovot 76100, Israel.

Chemical rearrangement processes in solids are often hindered by the packing forces in the crystals. However, when the void available to the molecules is large enough or when their shape permits, chemical transformation may occur in solids even at comparable rates to those in solution. Such processes require coupling between chemical transformation and reorientation in order for the molecules to preserve their orientation in the crystal. Solid state NMR experiments can provide detailed information about the pathways of such reactions. In the present work we report on studies, involving the Cope rearrangement in solid monosubstituted bullvalenes. These compounds interconvert via a specific seven-cycle  $(4\text{f}^* 1^{\wedge} \pm 3^{\wedge} 2^{\wedge} ?^{\wedge} 3^{\wedge} 1\ll^{\wedge})_r$  (where the numbers refer to the substitution site, 4 being the bridgehead carbon and 1 the cyclopropane ring). In solution these compounds exist as mixtures of interconverting isomers, while in the solid they usually crystallize in the form of a single isomer. One would therefore expect complete quenching of any rearrangement in the solid, unless the process involves a cycle of transformations which ends up with the original isomer in the original crystal site. Solid state NMR measurements including dynamic ID MAS, magnetization transfer and 2D MAS exchange spectroscopy applied to several monosubstituted bullvalenes, showed that all of them indeed undergo Cope rearrangement, although at slower rates than in solution. Analysis of the experimental data provided detailed information on the reaction pathway and uniquely identify the transient intermediates involved in the process. For example, cyanobullvalene and bullvalene-carboxylic acid, which crystallize as the 3-isomer rearrange via the cycle 3-L3, while fluorobullvalene, which crystallizes as the 4-isomer, rearranges via the cycle 4-1-3-1-4.



**290 1H CRAMPS SPECTROSCOPY OF RIGID SOLIDS, POLYMERS, TRANSITION METAL COMPLEXES AND CLUSTERS. A. I. Rehrov, S. V. Rykov, M. P. Filatova, Institute of Petrochemical Synthesis, Russian Academy of Sciences, Moscow, Russia.**

The value of the CRAMPS (combined magic angle spinning and multiple pulse spectroscopy) technique for the observation of  $^1H$  spectra of solids, insoluble polymers, including synthetic organic polymers and selective complex-forming polymeric sorbents, as well as transition metal complexes and clusters in high resolution spectra, is discussed. The resolution varies from 0.5 ppm to about 2 ppm which is sufficient to resolve resonance signals of protons of the different molecular groups, such as olefinic, aromatic, and aliphatic protons, but the lines are too broad to obtain the microstructure due to tacticity. As a result, it is possible to determine the common structure of the polymeric matrix, establish the presence of the polycrystalline areas in it, and the degree of compatibility of the components in the polymeric composition. Averaged chemical shifts of a series of selective complex-forming polymeric sorbents are discussed. The resolution is expected to be increased by combination the high-field MAS experiment and a more effective multiple-pulse sequence.

**291 STUDY OF  $^{69}Ga$  OVERHAUSER EFFECT BY DIRECT NMR DETECTION IN OPTICALLY PUMPED GaAs. T. Room, E.L. Hahn, *Department of Physics*, and T. Pietrafi, Y.-Q. Song, A. Pines, *Department of Chemistry, University of California, Berkeley, CA94720***

Polarization of electron spins by optical pumping (OP) of interband transitions in semiconductors enhances the sensitivity of NMR. Optical detection of NMR by means of the Hanle effect senses only the polarization of nuclei that are hyperfine-coupled with the localized electron spins. This method is applicable in applied magnetic fields no more than few kG. Directly detected NMR measures the entire nuclear magnetization and is not limited to those nuclei within the electron localization Bohr radius. The NMR of optically pumped GaAs quantum wells has been reported by Barrett *et al.* (*Phys.Rev.Lett.*72(1994)1368). Here we present results of high field OP in un-doped bulk GaAs sample. The OP enhancement is found to peak at photon energies below the bandgap and is negligible above the bandgap which indicates that polarization transfer is from localized electrons to nuclei. Enhancement of the nuclear magnetization by OP increases when higher magnetic fields and lower temperatures are applied. Direction of the nuclear magnetization depends on temperature, magnetic field, and light helicity. For example, the nuclear magnetization is inverted for both light helicities at  $T = 1.5$  K and  $B = 9.3$  T. We apply the Overhauser model of spin-polarization transfer from polarized trapped electrons to nuclear spins at low temperatures and in high magnetic fields. Our data indicates that the  $g$ -factor of the trapped electrons is negative as it is for the conduction band electrons in GaAs.

292

**SOLID AND LIQUID STATE NMR STUDIES OF THE R3230AC MAMMARY ADENOCARCINOMA IN MODEL FISCHER RATS. R.A. Santos, B.A. Concannon, K.M. Groch, D.N.Rommereim, R.A. Wind**

It is investigated whether solid state NMR can contribute to an improved detection and characterization of tumors. The solid state results contain information that can describe the composition and concentration of dipolar-broadened components, invisible to the standard liquids experiment. In cellular systems the high-molecular weight, slow tumbling molecules predominantly inhabit the cell membrane in the form of glycolipids and glycoproteins. Cancer induced differences in cell membrane composition are marked by altered surface and transport properties that may be investigated by NMR.  $^1\text{H}$ ,  $^{13}\text{C}$  and  $^{31}\text{P}$  variable-temperature (-100 to -10 °C) data will be presented of healthy mammary epithelial cells and transplanted mammary R3230AC tumor cells in female Fischer rats. Liquid state results will be shown as part of our overall research strategy.

Pacific Northwest Laboratory is a multiprogram laboratory operated by Battelle Memorial Institute for the U.S. Department of Energy under contract DE-AC06-76RL0 1830. BAC and RAS are supported by the Associated Western Universities Inc., Northwest Division under grant DE-FG06-89ER-75522 under the U.S. Department of Energy.

293 **ANALYSIS OF THE TEMPERATURE DEPENDENCE OF THE  $^1\text{H}$  CONTACT SHIFTS IN MODEL HEMES AND HEME PROTEINS: EXPLANATION OF "CURIE" AND "ANTI-CURIE" BEHAVIOR WITHIN THE SAME MOLECULE. Nikolai V. Shokhirev and F. Ann Walker. Department of Chemistry, University of Arizona, Tucson, AZ 85721.**

Deviation of the observed temperature dependences of the contact shifts of the protons of paramagnetic complexes from the Curie law, and the presence of both "Curie" and "anti-Curie" dependences within the same molecule have been observed previously. The existence of these types of behavior can be explained on the basis of a two-level model, taking into account the ground state and a single low-lying excited state. The conditions for the presence of different types of temperature dependences for protons in the same molecule have been determined, and procedures for fitting the experimental data have been proposed and tested on model numerical experiments. Experimental temperature dependences for four types of compounds, including two types of low-spin iron(III) porphyrinates,  $[\text{PorJFeLj}]^{m+}$  (both of which have unsymmetrical substitution patterns, but one of which also has an axial ligand in fixed orientation), several low-spin Fe(III) heme proteins, and a group of Fe(III) model hemes having  $S=3/2, 5/2$  admixed spin ground states, have been processed and the energy gap between the ground and excited states determined. Spin densities at the carbons to which protons of interest are attached have been obtained for the two states and are interpreted in terms of MO Theory.

294 **MULTIPLE QUANTUM NMR OF METHYL- AND CHLORO-BENZENE IN NEMATIC LIQUID CRYSTALS. Raymond T. Syvitski and Elliott Burnell, University of British Columbia, 2036 Main Mall, Vancouver, B.C. Canada V6T 1Z1**

NMR spectroscopy has been used for determining the orientational order parameter of methyl- and chloro-benzene in a nematic liquid crystal. Solute order parameters strongly depend on the size and shape of the molecules. Since methyl- and chloro-benzene are of similar size and shape but have different dipole moments, the difference between the order parameters may be an indication of strong solute-solvent electrostatic interactions. We discuss the effect of solute-solvent interactions on the order parameter of similar size and shape solutes.

- 295 B11-A127 Double Resonance NMR on Alumoborate Glasses.** \*Lco van Wtilen, †Lars Zuchner and \*Hellmut Eckerl  
Department of Chemistry, University of California, Santa Barbara, CA  
93 106

† Institut für Physikalische Chemie, Universität Münster, Germany

**Abstract:**

The question of connectivity in glasses can be elegantly addressed by means of double resonance techniques. In this study we focus on the applicability of the REDOR (Rotational Echo Double Resonance) and CP MAS experiments involving  $1\ ^{10}\text{B}$  and  $2\ ^{7}\text{Li}$  nuclei, whose connectivity in sodialumoborate glasses is under study. In addition to the MAS experiments, some results of static CP experiments will be presented. A new technique of spectral editing by utilizing the different T<sub>1</sub> behaviour of different boron environments is introduced.

- 296 SPECTRAL EDITING OF  $^{19}\text{F}$ - $^{13}\text{C}$  CPMAS SPECTRA**

\* Stephanie A. Vierkotter and Edward W. Hagaman  
Chemical and Analytical Sciences Division  
Oak Ridge National Laboratory, Oak Ridge, TN 37831, USA.

Recent results from spectral editing of  $^{13}\text{C}$  CPMAS spectra of fluorinated organics are presented.  $^{13}\text{C}$  NMR spectra obtained via direct fluorine-carbon cross-polarization are edited by utilizing the  $^{19}\text{F}$ - $^{13}\text{C}$  dipolar coupling and the ratio of heat capacities of a  $^{13}\text{C}$  nucleus to its group of directly bonded fluorine nuclei. Two goals are being pursued: First, the distinction of  $\text{CF}_2$ ,  $\text{CF}$ ,  $\text{CF}_3$  and non-fluorinated carbons, and second, the distinction of carbons one- and two bonds removed from fluorine. The latter separation gives local structure information about the environment of the fluorine nuclei. In compounds with low fluorine content the rate of  $^{19}\text{F}$ - $^{19}\text{F}$  spin diffusion is lower than in perfluorinated compounds. The fluorine spin diffusion rate determines for how long the  $\text{CF}_x$  spin pairs are isolated from the other spins during the initial stage of the  $^{19}\text{F}$ - $^{13}\text{C}$  cross-polarization and thus how easily selectivity can be achieved in the editing.

- 297 A HIGH RESOLUTION SOLID STATE  $^{13}\text{C}$  NMR INVESTIGATION OF THE LOCAL CHAIN DYNAMICS OF COMPATIBLE BLENDS OF POLYSTYRENE AND POLYVINYL METHYL ETHER).** Todd A. Waaler, Peter L. Rinaldi, and Chang D. Han, The University of Akron, Akron, OH., 44325-3601, (216)-972-7352.

Compatible blends of polystyrene and polyvinyl methyl ether) were studied by high resolution solid state  $^{13}\text{C}$  NMR. Measurements of  $^1\text{H}$  spin-lattice relaxation times in the rotating frame have been obtained as a function of both temperature and blend composition. By varying the blend composition, it has been possible to study the effect of intermolecular interactions on local chain dynamics. Results indicate a strong temperature dependence on local chain motions. At temperatures above 35°C the difference in motional frequencies between the two components becomes very pronounced. This deviation in local chain motions demonstrates that on a molecular scale the blends are not compatible and there may exist micro-domains of each component.

- 298 **INVESTIGATION OF THE STRUCTURE AND DYNAMICS OF SURFACTANT MOLECULES DURING NUCLEATION OF MESOPHASE SILICATES USING SOLID-STATE NMR.** Li-Oiong Wang, Jun Liu, Rodolfo A. Santos, and Anthony Y. Kim. Pacific Northwest Laboratories, MS. K2-44, Richland, WA 99352

A variable-temperature  $^{13}\text{C}$  solid-state nuclear magnetic resonance (NMR) has been used to investigate the structure and dynamics of surfactant molecules in mesophase silicates. The functional groups and side groups were identified from the high resolution  $^{13}\text{C}$  MAS NMR spectra obtained using high-power  $^1\text{H}$  decoupling. Although the surfactant bound to the silicate to form amorphous precipitate upon mixing, the behavior of the surfactant in the amorphous phase is quite different from the behavior of the ordered phase. An additional peak at 57.4 ppm appeared in the ordered mesophase suggesting that methyl groups next to the head group are affected by ordering, but not by electrostatic binding. The relative peak intensities observed in the  $^{13}\text{C}$  MAS NMR spectra of surfactant/silica were found to be dependent on whether cross-polarization (CP) or single-pulse (SP) excitation is used, an observation interpreted in terms of the mobility of the surfactant on the silica surfaces. Parameters including  $T_{\rho}$ ,  $T_1$ , and  $T_{1\rho}$  at different temperatures (300K and 170K) were obtained from a series of relaxation measurements.

- 299  **$^7\text{Li}$  SOLID STATE NMR STUDY OF NONLINEAR OPTICAL  $\text{Li}_{1-x}\text{Nb}_x\text{W}_3\text{O}_{13}$  MATERIALS.** Yin Xia\*, Leo van Wullen\*, Xuehua Wu\*\*, Charles Lakeman\*\*, Hellmut Eckert\*, Fred Lange\*\*, and Stan Anderson\*\*\*. \*Chemistry Department, \*\*Materials Science Department, University of California, Santa Barbara, CA 93106. \*\*\*Westmont College, Santa Barbara, CA 93108.

Cation mobility and spatial distribution of lithium ions have been studied on a series of solid solutions  $\text{Li}_{1-x}\text{Nb}_x\text{W}_3\text{O}_{13}$  ( $0 < x < 0.5$ ). For each tungsten atom substituting on a niobium site, a lithium vacancy is produced. Low temperature second moments depend linearly on lithium content, consistent with a random distribution of vacancies. Variable-temperature (30-550 °C)  $^7\text{Li}$  NMR studies as a function of composition give evidence for two distinct motional processes- a low-temperature local hopping mechanism and high-temperature long-range diffusion. The former process appears to be suppressed with increasing tungsten substitution, whereas the long-range diffusion is significantly enhanced with increasing vacancy concentration. The compositional dependence of the lithium mobility is compared with simulations based on a percolation model.

- 300 **MOLECULE STRUCTURE AND DYNAMICS OF COAL AT HIGH TEMPERATURE AND UNDER SOLVENT SATURATION AS STUDIED BY  $^1\text{H}$  CRAMPS** Jincheng Xiong and Gary Maciel, Chemistry Department, Colorado State University, Fort Collins, CO 80523

Extensive time-domain  $^1\text{H}$  CRAMPS experiments were used to investigate molecular structure and dynamics of coals, and to correlate the molecular motion with  $^1\text{H}$  CRAMPS resolution. Moderately high temperature (up to 230°C) does not result in a dramatic increase in  $^1\text{H}$  CRAMPS resolution. The results are not what we expected, based on our previous studies in which we found dramatic line narrowing when coal is saturated with pyridine. To examine explicitly the dependence of molecular motion on temperature, we carried out proton dipolar-dephasing experiments and proton spin-exchange experiments on coals with and without solvent saturation. We also measured the temperature dependence of proton  $T_1$  and  $T_{1\rho}$  values of coals.  $^1\text{H}$  CRAMPS detection was used in all of the time-domain experiments, this provided molecular dynamic information on aliphatic and aromatic protons separately. To separate inhomogeneous line broadening from broadening due to effects of motion on CRAMPS efficiency, time suspension experiments were also employed. We found that thermal treatment and solvent saturation have quite different effects on the structure and dynamics of coals. A structural model of coal based on our new results will be discussed. Reasons for the apparent CRAMPS resolution enhancement under solvent saturation will also be discussed.

301 **NQR, NMR AND SQUID DETECTION OF  $^{14}\text{N}$  AND  $^{13}\text{C}$  IN COCAINE BASE AND HYDROCHLORIDE**

**James P. Yesinowski, Michael L. Buess,<sup>1</sup> Allen N. Garroway, Marcia Ziegeweid<sup>5</sup> and Alexander Pines<sup>5</sup>**  
 Chemistry Division, Naval Research Laboratory, Washington DC 20375-5342;<sup>1</sup> SFA, Inc., Landover, MD 20875; <sup>5</sup> Materials Sciences Division, Lawrence Berkeley Laboratory, and Department of Chemistry, University of California, Berkeley, CA 94720.

Detecting low-frequency pure NQR transitions (e.g. those in the range 500 kHz to several MHz) in new samples is difficult due to the intrinsic insensitivity of resonant circuits in this region and the limited accuracy with which nuclear quadrupole coupling constants (NQCC) can be predicted. We have used a cw SQUID double-resonance CH- $^{14}\text{N}$ ) spectrometer to obtain the  $^{14}\text{N}$  NQR ( $I=1$ ) frequencies in cocaine hydrochloride. Subsequently, pure  $^{14}\text{N}$  NQR signals were observed by pulsed techniques, relaxation times measured at various temperatures, and the 806 kHz and 961 kHz transitions assigned to *v.* and *p.*, respectively, by application of a weak Zeeman field. Similar pure  $^{14}\text{N}$  NQR measurements were made in cocaine base at ca. 3.8 MHz. We used high-field  $^{13}\text{C}$  NMR ( $I=3/2$ ) at 7.0 T to obtain the NQCC from the second-order quadrupolar powder pattern in both cocaine and heroin hydrochloride, which contain a chloride anion hydrogen-bonded to a (protonated) nitrogen. The experimental spectrum observed by stepping a spin-echo carrier frequency is compared with simulations. The cocaine salt exhibits a  $^{13}\text{C}$  pure NQR peak at 2.53 MHz (asymmetry parameter  $\eta = 0.2$  from NMR), but the corresponding NQR peak for the heroin salt predicted to be at 1.912 MHz has not yet been observed. General strategies for observing low-frequency  $^{14}\text{N}$  and  $^{13}\text{C}$  NQR transitions will be discussed.

302  **$^{13}\text{C}$  CHEMICAL SHIFT PRINCIPAL VALUES IN AN ANALOGOUS SERIES OF HETEROCYCLIC AROMATIC COMPOUNDS** Wei Wang, D.W. Alderman, Mark S. Solum, Ronald J. Pugmire\* and David M. Grant, Department of Chemistry and Chemical and Fuel Engineering\*, University of Utah, Salt Lake City, UT 84112

The electronic, molecular and crystal structures of Fluorene, Carbazole, Dibenzofuran and Dibenzothiophene are important not only for their significance in basic chemical science but also for their roles as model compounds in various technological and industrial processes. Advances in solid state NMR methods and computational chemistry now afford us to study their structures in detail. Since these aromatic compounds all have very long  $^1\text{H}$  spin-lattice relaxation time, relaxation-agent doping is employed to shorten their proton T<sub>1</sub>, substantially. A Flip-back MAT experiment is utilized to further reduce the experimental time. Spectral assignments are aided by *ab initio* calculated shielding tensors using GIAO method. The availability of three principal shift values instead of single isotropic shift has enhanced the reliability of these assignments. Influences of heteroatoms and biphenyl linkage on the  $^{13}\text{C}$  shift principal values of the central five-membered ring and two flanking benzene rings are discussed.

303  **$^{13}\text{C}$  DIPOLAR SPECTRUM OF MATRIX ISOLATED BENZYNE-1,2- $^{13}\text{C}_2$**

Anita M. Orendt, J. G. Radziszewski, J. C. Facelli, J. Michht, and D. M. Grant  
 Department of Chemistry, University of Utah, Salt Lake City, UT 84112 and <sup>^</sup>Department of Chemistry and Biochemistry, University of Colorado, Boulder, CO 80309.

The  $^{13}\text{C}$  dipolar spectrum of o-benzyne-1,2- $^{13}\text{C}_2$  in argon matrix at a temperature of about 25K is reported. This species has been the focus of a number of matrix isolation IR spectroscopic and theoretical studies in order to characterize the strained aryne bond. However, dipolar spectroscopy remains the only method available to experimentally determine this bond length. The benzyne was generated photochemically from phthalic anhydride-1,2- $^{13}\text{C}_2$  with a conversion to benzyne of about 55%. Simulations of the dipolar patterns of pure phthalic anhydride and the phthalic anhydride - benzyne mixture have been completed. The results of the simulations give the principal values of the chemical shift tensor of the labeled carbon in benzyne as 275, 235, and 70 ppm with respect to TMS, in good agreement with *ab initio* calculations. The 833 component is not perpendicular to the molecular plane as is common in aromatic systems; instead 833 is found to be nearly along the triple bond with 822 perpendicular to the molecular plane. The dipolar coupling gives a bond length of 1.25 Å, again in good agreement with the results of geometry optimizations. The dipolar spectra, simulations, and theoretical treatment of benzyne will be presented in this poster.

- 3 0 4** CHEMICAL SHIFT TENSOR MEASUREMENTS AND THEIR UTILITY IN THE THREE DIMENSIONAL WORLD OF CHEMISTRY. David M. Grant, Dept. of Chem., Univ. of Utah, Salt Lake City, UT 84112  
*Associates:* J. C. Facelli, D. W. Alderman, R. J. Iulucci, W. Wang, M. S. Solum, F. Liu, C. Phung.

In liquids, the shielding tensor averages to its isotropic value. In solids the measurable chemical shift tensor is symmetric and involves six parameters that provide increased information on both electronic and molecular structure. The added benefit, however, is obscured in solid powder samples by severely overlapping spectral bands. Single crystal samples provide all six components of the tensor from sharp NMR peaks. The traditional method for single crystals uses a goniometer approach usually limited to crystals with less than 15-20 magnetically different  $^{13}\text{C}$  nuclei per unit cell. A new 2D chemical-shift/chemical-shift (CS/CS) correlation method, to be described, improves resolution and allows indexing of crystals with 50-100 magnetically different nuclei. When only powder samples are available, a new 2D magic angle turning, MAT, technique is now available that portrays the isotropic shifts along the evolution dimension and provides solid powder patterns in the acquisition dimension. The increased information in shift tensors is sensitive to small variations in atomic positions, establishing a connection between diffraction results and tensor shifts. Quantum chemical calculations now appear to be able to correlate shifts with diffraction data within  $\pm 2$  ppm and indicate that an appreciable portion of the theoretical scatter may be attributed to intrinsic limitations in the diffraction distances. Single crystal results have validated the use of quantum mechanical methods for correlating the simpler powder shift results which still have greater structural information than obtainable in liquids. Results from MAT data illustrate the nature of chemical information that is available for model solids and even for very complex materials such as pitches and coals.

- 3 0 5** CONNECTIVITIES AND CATION DISTRIBUTIONS IN GLASSES: SOLID STATE NMR STUDIES. Hellmut Eckert, Becky Gee, Leo van Wullen, Lars Zuchner, Werner Muller-Warmuth, Institut für Physikalische Chemie, Westfälische Wilhelms-Universität Münster, D-48149 Münster, Germany.

Dipolar single and double resonance NMR techniques are becoming valuable structural probes in glasses of increasing complexity. For example, heteronuclear CPMAS and REDOR provide important details on connectivities in mixed network former glasses. Results will be shown for phospho- and borosilicate glasses as well as aluminoborate and -phosphate systems. Together with standard NMR techniques these new approaches allow detailed quantitative descriptions of short- and intermediate range order.

A second important aspect of glass structure is the spatial distribution of the network modifier ions, a topic that has received less attention to date due to the lack of suitable structural probes. We have shown that  $^{23}\text{Na}$  spin echo decay spectroscopy is a promising technique for studying the distribution of sodium ions in sodium silicate glasses. Of particular interest is further the „mixed alkali effect“, a transport phenomenon that has been previously linked to correlations among unlike alkali ions in mixed alkali glasses. Such structural models are considered in quantitative detail by means of  $^{23}\text{Na}$ - $^7\text{Li}$  SEDOR NMR in mixed sodium-lithium silicate glasses.

- 3 0 6** SOLIDS NMR OF COMPLEX MIXTURES AND MACROMOLECULES: SPECTRAL EDITING AND 2D NMR OF UNIFORMLY LABELED MOLECULES. Sean Burns, Anil Mehta, Xiaoling Wu, Matthew P. Augustine, Brett Tounge, Iwen Wu and Kurt W. Zilm. Department of Chemistry, Yale University, 225 Prospect Street, New Haven, CT. 06511.

Improvements in pulse sequences for manipulating Hartmann-Hahn spin exchange or cross polarization have allowed us to devise a number of methods for simplifying complex  $^{13}\text{C}$  MAS NMR spectra. These spectral editing techniques have numerous applications in the study of polymers, kerogens and other complex mixtures. Selective cross polarization techniques of this type can also be put to good advantage in 2D correlation spectroscopy of organic solids which have been uniformly labeled in  $^{13}\text{C}$  and  $^{15}\text{N}$ . In this talk we will discuss recent developments in spectral editing methods for complex mixtures and extensions of this type of technique to the study of model RNAs. Combinations of these techniques with various homonuclear spin exchange or dipolar recoupling schemes hold great promise for structural studies in a variety of complex solids. Strategies for using solids NMR methods of this type in structure determinations of large RNAs at high fields will be discussed.

**CHEMICAL SHIFTS AND DISTRIBUTIONS OF RARE GAS CLUSTERS IN ZEOLITES, Cynthia J. Jameson, University of Illinois at Chicago, Chicago, IL 60607-7061**

The NMR chemical shift is extremely sensitive to intermolecular effects, as has been quantitatively documented in the gas phase and in gas-to-liquid shifts. The observed chemical shift carries information about where the rare gas atom has been, with whom, and for how long. We show that the results of  $^{129}\text{Xe}$  NMR studies of Xe in zeolite NaA provide information about the zeolite environment, the nature of the averaging for  $n$  Xe atoms within the same cavity, as well as the distribution among the cavities. The  $^{129}\text{Xe}$  nucleus reports on the changes in the structure of the zeolite cage, cation-induced differences between cages, average number of coadsorbed molecules in a cage with  $n$  Xe atoms, and even the distribution and chemical shifts of mixed clusters such as Xe,Kr. The shielding function describing the intermolecular effects on the rare gas atom by fragments of the zeolite frame work with various cations ( $\text{Na}^+$ ,  $\text{K}^+$ ,  $\text{Ca}^{2+}$ ) has been obtained by *ab initio* calculations. The assumption of pairwise-additive shielding contributions permits computation of average chemical shifts in a Grand Canonical Monte Carlo simulation which can be compared directly with experiment, for Xe, as a function of temperature, for XeKr clusters, and for Xe, observed in various loadings of Xe and Ar in competitive adsorption,  $n = 1-8$ .

**308 Study of Molecular Transport within Microporous Solids by MRM\*  
George D. Cody, Rex E. Gerald II and Robert E. Botto. Chemistry Division, Argonne National Laboratory, Argonne, IL 60439**

Magnetic resonance microscopy (MRM) has been employed to study molecular transport of solvents and gases within microporous solids. Sequential imaging studies of solvent uptake in polymeric materials differentiates two different transport mechanisms. Exponential solvent concentration profiles observed for rubbery networks are consistent with Fickian behavior. In glassy systems, where solvent induces a phase transition of the network, a sharp solvent propagation front is observed which is typical of anomalous Case II transport. MRM analysis forms the basis of a model of anomalous transport in macromolecular solids which couples diffusion of solvent with kinetics of the 1st-order phase transition of the network and yields basic information about molecular architecture. Chemical-shift selective MRM of competitive gas diffusion experiments within porous media is being applied to monitor diffusivities of methane and other gases into materials designed for methane storage.

**309 NMR IMAGING OF PORE STRUCTURES AND LIQUID FLOW PATHS IN POROUS MEDIA, Donald E. Woessner (\*), The University of Texas Southwestern Medical Center at Dallas, Rogers Magnetic Resonance Center, 5801 Forest Park Road, Dallas, Texas 75235-9085.**

Because NMR imaging ordinarily gives signals only from liquids, it can be used to map the pore space distribution in liquid-saturated porous media. When the imaging resolution is sufficient, the actual pore structure can be obtained. Three-dimensional imaging is especially powerful for obtaining the structure of the system of pores. By use of connectivity algorithms, one can select networks of connected pores and estimate the liquid flow paths through the porous medium. Alternatively, the imaging protocol can be chosen so as to greatly attenuate the imaging signal of stationary liquid when liquid is flowing through the sample. The relatively unattenuated signal indicates the major flow paths. Because of dead-end pore spaces, the latter method is the more accurate. In some cases, only a fraction of the connected pore space is in the liquid flow path. Examples of various pore structures and flow paths using two-dimensional slices and three-dimensional rendering have been visualized.

(\* ) Work performed at MEPTEC, 13777 Midway Road, Dallas, Texas 75244.

- 310 **HIGH-VOLUME FRACTION SUSPENSION FLOWS STUDIED BY NMR IMAGING, S. W. Sinton, A. W. Chow, J. H. Iwamiya, Lockheed Martin Missiles & Space, 3251 Hanoever St, Palo Alto, Ca 94304, Mail Stop 93-50/204**

The flow behavior of highly filled suspensions often deviates from that of the underlying Newtonian suspending liquid. Phenomena such as shear-induced particle migration and particle bridging become important and have lately been subjected to theoretical and experimental efforts. On the experimental side, NMR imaging has proven useful for quantitative measurement of local particle concentrations and suspension velocities. We will describe our ongoing and recent MRI studies of suspension flows in various geometries. Results on the evolution of particle concentrations in different rheometer cell geometries will be presented and interpreted in terms of particle migration effects and the impact on viscometric measurements. These studies are helping us develop improved rheological characterization methods for these industrially important suspension materials.

- 311 **MR IMAGING OF THE HEART: FROM FLOW TO PERFUSION. Michael Jerosch-Herold and Norbert Wilke, University of Minnesota, Department of Radiology, UMHC Box 292, Minneapolis, MN 55455**

Flow in the microcirculatory system of the heart muscle can be assessed by measurement of the regional time course for the concentration of a blood borne indicator following injection. We have used ultra-fast MR imaging techniques to track with adequate spatial and temporal resolution the passage of extracellular and intravascular indicators through the myocardium. The MRI measurements were carried out on a fully instrumented canine model. The MR results were compared with flow measurements using radio-labeled microspheres and simulations of the signal dynamics and tracer kinetics during passage of the indicator. Quantification of flow in the myocardium requires models which account for the flow heterogeneity, dispersion and complex distribution of pathways in the vascular architecture. This has been successfully applied in our group for intravascular indicators. For extracellular indicators we have instead derived semi-quantitative parameters which characterize flow in the microvasculature over a wide flow range encountered in animals and humans under resting and stress conditions. Such noninvasive quantitative MR assessment of perfusion would be of great value to assess the significance of a coronary stenosis and monitor treatment of coronary heart disease. Finally we have developed image processing algorithms to generate parametric maps of the myocardium displaying regional variations in flow with excellent spatial resolution.

- 312 **HOW ARE MOLECULES DISPLACED AND REORIENTED ON SURFACES? FIELD-CYCLING RELAXOMETRY AND FIELD-GRADIENT DIFFUSOMETRY.**

**Rainer Kimmich and Siegfried Stapf, Universitat Ulm, Sektion Kernresonanz, 89069 Ulm, Germany.**

The molecular dynamics of fluids in porous media has been studied using field-cycling NMR relaxometry and NMR field-gradient diffusometry. The frequency dependences of the  $^1\text{H}$  and  $^2\text{H}$  spin-lattice relaxation times  $T_1$  of various liquids in porous glass reveal weak and strong adsorption behaviour depending on the polarity of the adsorbates. Correlation times eight orders of magnitude longer than in bulk have been observed. The  $T_1$  dispersion moreover reflects geometrical details of the matrix in a length scale three orders of magnitude longer than the adsorbate molecules. The mean-square displacements of adsorbate molecules on the surface are only one order of magnitude less than in bulk in a given interval. The observed phenomena can be explained by "bulk-mediated surface diffusion", i.e., Levy walks, and adsorbate "reorientations mediated by translational displacements". The dynamics of polymer chains much longer than the pore size is characteristically different from that in bulk melts. There is evidence that the reptation mechanism explains at least a part of the phenomena observed for the porous matrix in contrast to findings with bulk polymer melts.



**313 IN VIVO AND IN VITRO INVESTIGATION OF HUMAN SKIN BY NMR MICROSCOPY: UPTAKE OF DIFFERENT OINTMENTS INTO THE SKIN. M. Szavna and W. Kuhn, Fraunhofer Institut für Biomedizinische Technik, D-66386 St. Ingbert, Germany.**

Skin, with its crucial importance of water content, constitutes a very interesting object for NMR studies. *In vivo* measurements performed on the skin from human finger provided valuable information about transparency and occlusion processes taking place in particular skin layers, like epidermis (with its Stratum Corneum) and dermis, when different ointments are applied. Studies have included parameter selective (T<sub>1</sub> and T<sub>2</sub>) and chemical selective (water and fat) imaging. Based on the obtained results we were able to observe the quantitative changes in the hydration of the skin as a consequence of treatment by different ointments (creams and drugs). From calculated proton density images regarding the type of used ointment (W/O or O/W) 20 to 40% increase of skin hydration was observed. Changes of T<sub>2</sub> values for the outer part of epidermis caused by uptake of creams covering the skin were in the range of 50%. All of the previously described findings were in agreement with chemical shift selective (water and fat) images. In addition, an almost negligible content of lipids was observed penetrating skin layers. Obtained results concerning hydration of the skin were correlated with information about physico-chemical structure of applied ointments. From the diffusion measurements we were able to distinguish between different fractions of "bound" and "free" water, which play an important role in cosmetic industry. All *in vivo* data were collected using a standard Bruker Biospec System (4.7 T) equipped with home built microimaging probes. Achieved spatial resolution was better than 100 μm in plane and 500 μm slice thickness in a time range of 10 minutes.

**314 MULTIDIMENSIONAL NMR CORRELATIONS ON QUADRUPOLEAR NUCLEI. Ales Medek, Joseph R. Sachleben, John S. Harwood and Lucio Frydman. Department of Chemistry (M/C 111), University of Illinois at Chicago, Chicago, Illinois 60607**

The transitions of half-integer nuclei with spin  $S > 1$  are dominated by quadrupolar and chemical shift effects. These interactions transform as zero-, second- and fourth-rank spherical harmonics, and yield upon sample rotation average evolution frequencies

$$\langle a(m,P) \rangle = a^{\langle \cdot \rangle} + af^A A^{TM} P_2(\cos\beta) + af^A A^{TM} P_4(\cos\beta) \quad ;$$

where  $P_l(\cos\beta)$  are  $l$ -order Legendre polynomials and  $m$  denotes a transition of the spin manifold. We discuss here how this  $P$  and  $m$  dependence can be used to develop a series of new multidimensional NMR experiments. These include 3D correlations where spinning axes  $P$  are made time-dependent, and 2D experiments where  $P$  is kept constant but different  $m$  transitions are correlated. The first of these approaches yields highly resolved bidimensional powder patterns whose line shapes carry the relative orientations of quadrupolar and chemical shift tensors; the second approach can lead to the long-sought goal of high-resolution quadrupolar NMR spectroscopy under conventional magic-angle spinning conditions.

**315 MOLECULAR DYNAMICS IN A <sup>19</sup>F-LABELED POLYCARBONATE. J. M. Goetz<sup>1</sup> J. H. Wu,<sup>2</sup> A. F. Yee,<sup>2</sup> J. Schaefer<sup>1</sup>**

<sup>1</sup>Department of Chemistry, Washington University, St. Louis, MO 63130

<sup>2</sup>Materials Science and Engineering, University of Michigan, Ann Arbor, MI 48109

Polycarbonate has the highest impact resistance of any rigid, transparent plastic. Many of the desirable physical characteristics of this glassy polymer have been attributed to backbone undulations which gate aromatic  $n$  flips. Fluorine has been substituted for an aromatic proton on every second monomer repeat (one <sup>19</sup>F per four rings), and the effect upon molecular dynamics is investigated using three channel, solid state, MAS NMR. Intramolecular <sup>13</sup>C-<sup>19</sup>F dipolar couplings are measured with a two-dimensional REDOR experiment and a newly developed two-dimensional TEDOR experiment. Intramolecular <sup>13</sup>C-<sup>1</sup>H couplings are measured using a dipolar rotational spin-echo experiment. Results from our experiments indicate that the <sup>19</sup>F-labeled rings are static, while all other rings on the polymer chain are flipping. These experimental results are inconsistent with some molecular dynamics simulations which predict that within a repeat unit, pairs of rings flip cooperatively.

- 316 **MEASUREMENT OF  $^1\text{J}^{13}\text{C}-^{13}\text{C}$  DIPOLAR COUPLINGS BY MAS NMR.** Terry Gullion and Joel R. Garbow<sup>^</sup>, Department of Chemistry, Florida State University, Tallahassee, FL 32306 and <sup>^</sup>Monsanto Corporate Research, Monsanto Company, St. Louis, MO 63198.

The development of techniques to recover and accurately measure homonuclear dipolar couplings between specific isotopically-enriched spin pairs (e.g.,  $^{13}\text{C}-^{13}\text{C}$ ) in samples spinning at the magic angle is an active area of research. Recently, progress has been made in measuring long-range distances (i.e., 5 - 6Å) by dipolar dephasing techniques. The measurement of such distances is difficult, since the Pake powder pattern for a weakly-coupled spin pair is small. One strategy that eliminates the need for hneshape analysis is to measure the dipolar coupling between homonuclear spin pairs with a *difference* experiment, similar to the REDOR technique developed for heteronuclear spin pairs. Such difference methods consist of a *control* experiment, which accounts for  $T_2$  decay, and a *dephasing* experiment, which is dominated by dipolar evolution. These difference experiments are demanding and require that the *control* and *dephasing* experiments be balanced so that, in the absence of dipolar interactions, they produce identical results. We present results illustrating that difference experiments can be designed in which the *control* and *dephasing* experiments differ only in the placement, but not the number or relative phases, of the pulses. Numerical and experimental results will be presented to illustrate this concept.

- 317 **XENON NMR IN PORES: OBSERVATIONS ON CHEMICAL SHIFTS AS A FUNCTION OF TEMPERATURE.** Yong-Wah Kim, Douglas M. Smith and William L. Earl. Quantum Magnetics, San Diego, CA 92121; Department of Chemical Engineering, University of New Mexico, Albuquerque, NM 87131; and Chemical Science and Technology Division, Los Alamos National Laboratory, Los Alamos, NM 87545

Xenon NMR has been used extensively over the last 10 years as a tool for measuring pore sizes in many porous materials. Out of this work has come a useful but very empirical method of interpreting  $^{129}\text{Xe}$  chemical shifts in pores. For several years ago we have studied  $^{129}\text{Xe}$  NMR as a function of temperature with the goal of adding physical understanding to the empirical equations. Several interesting features are observed in the  $^{129}\text{Xe}$  spectra in porous materials near the freezing point. The simplest phenomenon to understand is a freezing point depression due to containment. We also observe an unusual fluid phase which we associate with xenon on the wall of the pore at low temperature. Variable temperatureresults on a number of porous materials will be presented and a physical-chemical basis for the dense fluid phase will be discussed in detail. We will also discuss probe design, experimental details and the intrinsic problems related to low temperature  $^{129}\text{Xe}$  NMR.

- 318 **INORGANIC GLASS STRUCTURE FROM NMR SHIFTS AND LINESHAPES,** Josef W. Zwanziger, Department of Chemistry, Indiana University, Bloomington, IN 47405, (812) 855-3994

Typical oxide-based inorganic glasses consist of a network former, such as boron oxide ( $\text{B}_2\text{O}_3$ ), that provide a covalently-bound network; modifiers such as alkali oxides that disrupt the network; and various dopants used to alter the mechanical and electrical properties of the bulk glass. Recent developments in NMR methodology, especially isotropic-anisotropic correlation experiments, have enabled the acquisition of a wealth of results on the structure of the network former and the chemistry of the modification process. These results are of both fundamental and practical importance. The specific experiments will be reviewed in the talk, as will the new results they have produced on glass structure. A method for extracting information from the NMR lineshapes of disordered materials will also be presented, which is based on inverse theory and avoids making assumptions about the particular type of disorder present.

**319 NMR MEASUREMENT OF WEAK HOMONUCLEAR INDIRECT COUPLINGS IN GaAs** Larry. D. Potter and Yue. Wu Department of Physics and Astronomy, University of North Carolina, Chapel Hill, NC 27599-3255

Understanding of indirect couplings in semiconductors and accurate measurements of indirect couplings could provide unique information on the electronic structures of semiconductors and semiconductor nanocrystals. The difficulty in measuring indirect couplings in DI-V compounds arises from the fact that isotropic homonuclear indirect couplings do not contribute to the second moment of the NMR line. We demonstrate both theoretically and experimentally that small isotropic homonuclear indirect couplings in GaAs can be measured from the Hahn-echo decay under fast MAS; the time  $x$  associated with the echo top after applying the  $iz$  pulse is related to the dephasing time  $t_i$  between the  $n/2$  and the  $n$  pulses by  $x = cct_i$  and  $a$ , depending both on the isotropic heteronuclear and homonuclear indirect couplings, is a constant smaller than one. This  $a$  and the homonuclear indirect couplings determined from the echo decay were used to determine the heteronuclear indirect couplings. The heteronuclear couplings can also be evaluated independently from the MAS linewidth which provides a strict verification of the theory and experimental procedures. The measured isotropic indirect couplings were used to assess the accuracy of the Anderson theory on indirect couplings in semiconductors.

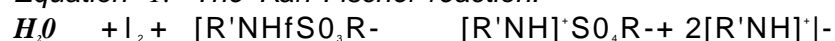
**320 Characterization of Protein Secondary Structures Using Fourier Transform Infrared Spectroscopy.** Aichun Dong, Pin Huang, Winslow S. Caughey, and John F. Carpenter. Department of Pharmaceutical Sciences, School of Pharmacy, University of Colorado Health Center, Denver, CO 80262, and Department of Biochemistry & Molecular Biology, Colorado State University, Fort Collins, CO 80523

For a successful development of natural or recombinant proteins as therapeutic agents, structural knowledge about the protein products and their behavior during purification, formulation, and storage are extremely important. FT-IR is an excellent tool for characterizing quantitatively as well as qualitatively the secondary structures of protein and to monitor conformational changes induced by selected variables such as ligand, redox state, pH, temperature, zymogen activation, mutation, denaturation, lyophilization, and cryopreservation. The criteria and procedures for liquid and gaseous water spectra subtraction are discussed. On the basis of empirical analysis of over 40 proteins with known crystal structures, a total of 14 characteristic band frequencies in amide I region have been assigned to different types of secondary structures such as  $\alpha$ -helix,  $\beta$ -sheet,  $\beta$ -turn, and unordered structures.

- 321 **KARL FISCHER MOISTURE ANALYSIS OF CHEMICAL AND PHARMACEUTICAL PRODUCTS-TIPS, TRICKS AND TECHNIQUES-**. Andreas Dietrich, Hoechst Celanese Corp., HWY 43 North, Bucks, AL 36512.

Determining the moisture content of chemical products via the Karl Fischer (KF) Titration belongs today to one of the most common tasks. The KF method is based on a simple red-ox reaction (equation 1) and gained increasing popularity since its discovery by Karl Fischer in 1935. The main advantages of the KF titration are speed, accuracy, and very few product limitations. Today's analyst expect instrumentation and analytical reagents to be fast, accurate, and precise. Constantly advancing instrumental and KF reagent methodology along with an increasing demand for the exact and precise sample water content have determined the research and development over the last twenty years.

*Equation 1: The Karl Fischer reaction:*



A summary of KF titration fundamentals, developments in areas of instrumentation, reagent technology and Karl Fischer titration theory will be presented. Volumetric and coulometric methodologies will be compared. The reaction chemistry of the modern Karl Fischer reagent will be explained with respect to interferences. A practical approach will help to identify and solve interference problems. Selected pharmaceutical and chemical samples will be discussed and analyzed for possible side-reactions.

- 322 **IN VIVO AND IN VITRO INVESTIGATION OF HUMAN SKIN BY NMR MICROSCOPY: UPTAKE OF DIFFERENT OINTMENTS INTO THE SKIN.** M. Szayna and W. Kuhn, Fraunhofer Institute for Biomedical Engineering, Magnetic Resonance Department, Ensheimer Str. 48, D-66386 St. Ingbert, Germany

Skin, with its crucial importance of water content, is a very interesting object for NMR studies. *In vivo* measurements performed on skin from human fingers provided valuable information about transparency and occlusion processes taking place in particular skin layers, like the epidermis (with its Stratum Corneum) and the dermis, when different ointments are applied. Studies have included parameter selective ( $T_1$  and  $T_2$ ) and chemical shift selective (water and fat) imaging. Based on the results we were able to observe the quantitative changes in skin hydration as a consequence of treatment by different ointments. From calculated proton density images, a 20% - 40% increase in skin hydration was observed from calculated proton density images, depending on the type of ointment used (W/O or O/W). After application of creams, changes in  $T_2$  values for the outer part of the epidermis were in the range of 50%. Lipid penetration of skin layers was found to be almost negligible. Skin hydration results were correlated with the physico-chemical structure of the applied ointments. From the diffusion measurements we were able to distinguish between different fractions of "bound" and "free" water. All *in vivo* data were collected using a standard Bruker Biospec System (4.7 Tesla) equipped with home built microimaging probes. Achieved spatial resolution was better than 100pm in plane and 500pm slice thickness in time range of 10 minutes.

- 323 **PHYSICO-CHEMICAL CHARACTERIZATION OF EMULSIONS BY NMR TECHNIQUES.** W. Kuhn and M. Szayna, Fraunhofer Institute for Biomedical Engineering, Magnetic Resonance Department, Ensheimer Str. 48, D-66386 St. Ingbert, Germany

Pharmaceutical drugs provided as ointments, and beauty care products such as cosmetic creams, are usually prepared as water in oil or oil in water emulsions. In addition, they may contain other ingredients such as vitamins, amino acids, penetration enhancers like urea, etc. The effectiveness of creams and ointments in penetrating the skin depends strongly on the physico-chemical properties of the emulsion. NMR parameters which can be used to characterize emulsions are the relaxation times and diffusion coefficients for the different compounds. In particular, the relative contribution of differently bound water seems to be one of the important parameters to describe the potential of skin care products. We present the chemical selective characterization of creams and ointments using the NMR parameters for the different compounds. The measurements reveal the presence of water bound in at least two different stages, which is reflected in diffusion coefficients measured not only for water but for lipids and other ingredients as well. From the diffusion values the average free moving distance of the molecules could be estimated, giving an idea of the water droplet size in the emulsion. Also the aging process and the phase separation of water and fat can be investigated by this technique.

- 324 **ANALYSIS OF AMT, A TOXIC AZT METABOLITE, BY HPLC/MS/MS.** Robert K. Lantz and Patricia L. Sulik, Rocky Mountain Instrumental Laboratories, Inc., 456 S. Link Ln., Ft. Collins, CO 80524

AMT (3'-amino-3'-deoxythymidine) is a toxic metabolite of AZT (zidovudine) which also exhibits anti-cancer activity. Much of the toxicity of AZT appears to be due to the effects of AMT. AMT was analyzed in samples from AIDS patients who had been treated with AZT during clinical trials of a new formulation of AZT. AMT was quantitated following deproteinization with internal standard-containing Acetonitrile. A Perkin-Elmer SciEx APT III triple quadrupole MS, using the daughter ion (126.8 amu) generated from the parent ion (242.4 amu), and MacQuan software was employed to quantitate the AMT. HPLC conditions were: Zorbax SB-CN analytical and guard columns; mobile phase: 30mM NH<sub>4</sub>Acetate, pH 6.0, 40% acetonitrile. Limit of quantitation was 1ng/mL for the AMT.

- 325 **STABILIZATION OF PROTEINS DURING FREEZING AND DRYING.** John F. Carpenter. School of Pharmacy, University of Colorado Health Sciences Center, Denver, CO 80262

To obtain a functional, native protein after lyophilization and rehydration, the protein must be stabilized during both freezing and drying. The mechanism for protection against each acute stress is distinctly different. Stabilization during freezing (e.g., by sucrose, polyethylene glycol) is due to the same universal mechanism that Timasheff and Arakawa have defined for solute-induced protein stabilization in nonfrozen, aqueous solution. The solutes are preferentially excluded from the protein, increase the protein's chemical potential and make it more thermodynamically unfavorable for the protein to denature. Protection of proteins against dehydration appears to be fundamentally different. We have found, using solid-state Fourier transform infrared spectroscopy, that the hydrogen bonding of the sugar to the dried protein is necessary for protein preservation. Recent studies have provided additional data supporting this "water replacement" hypothesis. Perhaps more importantly, from a practical viewpoint, we have found with resolution-enhanced infrared spectroscopy that labile proteins, lyophilized in the presence of sugars, retain their native structure in the dried solid. And the storage stability of the dried formulation is greater for the native than for the unfolded protein. Thus, in terms of prediction of storage stability, the minimum criterion for a successful formulation should be retention of native structure in the dried solid. Finally, many proteins that unfold during lyophilization will refold, if rehydrated immediately. Therefore, it is crucial that the structure be analyzed directly in the dried sample.

327 SAMPLE PREPARATION FOR FTIR ANALYSIS. Robert J. Dhyse, Midac Corporation, 1196 East Dry Creek Place, Littleton, CO 80122

A general review of sampling techniques useful to manufacturers of Pharmaceuticals. We will cover the use of different types of sampling accessories used for the analysis of incoming raw materials as well as the analysis of finished products.

329 IMPLEMENTING A QUALITY ASSURANCE PLAN FOR THE ETHANOL PROJECT AT THE NATIONAL RENEWABLE ENERGY LABORATORY. David W. Templeton, Christine I. Ehrman, Raymond O. Ruiz, John S. Brigham, National Renewable Energy Laboratory, 1617 Cole Blvd. Golden CO, 80401.

The ethanol project at the National Renewable Energy Laboratory (NREL) is seeking cost-effective technologies to convert biomass to ethanol for transportation fuels. The ethanol project strives to achieve its goal through the coordination of many scientific and engineering research efforts. It is vital to continued progress that all experimental data generated, both in-house and subcontractor, be comparable and of appropriate quality. The project has endeavored to produce a quality assurance plan (QAP) to meet this quality goal. The concepts and tools described in the QAP are designed to be general and flexible enough to be applicable to all project research. The creation, substance, and implementation of the QAP are discussed.

330 A QUALITY ASSURANCE PROGRAM FOR *IN-SITU* RADIOLOGICAL SURVEILLANC. Peter D. Fledderman and Moheb M. Khalil, Westinghouse Savannah River Company, Aiken, South Carolina 29808

During the past five years, a comprehensive Quality Assurance Improvement Program has been established for the radiological and nonradiological environmental monitoring programs at the Savannah River Site(SRS). The primary objective of the program is to ensure that accurate, precise, and defensible environmental monitoring data are produced. The program is built into the routine activities of the site's Environmental Monitoring Section (EMS)as established in DOE Order 5700.6c/NQA-1. The program's elements include enhanced QA activities in all work groups and QA training specially designed for EMS. Examples of the improvements within EMS QA program can be found in the annual site - controlled wildlife hunts, which are conducted to control the deer and feral hog population at SRS. EMS is responsible for monitoring each animal for radiological contamination before releasing it off site. In 1991, a series of improvements in the hunt monitoring program were implemented, including establishment of equipment operating-control limits; performance of regular routine QA source checks of the monitors to ensure compliance with control limits; collection and analysis of tissue samples as an independent verification of equipment accuracy; and improvement of records. These actions have increased monitoring accuracy and quality without compromising animal-processing speed.

- 331 **IPEP - THE INTEGRATED PERFORMANCE EVALUATION PROGRAM FOR THE DEPARTMENT OF ENERGY'S OFFICE OF ENVIRONMENTAL MANAGEMENT.** P. C. Lindahl, W. E. Streets, D. A. Bass, P. L. Johnson, J. J. Marr, A. E. Scandora, Jr., J. E. Hensley, and K. J. Parish, Argonne National Laboratory, Argonne, IL 60439; W. R. Newberry and M. H. Carter, U.S. Department of Energy, Office of Environmental Management, Analytical Services Division, Washington, DC 20585.

In support of environmental restoration and waste management efforts by the Department of Energy (DOE), the Office of Environmental Management's (EM's) Analytical Services Division (EM-263) has been charged with developing and implementing a program to assess the performance of laboratories providing analytical services for environmental management (EM) programs. Argonne National Laboratory (ANL) and the DOE's Radiological and Environmental Sciences Laboratory (RESL) and Environmental Measurements Laboratory (EML) have been collaborating on the development of a comprehensive Integrated Performance Evaluation Program (IPEP) for DOE-wide implementation. The IPEP incorporates several unique aspects in its approach. At the outset, it will use results from existing inorganic, organic, and radiological performance evaluation (PE) programs when these are available and appropriate. To complement these PE programs, the DOE has begun the development of the Mixed Analyte Performance Evaluation Program (MAPEP) at RESL to address the needs of the DOE Complex for a mixed-waste PE program. In addition, the IPEP will expand its assessment approach by reviewing a laboratory's historical PE program performance, as well as results from multiple PE programs, to provide an enhanced perspective of the laboratory's overall performance. (Work supported by the U.S. Department of Energy under Contract W-31 -109-ENG-38.)

- 332 **COMMON NONCOMPLIANCE ISSUES WITHIN LABORATORIES THAT CONDUCT TESTING FOR NATIONAL POLLUTANT DISCHARGE ELIMINATION SYSTEM PERMITTED PARAMETERS.** Jimmy L. Seidel, U.S. Environmental Protection Agency, National Enforcement Investigation Center, Building 53 Box 25227, Denver Federal Center, Denver, Colorado 80225.

Inspections of corporate laboratories, which are involved in testing for National Pollutant Discharge Elimination System (NPDES) permitted parameters, have revealed several noncompliance issues which commonly occur. Most instances of noncompliance could be avoided by a careful review of sampling practices, testing procedures and documentation, and quality assurance/quality control systems by the laboratory's senior management. In order to better understand some of the more common areas of noncompliance encountered, an overview and discussion of these areas will be presented.

- 333 **ANALYSIS OF URINARY ESTROGENS BY GC/MS FROM PATIENTS WITH CHOLESTASIS OF PREGNANCY.** A. W. Pike, K. Leslie, L. Reznikov, and P. V. Fennessey. Departments of Pediatrics, Obstetrics and Gynecology, UCHSC, Denver, CO USA.

Cholestasis of pregnancy usually presents by the third trimester of pregnancy. It appears to have a particular high incidence in Scandinavia and Chile, and has been shown to have a genetic link. Previous studies have demonstrated that the condition can be induced using high doses of estrogen in both males and females of the affected family. The major clinical symptoms include marked psoriasis (skin irritation), and acute jaundice. Untreated, the condition not only causes acute maternal distress, but can result in high infant mortality. Blood chemistries reveal elevated bile acids and liver enzymes. Previous treatment has been accomplished by attempts to decrease plasma bile acid levels. We have analyzed urinary steroids by gas chromatography mass spectrometry from patients who have clinically been defined to have mild and severe forms of the condition during each trimester of their pregnancy, and compared them to corresponding controls. Similarly, urine was analyzed from those patients who were successfully treated during their pregnancy. Results from these analyses will be presented and compared to those from affected and treated patients.





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